Biogeochemistry of selenium and food chain quality

Helinä Hartikainen
Department of Food and Environmental Sciences
University of Helsinki

in co-operation with Nashmin Ebrahimi, Anthony Owusu-Sekuere,
Martina Metzler and Mervi Seppänen
Contents

- Soils as source of selenium
- Selenium as a problem in Finland
- Agronomic biofortification
- Effects of selenium fertilization on food chain quality
Soils as primary sources of selenium

- concentration spectrum is very large ~ 0 – 1250 ppm
- low-Se soils are more common than seleniferous ones

The geographical distribution can be very uneven
- Se toxicity and deficiency may occur within short distances

Generally:
- marine sedimentary deposits (shales) are high in Se
- soils derived from igneous rocks tend to be low in Se

High-Se soils were recognized far before those deficient in Se
- hyperaccumulating plants
- dramatic toxicity symptoms in domestic animals (necrotic and sloughed hooves, hair loss, emaciation, etc.)
Se hyperaccumulators – an invention of 1930’s

- The first description of disease of horses now known to be a form of Se poisoning was written in 1857 by Madison

  Astragalus bisulcatus

  Morinda reticulata

- Palatable only to horses, they may even become addicted to this plant
- able to accumulate Se from soils not very high in this metalloid
Selenium cycle begins and ends with soil

- Bedrock $\Rightarrow$ soil $\Rightarrow$ plants $\Rightarrow$ animals/humans

= geomedicine
From a toxicant to an essential nutrient

- Low-Se soils are more difficult to identify than those high in Se.

- In Finland, the first signals of Se deficiency were unknowingly described in a veterinary report in 1933. Symptoms of nutritional muscular degeneration (NMD).

- In 1950’s isolated cases throughout the country:
  - Feed low in Se.
NMD disease in Finland 1950’s

- Most frequently observed in Ostrobothnia

  - bottom sediments deposited during Littorina stage (salty water high in S) of Baltic Sea
  - rich in FeS₂ (pyrite) and relatively high in Se
  - now acid sulfate soils

Uppermost shoreline of the ancient Littorina Sea
Total Se vs. bioavailable Se

- Total Se in soil does not necessarily correlate with Se in the food chain

**Bioavailability** of Se depends on

- **chemical pool**
  - dissolved in soil solution
  - sorbed on oxide surfaces
  - constituent in organic matter or minerals

- **chemical species**
  - oxidation states vary from +6 to -2
    - differ in their soil chemistry
  - catenated organic species (e.g. volatile diselenides (RSeSeR))
Selenium problems in Finland

- Soils are not exceptionally low in Se but the **bioavailability** of Se is low
  - soils are geologically young and weakly weathered
  - acidity promotes the sorption reactions

- Situation of domestic animals improved when the Se-supplementation of feeds started in 1969

- ”Mineral Element study” in 1970’s revealed that
  - cereal crops, beef, milk and dairy products very poor in Se
  - the average daily Se intake was clearly below the adequate level

- Supplementation of fertilizers with Se started in 1985
  - Se concentrations in foodstuffs markedly increased
    - throughout the monitoring program, milk has been the most sensitive indicator to reveal the changes in food quality
Se concentration of milk in Finland 1984-2006

Se fertilization

Se concentration of milk in Finland 1984-2006
Se concentration of cereal grains in Finland 1984-2006
Se concentration of beef and pork  Finland 1981-2006

Se-supplementation of feeds started in 1969
The average daily Se intake in Finland.
Agronomic biofortification in Finland

- Se is given as selenate ($\text{SeO}_4^{2-}$)
  - less toxic than selenite ($\text{SeO}_3^{2-}$)

- Selenate is weakly sorbed on Al and Fe oxide surfaces
  - the most mobile species, present in oxic conditions
  - uptake by plant through sulfate transporter (competition S/Se)
    - competition causes problems in acid sulfate soils
    - translocated efficiently from roots to shoots
  - can act as electron acceptor in soil $\Rightarrow$ reduction to selenite

- Selenite has a high sorption affinity
  - ligand exchange on Fe and Al oxide surfaces, favoured by low pH
  - uptake by plants through phosphate transporter
    - tends to accumulate in roots $\Rightarrow$ weaker translocation to shoots
Plants – pivotal Se carriers

- Prevailing concept that higher plants do not require Se raised a doubt in Finland:
  Why are plants forced to take up an element they don’t need?

