Tungsten: A Preliminary Environmental Risk Assessment

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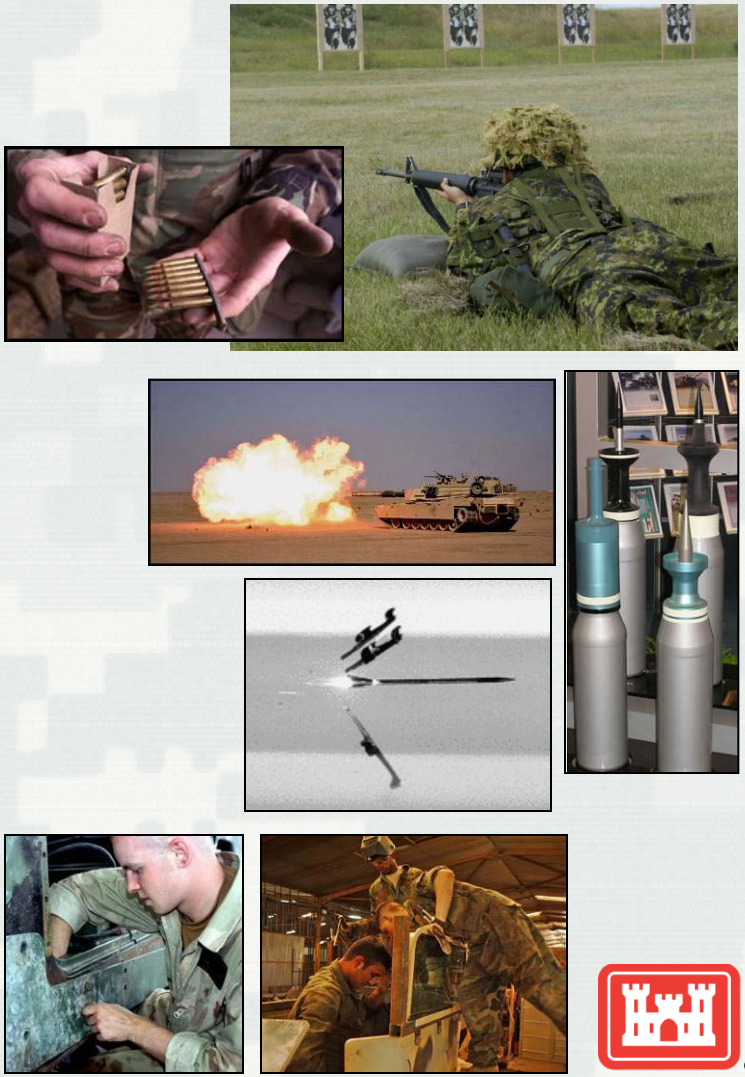
Tungsten: Characteristics & Military Applications

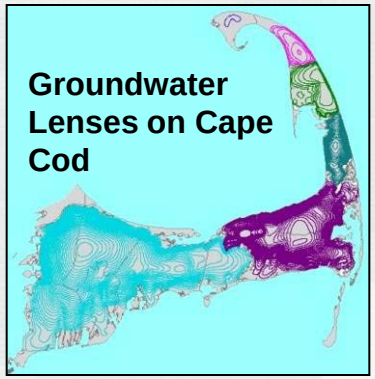
- Only small percentage of earth metals
  ~1 mg/kg (ppm)
- Found in ores in multiple oxidative states (W^{-4}, W^{-2}, W^{-1}, W^{+3}, W^{+5}, W^{+6})
- 2nd most dense metal
- Highest melting point
- Highest tensile strength
- Military uses:
  - Small arms munitions
  - Penetration ammunition
  - Protective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

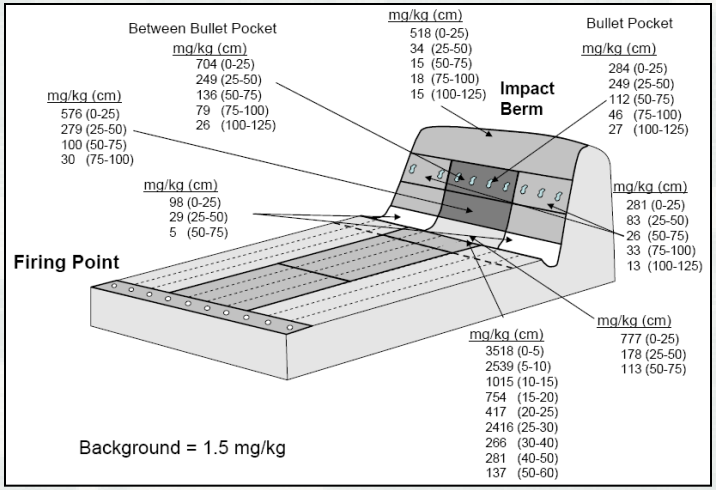


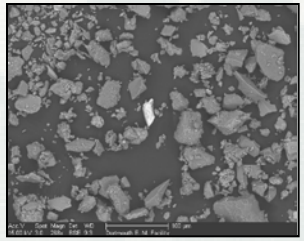
Problems with Tungsten: Environmental Mobility

- "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

Map of southeastern Massachusetts showing Cape Cod and the Massachusetts Military Reservation







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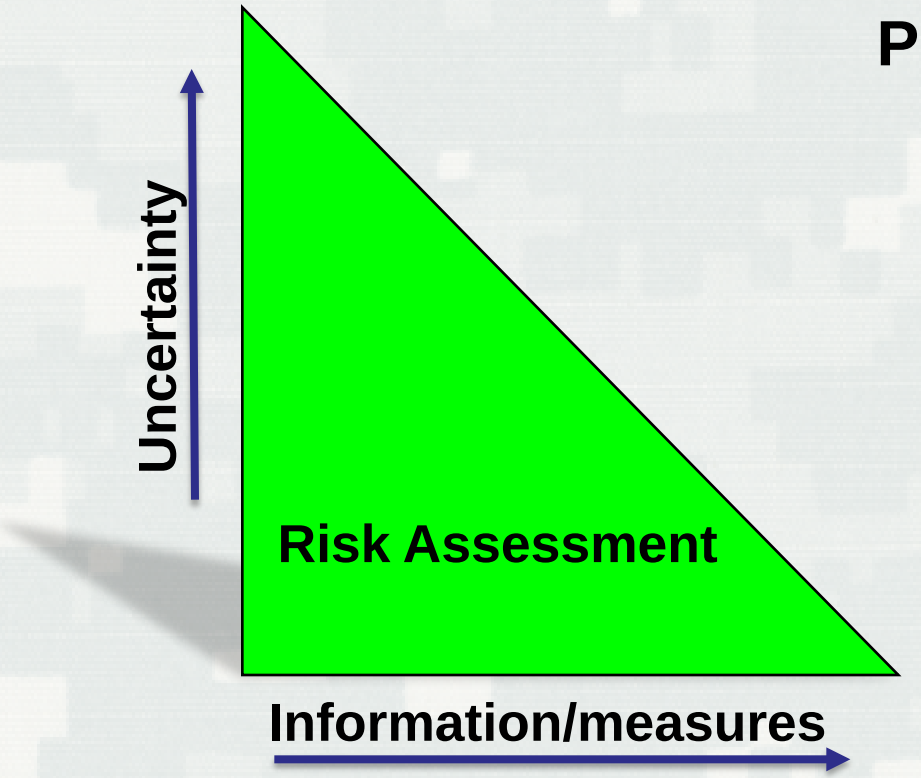
Reducing Uncertainty in Risk Assessment



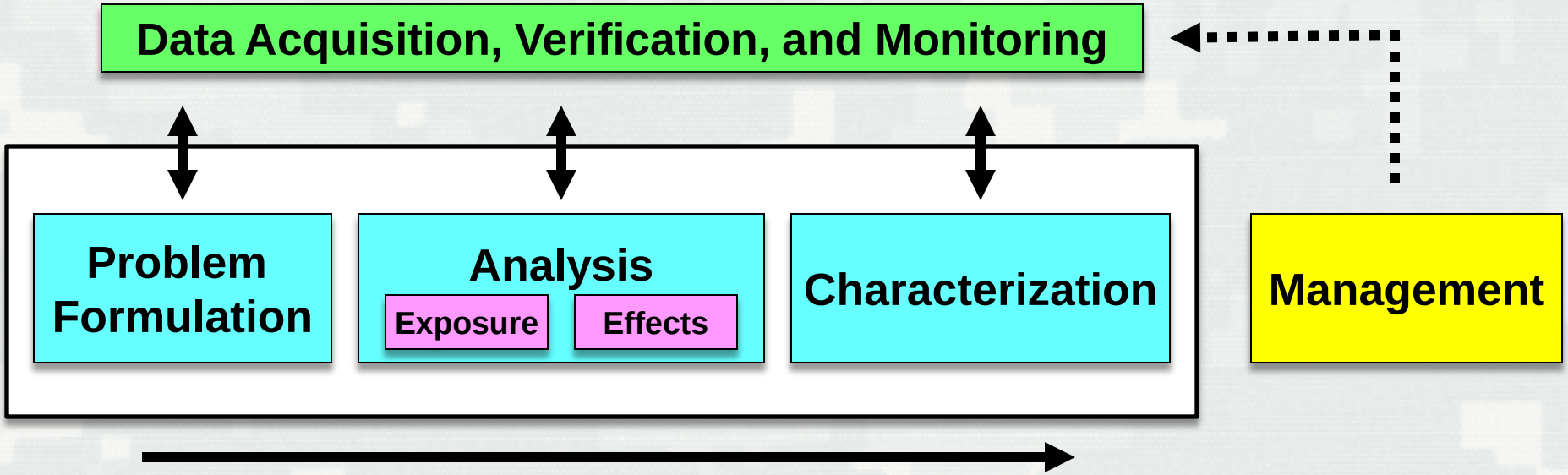
Problem: Need to increase knowledge of the potential impacts of military unique compounds and industrial compounds on aquatic and terrestrial wildlife species

