

CONSIDERATIONS FOR SOIL SILENIUM GUIDELINES AND RESULTS OF INITIAL TOXICITY TESTING

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OVERVIEW

- **Background**
 - Distribution, uses, basic chemistry
- **Selenium speciation and thermodynamics**
- **Selenium toxicity**
 - Accumulator & non-accumulator species
- **Soil Guidelines**
- **Initial plant toxicity testing**
 - Role of sulfate, hormesis, results
- **Discussion**



SELENIUM DISTRIBUTION

- 69th most abundant element (*ATSRD, 2003*)
- Natural soil concentrations are largely dependant on weathering of parent materials
- Worldwide soil distribution varies
- Soil concentrations range up to 4.7 mg/kg in Canada (*CCME, 2009*) and 2.3 mg/kg in Alberta (*Penny, 2003*)



SOIL SELENIUM DISTRIBUTION IN THE UNITED STATES

Se (ppm, AA)

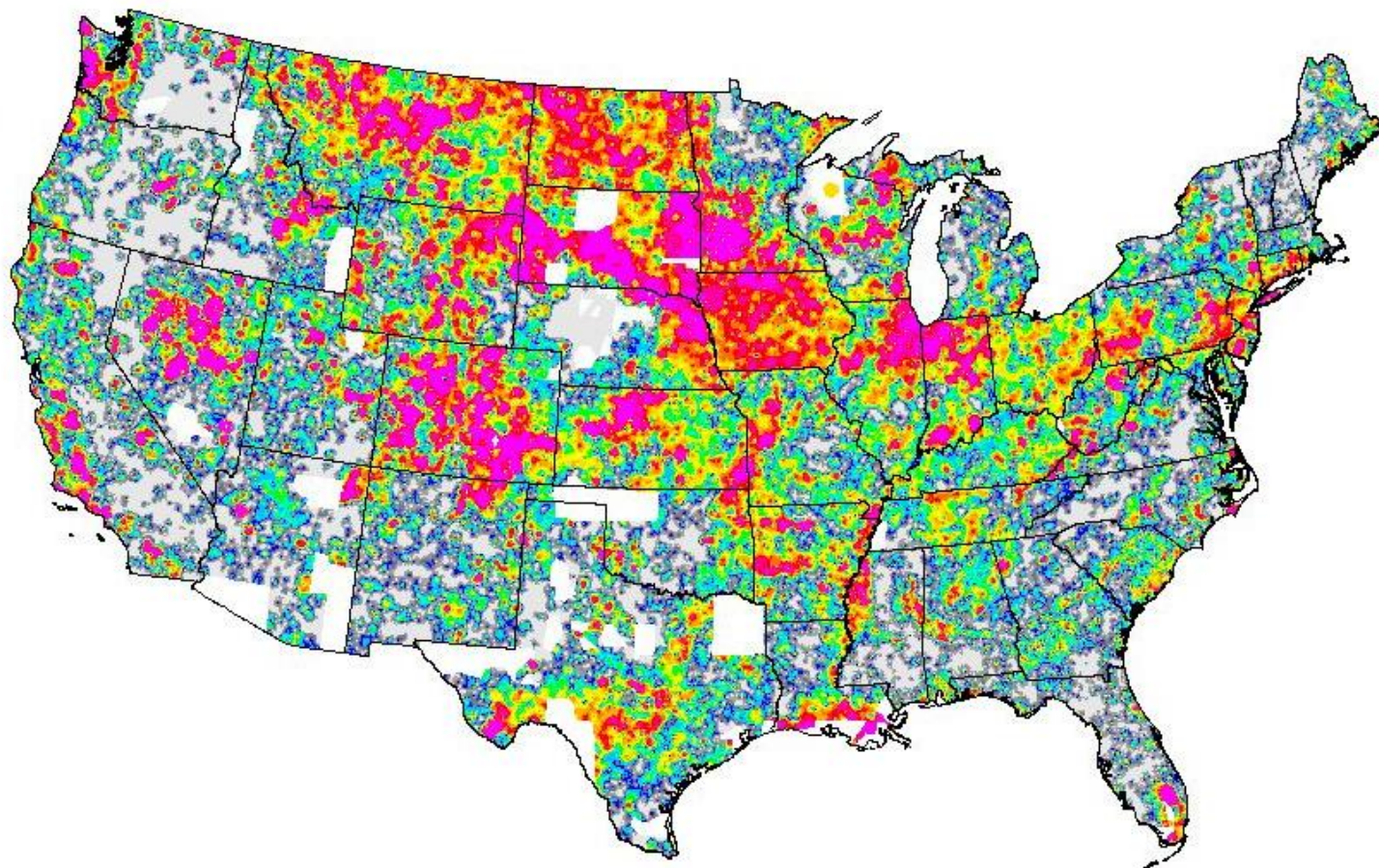
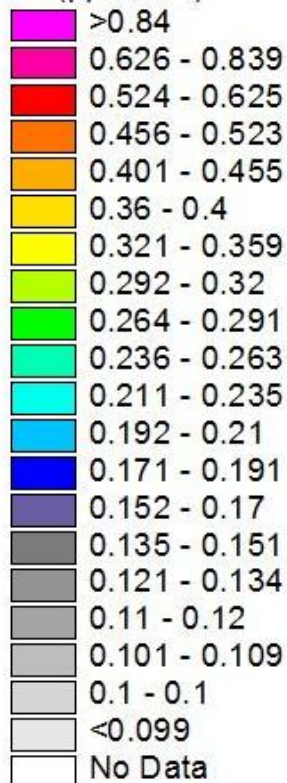


