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Report of the Selenium Working Group 2022

Merja Eurola, Tarja Alainen, Titta Berlin, Päivi Ekholm, Iris Erlund, Veli Hietaniemi, Jaakko Mannio, Satu Mykkänen, Marjo Pulkkinen, Tarja Root, Mervi Seppänen, Katri Siimes, Eija-Riitta Venäläinen and Kari Ylivainio

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Summary

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In Finland selenium has been added to compound fertilizers since 1984. In the background of this action were studies of the low selenium contents of domestic foods and feeds and concern about its negative effects for public health. Climatic and soil conditions increase the conversion of selenium into forms unavailable to plants and selenium fertilization is needed annually to maintain adequate selenium levels in domestic foods and feeds.

During the growing season plants convert inorganic fertilizer selenium into organic selenium compounds that humans and animals can utilize more efficiently than inorganic selenium. Already in the growing season 1985 the effects of selenium supplemented fertilization were seen in domestic foods and feeds. Selenium contents increased 3–4-fold. With fertilization selenium concentrations in foods have been at adequate level to maintain the selenium adequate intake which is in accordance with recommendations. Additional selenium supplements are not needed. Selenium intake can be regulated by the amount of selenium in fertilizers (changed in 1990, 1998, 2007, 2013). Reasons behind these revisions were the changes in fertilization practises. Recent years interest towards bio-based fertilizers (BBFs) have increased due to both environmental and economic reasons. Fertilizing Products Regulation provides means for free movement of BBFs within the EU and a way to reduce EU:s dependency on imported mineral fertilizers. Due to various nutrient sources for producing BBFs concentrations of selenium varies as well. However, bioavailability of selenium was poor.

Changes in the selenium contents of fertilizers affect directly to the selenium intake of the population and selenium concentrations in human serum. 2010s selenium intake was about 0.08 mg/day/10 MJ and the serum selenium level 1.5 µmol/l. Both intake and serum selenium are at good and adequate level.

Soluble selenium concentration in cultivated soils has remained about the same low level during the past 37 years despite annual application of selenium supplemented fertilizers. This is probably due to small annual application rates of selenium and its binding to insoluble form and thus requiring annual application to ensure adequate selenium uptake by plants. The selenium concentrations in surface waters and fishes have been at acceptable level. During floods and heavy rains soil erosion can increase selenium losses somewhat, but generally selenium fertilization has not affected surface waters. However, environmental issues should be followed regular basis.

Keywords: selenium, fertilizer, bio-based fertilizer, fertilization, food, feed, soil, surface water, intake, human serum

Tiivistelmä

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Seleeniä on Suomessa lisätty moniravinteisiin lannoitteisiin vuodesta 1984 lähtien. Toimenpiteen taustalla olivat tutkimukset elintarvikkeiden ja rehujen pienistä seleenipitoisuuksista ja huoli alhaisen seleeninsaannin vaikutuksista väestön ja tuotantoeläinten terveyteen.

Kasvukauden aikana kasvit muuttavat epäorgaanisen lannoiteseleenin orgaanisiksi seleeniyhdisteiksi, joita ihmiset ja eläimet pystyvät hyödyntämään tehokkaammin kuin epäorgaanista seleeniä. Seleenin lisäys epäorgaanisiin lannoitteisiin näkyi kotimaisissa elintarvikkeissa ja rehuissa heti kasvukaudella 1985, jolloin niiden seleenipitoisuudet nousivat noin 3–4 kertaisiksi. Seleenilannoituksen myötä kotimaisten elintarvikkeiden seleenipitoisuudet ovat olleet riittävällä tasolla ylläpitämään suositusten mukaista seleenisaantia väestössä, eikä ylimääräisen seleenilisän käyttöön ole ollut tarvetta. Epäorgaanisten lannoitteiden seleenimäärää säätämällä (muutokset vuosina 1990, 1998, 2007, 2013) voidaan vaikuttaa seleeninsaantiin. Muutosten taustalla ovat olleet lannoituskäytäntöjen muutokset. Kiinnostus kierrätyslannoitteita kohtaan on lisääntynyt viime vuosina johtuen sekä ympäristöllisistä että taloudellisista näkökohdista. EU:n uusi lannoitevalmisteasetus mahdollistaa kierrätyslannoitteiden vapaan liikkuvuuden ja voi siten vähentää EU:n riippuvuutta tuontilannoitteista. Koska kierrätyslannoitteiden valmistamiseen käytettävät raaka-aineet vaihtelevat, vaihtelevat myös niiden seleenipitoisuudet. Kierrätyslannoitteiden sisältämä seleeni oli kuitenkin heikosti ohralle käyttökelpoisessa muodossa

Muutokset lannoitteiden seleenipitoisuuksissa vaikuttavat suoraan väestön seleeninsaantiin ja ihmisen veren seerumin seleenipitoisuuksiin. Seleeninsaanti on ollut 2010-luvulla noin 0,08 mg/päivä/10 MJ ja väestön seerumin keskimääräinen seleenitaso, 1,5 µmol/l. Sekä seleenin saanti että seerumin seleenitaso ovat nyt hyvällä ja riittävällä tasolla.

Seleenilannoitus ei ole vaikuttanut liukoisen seleenin määrään viljelymaissa 37 vuoden aikana. Lannoitteista viljelymaihin tulevan seleenin määrä on suhteellisen pieni ja se muuttuu kasvukauden kuluessa niukkaliukoiseen muotoon sitoutuen maaperään. Pintavesien ja kalojen seleenipitoisuudet ovat olleet hyväksyttävällä tasolla. Tulvien ja sateiden aiheuttaman maa-aineksen eroosion myötä seleeniä voi kuitenkin siirtyä pelloilta vesistöihin normaalia enemmän. Yleisesti suuria vaikutuksia vesistöihin ei ole havaittavissa, mutta vesistöjen seurantaa tulisi tehdä säännöllisesti.

Avainsanat: seleeni, lannoitus, lannoite, kierrätyslannoite, elintarvike, rehu, maa, luonnonvesi, saanti, seerumi

Sammandrag

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Selen har tillsatts i gödselmedel med flera näringsämnen i Finland sedan 1984. Åtgärden baserades på forskning om det låga seleninnehållet i livsmedel och foder och oro för effekterna av lågt selenintag på befolkningens och husdjurens hälsa.

Under växtsäsongen omvandlar växter oorganiskt gödningsmedel selen till organiska selenföreningar, som människor och djur kan använda mer effektivt än oorganiskt selen. Tillsatsen av selen till oorganiska gödningsmedel var synligt i hushålls mat och foder redan under växtsäsongen 1985, då deras selenhalt ökade cirka 3–4 gånger. Med selengödsling har selenhalten i inhemska livsmedel legat på en tillräcklig nivå för att bibehålla det rekommenderade selenintaget för befolkningen, och det har inte funnits något behov av att använda ett extra selentillskott. Genom att justera mängden selen i oorganiska gödselmedel (förändringar 1990, 1998, 2007, 2013) kan selenintaget påverkas. Förändringar i gödslingsmetoderna har legat bakom förändringarna. Nuförtiden kan den ökande användningen av biobaserade gödselmedel minska selenhalten i grödor och foder, eftersom deras selenhalt är låg och växterna inte kan utnyttja det selen de innehåller dåligt. Intresset för återvunna gödselmedel har ökat de senaste åren på grund av både miljömässiga och ekonomiska synpunkter. EU:s nya gödselproduktförordning möjliggör fri rörlighet för återvunna gödselmedel och kan därmed minska EU:s beroende av importerade gödselmedel. Eftersom råvarorna som används för att tillverka återvunna gödselmedel varierar, varierar även deras selenhalt. Selenet i återvunnet gödningsmedel var dock svagt användbart för korn.

Förändringar i selenhalterna i gödselmedel påverkar direkt selenintaget hos befolkningen och selenhalterna i humant blodserum. Selenintaget under 2010-talet har varit runt 0,08 mg/dag/10 MJ och den genomsnittliga selenhalten i befolkningens serum, 1,5 µmol/l. Både selenintaget och serumselennivån är nu på en bra och tillräcklig nivå.

Selengödsling har inte påverkat mängden av lösligt selen i jordbruksmark under 37 år. Mängden selen som kommer från gödningsmedel till jordbruksmark är relativt liten och under växtsäsongen övergår den till en svårlöslig form som binder till jorden. Selenhalterna i ytvatten och fisk har legat på en acceptabel nivå. Men på grund av jorderosion orsakad av översvämningar och regn kan selen flytta från åkrar till vattendrag mer än normalt. Generellt sett kan inga större effekter på vattenförekomster observeras, men övervakning av vattenförekomster bör göras regelbundet.

