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Biogeochemistry of selenium and food chain quality

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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

- Selenium World Atlas (Oldfield 2002):
  - 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 sloughted 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

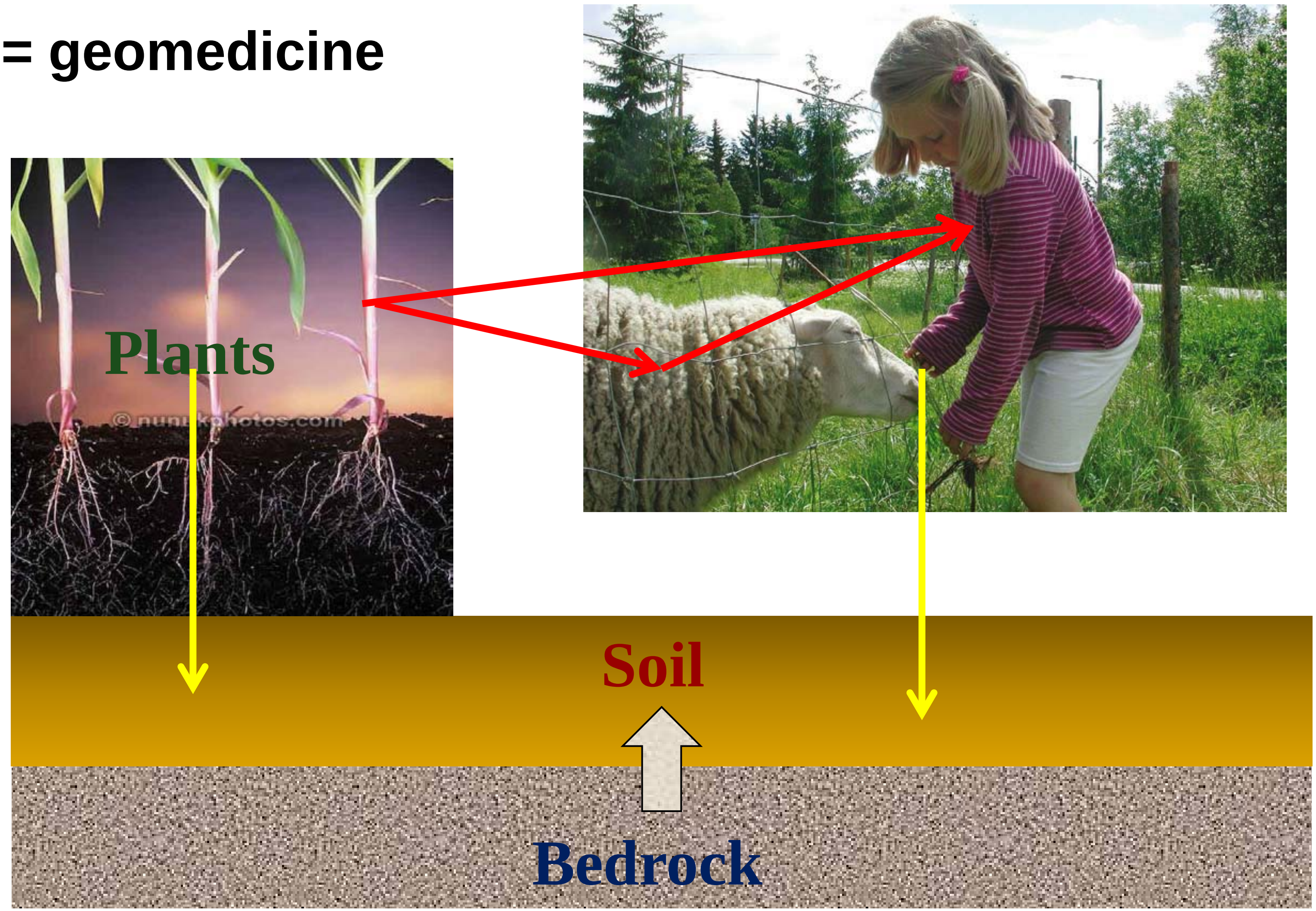
Astragalus bisulcatus

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