Image Source: USGS, 2012. Sampling density = 1/289 km²

25th% = 0.1 ppm; Median = 0.2 ppm; 75th% = 0.5 ppm; Max: 223 ppm



USES AND ANTHROPOGENIC SOURCES

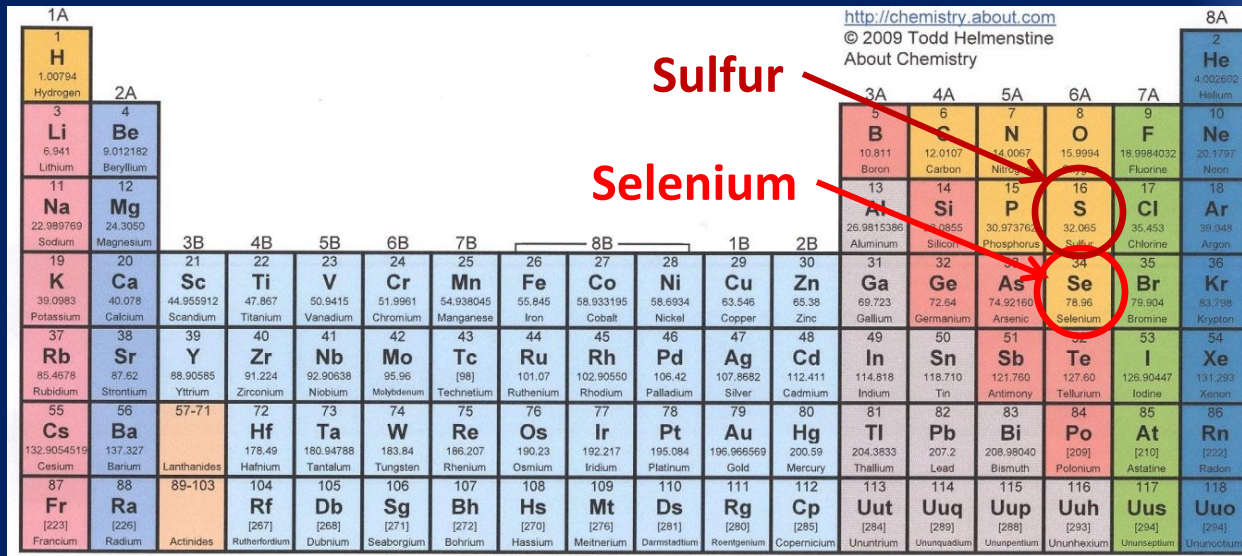
- Electronics, glass manufacturing, medicine, pesticides, pigments, shampoo, photoreceptors, etc. *(ATSDR, 2003)*
- In 2003, Japan was the largest Se producer, followed by Canada *(CCME, 2009)*
- Primary source of Canadian Se is from smelting in Ontario *(CCME, 2009)*



SELENIUM CHEMISTRY

- Metalloid located between sulfur & tellurium on Periodic Table
- Similar in resemblance & properties to sulfur

<http://chemistry.about.com>
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About Chemistry