Nyckelord: selen, gödsel, gödsling, livsmedel, foder, jord, råvatten, intag, serum

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1. Introduction

Since discovery of the essentiality of selenium (Se) to humans and animals in 1957 (Schwartz & Folz 1957), it has been studied extensively. Selenium enters to food chain almost exclusively through plants, thus in the low selenium regions agronomic biofortification both food and crops with selenium is especially important for human nutrition and health. In Finland selenium concentration in plants is determined by geological and climatic factors. In Finnish conditions soluble, plant available forms of selenium are easily reduced and bound into iron, aluminum and manganese oxides making selenium poorly available to plants. In 1960s selenium deficiency diseases of farm animals were treated with selenium and vitamin E. In 1969 supplementation of animal feeds with selenite was started. In 1970s extensive mineral element study (Koivistoinen 1980) of Finnish foods confirmed very low selenium content of domestic agricultural products, as well. The selenium intake of the population was well below the recommendations and concern about the possible selenium deficiency effects on the Finnish population appeared. An extensive research program was started to study the possible ways to increase dietary selenium intake of the Finnish population.

In 1983 Ministry of Agriculture and Forestry appointed the Selenium Working Group which includes authorities, experts from research institutes and companies. This group made an action proposal of adding selenium into compound fertilizers used for cereal and grass production and developed the consequent long-term follow up study. Target was to add sodium selenate into fertilizers, so that the selenium level of cereal grains would rise to about 0.1 mg/kg. This was considered adequate amount to increase the selenium content in domestic foods and feeds to the level that wound maintain sufficient selenium intake for Finnish population. The intervention started 1.7.1984 and has continued now for 37 years. Large amount of data has been collected and reported during this period.

In Finnish conditions selenium supplemented fertilization has been an easy, economical, and effective method to improve selenium status of the whole population and Se levels can be controlled by chancing the permitted levels of selenium in fertilizers and feeds. It is also safe way, as plants act as buffers minimizing the risk of excessive Selenium intake. Responsible use of fertilizers combined to the Finnish climatic and environmental conditions lower the risk of selenium accumulation and leaching. In collaboration, selenium levels are constantly monitored and it is possible to quickly react and reformulate selenium concentration in mineral fertilizers.

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We thank all the persons and companies who have been voluntarily involved in the activities of the Selenium Working Group. Eurofins Agro Ltd. has given the results of the soil selenium analyses for the use of the Working Group. The selenium results of many other research projects of the participating organizations have also been included. We thank all those people who have donated blood samples for the research. Many thanks to the laboratory staff of the participating organizations for their valuable work with the selenium analyses.

2. Materials and methods

The effects of selenium fertilization are monitored constantly. Situation is assessed and controlled by analyzing the Se content in the most important domestic agricultural products, human serum, soil, and fertilizers at regular intervals. Also, environmental aspects have been studied at times. All the participating organizations have collected the samples according to their own sampling systems. Most of the samples come from the other follow-up studies of each institute. To make the Se monitoring as cost-effective as possible co-operation between the institutes is important. For example, cereal samples are collected From National Grain Quality Monitoring program, operated by Finnish Food Authority. National Resources Institute conduct sampling from this material for Se monitoring.

The division of the selenium monitoring between participating organizations is as follows:

Natural Resources Institute Finland

- foods and cereals: milk, cheese, bread, fish, vegetables, cereals (wheat, barley, oats, rye)
- soil, manure and organic soil improvement materials

Finnish Food Authority

- meat and liver (pork, beef)
- feeds
- fertilizers

Finnish Institute for Health and Welfare

- human serum and blood

University of Helsinki

- assessment of selenium intake

Finnish Environment Institute

- surface water

Eurofins Agro Ltd.

- Analyses of selenium from the soil samples taken by the farmers

2.1. Samples

2.1.1. Fertilizers

Mineral fertilizers: Finnish Food Authority carries out risk-based surveillance of the quality and safety of fertilizers placed on the market in Finland as part of official controls

Bio-based fertilizers: Nitrogen (N) and phosphorus (P) are the main nutrients limiting crop growth and they are supplemented either with synthetic mineral fertilizers or bio-based fertilizers (BBF), originating from nutrient-rich side-streams, e.g., manures, sewage sludges, biowaste or animal by-products. In addition to N and P, BBFs also contains variable amount of other plant nutrients as well, including Se. In a LEX4BIO-project (Horizon 2020, Grant No 818309) 38 BBFs (P-BBFs) were collected across Europe to cover wide range of production function categories (PFCs) and component material categories (CMCs) as stated in the new Fertilising Products Regulation (EU 2019/1009). Selenium concentration of BBFs was analysed with ICP-MS (Agilent Technologies 7800) after microwave digestion with aqua regia. In a growth trial, P fertilizing efficiency of these BBFs was tested by mixing equal amount of total P in a growing media (6.5 kg of P deficient soil) and providing other essential nutrients, except P, to ensure that only P was the growth limiting nutrient. Barley was grown up to the maturity and concentration of Se in both grain and straw yield was analysed after microwave digestion with ICP-MS (Agilent Technologies 7800).

2.1.2. Feeds

Feed samples have been taken according to the guide for feed sampling of Finnish Food Authority (previously Plant Production Inspection Centre, KTTK, and Finnish Food Safety Authority Evira). The guide is based on the Regulation of the European Commission (EU) No 152/2009 and its amendment (EU) N:o 691/2013. Silage samples were obtained from private farms from all over Finland in connection to official controls of feed operators in primary production. Surveillance of the selenium content of commercial compound feeds have been carried out in official control of feed manufacturers and retailers. Samples have been taken by inspectors authorized by Finnish Food Authority or inspectors in Centres for Economic Development, Transport, and the Environment (ELY Centres). Feed samples have been analysed in Finnish Food Authority.

2.1.3. Agricultural soil

Eurofins Agro Ltd. analyses hot water extractable selenium from the soil samples. The method is considered to represent plant available Se concentration in the soil. The samples have been taken by the farmers from their own fields. The number of samples received have varied annually depending on the farmers interests to evaluate Se status of their fields. These results have been provided for the use of the Selenium Monitoring Program anonymously, without any farmers data. Total of 1297 soil samples were analysed by Eurofins Ltd in Mikkeli, Finland during the years 2018–2021.

2.1.4. Surface water samples

Selenium was included into the national surface water monitoring program in 2009. In practice, total selenium is analysed with metals in water samples taken in selected rivers. One of the main purposes of the monitoring program is to gather data for the calculation of riverine loads of heavy metals to the Baltic Sea.

Sampling sites are typically in the downstream and samples are taken from the mean flow. In large rivers the mean flow is estimated to be in the depth of 1-meter in the middle of the river (samples are often taken from a bridge). At least 12 samples are annually taken in 24 rivers. If several intensive sampling sites are located on the same river, the results of only one of them are presented. In practice this means that in river Kymijoki results from sampling site Huruksela are presented while results from Ahvenkoski (western river branch) and Kokonkoski (eastern river branch) are not shown. Results from small rivers Kelopuro and Hietapuro in watershed number 04.963 were identical and only Hietapuro results are shown.

Regional environmental authorities in the Centres for Economic Development, Transport, and the Environment (ELY Centres) took samples until the end of 2015. Since the samples are taken by a consult with contract to ELY Centres. Samples are stabilized by adding concentrated nitric acid (ROMIL SpA) to bottles at field. In laboratory samples are centrifuged before analysis. A minor part of the samples is filtered in laboratory to obtain dissolved part.

2.1.5. Cereals

Finnish Food Authority`s Plant Laboratory monitors grain quality and safety of the annual grain harvest. The grain samples together with their background information are asked from the farmers around Finland. The samples represent both the grain sold on the grain market and grain that remains on the farm. From this material Natural Resources Institute collects randomly samples from different areas for the selenium monitoring. Samples of barley, oats, winter wheat, spring wheat and rye were collected. The quality criteria of wheat (falling number, hectolitre weight and protein) was of bread grain, if possible.

2.1.6. Foods

Food samples are collected from largest retail food stores of two cities. Samples of domestic milk (3,5–4,0 % fat and 1,5–1,8 % fat) cheese (Edam -type, 40 % fat), eggs, rye and wheat bread, rye and wheat flour and Baltic herring are collected four times during the year (March, June, September, and December), so that the seasonal variation will be observed. Samples of cabbage, potato and cultivated rainbow trout are also collected in December. Occasionally other food samples have been studied like milk-based baby foods and organic products.