UNCERTAINTY = $ COST $

SOLUTION:

MORE KNOWLEDGE = IMPROVED ASSESSMENTS = MORE TRAINING = BETTER SOLDIERS

Ecological Risk Assessment Framework



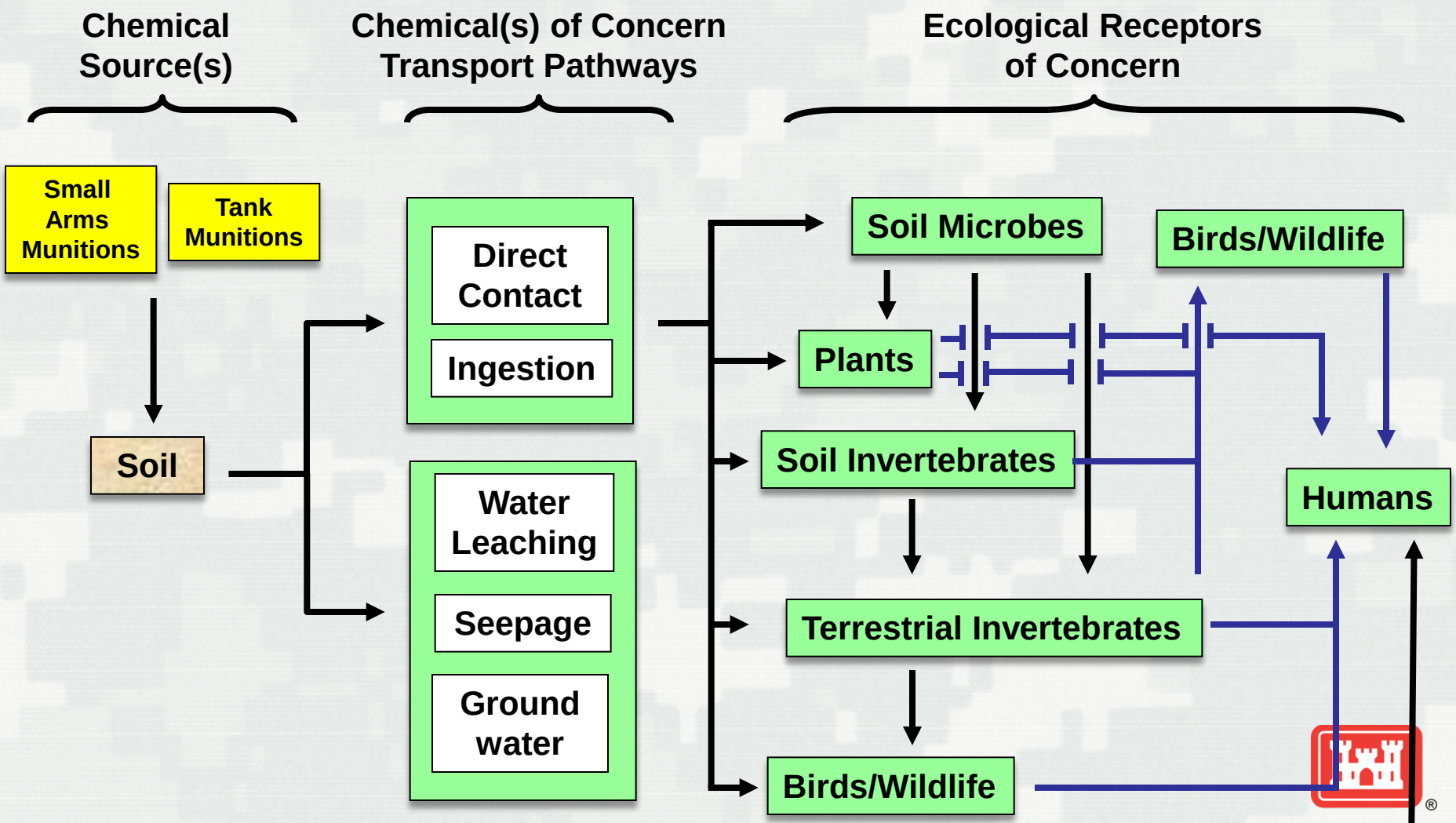
- Process that evaluates the likelihood that adverse effects may occur or are occurring as a result of exposure to one or more stressors (USEPA, 1997)

- 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?

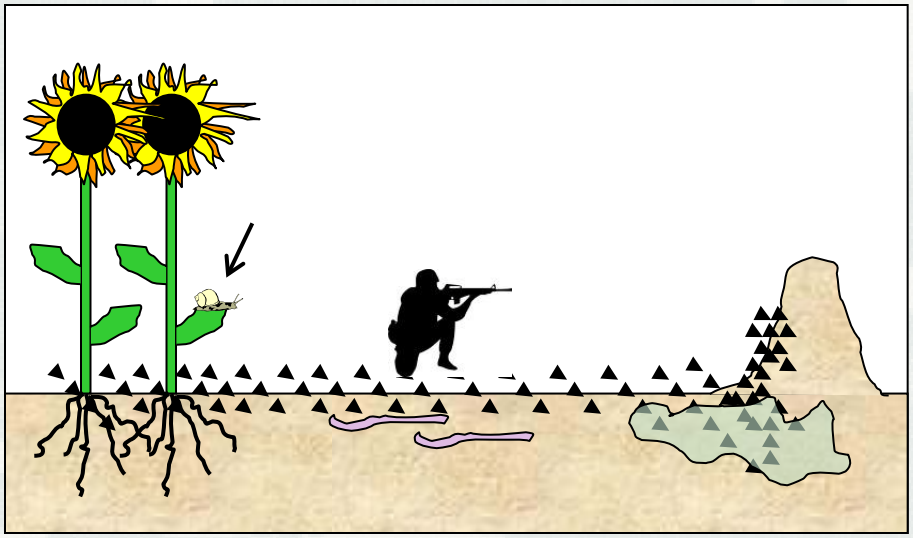
Dietary uptake:	**~0.01 mg** **0.2-16 mg/kg (vegetables)**
Drinking water:	**generally not measured** **0-217 μg/L (Fallon, NV)** **groundwater > surface water**
Soil:	**1-1.3 mg/kg (earth's crust)** **1-22 mg/kg (agriculture fields)** **0-5,500 mg/kg (tungsten mines, military ranges)**
Air:	**< 10 ng/m^3 (ambient)** **5 mg/m^3 (industry, OSHA)**

Tungsten: Ecological Risk Assessment Conceptual Model



Tungsten Research To Assess Exposure and Effects on Flora & Fauna

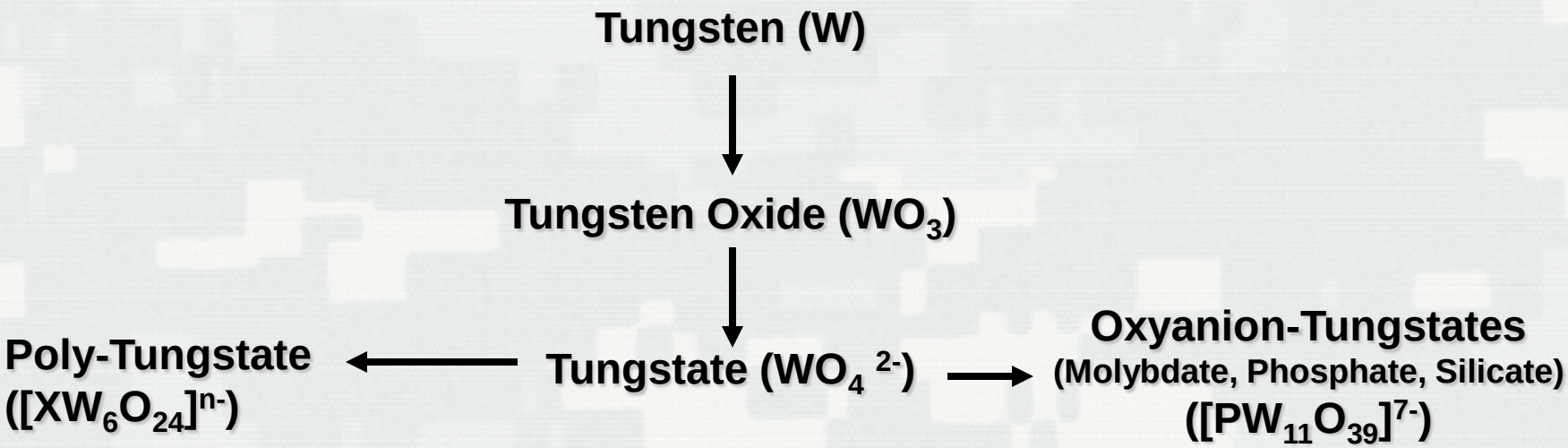
- **Geochemistry**
- **Soil microbial communities**
- **Plants**
- **Soil invertebrates**
- **Higher order animals**
- **Additional studies**