1A	2A	3A	4A	5A	6A	7A	8A
1 H 1.00794 Hydrogen	4 Be 9.012182 Beryllium	5 B 10.811 Boron	6 C 12.0107 Carbon	7 N 14.0067 Nitrogen	8 O 15.9994 Oxygen	9 F 18.9984032 Fluorine	10 Ne 20.1797 Neon
3 Li 6.941 Lithium	12 Mg 24.3050 Magnesium	13 Al 26.9815386 Aluminum	14 Si 28.0855 Silicon	15 P 30.973762 Phosphorus	16 S 32.065 Sulfur	17 Cl 35.453 Chlorine	18 Ar 39.948 Argon
11 Na 22.989769 Sodium	20 Ca 40.078 Calcium	21 Sc 44.955912 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938045 Manganese	26 Fe 55.845 Iron
19 K 39.0983 Potassium	38 Sr 87.62 Strontium	39 Y 88.90585 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.90638 Niobium	42 Mo 95.96 Molybdenum	43 Tc [98] Technetium	44 Ru 101.07 Ruthenium
37 Rb 85.4678 Rubidium	86 Kr 83.798 Krypton	55 Cs 132.9054519 Cesium	56 Ba 137.327 Barium	57-71 Lanthanides	72 Hf 178.49 Hafnium	73 Ta 180.94788 Tantalum	74 W 183.84 Tungsten
87 Fr [223] Francium	88 Ra [226] Radium	89-103 Actinides	104 Rf [261] Rutherfordium	105 Db [262] Dubnium	106 Sg [266] Seaborgium	107 Bh [264] Bohrium	108 Hs [277] Hassium
101 La 138.90547 Lanthanum	102 Ce 140.116 Cerium	103 Pr 140.90765 Praseodymium	104 Nd 144.242 Neodymium	105 Pm [145] Promethium	106 Sm 150.36 Samarium	107 Eu 151.964 Europium	108 Gd 157.25 Gadolinium
89 Ac [227] Actinium	90 Th 232.03806 Thorium	91 Pa 231.03588 Protactinium	92 U 238.02891 Uranium	93 Np [237] Neptunium	94 Pu [244] Plutonium	95 Am [243] Americium	96 Cm [247] Curium
109 Mt [268] Meitnerium	110 Ds [281] Darmstadtium	111 Rg [280] Roentgenium	112 Cp [285] Copernicium	113 Uut [284] Ununtrium	114 Uuq [289] Ununquadium	115 Uup [288] Ununpentium	116 Uuh [293] Ununhexium
117 Ts [294] Tennessine	118 Og [294] Oganesson	119 Uus [294] Ununseptium	120 Uuo [294] Ununoctium	121 Uut [293] Ununtrium	122 Uuq [293] Ununquadium	123 Uup [293] Ununpentium	124 Uuh [293] Ununhexium
125 Nh [286] Nihonium	126 Fl [289] Flerovium	127 Mc [288] Moscovium	128 Lv [293] Livermorium	129 Ts [293] Tennessine	130 Og [294] Oganesson	131 Uhs [294] Ununseptium	132 Uuo [294] Ununoctium
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SELENIUM CHEMISTRY (CONT')

- **Selenium fate gained attention in 1980s with Kesterson Reservoir in California**
- **Complex Biogeochemistry & Thermodynamics**
 - **Other minerals, microbiological activity, volatilization, Eh, pH, etc.**
- **Four common valence forms**

FOUR COMMON SELENIUM SPECIES

Selenide
 Se^{2-}

[-2]

Low pH, low Eh, relatively insoluble

Elemental
 Se^0

[0]

Not common in natural environments, relatively insoluble

Selenite
 SeO_3

[+4]

Neutral pH, well-drained soils, can be soluble, found in water. More reduced than selenate

