Special Topics
I. Selenium Ecotoxicology
II. Arsenic in Drinking Water

Learning Objectives

- Examine the chemistry of selenium in inorganic and organic molecules.
- Understand the role of seleno-amino acids in the expression of selenium toxicity in plant and animal systems.
- Examine chronic selenium toxicosis (selenosis).
- Understand the role of selenium in reproductive failure.

Environmental Selenium

- Sulfur analogue.
  - sulfate/selenate.
  - sulfite/selenite.
  - sulfide/selenide.
  - S(0)/Se(0).
- Organic compounds.
- Essential trace element, toxic at higher concentrations.

Forms of Selenium

<table>
<thead>
<tr>
<th></th>
<th>Se(^2)</th>
<th>Reducing environments. Forms metal complexes; highly immobile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylselenide</td>
<td>(CH(_3))(_2)Se</td>
<td>Volatilization from soil bacteria and fungi</td>
</tr>
<tr>
<td>Dimethylselenide</td>
<td>(CH(_3))(_2)Se(_2)</td>
<td>Volatilization from plants</td>
</tr>
<tr>
<td>Dimethylselenide</td>
<td>(CH(_3))(_2)SeO(_2)</td>
<td>Volatile metabolite</td>
</tr>
<tr>
<td>Hydrogen selenide</td>
<td>H(_2)Se</td>
<td>Unstable moist air; decomposes to Se(^0) in water</td>
</tr>
<tr>
<td>Seleno-amino acids</td>
<td>Selenomethionine, Se-cysteine, Se-methyl-selenocysteine, Se-cystathionone</td>
<td></td>
</tr>
</tbody>
</table>

Forms of Selenium, 2

<table>
<thead>
<tr>
<th>Elemental Selenium (0)</th>
<th>Se(^0)</th>
<th>Stable reducing environments; very slow oxidation and reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Se(0) in a Se reducing bacteria culture.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forms of Selenium, 3</td>
<td>Forms of Selenium, 4</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Selenium (+IV)</strong></td>
<td><strong>Selenate (+VI)</strong></td>
<td></td>
</tr>
<tr>
<td>SeO$_2^-$</td>
<td>SeO$_4^{2-}$</td>
<td></td>
</tr>
<tr>
<td>Soluble form</td>
<td>Se(VI) is stable in well-oxidized environments and very mobile in soils</td>
<td></td>
</tr>
<tr>
<td><strong>Trimethylselenonium</strong></td>
<td>(CH$_3$)$_3$Se$^+$</td>
<td></td>
</tr>
<tr>
<td>Important urinary metabolite</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Selenous acid</strong></td>
<td><strong>Selenic acid</strong></td>
<td></td>
</tr>
<tr>
<td>H$_2$SeO$_3$</td>
<td>H$_2$SeO$_4$</td>
<td></td>
</tr>
<tr>
<td>Common in soils</td>
<td>Common in soils</td>
<td></td>
</tr>
<tr>
<td><strong>Selenium dioxide</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SeO$_2^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formed as a product of fossil fuel combustion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Global Selenium Mobilization**

- **Atmosphere.**
  - Deposition to marine system; deposition to terrestrial system.
- **Marine.**
  - Volatilization; sea salt suspension; marine biota uptake; sediment deposition to land.
- **Terrestrial.**
  - Volatilization; dust particles; river dissolved and particulates.
- **Anthropogenic**
  - Mining; petroleum; irrigation.

**Distribution of Se (mg/kg)**

<table>
<thead>
<tr>
<th>Terrestrial</th>
<th>Earth's crust</th>
<th>0.09</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>0.1 - 14.0</td>
<td></td>
</tr>
<tr>
<td>Shales and phosphate rk</td>
<td>&lt; 1 - 55</td>
<td></td>
</tr>
<tr>
<td>Crude oil</td>
<td>0.06 - 0.39</td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>0.5 - 11.0</td>
<td></td>
</tr>
<tr>
<td>Soils:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-seleniferous</td>
<td>&lt; 0.1 - 2.0</td>
<td></td>
</tr>
<tr>
<td>Seleniferous</td>
<td>2 - 200</td>
<td></td>
</tr>
</tbody>
</table>

**Distribution of Se (mg/L)**

<table>
<thead>
<tr>
<th>Aquatic</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean water</td>
<td>$10^{-4}$ - $4 \times 10^{-3}$</td>
</tr>
<tr>
<td>River water</td>
<td>$10^{-4}$ - $4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Aquatic plants</td>
<td>0.02 - 0.14</td>
</tr>
<tr>
<td>Plankton</td>
<td>1.1 - 2.4</td>
</tr>
<tr>
<td>Fish</td>
<td>0.5 - 6.5</td>
</tr>
</tbody>
</table>

