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Considerations for Soil Selenium Guidelines and Results of Initial Toxicity Testing

Remediation Technologies Symposium

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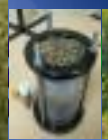
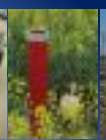









Overview

- 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

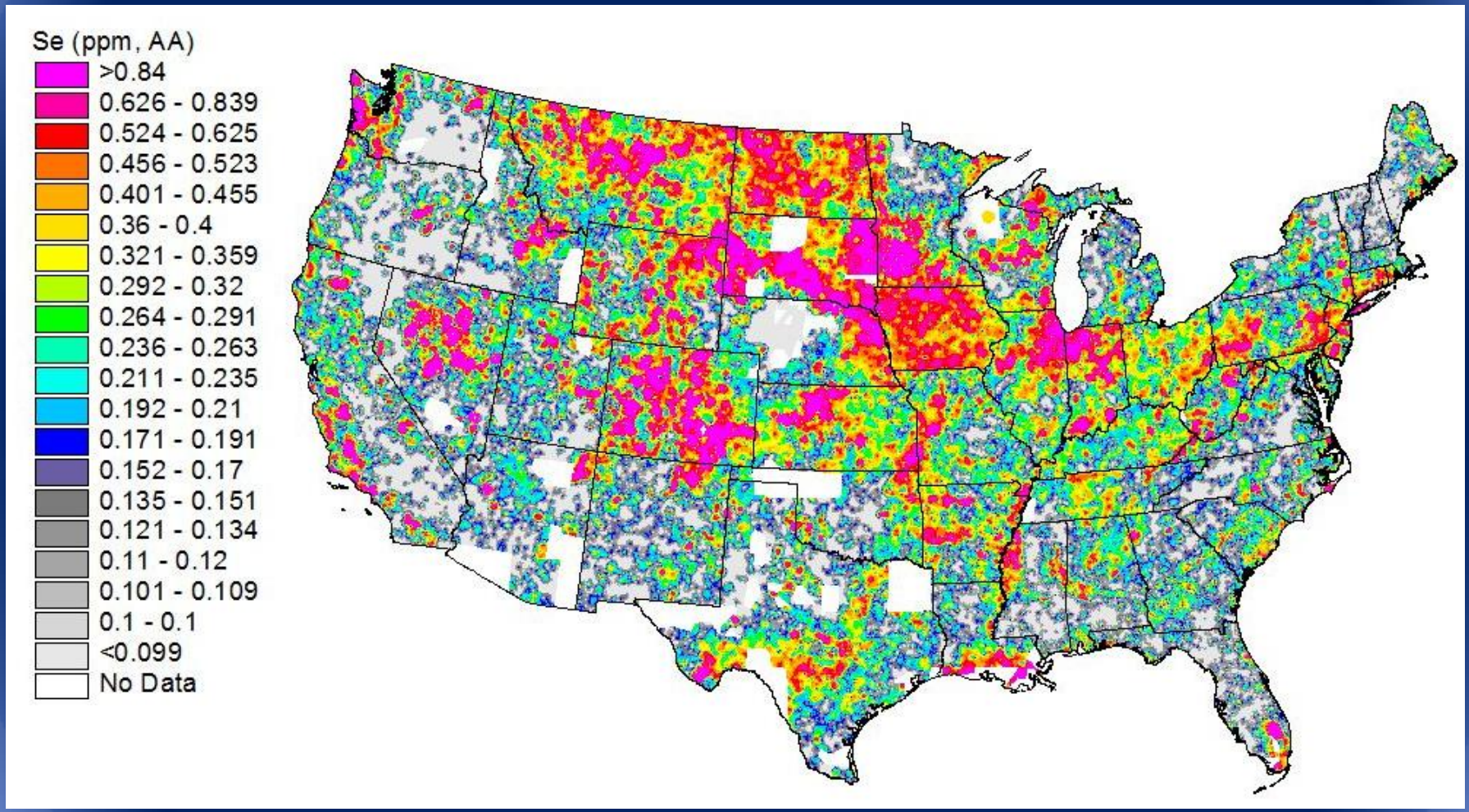


Image Source: USGS, 2012. *Sampling density = 1/289 km²*

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