- The concept places also the scientific community in a dilemma, for plants play a key role in cycling Se from soil to animals and humans

  - Are plants only conveyers in the soil-plant-animal-human chain?
  - Don’t they derive any direct benefit from Se for themselves?

  Nature is functioning on a rational way
Impact of Se on plants

Results of our first pot experiment with lettuce
- at proper levels Se promotes the plant growth

Lettuce yields at various Se fertilisation levels (µg kg⁻¹ of soil)
Development of dry weight of lettuce during 8-week cultivation without or with added Se (mg kg\(^{-1}\)).
Impact of Se on plants

- Growth-promoting effect is associated with the accumulation of energy reserves (starch and soluble sugars)

- In proper concentrations Se
  - defences plants against various internal metabolic (respiration, photosynthesis) or external (UV-B light, frost, drought, detrimental elements) stressors
  - reduces lipid oxidation and maintains cell membrane integrity
  - improves the quality of plant products
    - counteracts the impairment of nutritive value of senescent plants (e.g. the decrease of vitamin E)
    - improves e.g. the process quality of potato (reduces raw darkening of tubers)
    - e.g. garlic is found to incorporate Se into bioactive organic compounds with anticarsinogenic potential, etc.
Recent studies with *Brassica* species

- Fertilizer-Se was efficiently metabolized to valuable organic compounds
- 85% of Se taken up had accumulated in seeds as selenomethionine (SeMet) in the protein rich meal fraction
  - high quality cattle feed
- in *B. napus* selenomethionine selenocysteine (SeMetCys) accumulated in the leaves
- Se seemed to increase the photosynthesis rate
Studies with alfalfa (*Medicago sativa*)

- N₂-fixing plant are valuable protein source in feed ⇒ food chain
- Se fertilization increased
  - the number and fresh weight of nodules
  - concentration of carotenoids and chlorophyll a and b
- soluble sugars concomitantly with elevated activity of fructose-1,6-bisphosphatase
  - carbohydrate metabolism
Se ends up in soil with plant residues

- In Finnish soils, sequential Se extractions have revealed that:
  - only 1% (1%) is in soluble form
  - 15–20% (17%) is adsorbed on oxide surfaces
  - 50% (39%) is associated with organic matter
  - 10% (14%) is elemental Se$^0$
  - 20% (29%) in recalcitrant organic Se or metal selenides

Numbers in red refer to accumulation of fertilizer-Se during 12 years in experimental fields (mineral soils)

- Bioavailability of residual fertilizer-Se is rather low in acid soils in humid conditions favoring the reduction of selenate to selenite (efficient sorption onto Fe and Al oxides)

- Se fertilization is needed at every seeding
Thank you for your attention!
Agronomic measures to improve the animal and human health in Finland

Age-standardized mortality from coronary heart disease in 1952-1999, deaths per 100,000 of population aged 35-64 years. (G. Alfthan et al. 2011)
Biogenic Se emissions

- Plants, marine algae and soil microbes contribute to a larger-scale Se cycling

- Biogenic emission of dimethylselenide (DMSe) from soil, plants and algae
  - an important process decreasing the toxicity and mobility of seleno-oxyanions
  - DMSe is 500-700 times less toxic than selenate or selenite

- Phytovolatilization is a potential mechanism for bioremediation of high-Se soils

- Indian mustard (*Brassica juncea*), an superior species
  - rhizosphere microbes further enhance its efficiency in volatilization
Selenium as an environmental pollutant

Kesterson Reservoir in California

- build in 1968-1971 to counteract the irrigation-induced increase in groundwater level

- Se toxicity began to become a problem shortly after the drainage tiles were installed
  - deformities and death of livestock
  - later there was a large die-off of migrating waterfowl

- in 1987 the site was declared a toxic waste dump
Conclusions

- During the last 30 years many important milestones have been reached on the way to solve Se problems.

- Consensus: Se is an essential nutrient for animals and humans but toxic at high concentrations.

- Whether Se is required for the growth of higher plants is still a controversial and unresolved question.

- The present development in molecular biology and biochemistry may provide evidence that Se is a plant nutrient even though very tricky and two-edged by its very nature.