*Aquatic Biota Criteria: 0.005 mg/L, Drinking Water MCL: 0.050 mg/L*

<table>
<thead>
<tr>
<th>Anthropogenic</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum products</td>
<td>0.15 - 1.65</td>
</tr>
<tr>
<td>Fly ash</td>
<td>1.2 - 16.5</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>1.8 - 4.8</td>
</tr>
<tr>
<td>Paper products</td>
<td>1.6 - 19.0</td>
</tr>
</tbody>
</table>
The Selenium Conundrum

- Essential trace element for aerobes.
  - GSH-px (antioxidant); immune function.
- Poor control response.
  - Deficiency ↔ normal ↔ toxic ranges closer and less "controlled" than other essential trace elements.
- Can do sulfur chemistry in biosynthesis.
  - Results in seleno-amino acids.
  - Disulfide bridges in protein tertiary structure now changed.
- Toxic at high enough levels.
- Lentic vs. lotic aquatic systems.
- Species sensitivity variations.

Se Cycling in Soils

Acid, poorly aerated

\[ \text{Heavy metal selenides} \quad \text{Se}^{2-} \quad \text{Selenides} \quad \text{SeO}_4^{2-} \]

Well aerated, alkaline

\[ \text{Organo-Se} \quad \text{Se}^{0} \quad \text{Selenites} \quad \text{SeO}_3^{2-} \]

Plants

Leaching

Insoluble Fe(OH)SeO_3 complexes

Microbial Interactions: Sulfate Reducing Bacteria

The Selenium Debates

- Disagreement on impacts in different environmental systems.
  - Lentic (ponds, lakes); lotic (streams, rivers)
- Extrapolation of observations to low levels.
- Interplay of required vs. toxic exposures.
- Precaution or overly conservative?

Receptors

- Selenium is not usually essential to plants but is for animals.
- Can substitute for sulfur in biochemical systems.
- Incorporated into amino acids and therefore can form selenoproteins.
  - Basis of plant and animal toxicity.
- 1930s: Se levels in plants of interest because of grazing deaths in sheep and cattle.
- Food chain bioconcentration observed.

Se - Normal Plants

- Grown in the presence of Se
  - No separation of S from Se

Biosynthesis of

\[
\text{Selenomethionine} + \text{Selenocysteine}
\]

1. Incorporation into protein
2. Se — Se bridges less stable than S — S bridges
3. Enzymes lose activity
4. Death of plant

Se - Adapted Plants

- Grown in the presence of Se
  - S and Se separated

Synthesis of non-protein amino acid analogues

\[
\text{Se-methylselenocysteine}
\]

\[
\text{Selenohomocysteine}
\]

No toxic side effects

Methionine

Cysteine

Normal protein synthesis
Case Study: Belews Lake, NC

- Man-made reservoir; coal-fired power plant.
  - Lentic system.
  - Large amount of water re-circulated per day.
- Fly ash settling basin discharged 150-200 µg/L Se; lake = 10 µg/L
  - Other HMs and contaminants.

Belews Lake Observations

- Elevated rates of fish terata (10-70%).
- Some reaches w/ <5 µg/L had normal fish.
- Highly researched case with the result of lowering the chronic aquatic biota criterion from 35 to 5 µg/L.

Case Study: Kesterson NWR

- California Central Valley agricultural drainage.
  - Ancient marine basin; saline soils.
- Water from drainage developed as a national wildlife refuge by USFWS.
  - Late 1970s to early 1980s; lentic system.
  - Pacific flyway nesting grounds; > 95% of California wetlands have disappeared in the last century.
  - Monitored for biological productivity; chemical contamination.
- Observation of reproductive failure in aquatic birds and ducks.

Kesterson

- Selenium was leaching from agricultural soils and depositing in the drainage impoundments.
- Food chain bioaccumulation observed.
  - Water, sediments, aquatic plants, insects, fish, birds/ducks.
- Observation of teratogenesis in aquatic birds and ducks caused great public outcry.
  - “The Poisoning of the West”

Kesterson Observations, 1

- Stilts
- Coot

Kesterson Observations, 2
**Case Study: Selenium and Phosphate Mining**

**Phosphate Mining in Idaho**

- Considered, a clean strip mining operation where phosphoria layers are removed and overburden waste rock and soil is replaced.

**Geochemistry**

- Waste rock contains Chert, Limestone and Siltstone (Shale)
- Se primarily associated with the siltstone
  - Pyrite micro grains ~0.1-6% Se

**Chronic Selenosis**
Mining Challenges

- Control of Se release.
- Animal management.
- Control at historical mining sites.
- Monitoring of impact.