The sampling system of the food items has varied somewhat during the during the time of the monitoring. Since 2013 the samples have been collected from large retail food stores, located in two cities. From food store two retail packages of same food item from different manufactures are taken. These samples are freeze dried, homogenized, and combined, totaling of three combined samples/food item/sampling round for analyses.

Samples of meat and liver from pig and cattle were obtained from Finnish slaughterhouses. The samples were collected regularly every month according to an annual residue control plan from animals selected randomly from the slaughter line. The samples were packed separately and sent to the laboratory of Finnish Food Authority in temperature-controlled chambers containing coolant canisters before dispatch. Yearly about 120 samples were analysed (30 meat of cattle, 30 of pigs)

2.1.7. Blood samples

Human blood and serum samples were collected from two groups of adults during 1985–2012. One group (n = 30-35) was from Helsinki, the capital, which is located in Southern Finland. The second group (n = 35-45) was from Leppävirta, a rural municipality in Eastern Finland. None of the subjects used dietary supplements containing selenium on a regular basis.

FinHealth 2017 Survey serum samples were used for analyzing selenium in year 2017. This was a comprehensive nationally representative health examination survey (sample size 12 037 adult men and women) (Koponen et al. 2018). Serum samples from 732 men and 798 women were analyzed for serum selenium. For selenium analysis inductively coupled plasma mass spectrometry (ICP-MS) was used.

2.2. Analytical methods and quality control

Every organization analyse the selenium according to their methods (Table 1). Organizations also participate in intercomparison tests according to their quality protocols.

Table 1. Analytical methods

Sample type	Analytical method	Method accred-ited	Reference
Food (except meat and liver), cereals, manure and soil improvement materials	Wet digestion (HNO_3 + $HClO_4$ + H_2SO_4), reduction, extraction into MIBK, measured by ETAAS	X	Kumpulainen et al. 1983.
Meat and liver	Microwave digestion (HNO_3 + H_2O_2), measured by ICP-MS	X	In house-method
Commercial feeds	Microwave digestion (HNO_3 + H_2O_2), measured by ICP-MS	X	SFS-EN 15621, SFS-EN 15763/2010
Silage	Microwave digestion (HNO_3 + H_2O_2), measured by ICP-MS		
Mineral fertilizers	Nitric acid extraction Measured by ICP-OES	X	
Bio-based fertilizers	Agua Regia extraction Measured by ICP-MS		
Serum	ETAAS 2017- ICP-MS		Jacobsen 1988, Gardiner 1995
Soil (Eurofins Agro Ltd.)	Hot water extraction, measured by FI-AAS		Yläranta 1982
Surface water	ICP-MS	X	SFS-EN ISO 17294-2:2016:en

3. Results and discussion

3.1. Fertilizers

3.1.1. Mineral Fertilizers

Ministry of Agriculture and Forestry regulates the permissible amount of selenium in mineral fertilizers. Selenium is added to mineral fertilizers as sodium selenate, which is readily absorbed by plants. Selenium addition should not be made on the surface of the fertilizer granule as it poses an occupational safety risk. The amount of selenium in fertilizers has varied as follows:

- 1984–1990 6 mg kg^{-1} for grassland cultivation
  16 mg kg^{-1} for grain production
- 1990–1998 6 mg kg^{-1} for all fertilizers
- 1998–2007 10 mg kg^{-1} for all fertilizers
- 2007–2013 15 mg kg^{-1} for all fertilizers, exceptional cases 25 mg kg^{-1}
- 2013– 15 mg kg^{-1} for all fertilizers, exceptional cases 25 mg kg^{-1}
  0,0015 % liquid fertilizers, restrictions per hectare

In cases when farmers use mainly manure use mainly manure, it is permitted to use mineral fertilizers containing 25 mg/kg of selenium for grassland and cereal replenishment fertilization. When using liquid fertilizers during the growing season, maximum permissible doses are 10 g of selenium per hectare and when used as a foliar fertilizer maximum dose is 4 grams per hectare.

In recent years on average 10 fertilizer samples have been analyzed for selenium annually, and they have mainly fulfilled the requirements of the fertilizer legislation (Ruokavirasto 2020. Lannoitevalmisteiden tuotevalvonnan analyysitulokset (results of the product control of fertilizers)).

3.1.2. Bio-based fertilizers

Nowadays the Finnish Government has an increasing ambition to recycle nutrients effectively and the vision for 2030 is to have active market for recycled fertilizers (Ministry of Agriculture and Forestry 2022).

According to the EU Fertilising Products Regulation (EU 2019/1009), CE-marked fertilizers can be freely transported across the EU and legislation does not set limits for Se concentration. Selenium concentration varied between 0–166 mg kg^{-1} DW among the studied BBFs (Fig. 1), as compared to 15 mg kg^{-1} in commercially available mineral fertilizers in Finland. Highest values were found from laboratory scale produced struvite, originating from wastewater stream, whereas commercially available struvites, utilizing sewage streams as P sources, had Se concentration below 1 mg kg^{-1} DW. Excluding two laboratory scale produced struvites with high Se concentration, average concentration was 6 mg kg^{-1} DW (36 BBFs), highest concentrations being in biochar, produced from sewage sludge, and in hydrochars (plant based) and BBF produced out of animal proteins and vegetable by-products (Fig. 1). Out of the studied mineral P fertilizers (not supplemented with Se), single superphosphate had far lower selenium concentration (0.2 mg kg^{-1}) than in triple superphosphate (21 mg kg^{-1}).

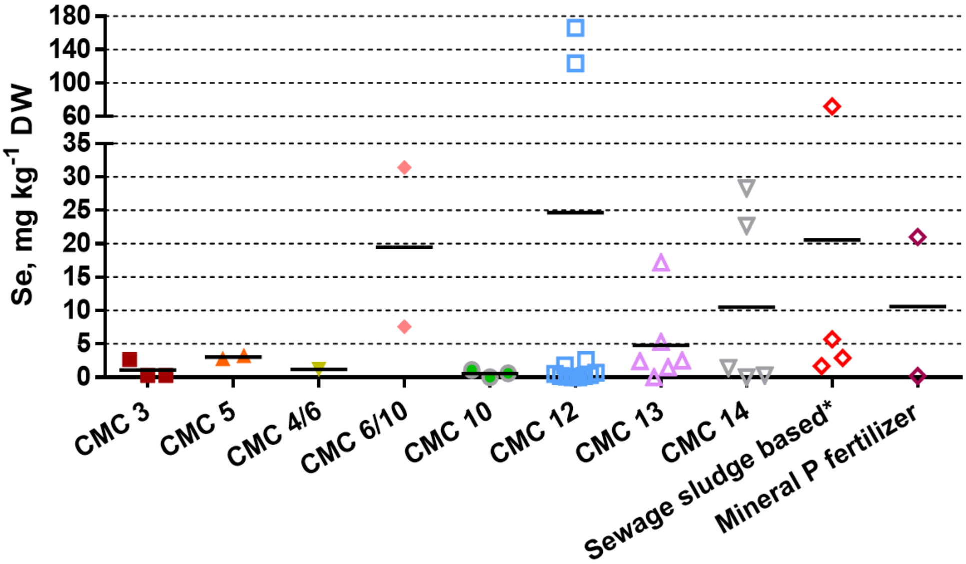

Figure 1. Selenium concentration of the studied bio-based fertilizers, divided according to their Component Material Categories (CMC) as stated in the Fertilising Products Regulation (EU 2019/1009). *Produced from sewage sludge by digesting or pyrolyzing and do not meet the criteria set for the CE-marked fertilizers.

In a greenhouse trials BBF application rates were adjusted according to total-P application, providing 50 mg total-P kg^{-1} soil. Due to different P and Se concentrations in various BBFs, application rate of total Se per pot varied from zero up to 811 µg. Highest Se application rates originated from hydrochars and biochars. Also, laboratory scale produced struvite provided high rates of Se (Fig. 2).

Despite great variation of selenium application rates from different BBFs, Se concentration in barley grains was far below the target concentration of 100 µg kg^{-1} (Fig. 3). In most of the cases Se concentration was below 5 µg kg^{-1} and ash-based (CMC 13) BBFs, originating either from sunflower husk or poultry litter, had the highest Se concentration of 19 and 28 µg kg^{-1}, respectively. Selenium concentration in straw followed the same pattern as in grain yield, highest values of 32 and 47 µg kg^{-1} being in the above-mentioned treatments and rest had Se concentrations below 13 µg kg^{-1}. This study showed that BBFs were poor source of selenium and selenium concentration in harvested yields needs to be followed if BBFs replaces the currently used selenium supplemented mineral fertilizers.