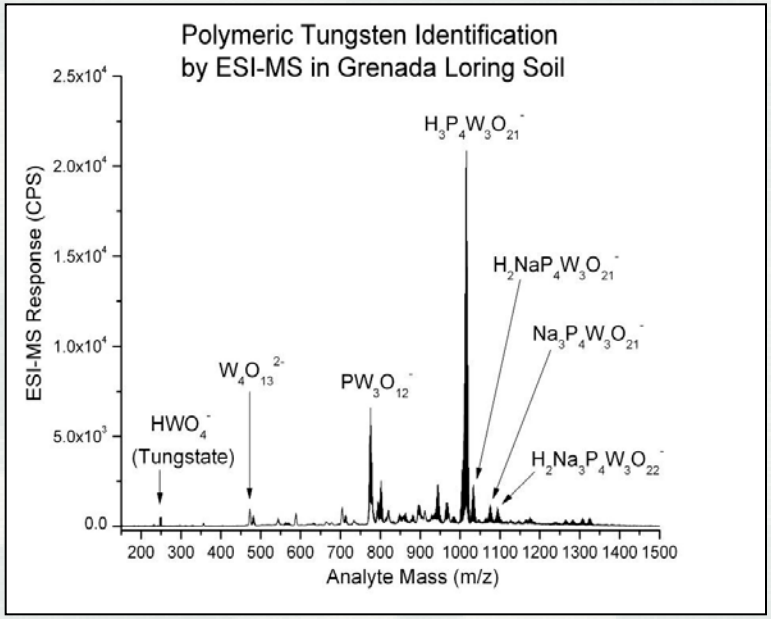
Tungsten Geochemistry

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



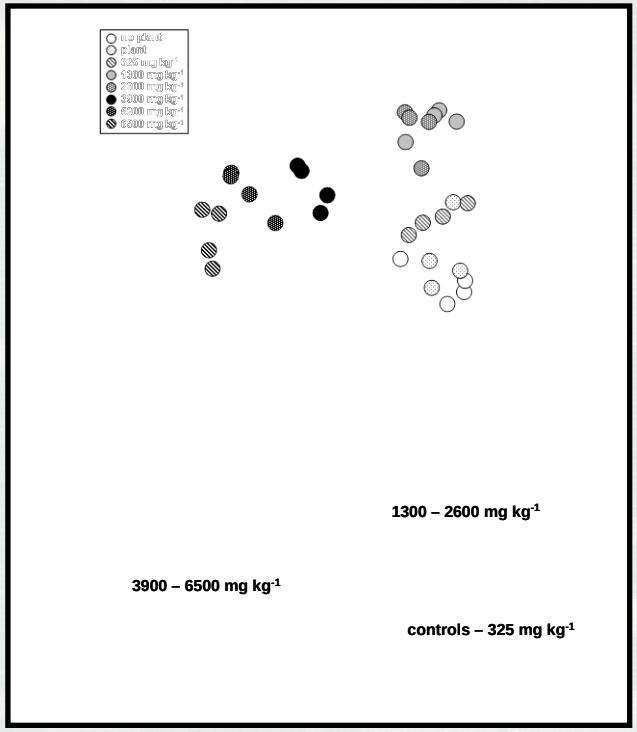
Tungsten Compounds	K_d 3 Days	K_d 4 Months
Tungstate	284	845
Polytungstate	92	135
Phosphotungstate	112	500
Tungstosilicic Acid	103	97

★ 1 yr aged soil K_d = 110

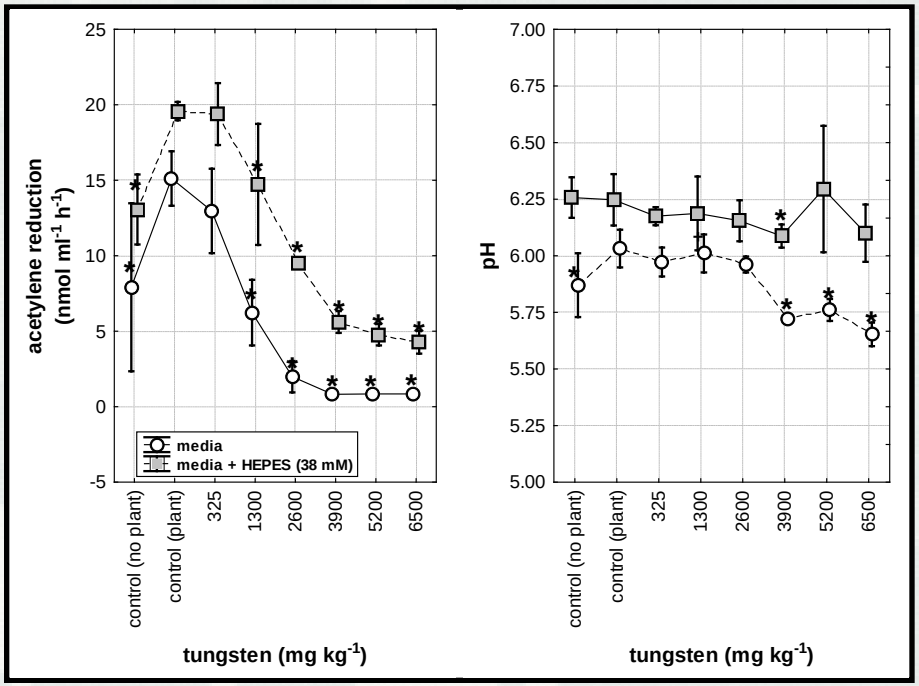
Partition coefficients (Kd), a measure of sorption, suggest that different species will have different mobility in soil

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]

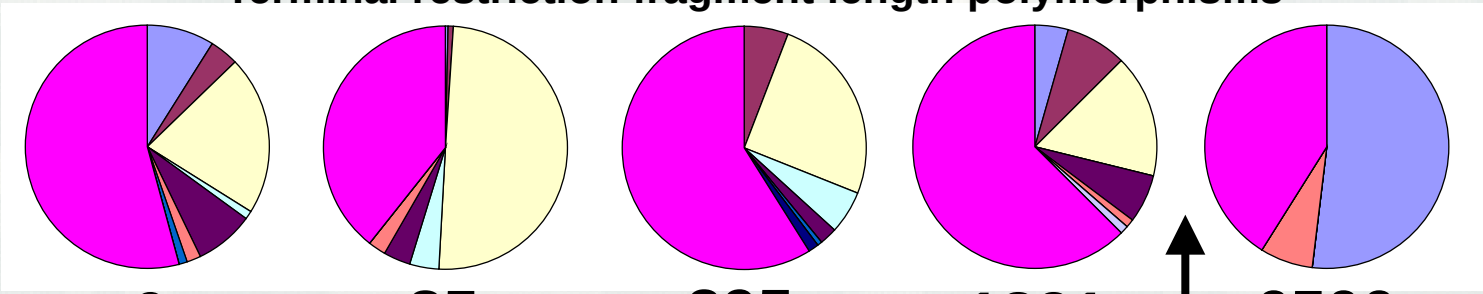


Nitrification activity inhibited by increasing [W] at neutral pH

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
  - γ-Proteobacteria – includes a variety of microbes