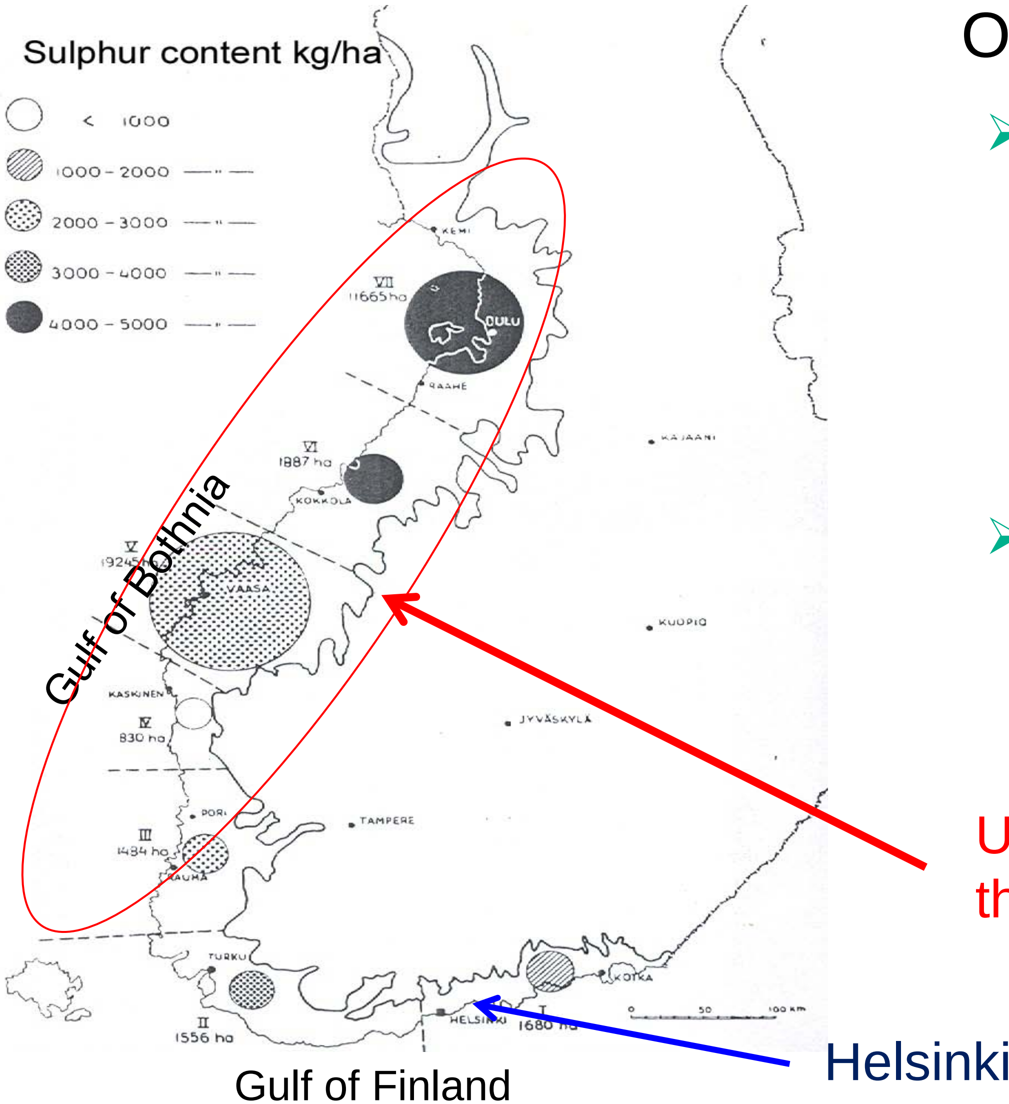
- Low-Se soils are more difficult to identify than those high in Se
- In Finland, the first signals of Se deficiency were unknowingly described in a veterinary report in 1933
  - symptoms of nutritional muscular degeneration (NMD)
- 1n 1950's isolated cases throughout the country

$\Uparrow$

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 FeS_2 (pyrite) and relatively high in Se
    - **now acid sulfate soils**