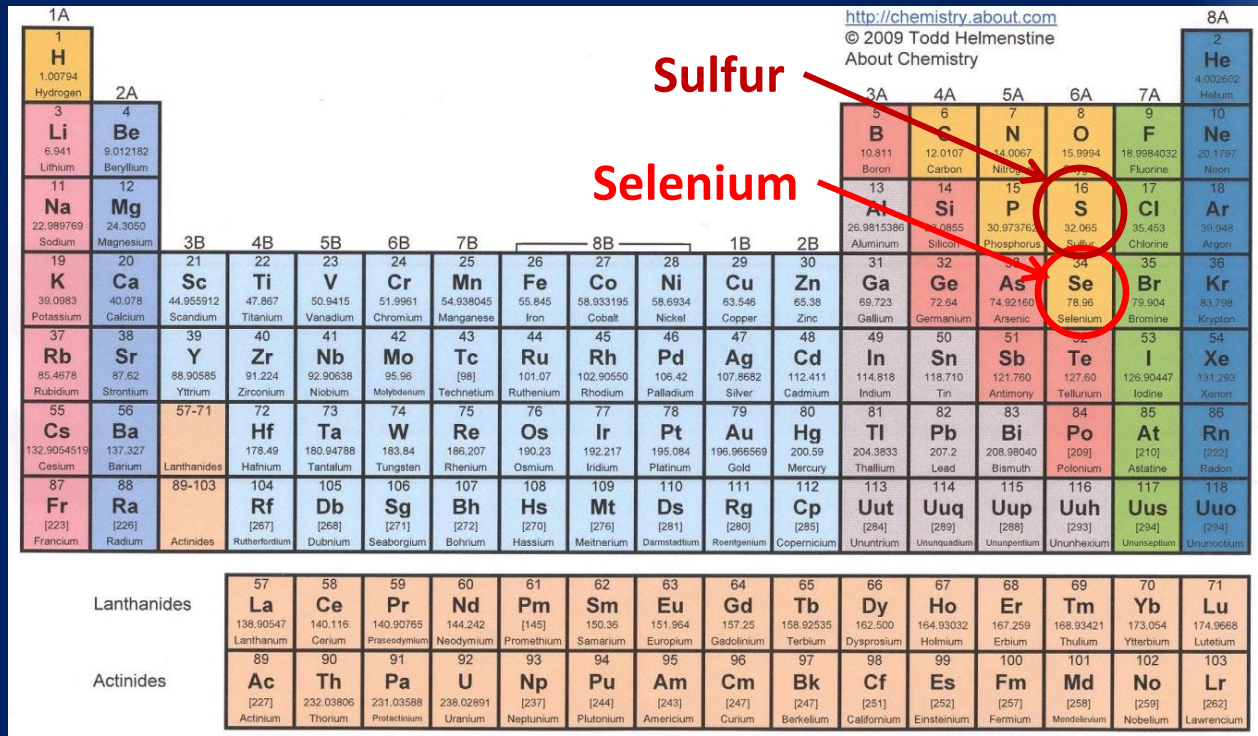


Image source: Helmenstine, 2012

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

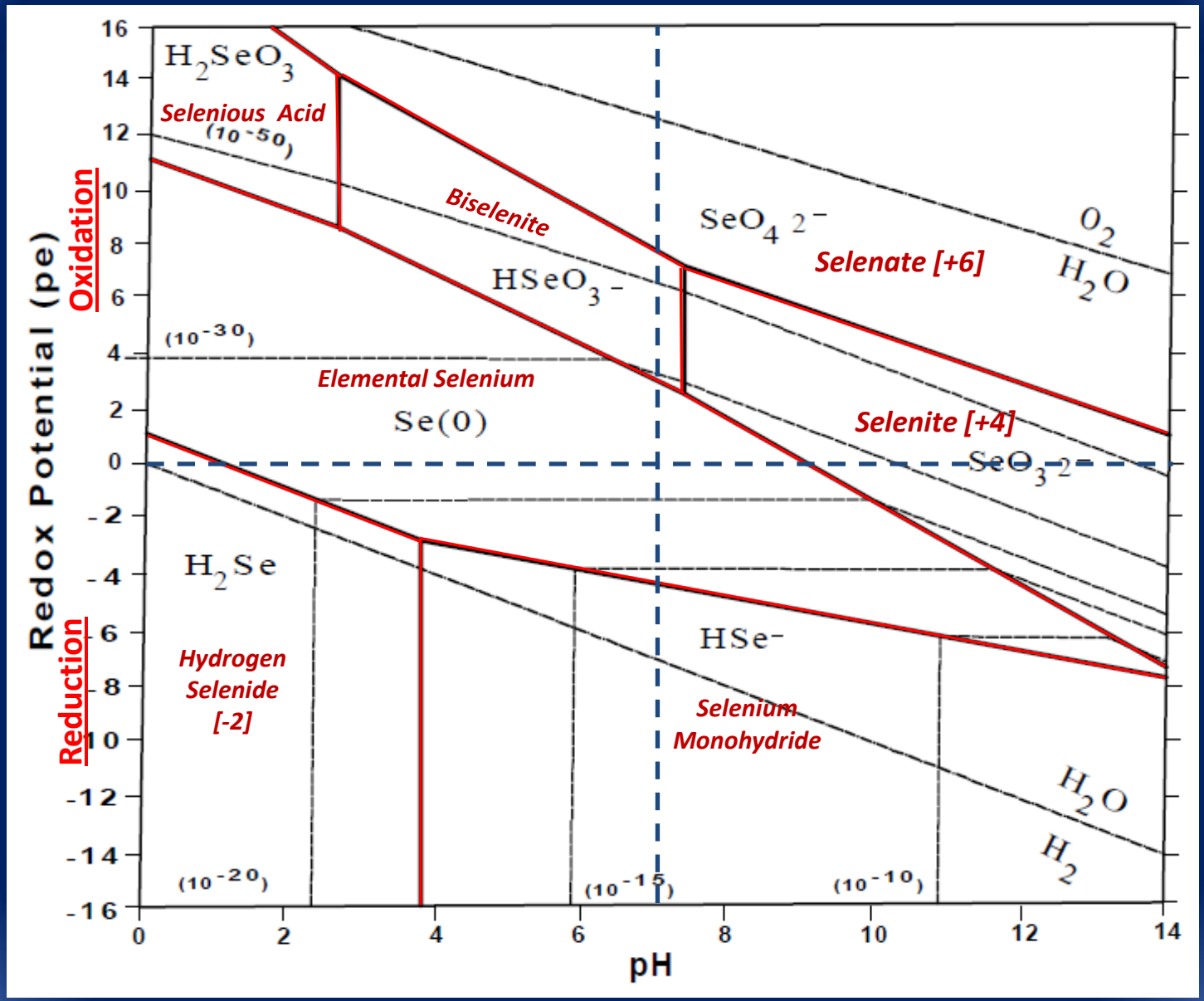
Four Common Selenium Species

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)

