CONSIDERATIONS FOR SOIL SELENIUM 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)
- >0.84
- 0.626 - 0.839
- 0.524 - 0.625
- 0.456 - 0.523
- 0.401 - 0.455
- 0.36 - 0.4
- 0.321 - 0.359
- 0.292 - 0.32
- 0.264 - 0.291
- 0.236 - 0.263
- 0.211 - 0.235
- 0.192 - 0.21
- 0.171 - 0.191
- 0.152 - 0.17
- 0.135 - 0.151
- 0.121 - 0.134
- 0.11 - 0.12
- 0.101 - 0.109
- 0.1 - 0.1
- <0.099
- No Data

Sampling density = 1/289 km²
25<sup>th</sup>% = 0.1 ppm; Median = 0.2 ppm; 75<sup>th</sup>% = 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

<table>
<thead>
<tr>
<th>Species</th>
<th>Charge</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenide (Se²⁻)</td>
<td>[-2]</td>
<td>Low pH, low Eh, relatively insoluble</td>
</tr>
<tr>
<td>Elemental (Se⁰)</td>
<td>[0]</td>
<td>Not common in natural environments, relatively insoluble</td>
</tr>
<tr>
<td>Selenite (SeO₃⁺⁴)</td>
<td>[+4]</td>
<td>Neutral pH, well-drained soils, can be soluble, found in water. More reduced than selenate</td>
</tr>
<tr>
<td>Selenate (SeO₄⁺⁶)</td>
<td>[+6]</td>
<td>Alkaline soils, highly soluble, found in water. Highest oxidation state</td>
</tr>
</tbody>
</table>
**Thermodynamic Predictions of Selenium Species**

Adapted from Masscheleyn & Patrick (1993)

- Selenious Acid
- Hydrogen Selenide [-2]
- Elemental Selenium
- Selenite [+4]
- Selenate [+6]
- Biselenite

pe = Eh(mV)/59.2

Black, dashed lines represent contours of equal selenide activities.
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 semi-arid 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
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)
Accumulators will preferentially uptake selenium over sulfur \((\text{Terry et al, 2000})\)

Most species are non-accumulators and will preferentially take up sulfate \((\text{Terry et al, 2000})\)

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 SO₄
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 SO₄
**BMD/EC Values for 25% Adverse Effect**

<table>
<thead>
<tr>
<th>Endpoint</th>
<th>EC$_{25}$ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root Mass</td>
<td>0.49</td>
</tr>
<tr>
<td>Shoot Mass</td>
<td>0.77</td>
</tr>
<tr>
<td>Root Length</td>
<td>0.86</td>
</tr>
<tr>
<td>Shoot Length</td>
<td>0.53</td>
</tr>
</tbody>
</table>

*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
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

Maximum Stimulation (averages 130-160% of control)

Distance to NOAEL (averages 5-fold)

NOAEL

Hormetic Zone (averages 10- to 20-fold)

Control

Stimulant Response

100%

Response

Dose

Image source: Calabrese, 2008
# ZED Values with Sulfate

<table>
<thead>
<tr>
<th>Sulfate Concentration (mg/kg)</th>
<th>Endpoint</th>
<th>500</th>
<th>1,500</th>
<th>3,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root Mass</td>
<td></td>
<td>13.27</td>
<td>&gt;15</td>
<td>13.17</td>
</tr>
<tr>
<td>Shoot Mass</td>
<td></td>
<td>13.29</td>
<td>NA</td>
<td>11.86</td>
</tr>
<tr>
<td>Root Length</td>
<td></td>
<td>6.01</td>
<td>&gt;15</td>
<td>5.66</td>
</tr>
<tr>
<td>Shoot Length</td>
<td></td>
<td>&gt;15</td>
<td>NA</td>
<td>7.30</td>
</tr>
</tbody>
</table>

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*

<table>
<thead>
<tr>
<th>Endpoint</th>
<th>0 mg/kg SO4</th>
<th>500 mg/kg SO4</th>
<th>1,500 mg/kg SO4</th>
<th>3,000 mg/kg SO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root Mass</td>
<td>ZED</td>
<td>ZED</td>
<td>BMD</td>
<td>ZED</td>
</tr>
<tr>
<td>Shoot Mass</td>
<td>ZED</td>
<td>BMD</td>
<td>ZED</td>
<td>BMD</td>
</tr>
<tr>
<td>Root Length</td>
<td>BMD</td>
<td>ZED</td>
<td>ZED</td>
<td>ZED</td>
</tr>
<tr>
<td>Shoot Length</td>
<td>BMD</td>
<td>ZED</td>
<td>BMD</td>
<td>ZED</td>
</tr>
</tbody>
</table>

Current Alberta & CCME Guideline

**Selenium (as Selenate) Concentration (mg/kg)**
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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