Bioaccumulation of Tungsten in Plants

Natural Sources

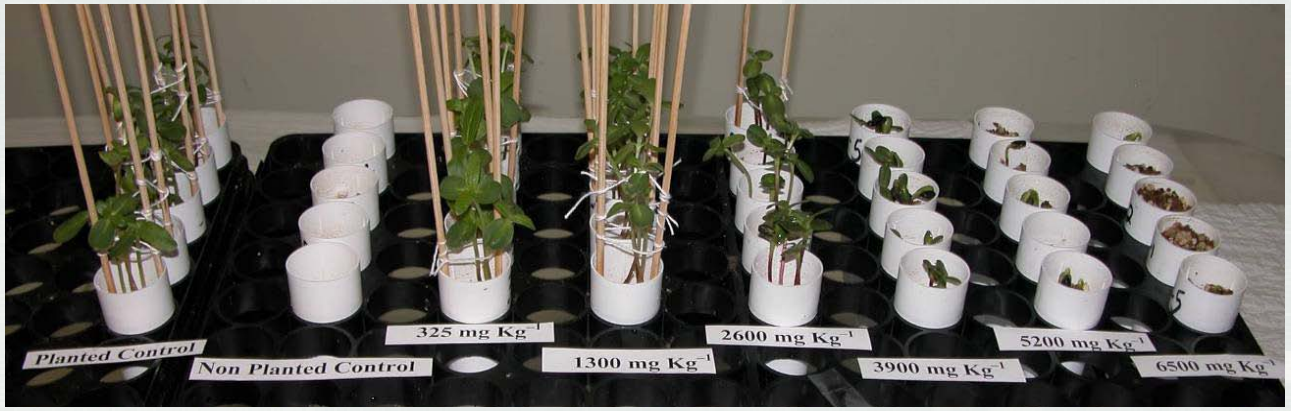
- Trees & shrubs in Rocky Mountain region, USA
- Siberian pine, willows, mosses & lichen in tungsten-rich fissures

Anthropogenic Sources

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




Effects of Tungsten-Spiked Soil on Sunflowers

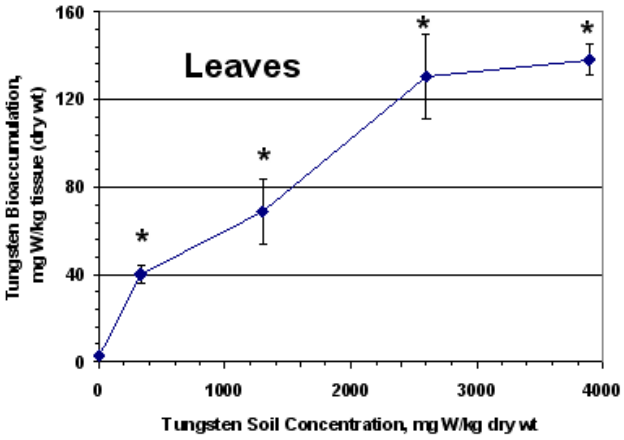


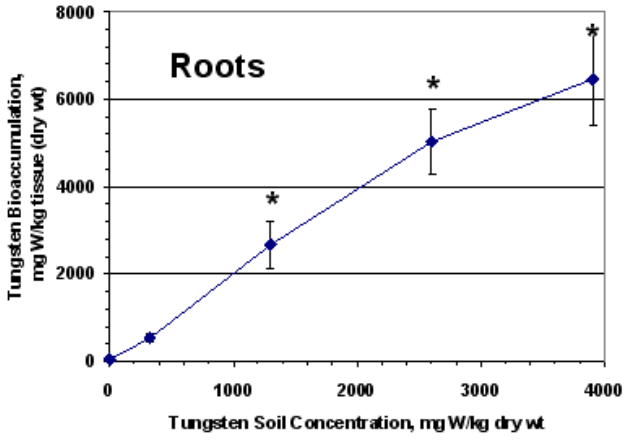
0 325 1300 2600 3900 5200 6500

Soil Tungsten Concentration, mg/kg

Statistically significant changes at ≥ [x]…

- **Stem Wt**
- **Leaf Wt**
  Total Wt
- **Root Wt**
  Shoot Length
  Root Length





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Effects of Tungsten on Earthworms (E. fetida)

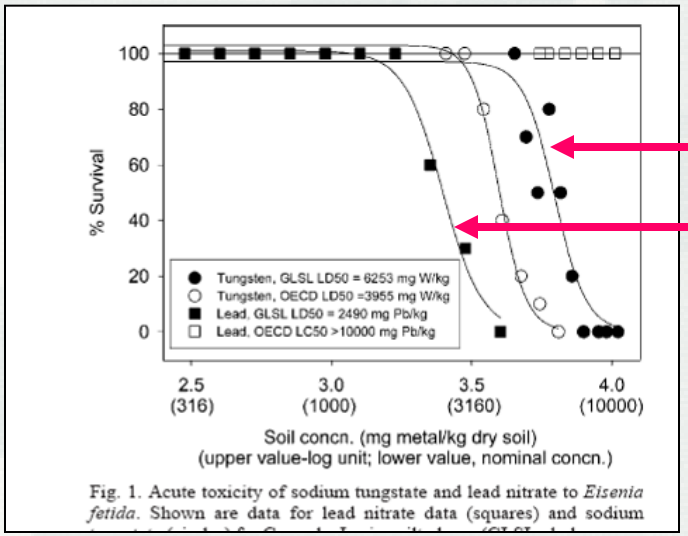
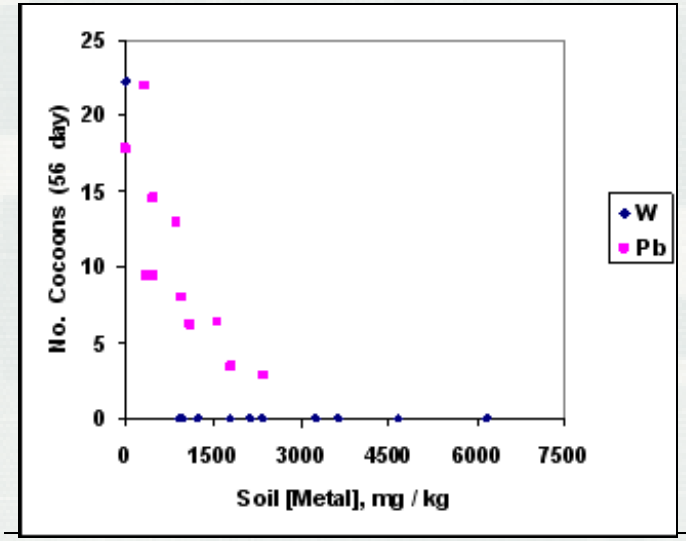


Fig. 1. Acute toxicity of sodium tungstate and lead nitrate to *Eisenia fetida*. Shown are data for lead nitrate data (squares) and sodium