Uppermost shoreline of the ancient Littorina Sea

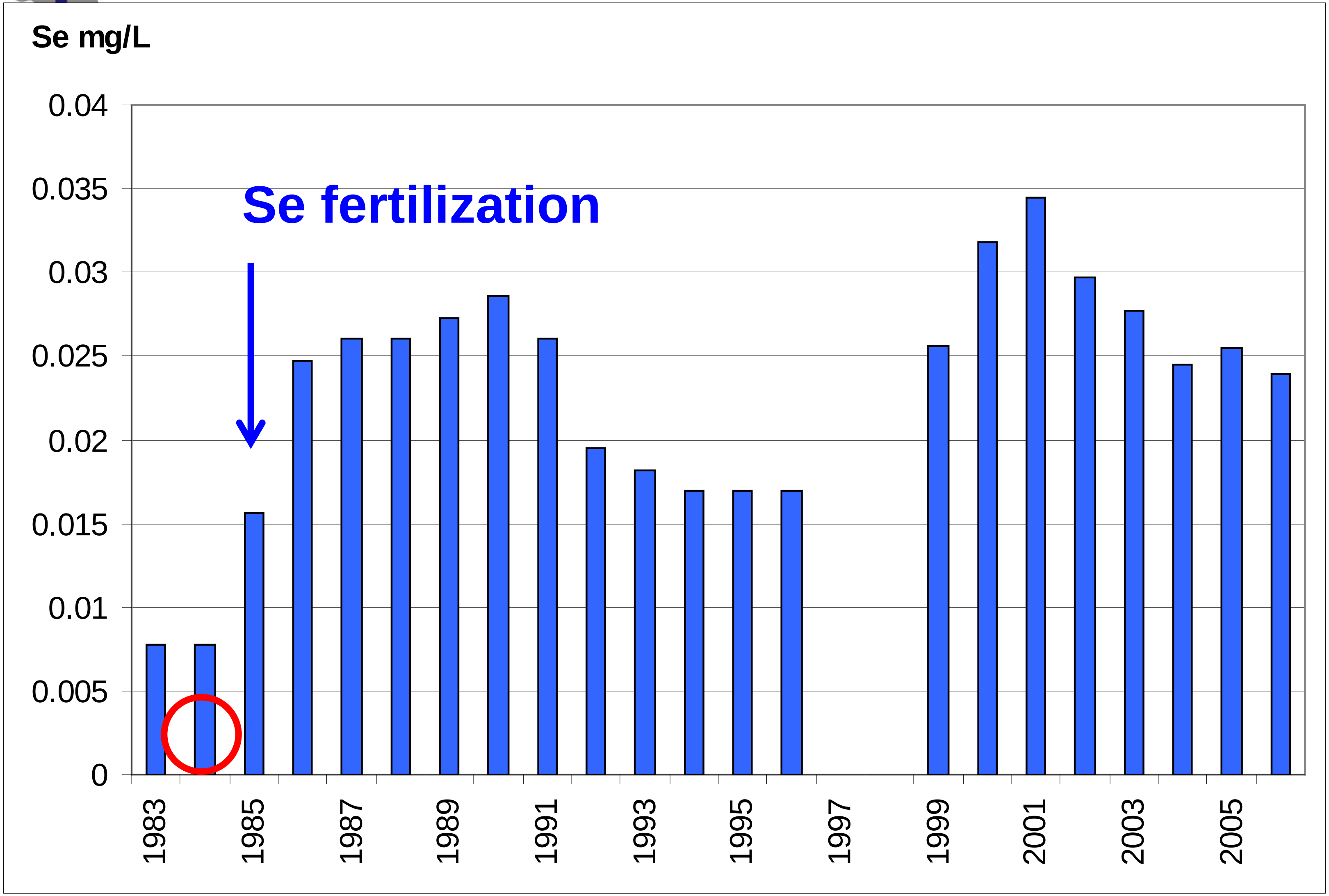
Total Se *vs*. bioavailable Se

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

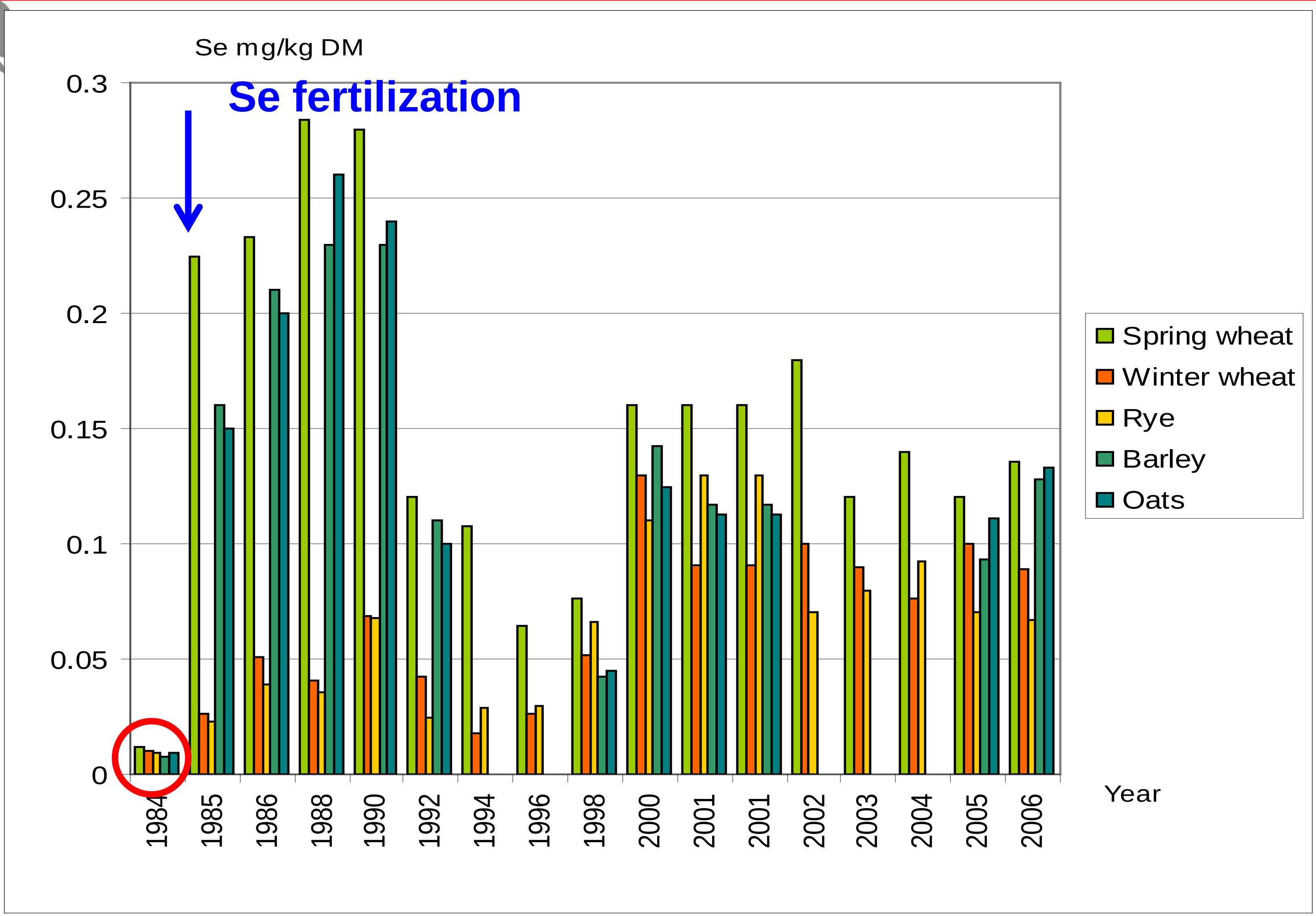
- **Bioavailability** of Se depends on
  - chemical pool
    - dissolved in soil solution
    - sorbed on oxide surfaces
    - constituent in organic matter or minerals
  - chemical species
    - oxidation states vary from +6 to -2
      - differ in their soil chemistry
    - catenated organic species (e.g. volatile diselenides (RSeSeR)