Selenate
 SeO_4

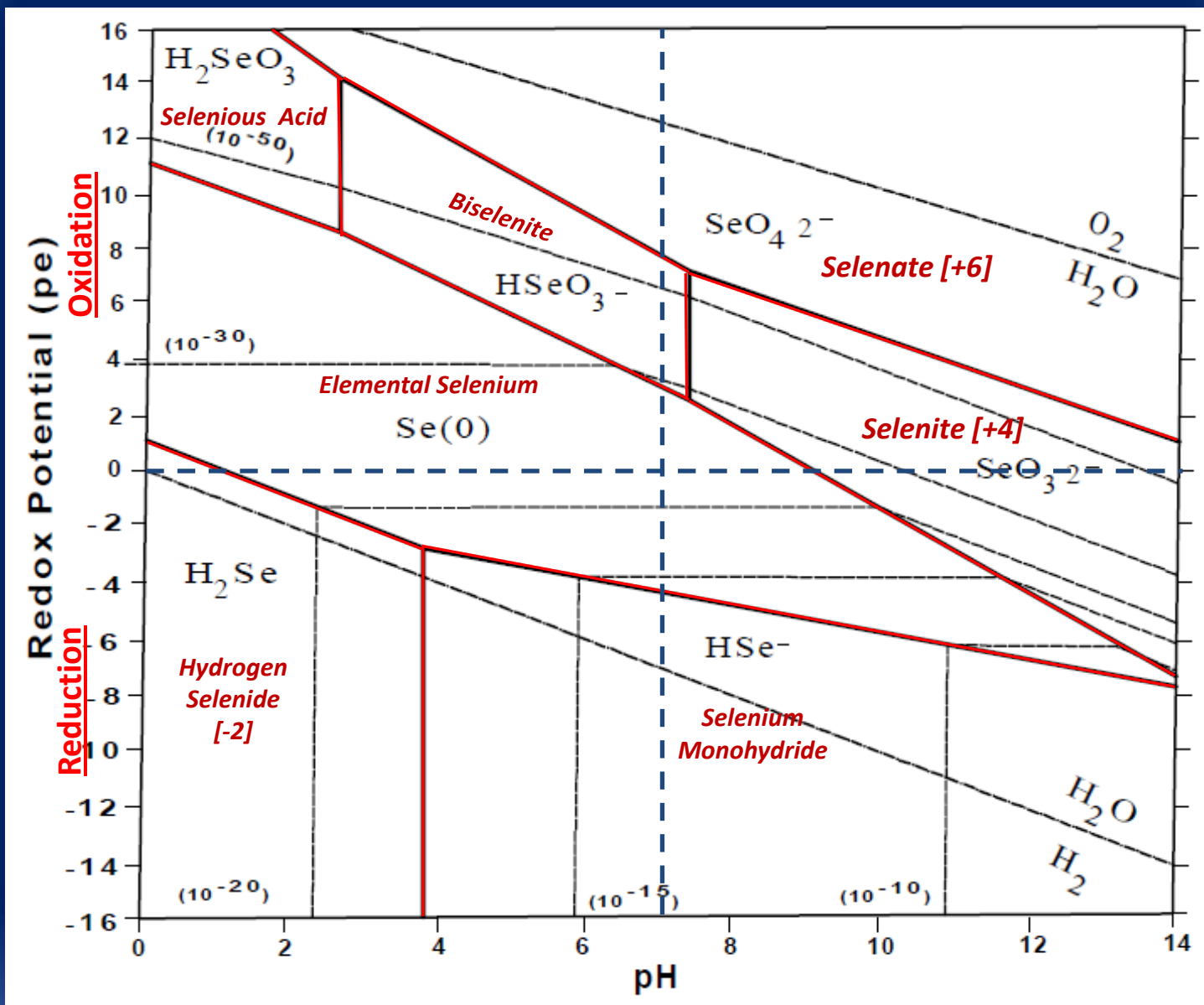
[+6]

Alkaline soils, highly soluble, found in water. Highest oxidation state

THERMODYNAMIC PREDICTIONS OF SELENIUM SPECIES

black, dashed lines represent contours of equal selenide activities

$$pe = Eh(mV)/59.2$$



Adapted from Masscheleyn & Patrick (1993)

SELENIUM TOXICITY

- Essential nutrient for animals and humans, *but not for plants*
- Essential & Toxic concentrations are quite close for humans and animals
 - “the essential toxin” (*Stolz et al, 2002*)
 - “double-edged sword element” (*Fernandez-Martinez & Charlet, 2009*)

