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

Principles of Environmental Toxicology
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University of Idaho

Learning Objectives

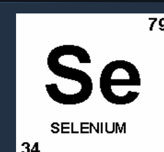
- Examine the chemistry of selenium in inorganic and organic molecules.
- Understand the role of seleno-amino acids in the expression of selenium toxicity in plant and animal systems.
- Examine chronic selenium toxicosis (selenosis).
- Understand the role of selenium in reproductive failure.

Learning Objectives

- Describe the biogeochemical cycle of selenium.
- Analyze environmental Se case studies.
- Examine the regulatory and scientific issues involved in Se risk assessment.
- Explore the occurrence of Arsenic in drinking water.
- Describe the US As regulatory changes
- Describe the clinical pathology of arsenicosis.
- Examine the arsenic in drinking water public health emergency in Bangladesh.

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

Selenides (-II)	Se^{2-}	Reducing environments. Forms metal complexes; highly immobile
Dimethylselenide	$(CH_3)_2Se$	Volatilization from soil bacteria and fungi
Dimethyldiselenide	$(CH_3)_2Se_2$	Volatilization from plants
Dimethylselenone	$(CH_3)_2SeO_2$	Volatile metabolite
Hydrogen selenide	H_2Se	Unstable moist air; decomposes to Se^0 in water
Seleno-amino acids	Selenomethionine, Se-cysteine, Se-methyl-selenocysteine, Se-cystathionone	

Forms of Selenium, 2

Elemental Selenium (0)	Se^0	Stable reducing environments; very slow oxidation and reduction

Red Se(0) in a Se reducing bacteria culture.

Forms of Selenium, 3

Selenite (+IV)	SeO_3^{2-}	Soluble form
Trimethylselenomium	$(CH_3)_3Se^+$	Important urinary metabolite
Selenous acid	$H_2SeO_3^-$ $HSeO_3^-$	Common in soils
Selenium dioxide	SeO_2	Formed as a product of fossil fuel combustion

Forms of Selenium, 4

Selenate (+VI)	SeO_4^{2-}	Se(VI) is stable in well-oxidized environments and very mobile in soils
Selenic acid	$H_2SeO_4^-$ $HSeO_4^-$	Common in soils

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)

Terrestrial

Earth's crust	0.09
Limestone	0.1 - 14.0
Shales and phosphate rk	< 1 - 55
Crude oil	0.06 - 0.39
Coal	0.5 - 11.0
Soils:	
Nonseleniferous	< 0.1 - 2.0
Seleniferous	2 - 200

Distribution of Se (mg/L)

Aquatic

Ocean water	10^{-4} - 4×10^{-3}
River water	10^{-4} - 4×10^{-4}
Aquatic plants	0.02 - 0.14
Plankton	1.1 - 2.4
Fish	0.5 - 6.5

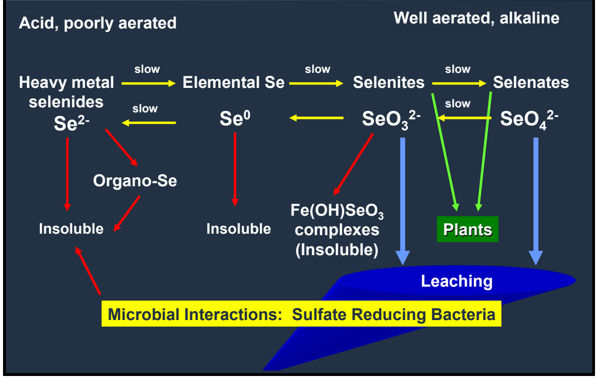
Aquatic Biota Criteria: 0.005 mg/L
Drinking Water MCL: 0.050 mg/L

Distribution of Se (mg/kg)

Anthropogenic

Petroleum products	0.15 - 1.65
Fly ash	1.2 - 16.5
Sewage sludge	1.8 - 4.8
Paper products	1.6 - 19.0

Se Cycling in Soils



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.

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.

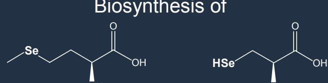
Se - Normal Plants

Harborne

Grown in the presence of Se

↓ *No separation of S from Se*

Biosynthesis of



Selenomethionine + 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

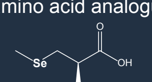
Harborne

Grown in the presence of Se

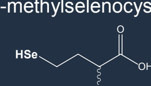
S and Se separated

Se ↓ ↓ S

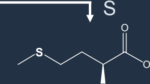
Synthesis of non-protein amino acid analogues



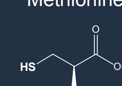
Se-methylselenocysteine



Selenohomocysteine
No toxic side effects



Methionine

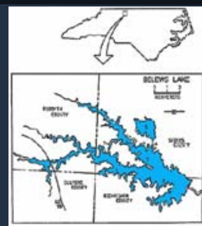


Cysteine

Normal protein synthesis

Case Study: Belews Lake, NC

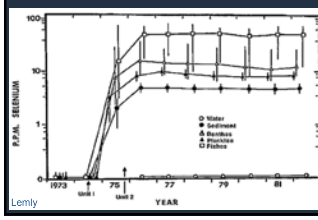
- Man-made reservoir; coal-fired power plant.
  - Lentic system.
- Initial filling in 1970, plant on-line in 1974.
  - Large amount of water re-circulated per day.
- Fly ash settling basin discharged 150-200 μg/L Se; lake = 10 μg/L
  - Other HMs and contaminants.