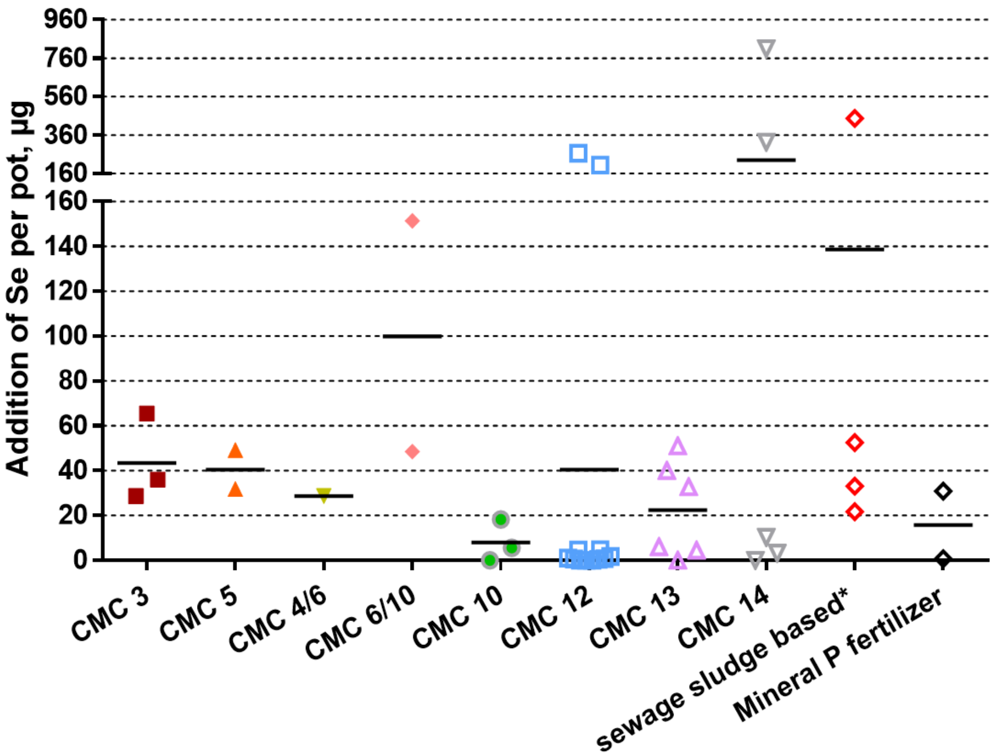

Figure 2. Supplemented rates of total Se per pot from various BBFs in a greenhouse trial when application of BBFs was based on total P (325 mg P kg^{-1} soil). Different BBFs were grouped according to Component Material Categories (CMC) as stated in Fertilising Products Regulation (EU 2019/1009). *Produced from sewage sludge by digesting or pyrolyzing and do not meet the criteria set for the CE-marked fertilizers.

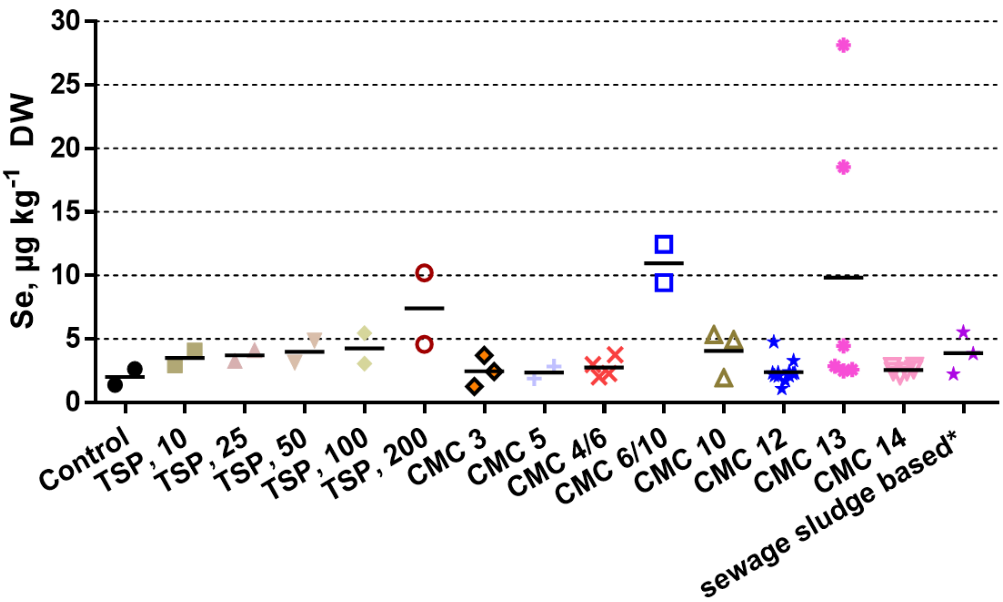

Figure 3. Effect of various BBFs on selenium concentration in barley grains in a pot trials. Triple superphosphate (TSP) was a reference P fertilizers and numbers after TSP indicate the amount (mg kg^{-1} soil) of added P at the start of the growth trial. All BBFs supplemented 50 mg P kg^{-1} soil. *Produced from sewage sludge by digesting or pyrolyzing and do not meet the criteria set for the CE-marked fertilizers.

3.2. Environment

3.2.1. Agricultural soil

Average hot-water extractable selenium concentration in the analyzed soil samples from farmer´s field was 0.014 ± 0.005 mg l^{-1}. Out of the 1297 soil samples analyzed, selenium concentration was below the detection limit (0.01 mg l^{-1}) in 498 samples and were not used for calculating the average value. Prior to the use of Se supplemented mineral fertilizers, hot water extractable Se concentration was reported to be 0.011 mg l^{-1} (n = 250, Sippola 1979). In this study selenium concentration in soil samples was at the same level as in those soil samples taken in years 2003-2006 (0.023 ± 0.036, 61 out of 129 samples above 0.01 mg l^{-1}, Eurola et al. 2008) and 2013-2015 (0.014 ± 0.004, n = 327/486 above 0.01 mg l^{-1}, Eurola et al. 2016).

Hot water extractable selenium concentrations were at the same level in mineral (n = 724, 0.013 ± 0.005 mg l^{-1}) and organic soils (n = 74, 0.014 ± 0.003 mg l^{-1}) and among soil textural classes selenium concentrations were at the same level (Fig. 4)

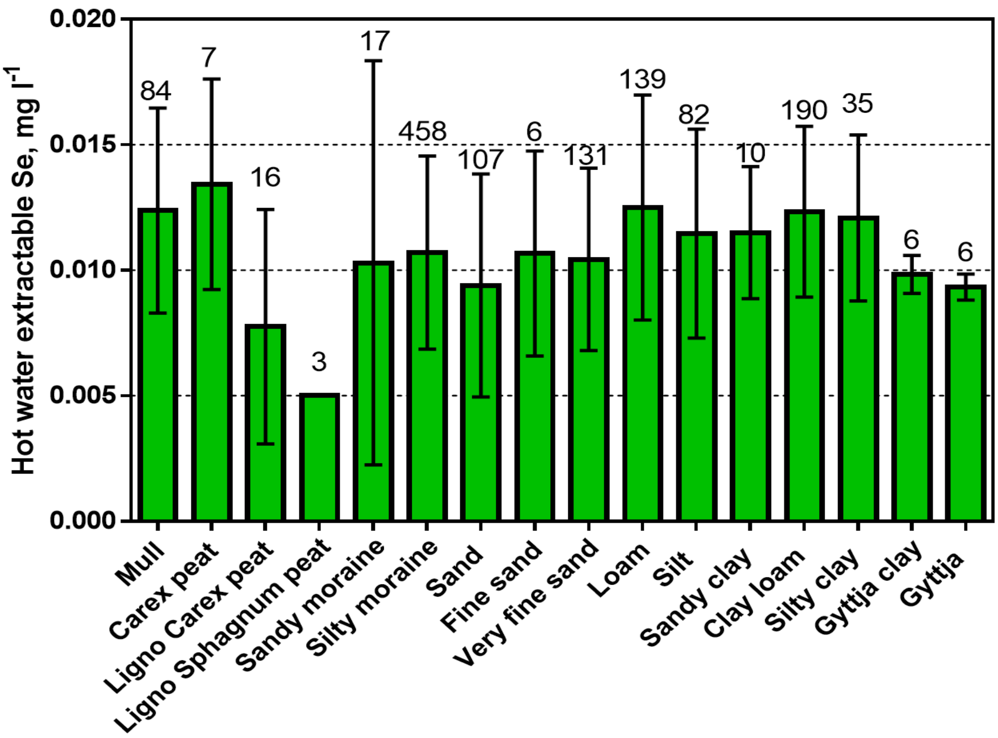

Figure 4. Hot water extractable selenium concentration in Finnish agricultural soils. Number above error bars indicate the amount of soil samples.