W (field soil) LD50 = 6253 mg/kg

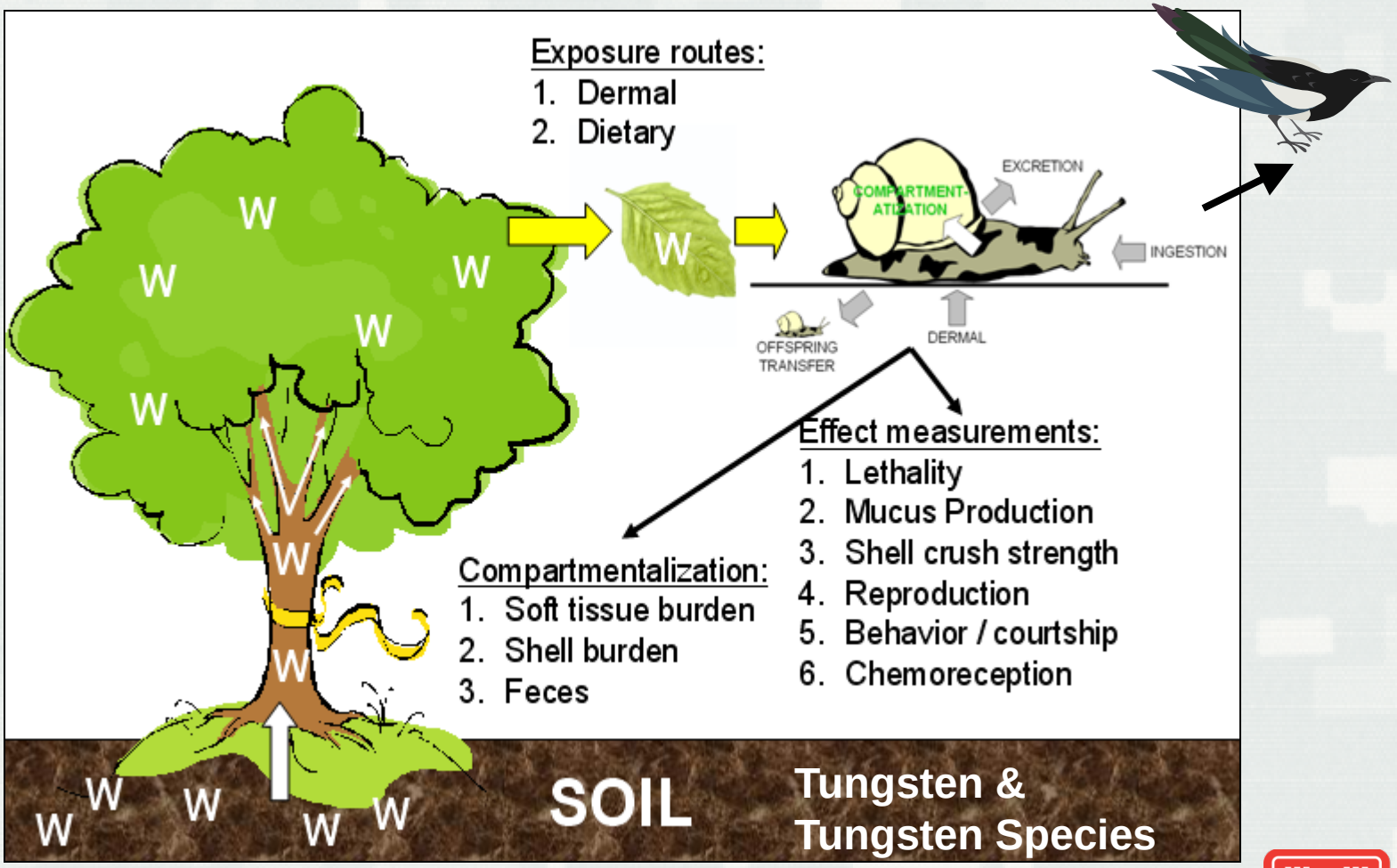
Pb (field soil) LD50 = 2490 mg/kg

- **W is less acutely toxic to earthworms than lead**

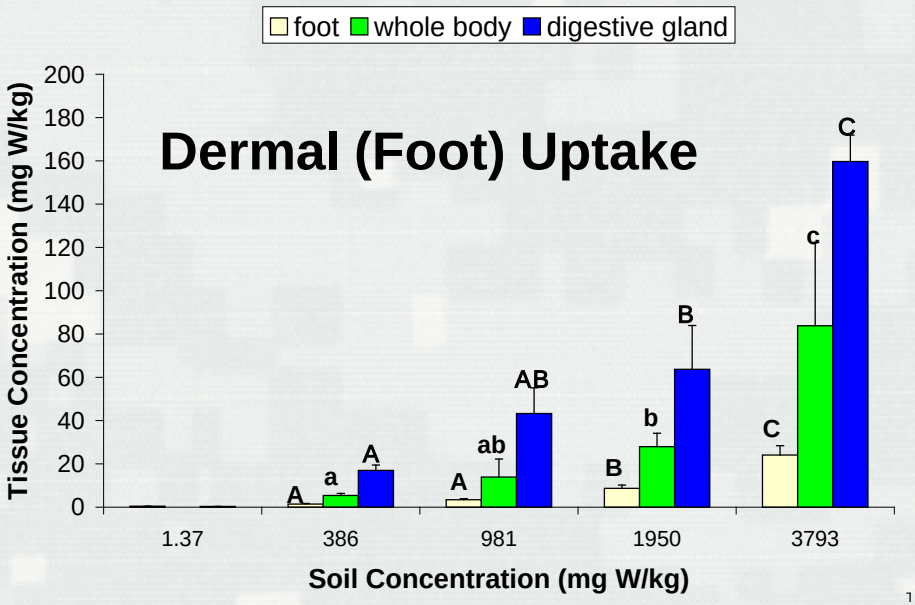


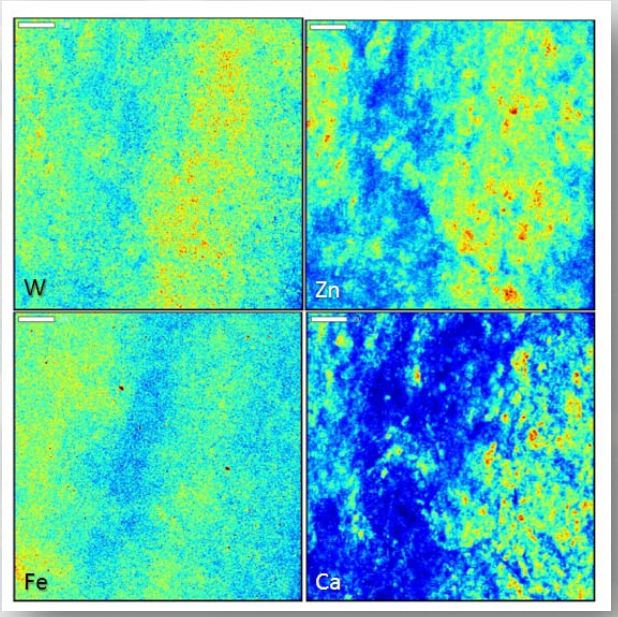
- **W is a potent reproductive toxicant to earthworms after 28 day exposure**

Is Tungsten Transferred Up the Food Web?



Uptake of W in Gastropods





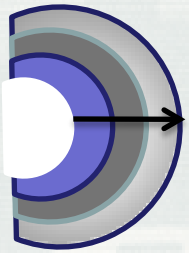
Synchrotron analysis of Snail hepatopancreas

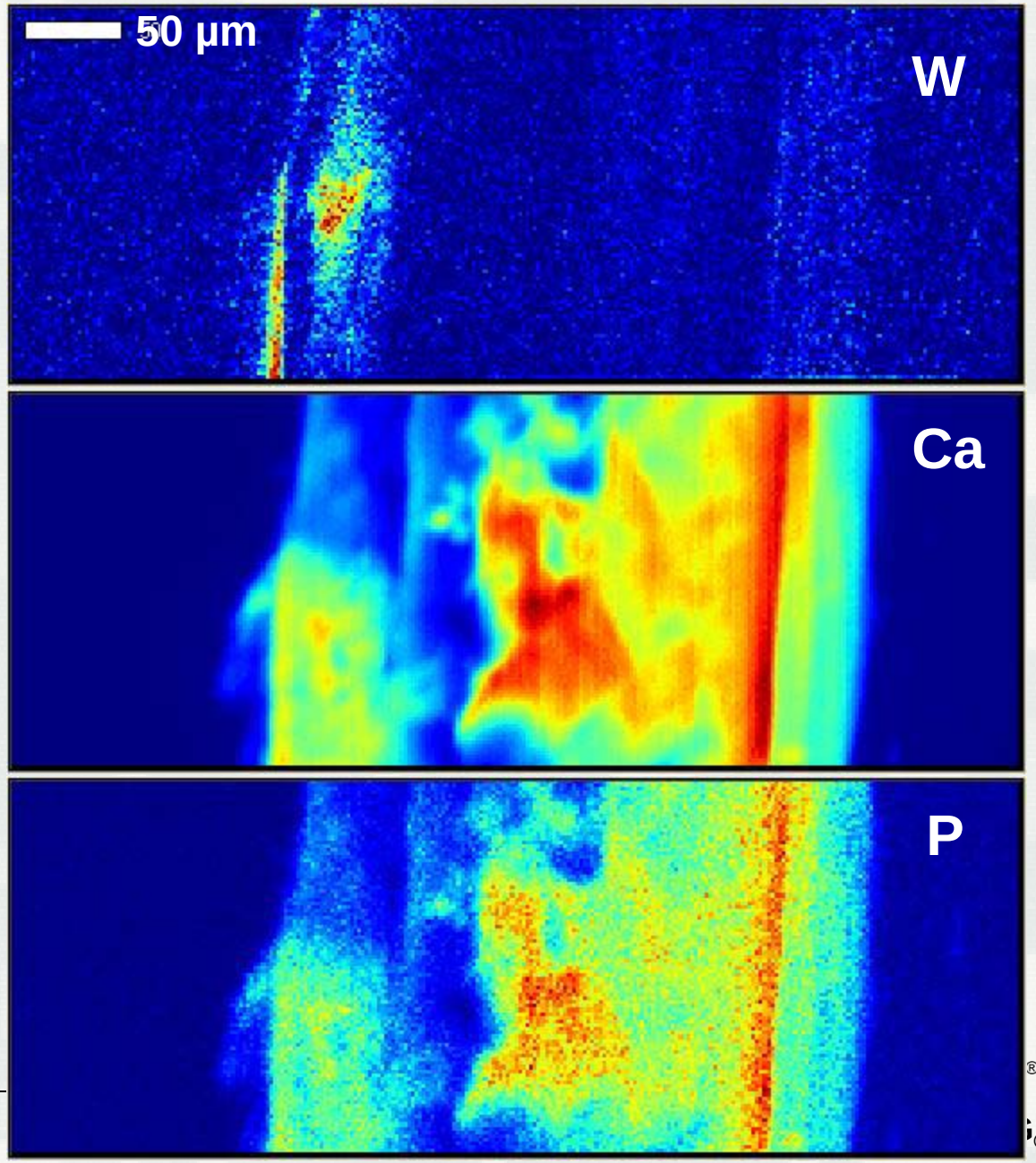
<u>Steady State</u>:
Body: 14 days
Hepatopancreas: 23 days
BAF: 0.09