Arsenic in Drinking Water

Natural Occurrence of As

- In rock: especially iron ores and magmatic sulfides.
- In sediments, soils and water: results from mineral dissolution.
- Anionic in solution: As(V) As(III)

Anthropogenic Sources

- In soil and water; sources include pesticides and wood preservatives.
- Anthropogenic activities can speed dissolution from parent rock and introduction to water

Health Effects - Acute

- 50 to 300 mg of inorganic As fatal to humans.
- Gastrointestinal injuries, kidney damage.
- Circulatory collapse, respiratory failure.
  - Industrial exposures
    - mining, agriculture
  - Environmental exposures
    - water, diet, treated wood, Paris Green
  - Intentional exposures
    - arsenical drugs

Health Effects, Chronic

- As builds up in tissues - skin, hair
- Melanosis, keratosis, unusual pigmentation
- Lesions, vascular system damage
- Skin, lung, bladder, lymph glands, kidney, prostate, and liver cancers

Evidence for damage to central nervous system
**Arsenic: Common Drinking Water Contaminant**

- US, Taiwan, Chile, Mexico, Argentina, Bangladesh, India...
- WHO drinking water standard 10 µg/L
- Many countries, especially the less industrialized, maintain a 50 µg/L standard
- US standard: 50 µg/L changing to 10 µg/L (compliance by 2006).

**As en México y América del Sur**

- Mucha gente ha sufrido en el mundo latino también.
- Especialmente en Chile, donde el agua contiene una parte por millón.
- La mayoría de lugares ahora tienen tratamiento para arsénico.

**U.S. Arsenic Regulation (past)**

- As is a Class A, known human carcinogen.
  - 1-2 in 1000 risk (1 in 100?) at 50 µg/L.
  - As was listed before 1987, and had no BAT.
- As MCL was 50 µg/L.

**US Arsenic Regulation (present)**

- EPA’s new MCL was 10 µg/L (Jan. 22, 2001)
  - Same level specified by WHO
  - Below this food becomes the predominant source
  - BAT’s were named
- Bush administration suspends new rule (March, 2001)
- New rule promulgated October 2001

**US Public Water Systems (PWSs)**

<table>
<thead>
<tr>
<th>As level exceeded</th>
<th>Large PWSs</th>
<th>Small PWSs</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µg/L</td>
<td>58</td>
<td>200</td>
</tr>
<tr>
<td>10 µg/L</td>
<td>508</td>
<td>1542</td>
</tr>
</tbody>
</table>

Large PWSs: >1000 people
Small PWSs: <1000 people
An Arsenic in drinking water public health emergency.

**Scope of the Bangladesh Problem**

"With more than an estimated 20 million of its 126 million people assumed to be drinking contaminated water and another 70 million potentially at risk, Bangladesh is facing what has been described as perhaps the largest mass poisoning in history."

(World Bank)

"Bangladesh makes the Chernobyl disaster look like a Sunday-school picnic."

(R. Wilson, Harvard U.)

**History of the Bangladesh Problem**

"The story beggars belief. In the 1970s, international agencies headed by the United Nations Children’s Fund (UNICEF) began pumping millions of dollars of aid money into Bangladesh for tubewells to provide “clean” drinking water. According to the World Health Organization, the direct result has been the biggest outbreak of mass poisoning in history. Up to half the country’s tubewells, now estimated to number 10 million, are poisoned. Tens, perhaps hundreds of thousands will die."

(F. Pearce, UNESCO)

**Arsenic Water Contamination Levels**

**Arsenic Lesions**
Arsenic Lesions, Cancer

Keratosis, Palm of a Patient

Arsenic Lesions on Feet, Cancer

Arsenic Lesions, Extreme

Arsenic Lesions, Chest & Arms

Gangrene Caused by Arsenic Poisoning
• Both died of arsenic related causes.

“
The social consequences of the arsenic crisis are far-reaching and tragic.
- Because of illiteracy and lack of information, many confuse the skin lesions caused by arsenicosis with leprosy.
- The most hard-hit villages where health problems have gripped a large population are treated much like isolated leper colonies. Within the community, arsenic-affected people are barred from social activities and often face rejection, even by immediate family members.
- Women are unable to get married, and wives have been abandoned by their husbands.
- Children with symptoms are not sent to school in an effort to hide the problem.”

- Green-safe, red-unsafe
Governmental and Agency Control Measures

- Immediate detection of the arsenicoses patients and ensure their treatment.
- Find alternate sources of safe drinking water.
- Find reasons of arsenic contamination in soil water.
- Conduct health education campaigns encouraging people to avoid arsenic contaminated drinking water.
- Training for health personnel.