Hot water extractable Se concentration is considered to represent plant available Se concentration, averaging 4 % of the total Se concentration in soil (Yläranta 1985). Total Se concentration prior to use of Se supplemented fertilizers was about 0.2 mg kg^{-1} (Sippola 1979) and after using Se fertilizers for 20 years it was reported to be about at the same level (Yli-Halla 2005).

Hot water extractable Se concentration in plough layer (25 cm) of agricultural soils corresponds roughly 25 g Se ha^{-1} (0.01 mg l^{-1}, bulk density 1 kg l^{-1}). This amount of Se will be applied already in four years with an annual mineral fertilization rate of 500 kg ha^{-1} (15 mg Se kg^{-1}), showing that since 1985, Se is applied in mineral fertilizers many times the amount of hot water extractable Se found in Finnish agricultural soils. Commonly only about 10 % of the applied Se will be taken up by the crops (Yli-Halla 2005) and rest will presumably retain in soil. Despite of the positive Se balances since the start of Se application, this is not evident in hot water extractable Se concentration. However, in the study of Keskinen et al. (2011), field applied Se in mineral soils was found in insoluble fractions as adsorbed, organically associated and recalcitrant form. It has also shown that residual fertilization value is poor and Se concentration in crop decreases to levels prior to Se application if fertilization is omitted (Yläranta 1984).

3.2.2. Surface water

While selenium is an important micronutrient to almost all animal cells, excess amounts can have toxic effects in the environment. This chapter tries to capture two important topics: (1) How selenium concentrations have changed in surface water over time; and (2) Are current selenium concentration levels in Finnish surface waters at environmentally safe level. Existing data is compiled to find the answers.

How selenium concentrations have changed in river water?

The current selenium monitoring in river water started in 2009. Results are available in the surface water quality database (VESLA) of Finnish environmental authorities. Monitoring and analysis is designed for metals and selenium has simply been included into the multiresidue analysis. Thus e.g. quantification limit is not optimized for selenium and it has been too high compared to the environmental concentration levels. On the other hand, these side-results have provided information on selenium concentration in over 1800 river water samples (2009–2020) and on-going monitoring is improving with time.

In non-agricultural areas, selenium concentration has mainly been lower than quantification limit (0.1 µg l^{-1} since 2013) (Table 2). This corresponds well to concentration level found in a screening project of Finnish headwater streams in 1990 (Wang et al. 1994). In 1990, the median value varied between regions being highest in South-West Finland (0.09 µg l^{-1}) and lowest in the West coast (rivers running to Gulf of Botnia) (0.03 µg l^{-1}). The headwater sites likely represented background conditions because concentration in stream water correlated with concentration in stream sediment and were at the same level as in wells.

In agricultural areas, the average selenium concentration was typically 0.15–0.25 µg l^{-1} but even higher average values were observed in rivers Kyrönjoki and Lapuanjoki (Table 2). The fluctuation of selenium concentrations in selected rivers are presented in Figure 4. The figure demonstrates that selenium concentrations increased in agricultural rivers in 2013–2015 but decreased close to estimated background concentrations in 2018–2020.

In river Vantaanjoki, selenium concentration range was 0.08–0.19 µg l^{-1} (n=47) in 1991–1992 (Wang et al. 1994). During 2009–2017 (every year) the annual average concentrations were higher than in 1990–1992. In 2018–2020, selenium concentration did not exceed 0.10 µg l^{-1} in river Vantaanjoki.

The highest selenium concentrations were detected in rivers Lapuanjoki (up to 4.0 µg l^{-1}) and Kyrönjoki in winter 2014–2015. The rivers locate in the region where upstream screening indicated the lowest natural selenium level in Finland in 1990 (Wang et al. 1994). Acid sulphate soils are predominant in the basin areas of the two rivers. Normally selenium adsorption in acid sulphate soils hinders the mobility and even crop uptake of selenium. Therefore, crop selenium content has reported to be lower in acid sulphate soils than in other areas (e.g. Harmanen

2007). It is likely that this has led to higher soil storage of selenium in acid sulphate soils – although the selenium is likely in immobile form.

Monthly riverine loads were calculated for selected rivers by multiplying the monthly flow volume with concentration. The dynamic of selenium loading was very similar in river Vantaanjoki and in rivers Kyrönjoki and Lapuanjoki. In period 2009–2020 without years 2013–2015 (so 9 years), the annual riverine loads were 62±22 kg (mean ± std), 319±193 kg and 220±141 kg in rivers Vantaanjoki, Kyrönjoki and Lapuanjoki, respectively. The highest loads were observed in 2015, when annual riverine loads were 3.1, 5.7 and 7.9 times higher than the presented average values.

Reasons for observed high concentrations in 2013–2015 are not known. Similar increase was not observed in rivers not affected by agriculture. There was no change in selenium addition in fertilizers. Selenium deposition is not measured in Finland. However, reported point source emissions to surface water or air were not higher than in other years (Finnish national YLVA database). A hypothetical explanation is that water driven erosion from agricultural areas was higher during 2013-2015 and, further, the differences between rivers were linked to the different selenium concentration in eroded soils. The selenium content in fertilized acid sulphate soils is likely higher than in soils, where higher proportion of added selenium is taken up by crops. However, the above explanation is not supported by measured erosion loads (fine material filtered by 0.4 µm mg l^{-1}).

Whilst other reasons have not be identified, the most likely explanation for observed selenium increase are related to weather conditions, hydrology and the mobility of selenium. Bioavailability and crop uptake are identified as one of the main reasons for the low recovery of added selenium in crops (Ebrahimi 2020). The same things influence on bioavailability and mobility (e.g. pH, oxidation status). River flow volumes in 2011 and 2012 were higher than on average. Summers 2013–2015 were warm and flows low in summers but high in November and December. However, warm and dry summers followed by high flows in late autumn have occurred after 2015 as well but they have not caused similar selenium concentrations.

Although not detected in after 2018, there has been a clear difference between selenium concentrations in agricultural and non-agricultural areas. This indicates that agricultural land use might have increased selenium concentration in surface waters. Unfortunately, site-specific long term trend analysis cannot be derived from pre-selenium fertilization time. However, long term changes can be derived from aged lake sediment profile samples. Wang et al. (1995) noticed that selenium concentration in lake sediments had increased during the previous century in most of the studied lakes. They explained the increase by agricultural activity and atmospheric fallout. They did not find clear evidence that selenium fertilization had increased selenium levels in lakes at that time. Cultivation has been linked to sediment selenium already before the start of the selenium fertilization (Koljonen 1974). Deposition has also increased during the industrial time. However, selenium deposition has declined in Europa and in Northern America – and it is expected to be further reduced globally (Feinberg et al. 2021). The role of this phenomenon during the monitoring period is not known.

Table 2. Selenium observations in 24 monitored rivers. The rivers are sorted according to the number of water basin (Nr) in descending order (from North to South and East). Background colors are set according to the average concentration in period 2014–2020: green for concentration <0.1 $\mu g\ l^{-1}$ and orange for values >0.2 $\mu g\ l^{-1}$. The quantification limits of selenium are given in the last row.

Studied rivers [A]					Number of quantified samples/number of analyzed samples				Average concentration[B] $\mu g\ l^{-1}$		
Nr	Name	Typ	Ec	Ag	1990-1993[C]	1994-2008	2009-2013	2013-2020	1994-2008	2009-2013	2013-2020
67	Tornionjoki	ESt	G			1/231	0/70	2/94	<QL	<QL	<QL
65	Kemijoki	Est	M			0/4	0/69	1/96	<QL	<QL	<QL
60	Kiiminkijoki	St	G				3/80	10/92		<QL	<QL
59	Oulujoki	ESk	M				7/96	9/114		<QL	<QL
54	Pyhäjoki	St	G	A			30/88	45/94		<QL	0.13
49	Perhonjoki	St	P	A			14/41	32/91		<QL	0.11
44	Lapuanjoki	St	M	A		2/2	48/68	57/95	1.03	0.33	0.38
42	Kyrönjoki	St	P	A		2/2	59/68	60/96	0.93	0.39	0.41
37	Lapväärtinjoki	St	M	A		0/2	24/69	56/108	0.20	<QL	0.18
35.13	Nokianvirta	ESk	G				3/59	3/58		<QL	<QL
35	Kokemäenjoki	ESk	M.	A			6/86	62/159		<QL	0.14
34	Eurajoki	Ssa	M	A			55/98	22/110		0.24	0.19
28	Aurajoki	Ksa	P	A			53/91	79/125		<QL	0.21
27	Paimionjoki	Ssa	P	A		9/55	54/84	96/135	0.32	0.20	0.25
25	Uskelanjoki	Ksa	P	A			68/97	90/145		0.21	0.24
24	Kiskojoki	Kk	P	A			1/69	27/126		<QL	0.16
23	Mustionjoki	Ssa	M	A			50/83	54/84		<QL	0.14
22	Siuntionjoki	Ksa	M	A			16/44	45/67		<QL	0.17
21	Vantaanjoki	Ssa	M	A	47/47[C]		55/83	75/85	0.12 [C]	0.21	0.21
19	Mustijoki	Ksa	P	A			50/83	70/76		0.21	0.26
18	Porvoonjoki	Ssa	M	A			52/83	74/84		0.21	0.23
16	Koskenkylänjoki	Ksa	P	A			28/83	57/83		<QL	0.23
14	Kymijoki	ESk	G			10/228	9/60	27/84	<QL	<QL	<QL
04.963	Hietapuro	Pt	H				0/102	1/111		<QL	<QL
Qantification limit (QL) $\mu g\ l^{-1}$					0.007[A]	0.2–0.5	0.200	0.100	0.2–	0.200	0.100