Dermal Uptake of W in Gastropods

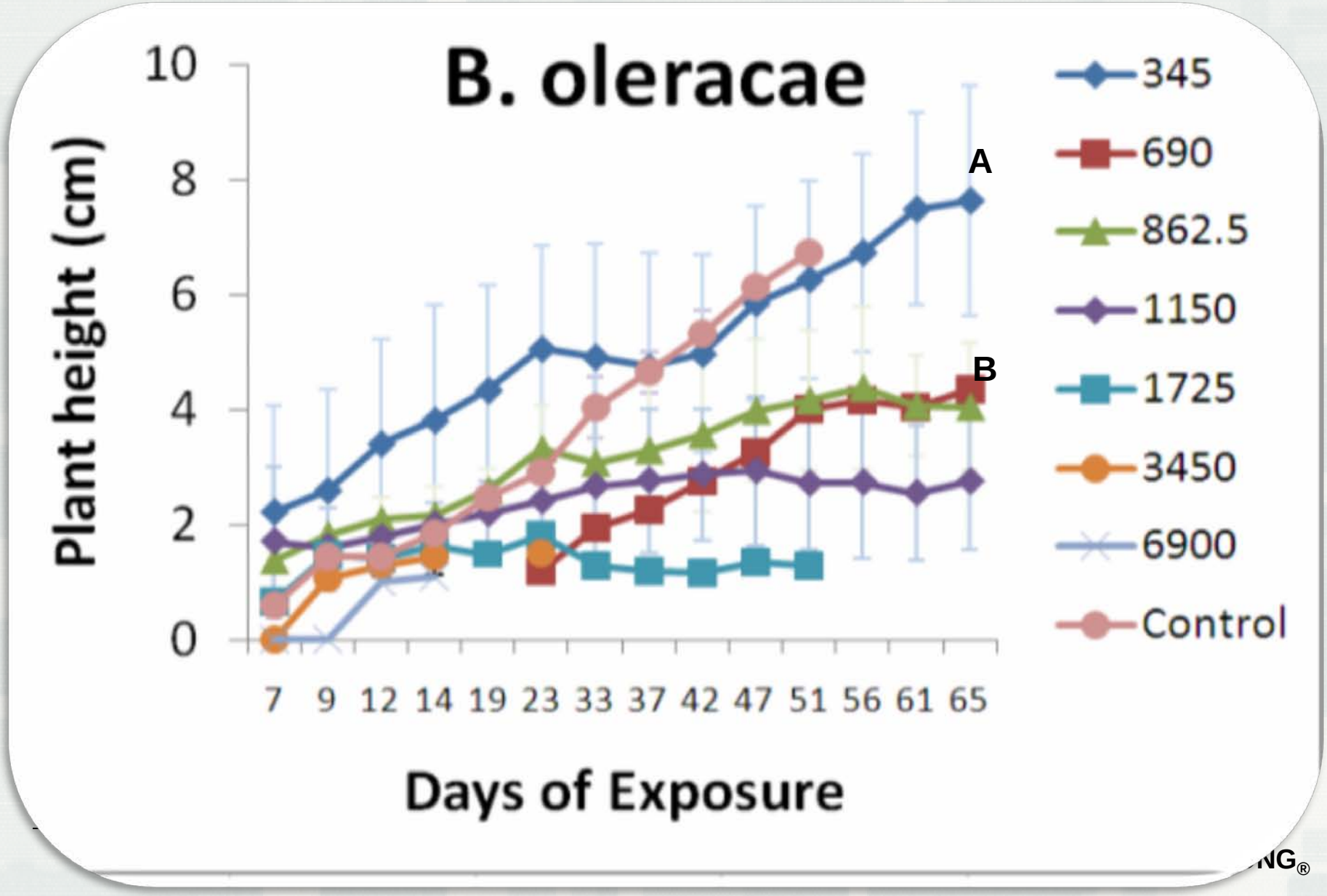
Snail Exposed to W

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 ± 34) mg/kg soil

Rates

Hepatopancreas

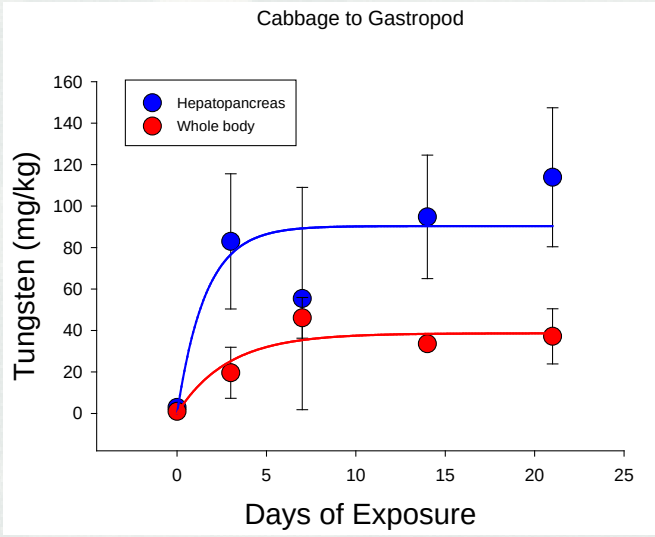
- Uptake (k_u): 0.23 ± 23 g/g/d (p=0.40)
- Elimination (k_e): 0.63 ± 0.68 1/t (p=0.43)
- Steady state: 5-days, 85.9 mg/kg
- BAF = 0.36

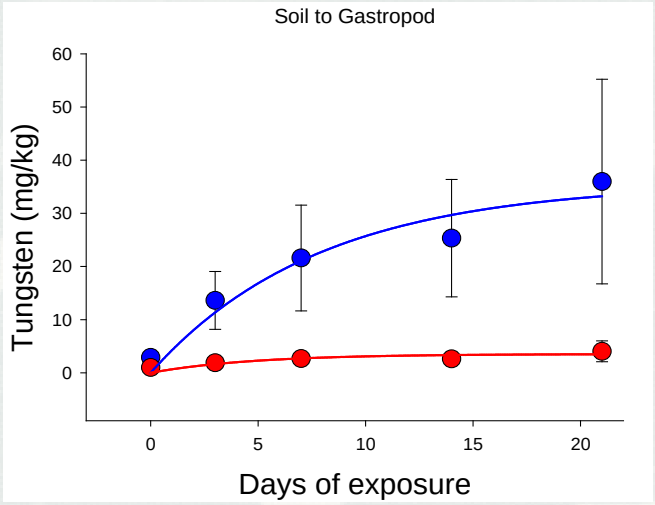
Body

- Uptake (k_u): 0.05 ± 0.03 g/g/d (p=0.15)
- Elimination (k_e): 0.35 ± 0.21 1/t (p=0.19)
- Steady state: 9-days, 36.7 mg/kg
- BAF = 0.15