Selenium problems in Finland

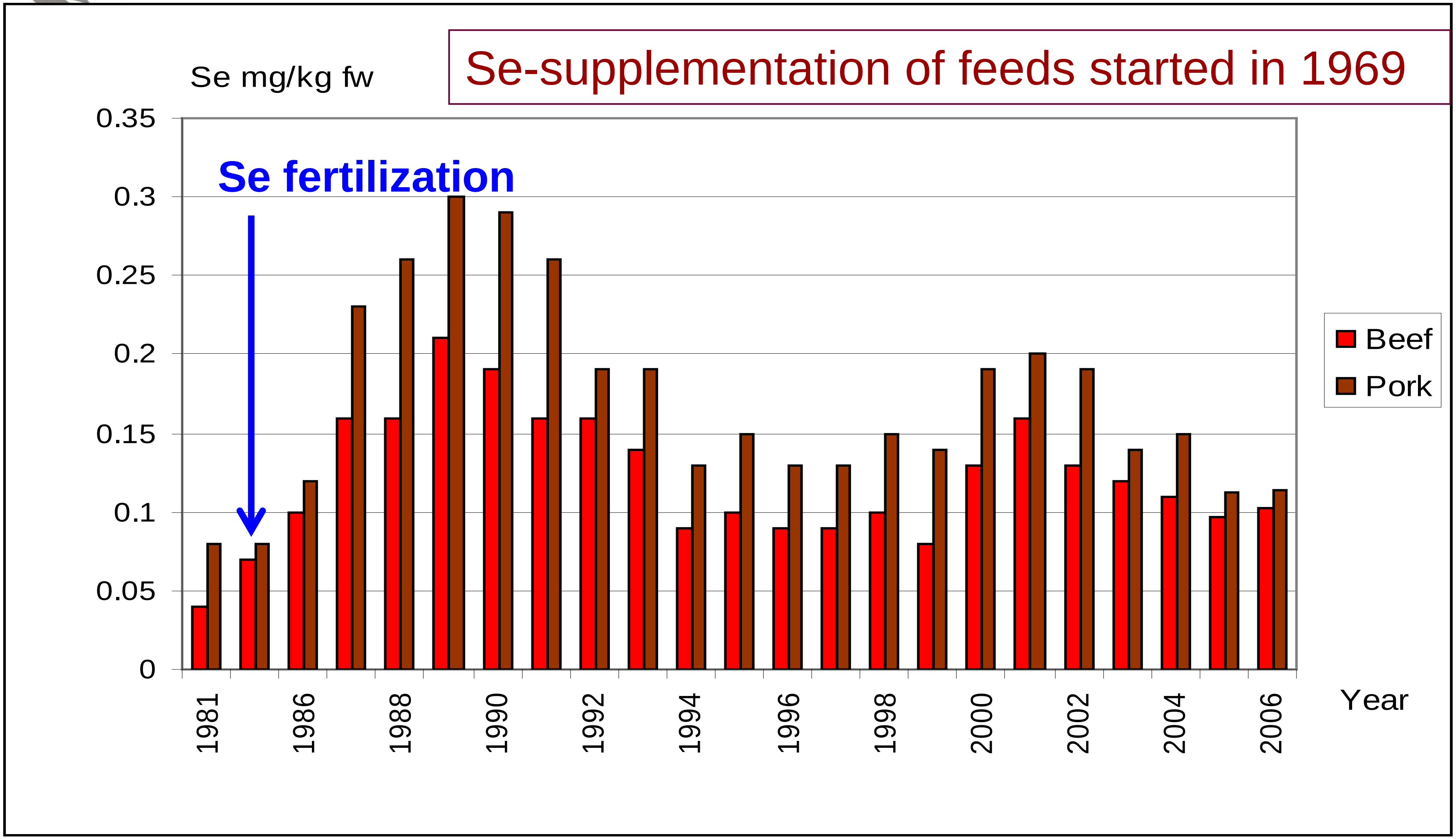
- Soils are not exceptionally low in Se but the **bioavailability** of Se is low
  - soils are geologically young and weakly weathered
  - acidity promotes the sorption reactions
- Situation of domestic animals improved when the Se-supplementation of feeds started in 1969
- ”Mineral Element study” in 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