A) Background information is taken from water management plans (WMP 2021): River type (Typ), ecological classification (Ec) and column Agr where A indicates that agriculture has been identified as a significant pressure in the water body of the sampling sites (for the largest rivers the whole basin is included and thus e.g. Kymijoki was not set to agricultural river).

River types are classified according to basin area soils and river size. Types in organic soil areas: Est =very large river, St = large river, Pt = small river; Types in clay soil areas: Ssa = large river, Ksa = middle sized rivers; Types in moraine soils (kangasmaat): ESk = very large river, Kk = middle sized river.

Ecological classes: H = high, G=good, M=moderate, P=poor, B=bad

B) In average calculation, half of the quantification limit is used for non-quantified samples. The numerical value of averages smaller than QL are not given but marked as <QL.

C) Vantaanjoki data (1991–1992) from Wang et al. 1994

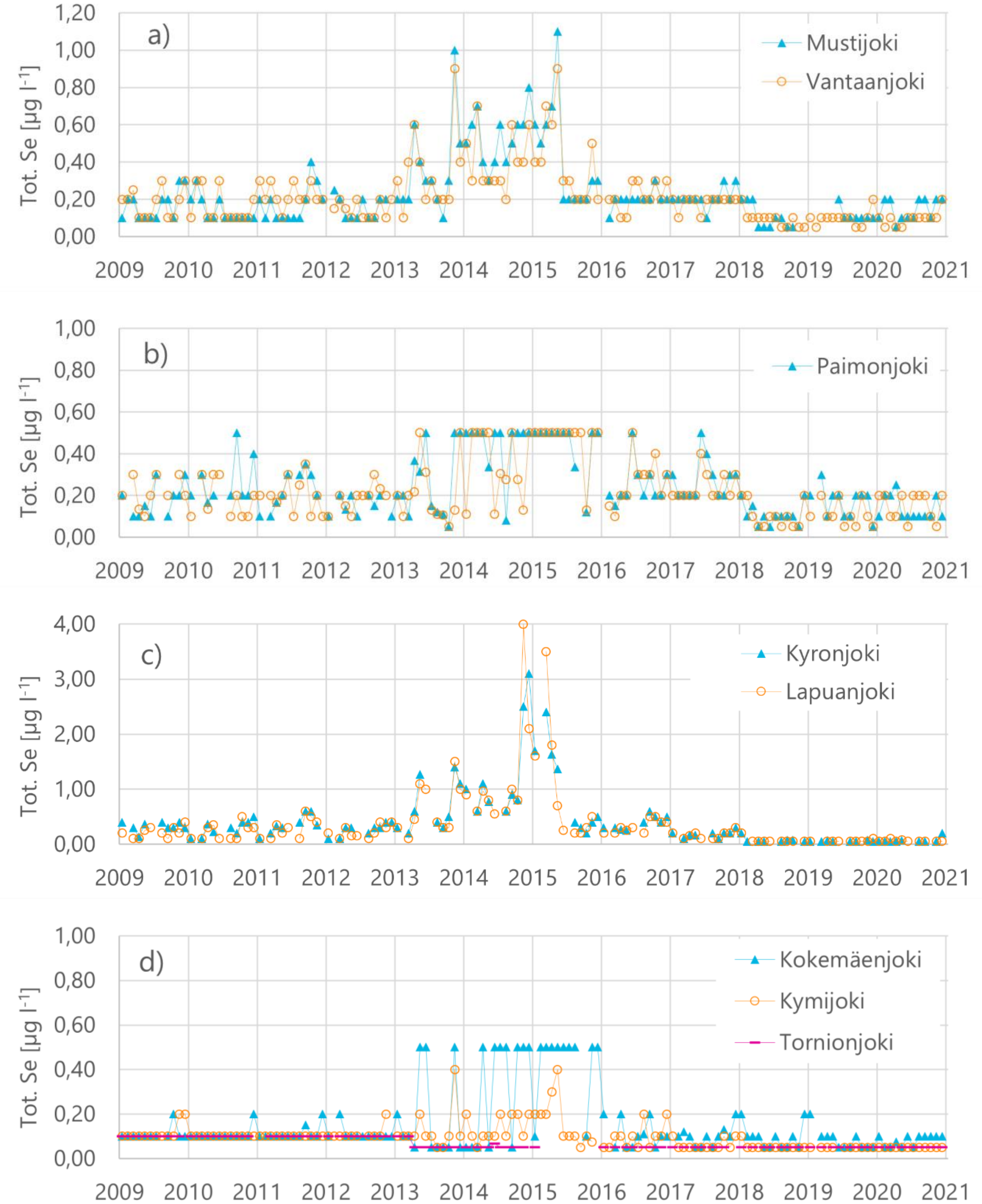

Figure 5. Monthly average concentration of selenium in selected rivers: a) Vantaanjoki and Mustijoki; b). Paimionjoki and Aurajoki; c) Kyrönjoki and Lapuanjoki (note the scale) and d) in three very big rivers: Kymijoki, Kokemäenjoki and Tornionjoki. For non-quantified samples concentration is set to half of the quantification limit.

Are observed concentrations harmful to the environment?

Currently, there is no valid environmental quality standard (EQS) for selenium in surface water in Finland. Selenium was a candidate substance to be added into the list of priority substances under the European union water policy. JRC drafted a selenium EQS dossier in 2016 but quality standard issues are still open. In risk assessment part JRC used predicted no effect concentration of 0.75 μ l^{-1}. Some European countries have set national environmental quality standards, e.g. in Germany and Belgium the quality standard for annual average concentration is 2.0 μg l^{-1} while both lower and higher national values exist in the EU. The high variation in risk assessments can be found in drinking water standards as well. The European drinking water limit value is 20 μg l^{-1}(EU 2020/2184) while e.g. the Canadian drinking water guideline is only 0.05 μg l^{-1} (Health Canada 2014). The measured selenium concentrations in Finnish surface waters have never exceeded the EU drinking water limit while the Canadian one is on the detection limit.

Selenium toxicity in surface waters is related to its bioavailability and bioaccumulation, and these depend on selenium species. Phytoplankton uptakes selenite (SeO_3^{2-}) rapidly from water and selenite is thus seen as the most toxic form. Selenate (SeO_4^{2-}) uptake is not as fast but in long term both selenite and selenate uptakes are related to their concentrations in the water (JRC 2017). Algae and other organisms in low trophic levels can tolerate rather high selenium concentrations. The potential problems are related to selenium bioaccumulation and transform through food web. Selenium can cause teratogenic effects in the higher trophic levels. Fish and water birds are the most sensitive aquatic species (Environment and Climate Change Canada 2021, US EPA 2021, JRC 2017).

Only total selenium concentration is currently analyzed of Finnish river waters – and concentrations by species are not known. In the early 1990's, the total selenium concentrations in rivers and lakes were 0.07 μg l^{-1} (0.03–0.18 μg l^{-1}, n=207) and 0,06 μg l^{-1}, (0.03–0.12 μg l^{-1}, n=76), respectively (Wang et al. 1994, Wang et al. 1995). The proportion of selenite of the total selenium was about the same in rivers and in lakes (8–10 %). However, selenate fraction was higher in stream water (mean 36 %) than in lakes (mean 9 %) and, visa verse, the proportion of humic selenium was higher in lake water (mean 52 %) than in rivers. Selenate was the dominant form of selenium in groundwater (Alfthan et al. 1995). Without current information on selenium species, it is difficult the estimate the harmfulness of selenium in river water.