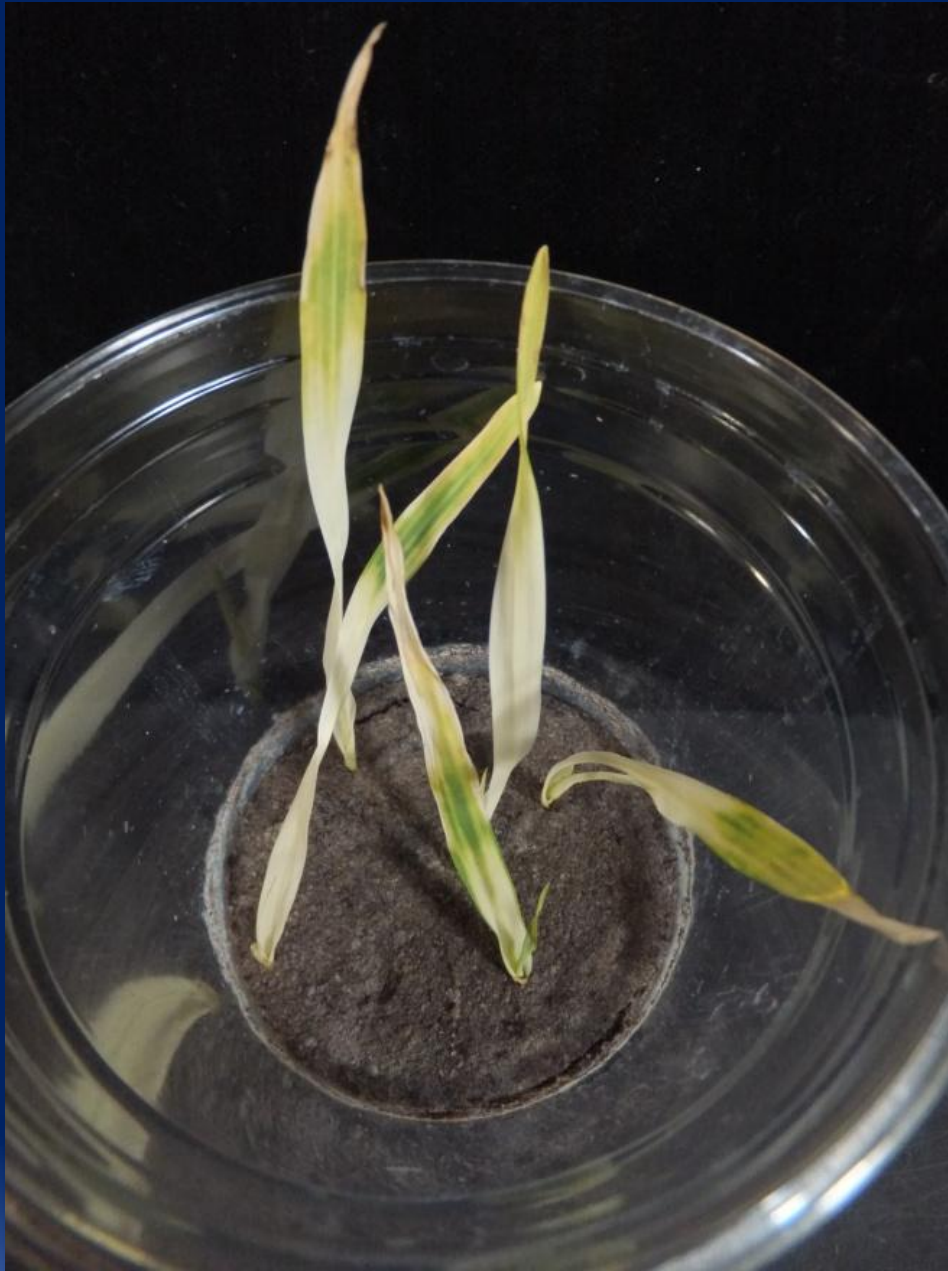


PLANT SELENIUM TOXICITY

- Arid and semiarid regions
- Plant toxicity is related to valence form
 - Selenate [+6] is generally most toxic form to plants, followed by Selenite [+4]
(ATSRD, 2003)
- White chlorosis



SELENIUM PLANT TOXICITY (CONT')



**White Chlorosis in
Hordeum vulgare (barley)**

grown in artificial soil spiked
with 15 mg/kg selenium (as
selenate) without added
sulphate

SELENATE [+6] / SULFATE ANTAGONISM

- Plant selenate uptake can be inhibited by sulfate salinity
 - Similar effect not present with chloride
(Mikkelsen et al, 1988)
 - Effect not present in other valence forms of selenium
(Gupta & Gupta, 2000)



SELENIUM ACCUMULATORS & NON-ACCUMULATORS

- Accumulators will preferentially uptake selenium over sulfur (*Terry et al, 2000*)
- Most species are non-accumulators and will preferentially take up sulfate (*Terry et al, 2000*)
- Non-accumulators have an increased sensitivity to selenium