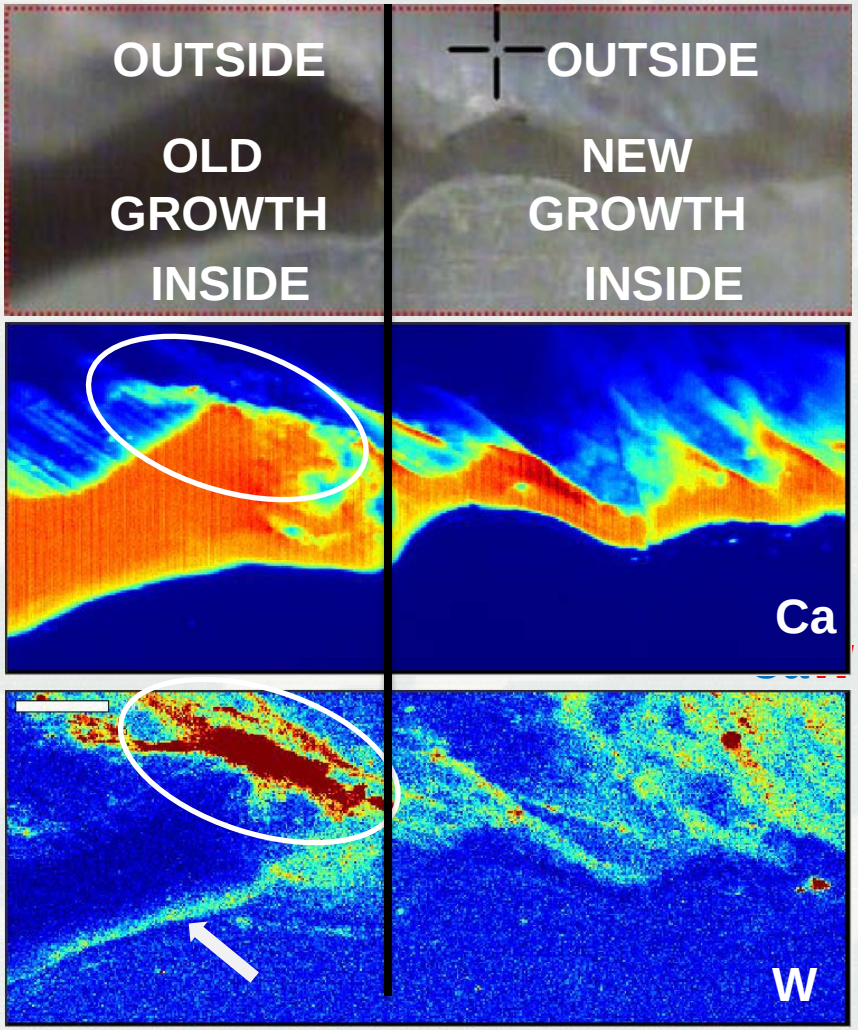
Body/liver = 0.43

- 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

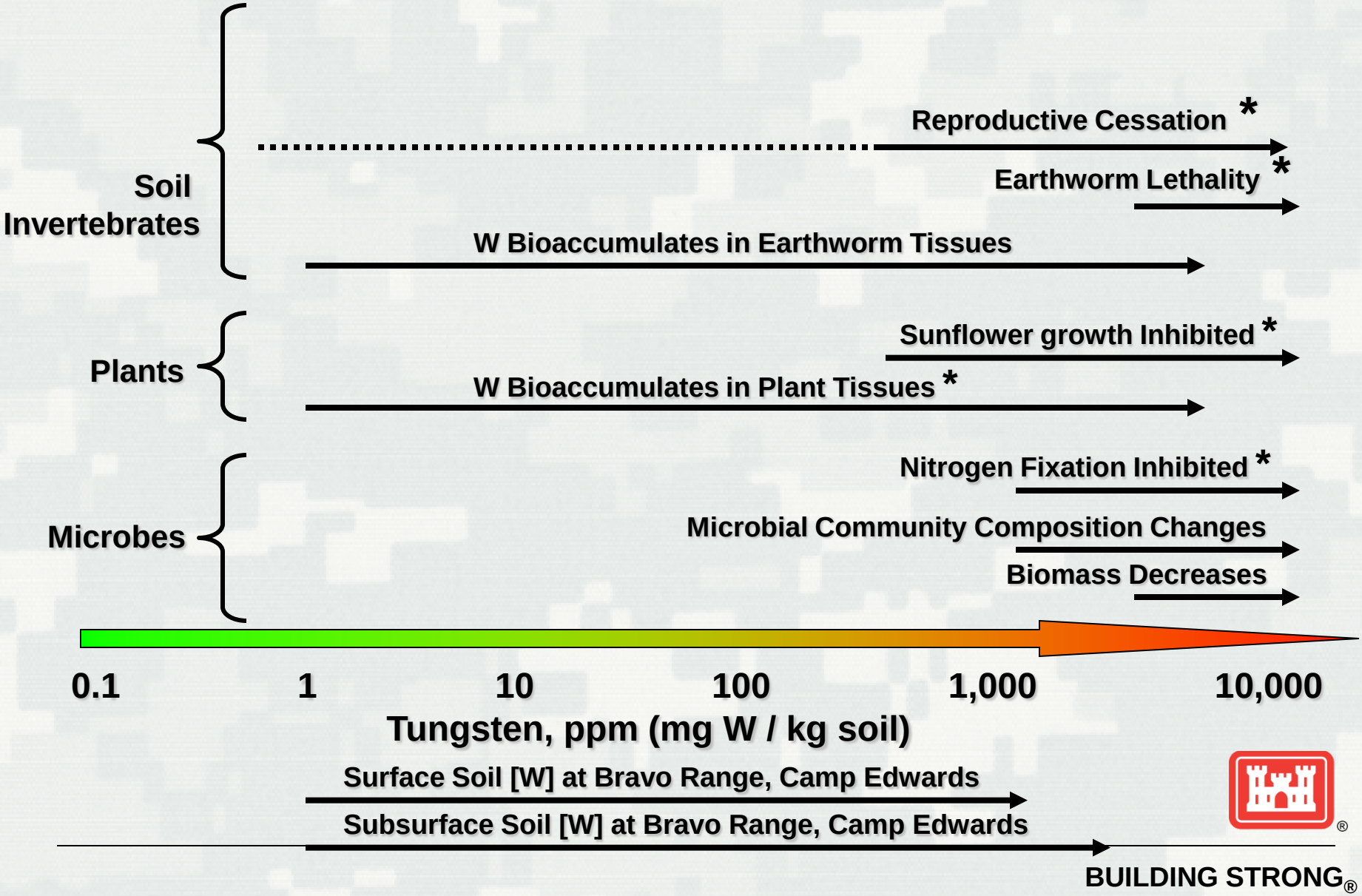
W clearly on the inside of the shell

Hot spot

ICP-MS:

5.7 vs. < 0.1 mg/kg

Tungsten Ecotoxicity: Fate & Effects



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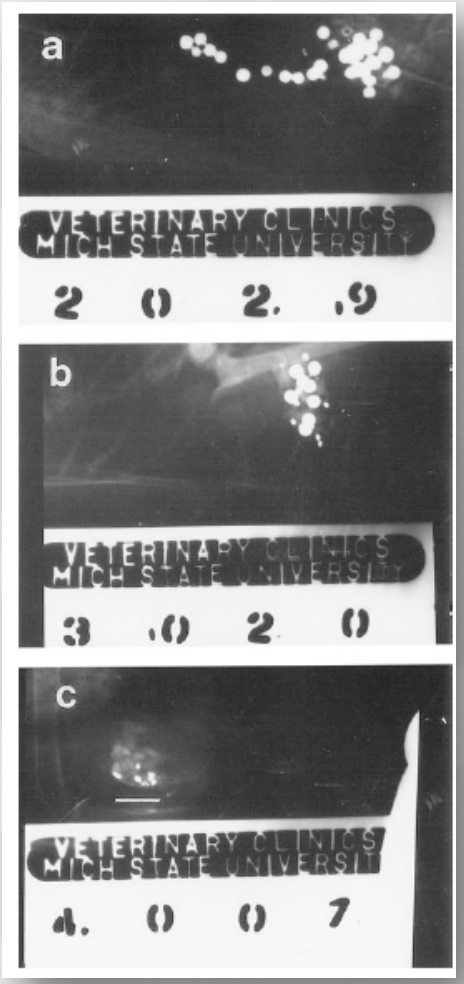
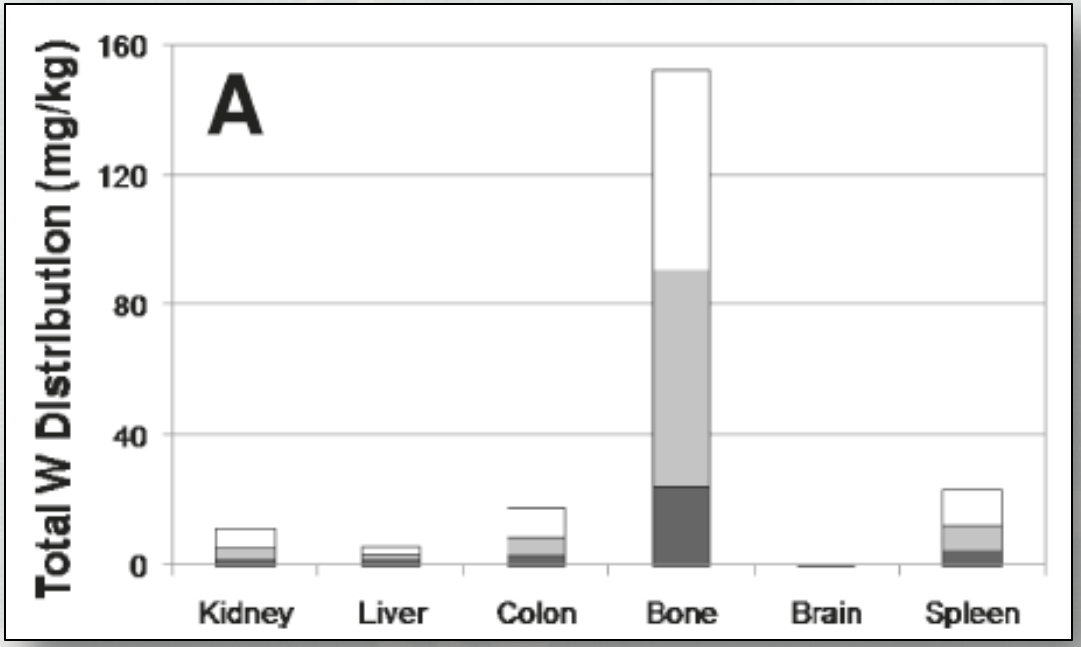
Tissue Distribution of W Uptake in Higher Organisms