Although direct effects of selenium on surface water biota are expected to be low in Finland, it must be noted that low selenite concentrations might limit algae blooms (Wang et al. 1995) and even a small selenite addition may facilitate algae growth.

Instead of concentrations in water, the selenium concentrations in top predators gives better indication of its potential risks. In USA, selenium concentration in eggs or ovaries of fish should not exceed 15.1 mg kg^{-1} DW, concentration in whole fish 8.5 mg kg^{-1} DW and in the muscle tissue of fish (skinless, boneless fillet) 11.3 mg kg^{-1} DW (U.S. EPA 2021). In addition, there is an US limit value for selenium concentration in water for special cases like if there are no fish in water body or if the loading has changed. The monthly average concentration in water should not exceed 3.1 μg l^{-1} in rivers nor 1.5 μg l^{-1} in US lakes.

Selenium concentration in Finnish wild-fish has ranged in 1–6 μg kg^{-1} DW, being mainly less than 2 μg kg^{-1} DW (e.g. Wang et al. 1995, Siimes and Junttila 2019, KERTYMÄ database of Finnish Environment Institute). The dataset for selenium is small and scattered in areas, times and fish species. Anyway, Wang et al. 1995 noticed that selenium concentration in perch was more related to the trophic level of the lake than selenium concentration in lake water, concentration being higher in oligotrophic than eutrophic lakes. No correlation between selenium concentration in water and in fish was observed. In addition, the biota trophic level matters.

Summary of selenium risks on Finnish surface waters

According to the monitoring data, selenium concentrations in surface water and fishes are in acceptable level in Finnish surface waters. However, the USA limit value for monthly concentration in surface water, was occasionally exceeded in Lapuanjoki and Kyrönjoki. Moreover, no high trophic level biota is monitored although the potential risk of selenium is highest among them.

Suggestions for further studies and monitoring:

The on-going selenium monitoring in river water should continue. The planned improvements in the analytical method will decrease the quantification limit and improve monitoring quality.

If the same analytical method can be used for selenium analysis in precipitation, it would be interesting to screen selenium wet deposition in order to study it's importance in the selenium mass balance in river basins. Selenium deposition is expected to decrease and increase the need for fertilization in the Northern hemisphere (see e.g. Feinberg et al. 2021).

The level and trend of selenium concentration in biota at high trophic level should be studied. In practice, this could be carried out as a part of other contaminant monitoring together with especially mercury but also other metals studied in fish. If a higher trophic level biota will be added into contaminant monitoring later (e.g. pike or seals) selenium should be included. If concentration levels are not expected to pose risks, the screenings could be repeated e.g. once in ca. a decade, but more often if risks are identified.

Fate of selenium in acid sulphate soils and selenium losses to surface water from these areas should be studied.

3.3. Selenium in animal feeds and nutrition

3.3.1. Selenium requirement of animals

The importance of selenium (Se) in animal nutrition was first discovered in the 1950's when it was shown that most myopathies in sheep and cattle as well as exudative diathesis in chickens could be prevented by adding selenium or vitamin E in the diet. Selenium is a component of the glutathione peroxidase molecule which explains its interactive role with vitamin E (McDonald et al. 2011). Further on mammals have been found to have several selenium containing selenoproteins, of which most act as antioxidants in tissues. Animals need selenium also in the production thyroid hormones (Suttle 2010). However, the difference between selenium requirement and harmfulness is narrow. In large quantities selenium is toxic.

Selenium is essential in growth and reproduction of all animals. The dietary requirement of selenium between animal species varies depending on their digestive system and type of production. In addition, the minimum requirement of selenium depends on its chemical structure and composition of the diet, especially the vitamin E content (Suttle 2010). Feeding organic selenium sources to animals have many benefits compared to inorganic selenium (Pehrson

2005). When assessing the selenium requirement of animals, the vitamin E supply should be assumed to be normal, because vitamin E deficiency enhances selenium requirement.

The Finnish recommendation of selenium for cattle is 0,1 mg kg^{-1} feed dry matter (DW), pigs 0,02 mg MJ NE-1 (0,2 mg kg^{-1} DW), poultry 0,1-0,2 mg kg^{-1} DW and fur animals 0,6-0,9 mg kg^{-1} ka (Luke 2021). Milk production increases selenium requirement in dairy cows (Donald et al. 2011, Suttle 2010).

The incidences of animal diseases have been monitored by the monthly information of veterinarians. In 1994 2846 muscular dystrophy cases in cattle were reported. In 2013 the number of cases was 71. The numbers in pigs, respectively, were 408 and 23 (Fig. 6). The numbers are approximate because all incidences have not necessarily been recorded. After the year 2013 notices about muscular dystrophy has not been given by veterinarians. It is likely that selenium fertilization for one has contributed to animal health. On the other had at the same time also the numbers of many other animal diseases have decreased.

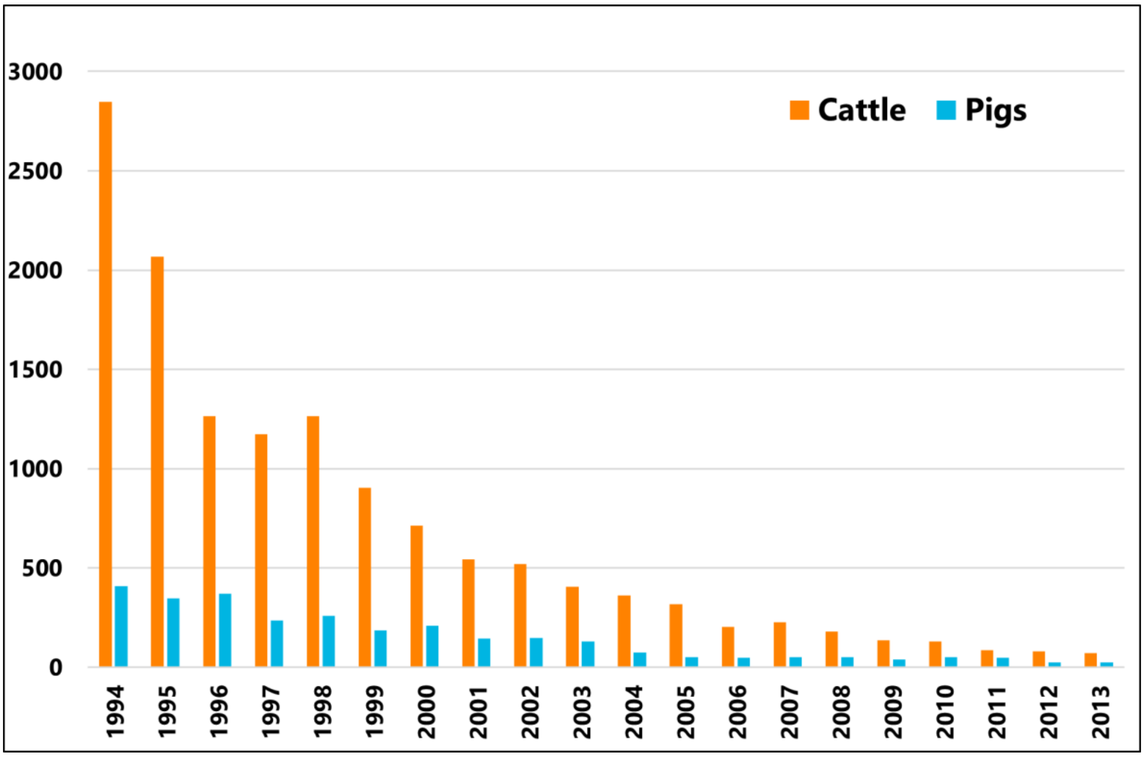

Figure 6. Muscular dystrophy cases **in cattle and pigs during** 1984–2013.

3.3.2. Feeds

Selenium in feed materials is mainly bound into organic protein as selenomethionine and in smaller quantities as selenocysteine as well as other selenocompounds. The amount of selenium in feeds of plant origin varies according to plant species, growth season and soil type. The content of selenium in legumes is generally smaller than grasses (Suttle 2010). The selenium content of soils in Finland is low, but in addition, due to weather conditions and geochemical reasons the selenium intake of plants is limited (Yläranta 1985).