CURRENT SOIL SELENIUM GUIDELINES

- CCME & Alberta Tier 1 Guideline is 1 mg/kg
 - Natural concentrations up to 4.7 mg/kg in Canada
- Primarily based on two studies
 - Singh & Singh (1979) and Carlson et al (1991)
 - Based on Selenate [+6]
 - LOEC approach



PRELIMINARY PLANT TOXICITY TESTING

- Two objectives:
 - To quantify selenate [+6] toxicity
 - To quantify the selenate-sulfate relationship
- Endpoints measured and test doses are not believed to have been assessed in previous research



METHODOLOGY & RESEARCH DESIGN

- Generally followed Environment Canada's plant toxicity standardized methodology
- Artificial soil
 - 8 concentrations of selenate, 4 sulfate concentrations
 - 4 – 5 replicates
 - *Medicago sativa* (alfalfa)
 - Grown in growth chambers at AITF
- EC₂₅ values for measured endpoints, based on threshold / point of departure approach



RESULTS – 0 mg/kg SULFATE

- Observable effects
- White chlorosis
- 100% mortality in 15 mg/kg Se

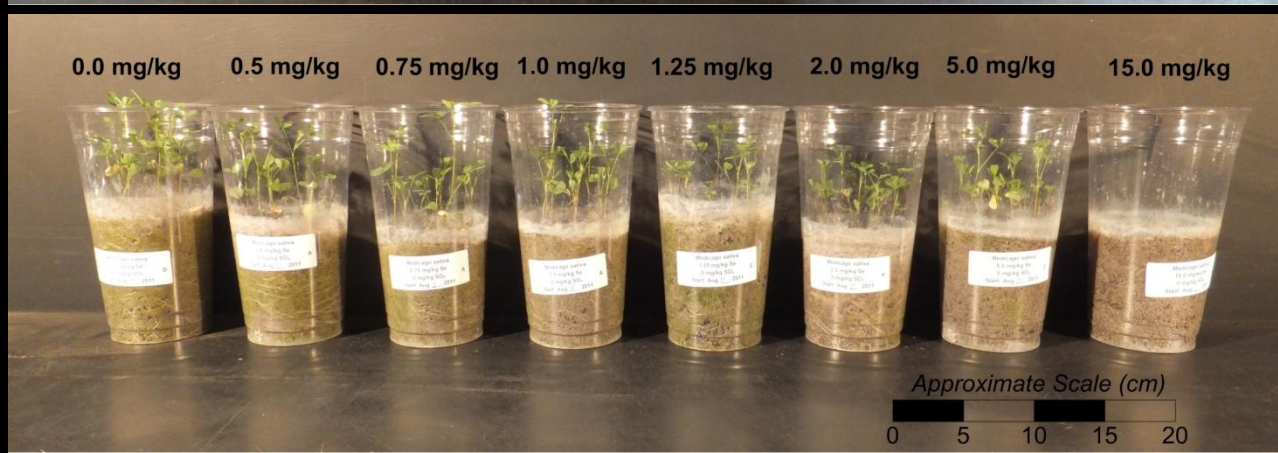


15 mg/kg Se vessel and 0 mg/kg SO_4

0 mg/kg SO₄



Note:
No 15 mg/kg
Se due to
100%
mortality





0 mg/kg Se vessel (left) and 15 mg/kg Se vessel (right), both with 0 mg/kg SO_4

BMD/EC VALUES FOR 25% ADVERSE EFFECT

Endpoint	EC ₂₅ (mg/kg)
Root Mass	0.49
Shoot Mass	0.77
Root Length	0.86
Shoot Length	0.53

Current Alberta & CCME guideline is 1 mg/kg



ADDED SULFATE RESULTS (500, 1,500, 3,000 mg/kg)

- Minimal observable effects
- 15 mg/kg Se had good vigor
- Stimulant response



15 mg/kg Se Vessel with 500 mg/kg SO₄



500 mg/kg SO_4



1,500 mg/kg SO_4



3,000 mg/kg SO_4



HORMESIS

- Low dose stimulation, high dose inhibition
- With added sulfate, an apparent hormetic effect was observed (J-Curve)
- Used zero equivalent dose (ZED) approach to assess *(Gaylor et al, 2003)*