Lemly

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.



Lemly

Case Study: Kesterson NWR

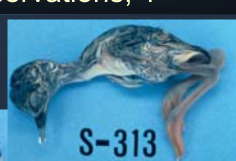
- California Central Valley agricultural drainage.
  - Ancient marine basin; saline soils.
- Water from drainage developed as a national wildlife refuge by USFWS.
  - Late 1970s to early 1980s; lentic system.
  - Pacific flyway nesting grounds; > 95% of California wetlands have disappeared in the last 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

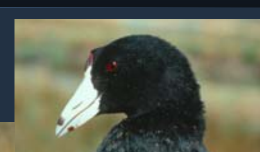
Stilts



Ohlendorf

Kesterson Observations, 2

Coot



Ohlendorf

Kesterson Observations, 3

Coot

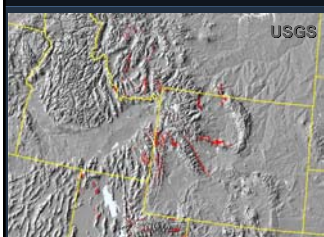
Ohlendorf

Kesterson Observations, 4

Mallard

Ohlendorf

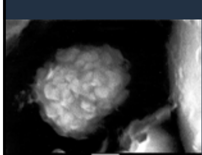
Case Study: Selenium and Phosphate Mining

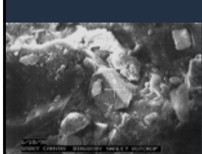


Phosphate Mining in Idaho

- 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

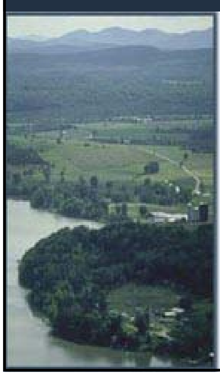
Chronic Selenosis

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 ug/L
- Many countries, especially the less industrialized, maintain a 50 ug/L standard
- US standard: 50 ug/L changing to 10 ug/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 ug/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

As in the United States

US Public Water Systems (PWSs)

As level exceeded	Large PWSs	Small PWSs
50 μg/L	58	200
10 μg/L	508	1542

Large PWSs: >1000 people

Small PWSs: <1000 people

As μg/L	% PWSs
1	36
2	25
5	14
10	8
20	3
50	1

Bangladesh

An Arsenic in drinking water public health emergency.

Encarta

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

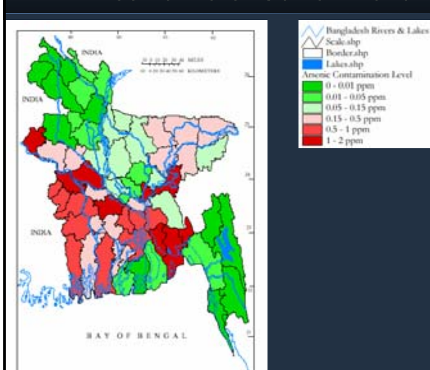
"The story beggars belief. In the 1970s, international agencies headed by the United Nations Children's Fund (UNICEF) began pumping millions of dollars of aid money into Bangladesh for tubewells to provide "clean" drinking water. According to the World Health Organization, the direct result has been 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)

Bangladesh – Public Health Concerns

World Bank

- In the early 1970s, most of Bangladesh's rural population got its drinking water from surface ponds and nearly a quarter of a million children died each year from water-borne diseases.
  - The provision of tubewell water for 97 percent of the rural population has been credited with bringing down the high incidence of diarrheal diseases and contributing to a halving of the infant mortality rate.
- Paradoxically, the same wells that saved so many lives now pose a threat due to the unforeseen hazard of arsenic.

Arsenic Water Contamination Levels



Arsenic Lesions

R. Wilson

Arsenic Lesions, Cancer

R. Wilson

Arsenic Lesions, Extreme

R. Wilson

Keratosis, Palm of a Patient

R. Wilson

Arsenic Lesions, Chest & Arms

R. Wilson

Arsenic Lesions on Feet, Cancer

R. Wilson

Gangrene Caused by Arsenic Poisoning

R. Wilson

Portrait of Pinjira Begum and Her Daughter

World Bank

- Both died of arsenic related causes.

Bangladesh – Cultural/Social Factors

- "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."

World Bank

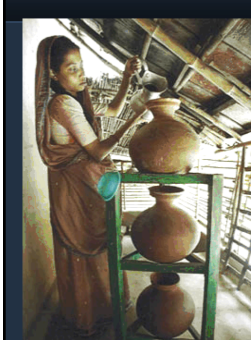
Collection and Testing of Tubewell Water

Coloring Tubewells After Testing

- Green-safe, red-unsafe

Chemical Treatment to Remove Arsenic

Home Water Treatment



Harvesting Rainwater

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.