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

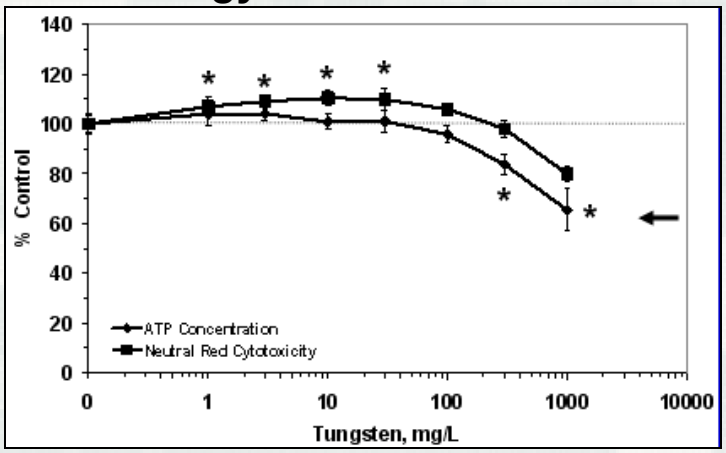
Uptake

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

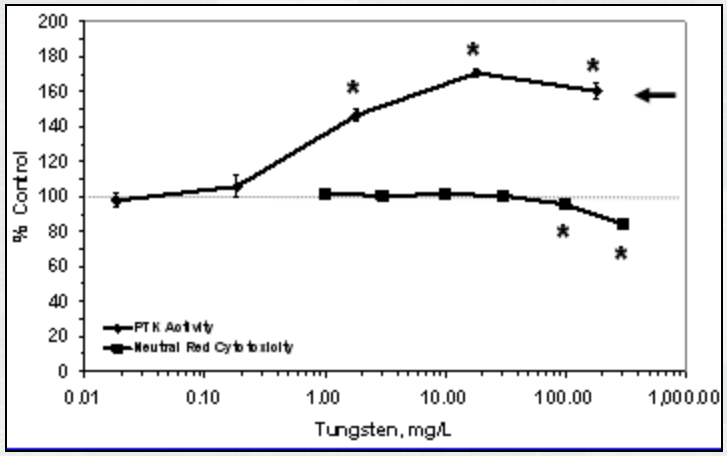
[a] Analyzed by ICP-MS

[b] Analyzed by SEC-ICP-MS

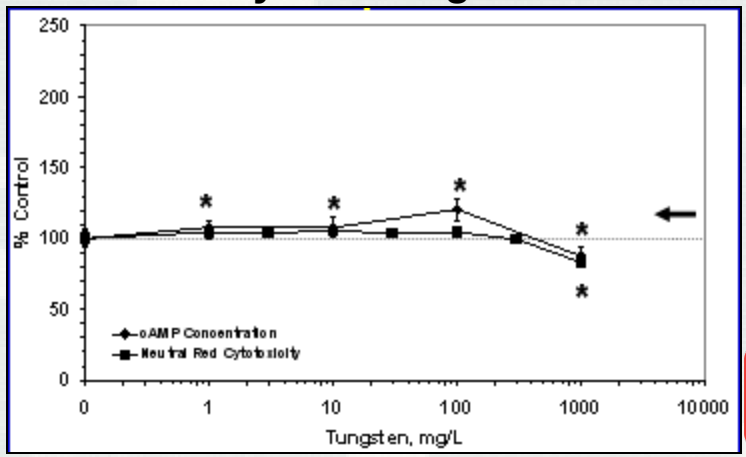
Energy Production: ATP



Cell Signaling: Tyrosine Kinase



Secondary Messengers: cAMP



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Toxicogenomic Effects of Tungsten on Rat Hepatocytes

1,822 Up-Regulated genes

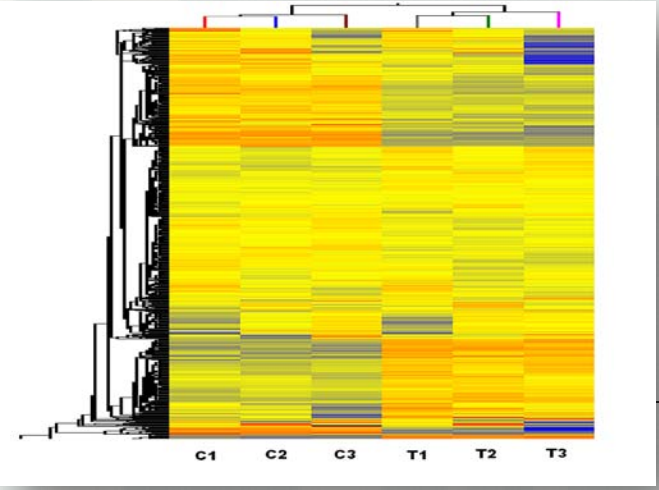
Major pathways affected:

- 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

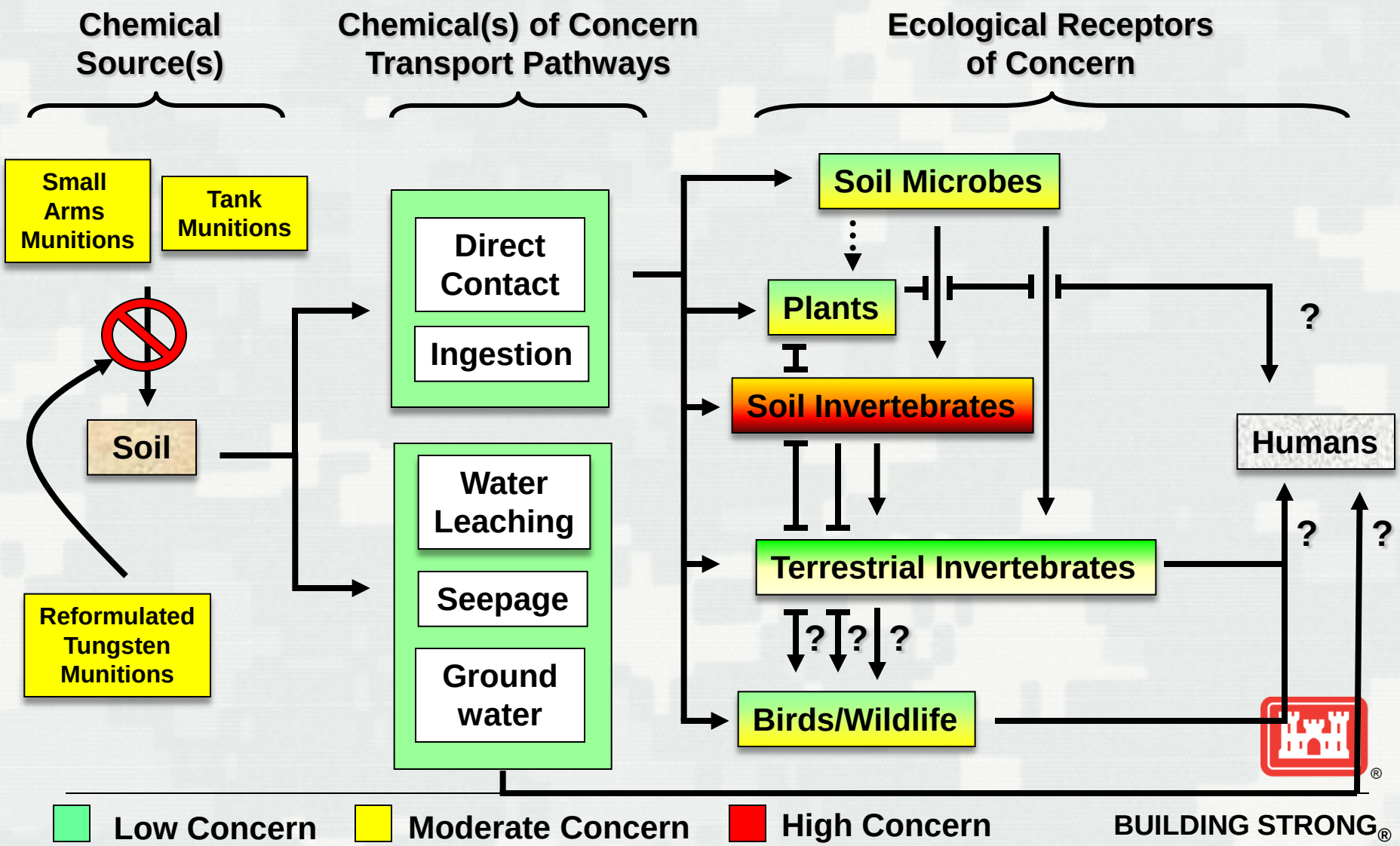
Invertebrates:

- 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



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**

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