HORMESIS

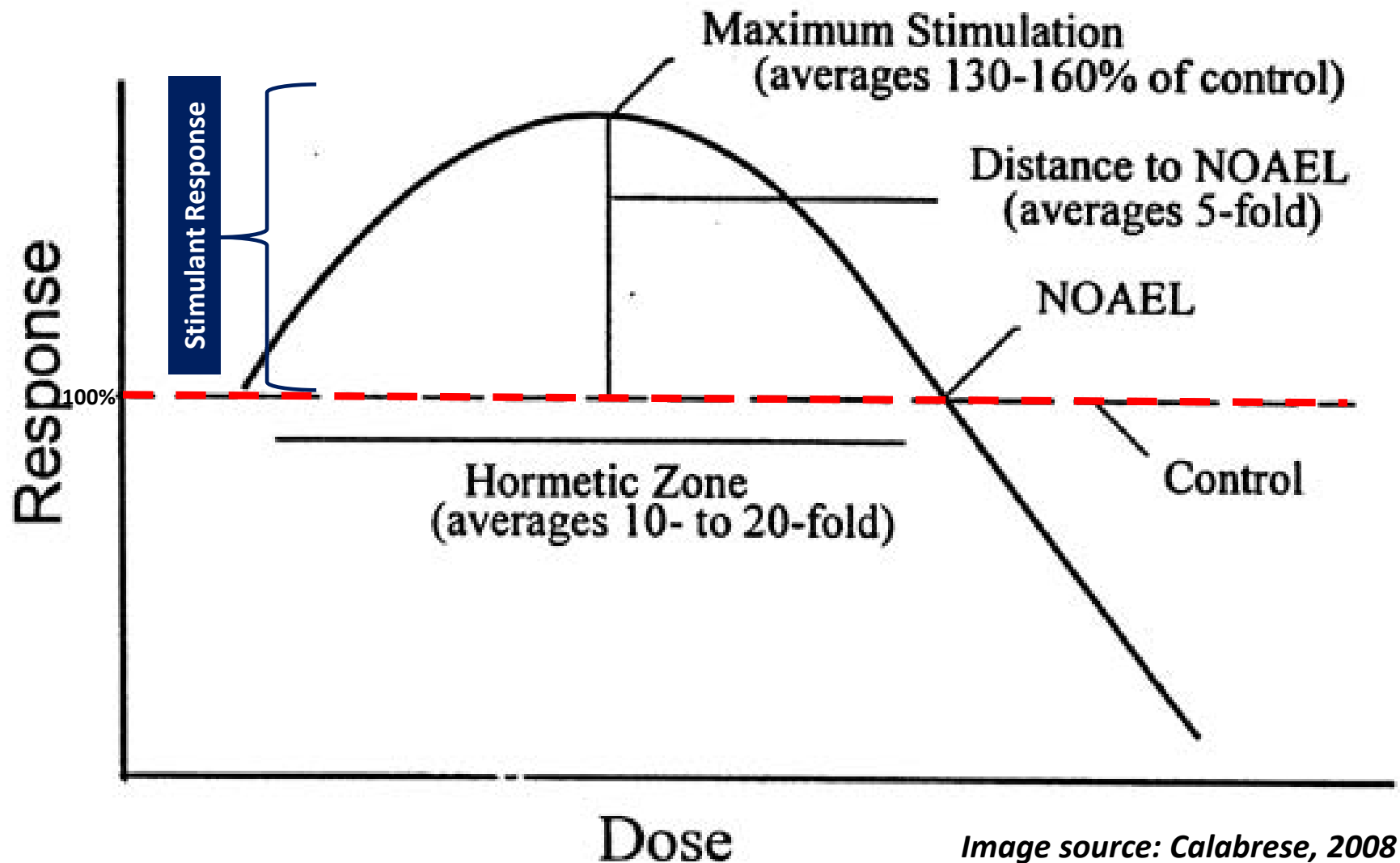


Image source: Calabrese, 2008



ZED VALUES WITH SULFATE

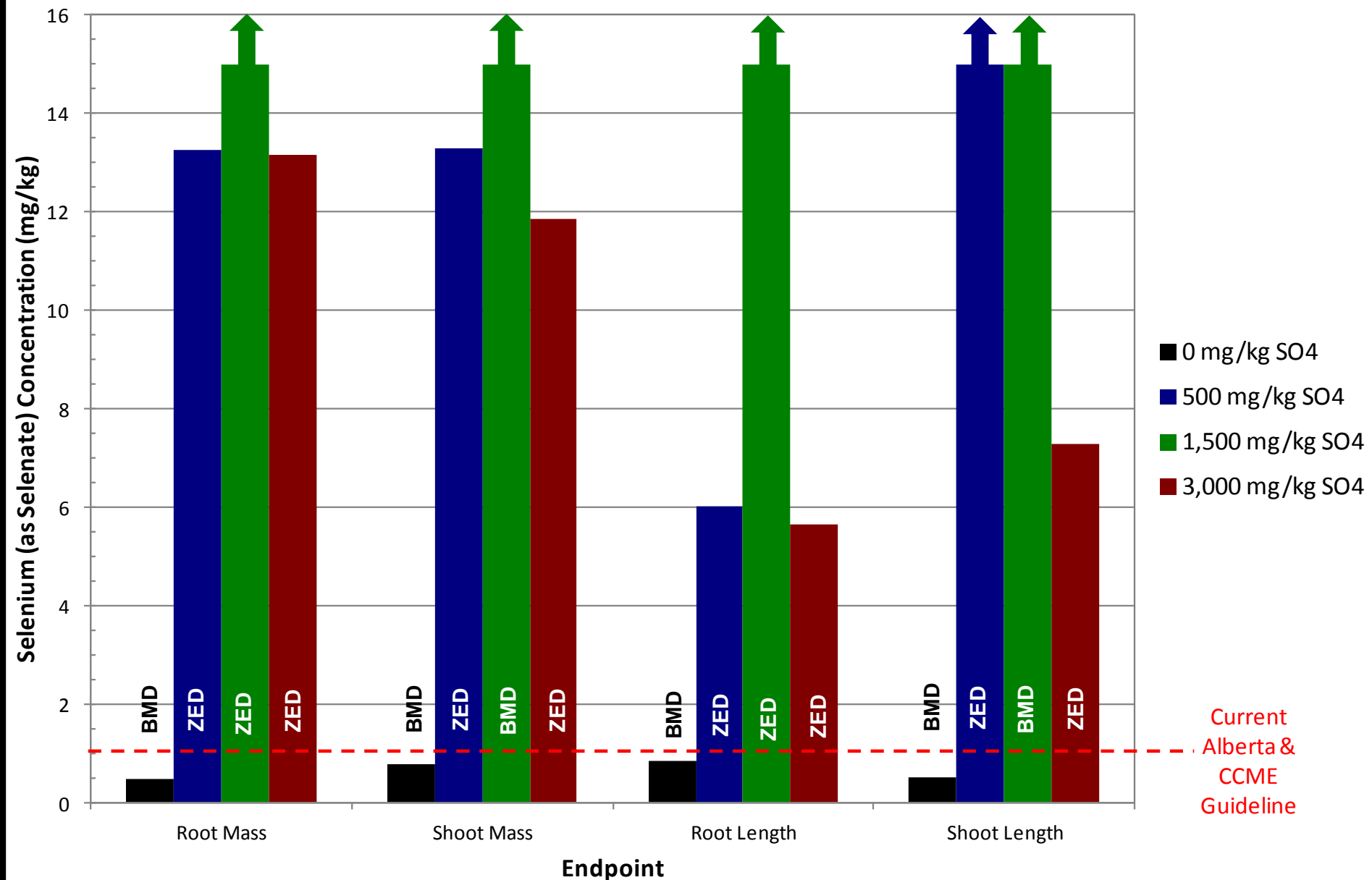
Endpoint	Sulfate Concentration (mg/kg)		
	500	1,500	3,000
Root Mass	13.27	>15	13.17
Shoot Mass	13.29	NA	11.86
Root Length	6.01	>15	5.66
Shoot Length	>15	NA	7.30

Current Alberta & CCME guideline is 1 mg/kg

NA = not assessed with ZED approach and were assessed with Hill model because of lack of apparent hormetic effect



Selenium (as Selenate) Concentrations Posing Negligible Risk to *Medicago sativa*



DISCUSSION

- **Selenium toxicity to plants is based on valence form and biochem/thermodynamics are complex**
- **Se accumulator Vs non-accumulator species/genera**
- **Antagonistic relationship of selenate [+6] and sulfate**
 - **Hormesis**
- **Socio-economic implications of the 1 mg/kg eco-contact guideline**



THANK YOU

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- Farideh Malek
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- Trevor Ahlstrom
Access Labs
- Bob Corbet
Access Labs
- Luanne Patterson
CN Rail
- Kyle Parkyn
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