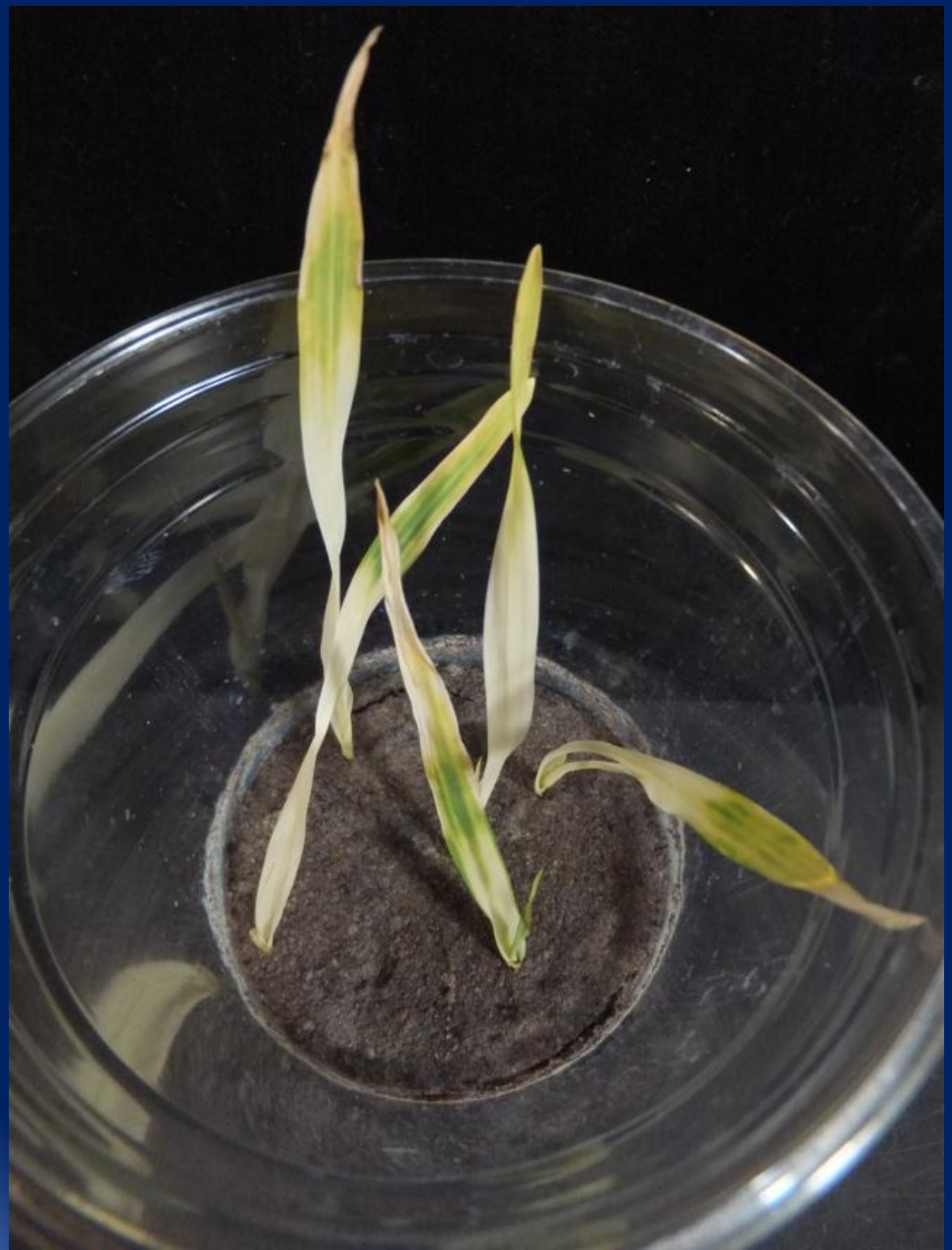
Selenium Toxicity

- 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" *(Fernandex-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

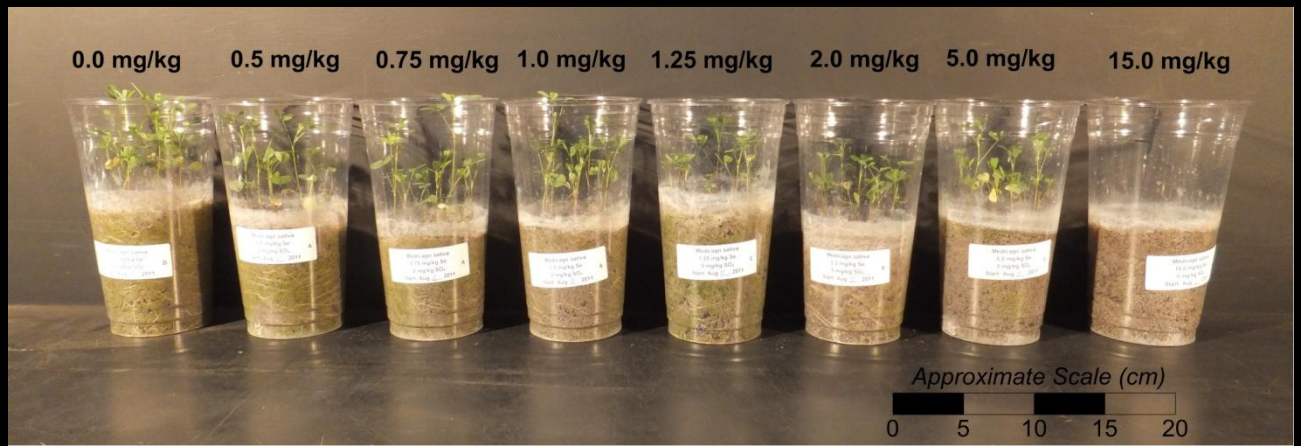
- Generally followed Environment Canada's plant toxicity standardized methodology
- Artificial soil
  - 8 concentrations of selenate, 4 sulfate concentrations
  - 4 – 5 replicates
  - *Medicago sativa* (alfalfa)
  - Grown in growth chambers at AITF
- EC_{25} values for measured endpoints, based on threshold / 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 SO_4