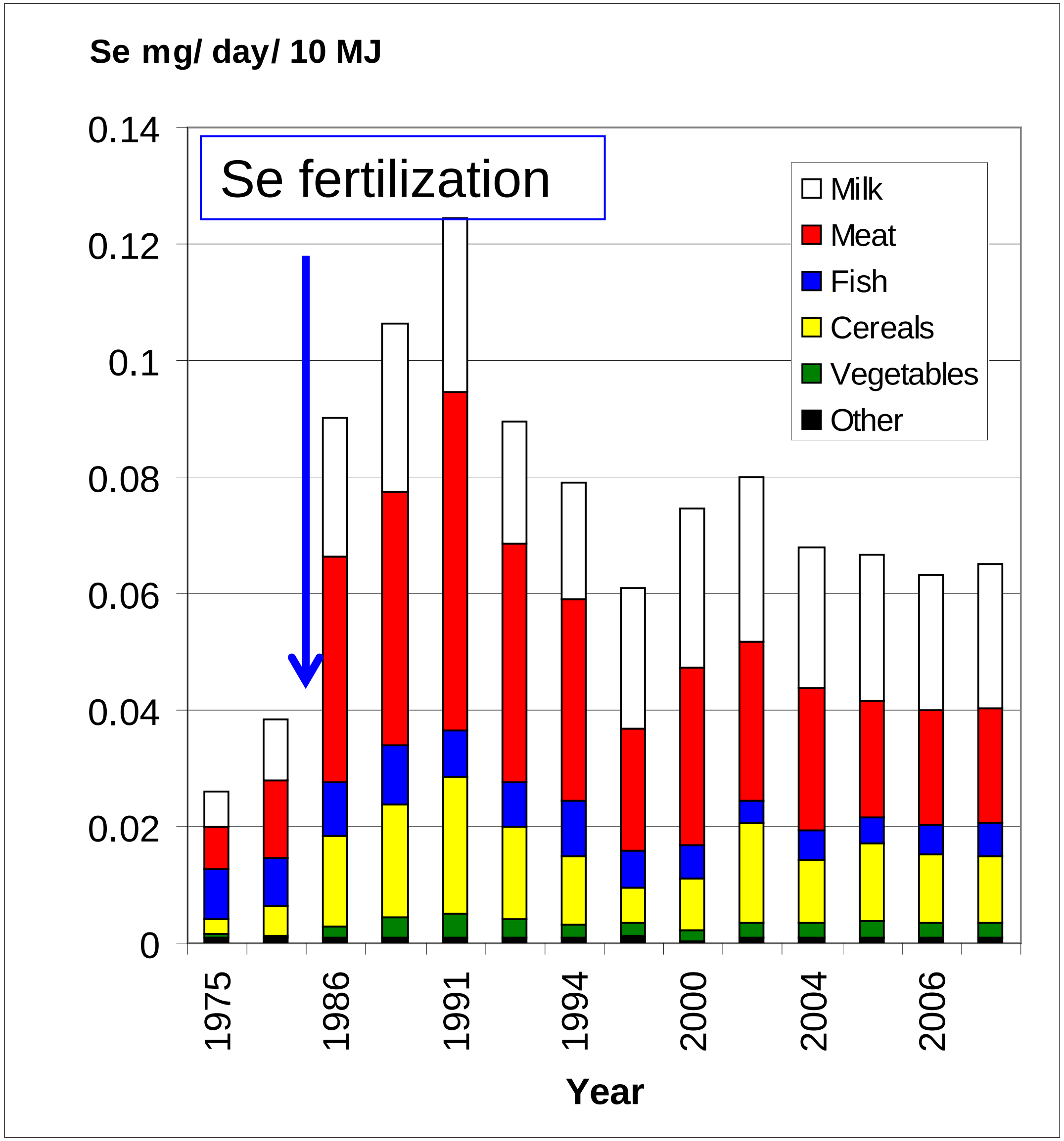
Se concentration of milk in Finland 1984-2006



Se concentration of cereal grains in Finland 1984-2006



Se concentration of beef and pork Finland 1981-2006



The average daily Se intake in Finland

Agronomic biofortification in Finland

- Se is given as selenate (SeO_4^{2-})
  - less toxic than selenite (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 ⇒ 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 ⇒ 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?

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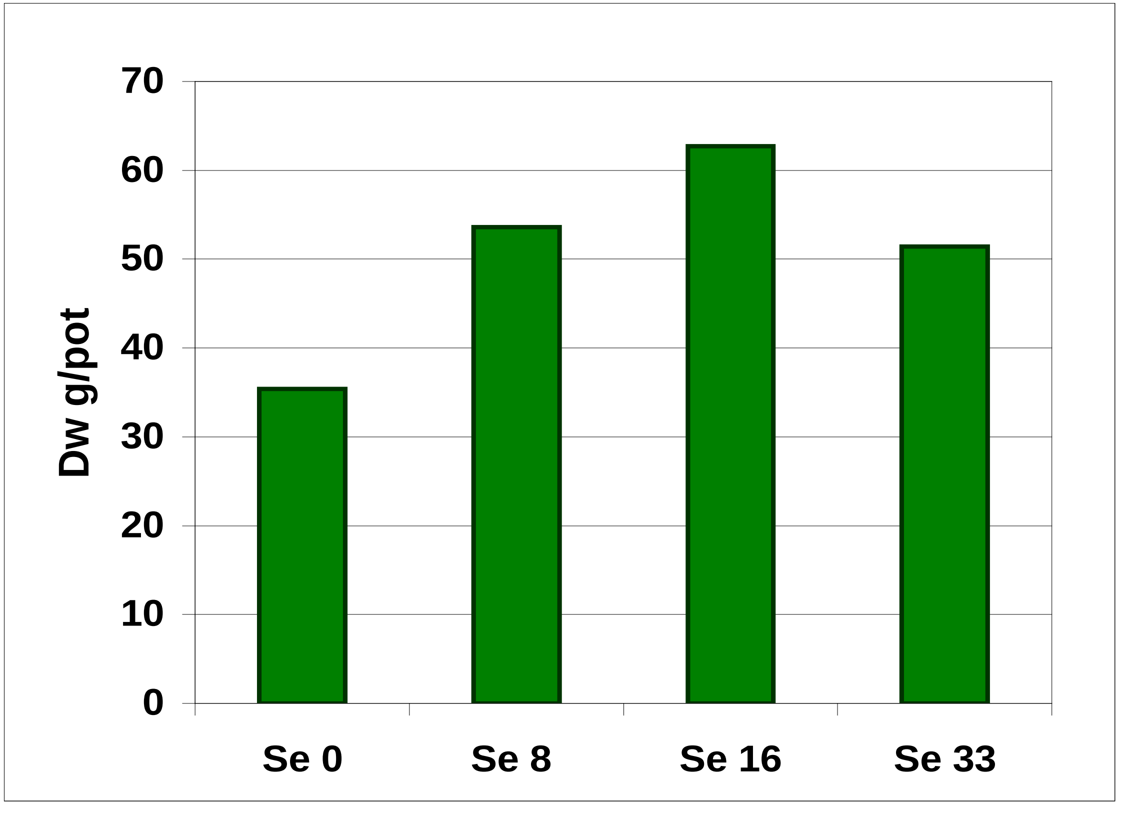
Nature is functioning on a rational way

Impact of Se on plants

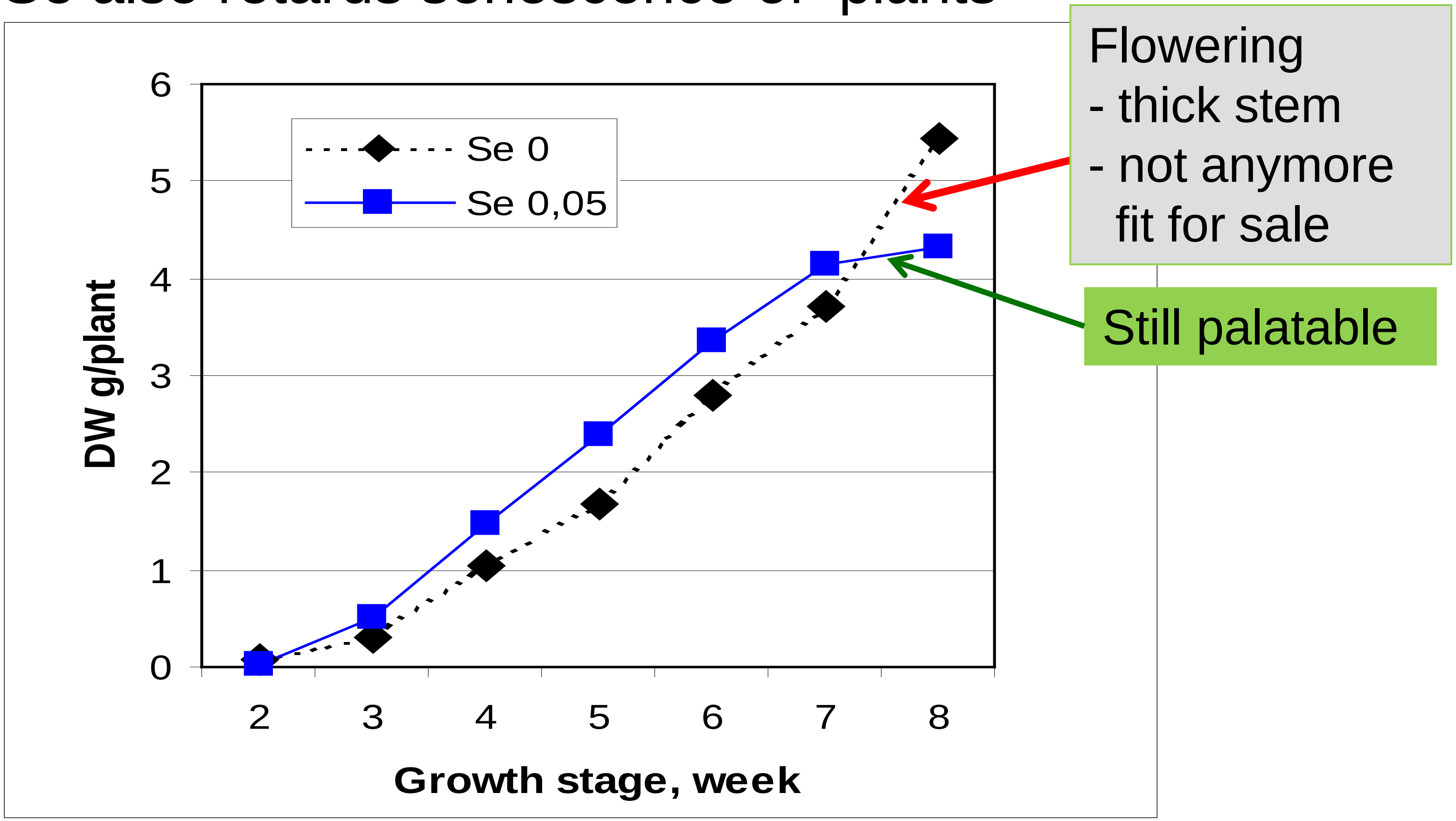
Results of our first pot experiment with lettuce