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

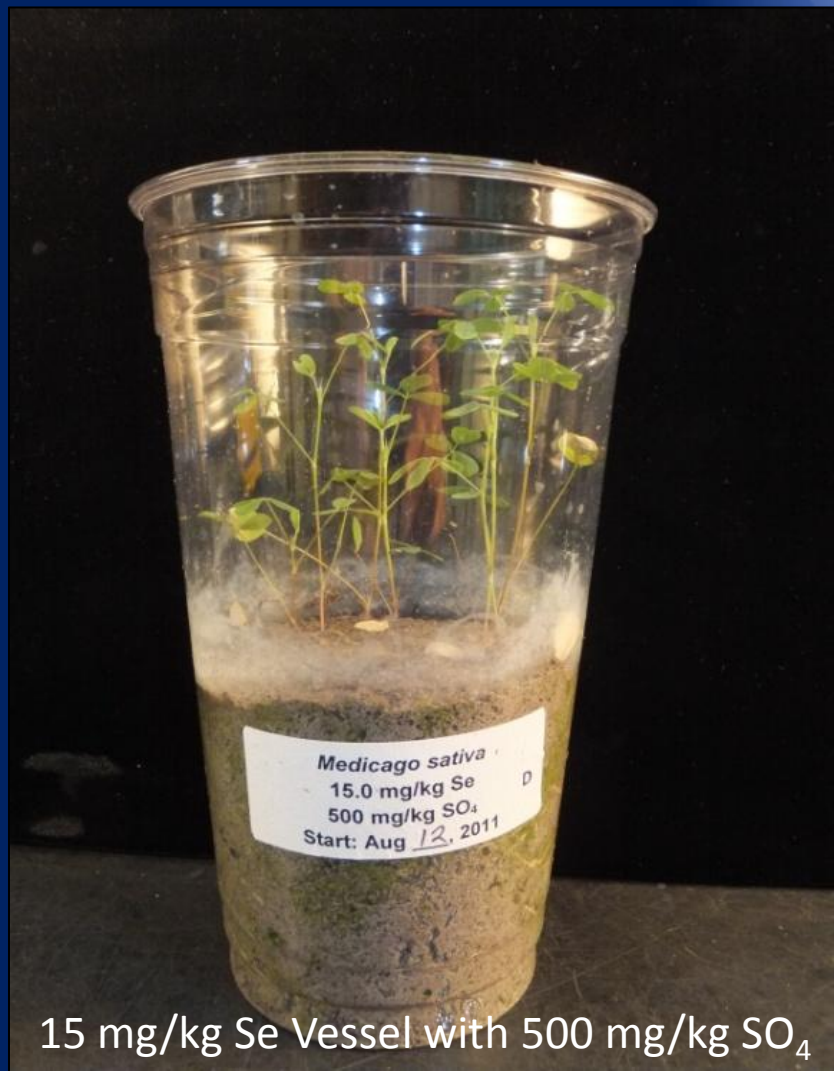
BMD/EC Values for 25% Adverse Effect

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 SO_4

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

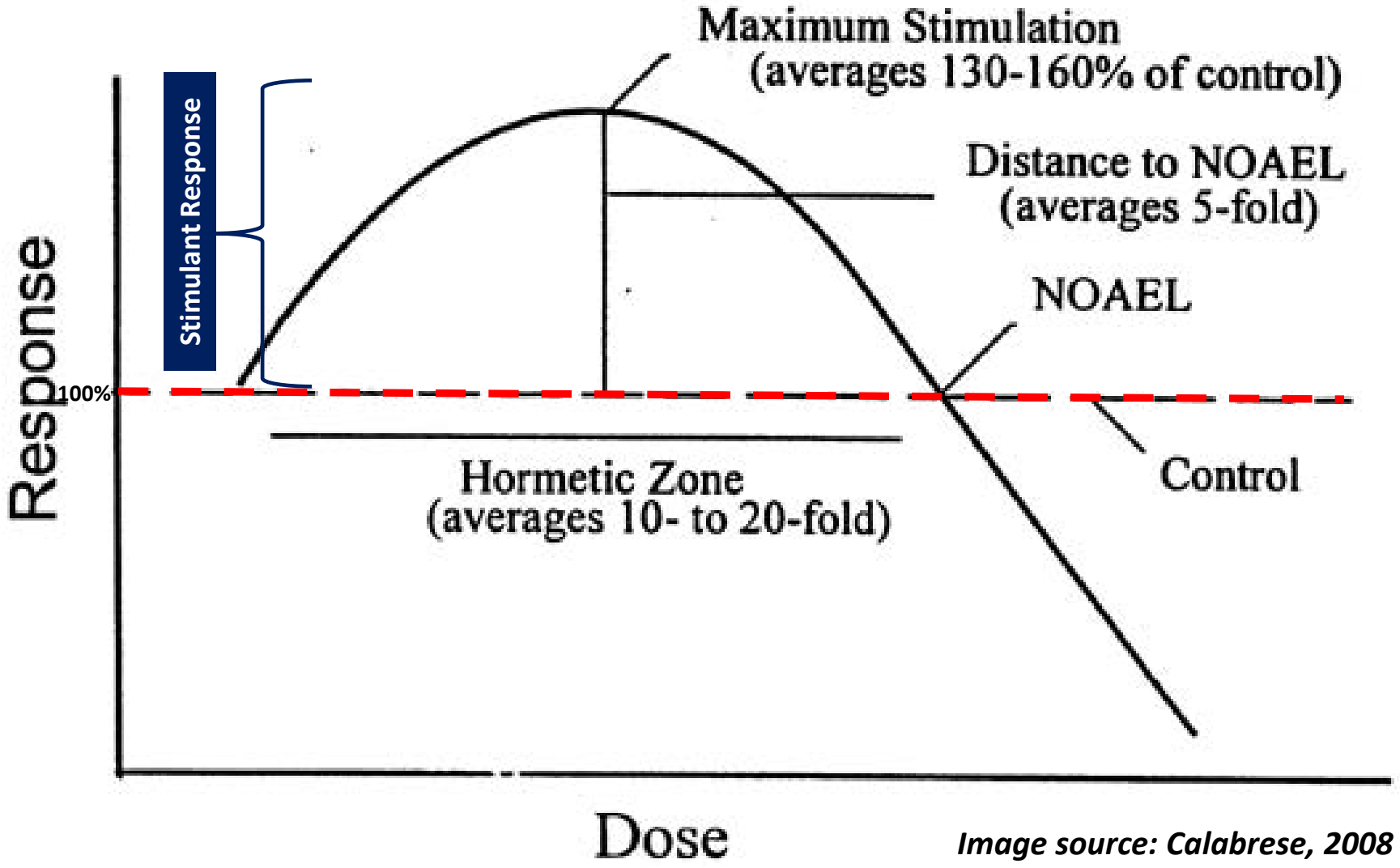


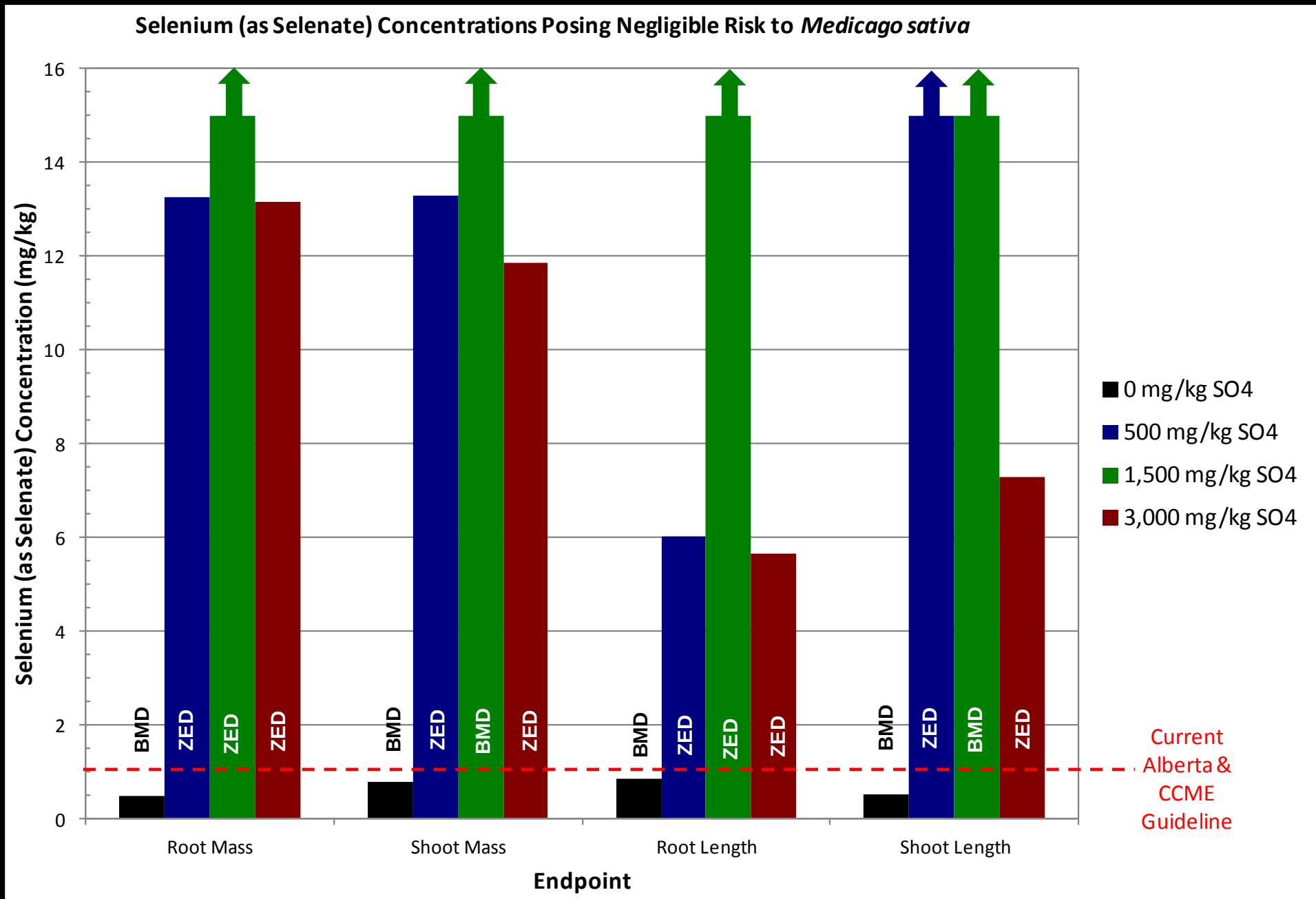
Image source: Calabrese, 2008

ZED Values With Sulfate

	Sulfate Concentration (mg/kg)		
Endpoint	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*
Selenium (as Selenate) Concentration (mg/kg)
16
14
12
10
8
6
4
2
0
BMD
ZED
ZED
ZED
BMD
ZED
BMD
ZED
BMD
ZED
ZED
ZED
BMD
ZED
BMD
ZED
Root Mass
Shoot Mass
Root Length
Shoot Length
Endpoint
0 mg/kg SO4
500 mg/kg SO4
1,500 mg/kg SO4
3,000 mg/kg SO4
Current Alberta & CCME Guideline

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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