- at proper levels Se promotes the plant growth



Lettuce yields at various Se fertilisation levels ($\mu g\ kg^{-1}$ of soil)

Subsequent studies with lettuce:
Se also retards senescence of plants



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*)

- N_2-fixing plant are valuable protein source in feed ⇒ food chain
- Se fertilization increased
  - the number and fresh weight of nodules
  - concentration of carotenoids and chlophyll 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

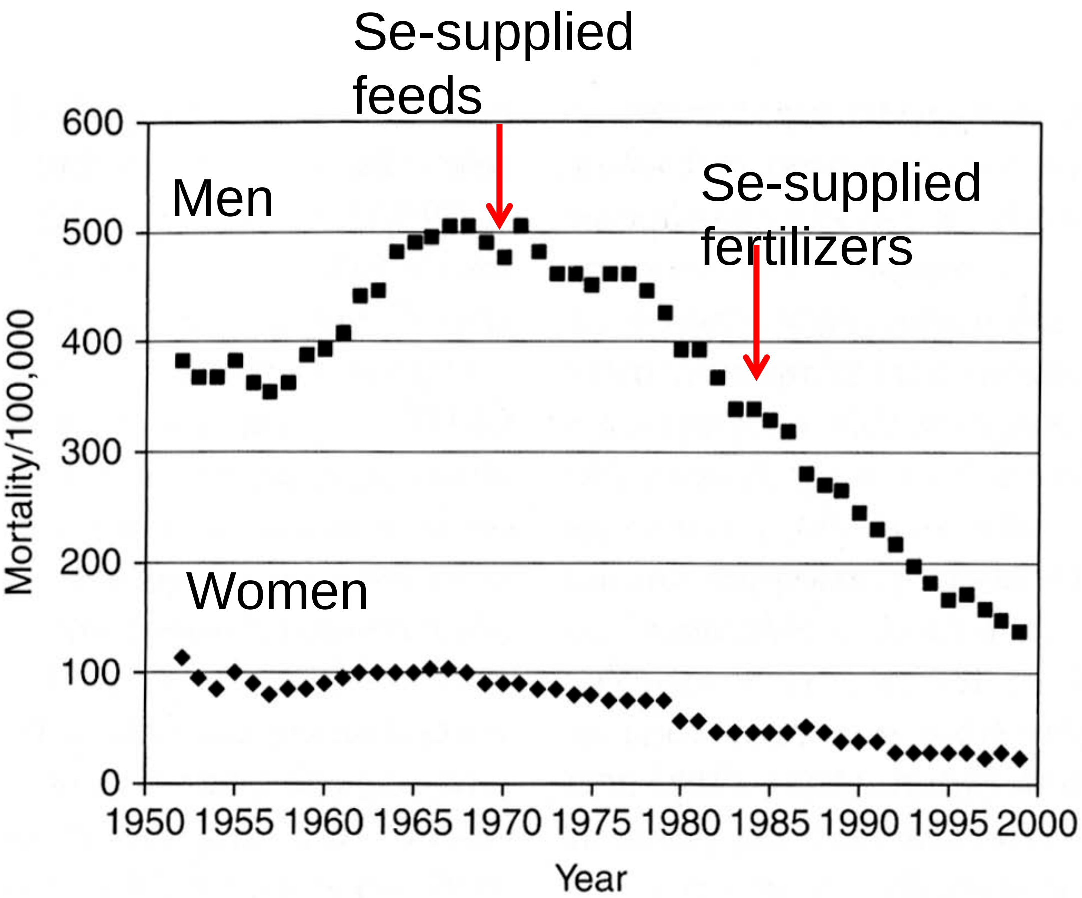
  Numbers **in red** refer to accumulation of fertilizer-Se during 12 years in experimental fields (mineral soils)

- 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 enchance 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-egded by its very nature