During 1984–2020 the average selenium content of grass silage samples taken by the Finnish Food Authority (former KTTK and Evira) has varied between 0,03-0,37 mg kg^{-1} DW (Fig. 7). Since 1984 the added sodium selenate in fertilizers has increased the amount of selenium in grass silage tenfold. The effect of changes in the amount of added selenium in fertilizers in years 1984, 1990, 1998, 2007 and 2013 seems to reflect on selenium content of silages with delay but the effect has not been permanent in long term. However, in recent years the amount of selenium in silages from conventional production has been increasing. On average 90 % of the silages from conventional production have been fertilized with commercial fertilizers containing selenium. In general, the selenium content of silages may be affected by the decrease in use of commercial fertilizers in farms (Tike 2014) and increased variety of commercial fertilizers on the market as well as the differences between selenium content in commercial fertilizers and their different way of use in farms (Ylhäinen 2014).

Silages from organic or other production systems which do not use commercial fertilizers have contained nearly ten times less selenium than silages from conventional production (figure 3). Increasing of organic cattle and sheep production (Tike 2014) increases the amount of such animals which do not get silage or grain fertilized with selenium rich fertilizers, and therefore the sufficient intake of selenium of these animals needs to be taken care of in other ways, mainly feeding them compound feeds which selenium.

The variation of selenium content of barley and oats since 1990's in Finland has levelled out to an average between 0,09-0,16 mg kg^{-1} DW. Since 2002 in the selenium monitoring programme barley and oats for feed has not been separated from the corresponding food grains, for which the results are reported in this report at point 3.4.

Only fishmeal contains substantial amounts of selenium compared to the other most commonly used feed materials (Suttle 2010). However, according to the Regulation (EU) No 999/2001 fishmeal is not allowed to be used in feeding of ruminants, except in the commercial milk replacers for young and unweaned ruminants. For the other species of production animals, fishmeal provides a good source of protein and selenium.

Compound feeds can be supplemented with both inorganic (sodium selenite or sodium selenate) and organic selenium (selenized yeast inactivated) as feed additives. According to the European feed additive regulation (EU) No 1831/2003 the allowed maximum level of selenium in complete feed or daily ration of animals is 0,5 mg kg^{-1} in feeds containing 12 % of dry matter (DM). This maximum level consists of both naturally occurring and added selenium in feeds. In recent years the importance of selenium in animal production has been widely acknowledged and the use of selenium in animal feeding has increased at farm level. To supply the demand feed manufactures aim to have the selenium content of compound feeds close to the maximum permitted level. Finnish Food Authority carries out monitoring of the quality and safety of compound feeds manufactured in Finland as part of official controls. In recent years on average 80 commercial feed samples have been analysed for selenium annually, and they have fulfilled the requirements of the feed legislation (Ruokavirasto 2020).

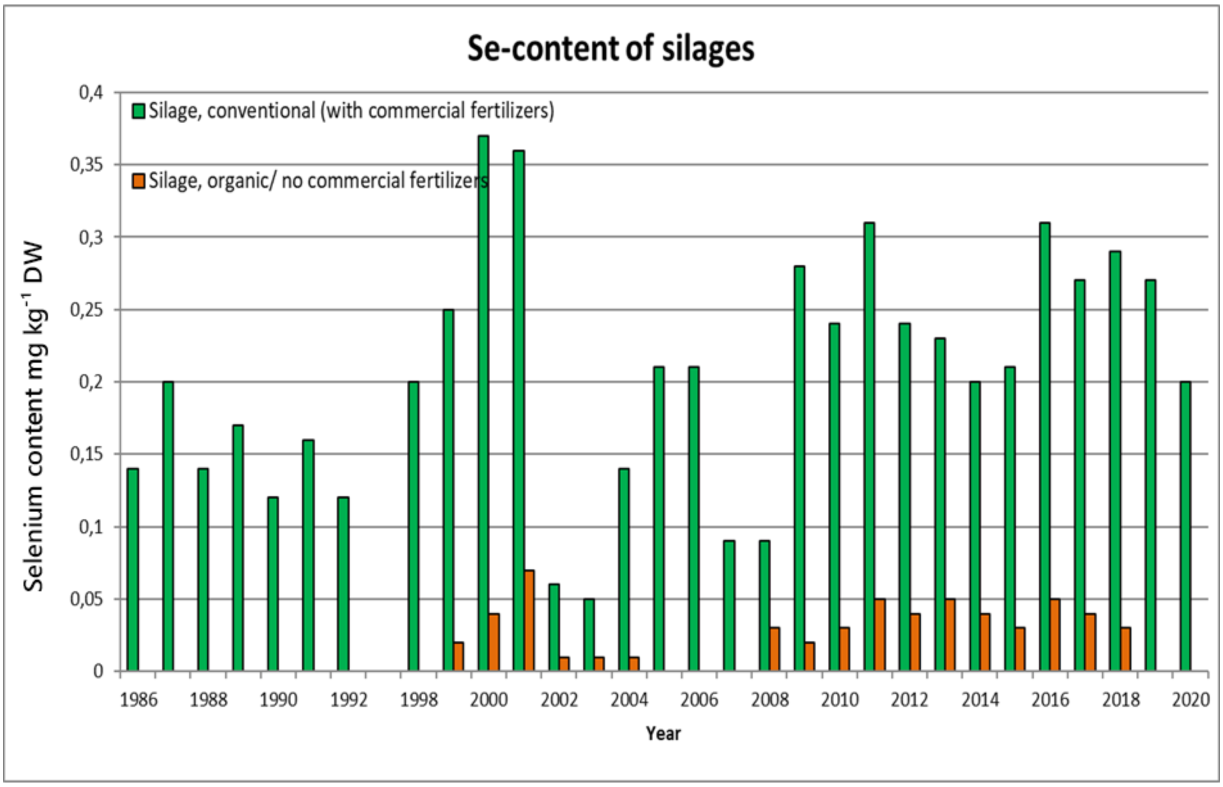

Figure 7. Selenium content of silages during years 1984–2020.

3.4. Cereal grains

In Finland the selenium content of domestic cereal grains depends on the selenium concentration of fertilizers (Table 2). In 1983 it was estimated that the selenium content of cereal grain should be about 0.10 mg kg^{-1} (0.11 mg kg^{-1} DW) to maintain the adequate selenium intake. Immediately after the selenium supplemented fertilization begun selenium content of spring cereals increased and reached the highest level in 1989 0.23-0.30 mg kg^{-1} DW. After this selenium concentration in fertilizer was decreased to 6 mg kg^{-1} to keep the variation and the mean selenium levels in more moderate levels. The selenium levels in domestic cereals can be easily controlled by changing the permitted selenium levels in fertilizers. Reducing selenium concentration in fertilizers to 6 mg kg^{-1} in 1998 dropped the mean selenium levels of spring cereals 50-70 %. The mean selenium levels and range increased again clearly when selenium concentration of fertilizers was increased into 10 mg kg^{-1}. The latest change to 15 mg ka^{-1} fertilizer had lesser effect on the selenium contents and variation. The variation in the farm samples is large as the fertilization practices, growing conditions like weather, soil type and other soil conditions can differ greatly in different farms and different parts of the country. Low selenium contents indicate the use of non-selenium fertilizers, low fertilization doses or use of manure or other type of organic materials and poor soil conditions. Figures 8-12 present the annual fluctuations of the selenium contents of cereal grains in Finland.

Table 3. Selenium content (mg kg^{-1} DW) of cereals grains during 1984–2019.

Year	Selenium concen-tration of fertilizers for cereals	Spring wheat	Winter wheat	Rye	Oats	Barley
	mg kg^{-1}	Mean ± Std Range	Mean ± Std Range	Mean ± Std Range	Mean ± Std Range	Mean ± Std Range
1984	0	0.012 ± 0.006 <0.010–0.026		0.009 ± 0.003 <0.010–0.015		
1989	16	0.300 ± 0.105 0.088–0.660	0.037 ± 0.018 0.016–0.081	0.034 ± 0.013 0.016–0.063	0.230 ± 0.150 <0.010–0.760	0.230 ± 0.140 <0.010–0.650
1993–1998	6	0.110 ± 0.028 0.030–0.160	0.043 ± 0.034 0.012–0.130	0.029 ± 0.018 <0.010–0.075	0.070 ± 0.058 0.023–0.470	0.068 ± 0.048 <0.010–0.320
1999–2007	10	0.140 ± 0.070 <0.010–0.360	0.100 ± 0.049 <0.010–0.250	0.071 ± 0.051 <0.010–0.210	0.130 ± 0.073 <0.010–0.340	0.120 ± 0.073 <0.010–0.450
2008–2019 2013-	15 (25) 15 (25) 0.0015% liquid	0.150 ± 0.110 <0.010–0.530	0.110 ± 0.081 <0.010–0.290	0.080 ± 0.071 <0.010–0.380	0.120 ± 0.094 <0.010–0.430	0.120 ± 0.093 <0.010–0.480

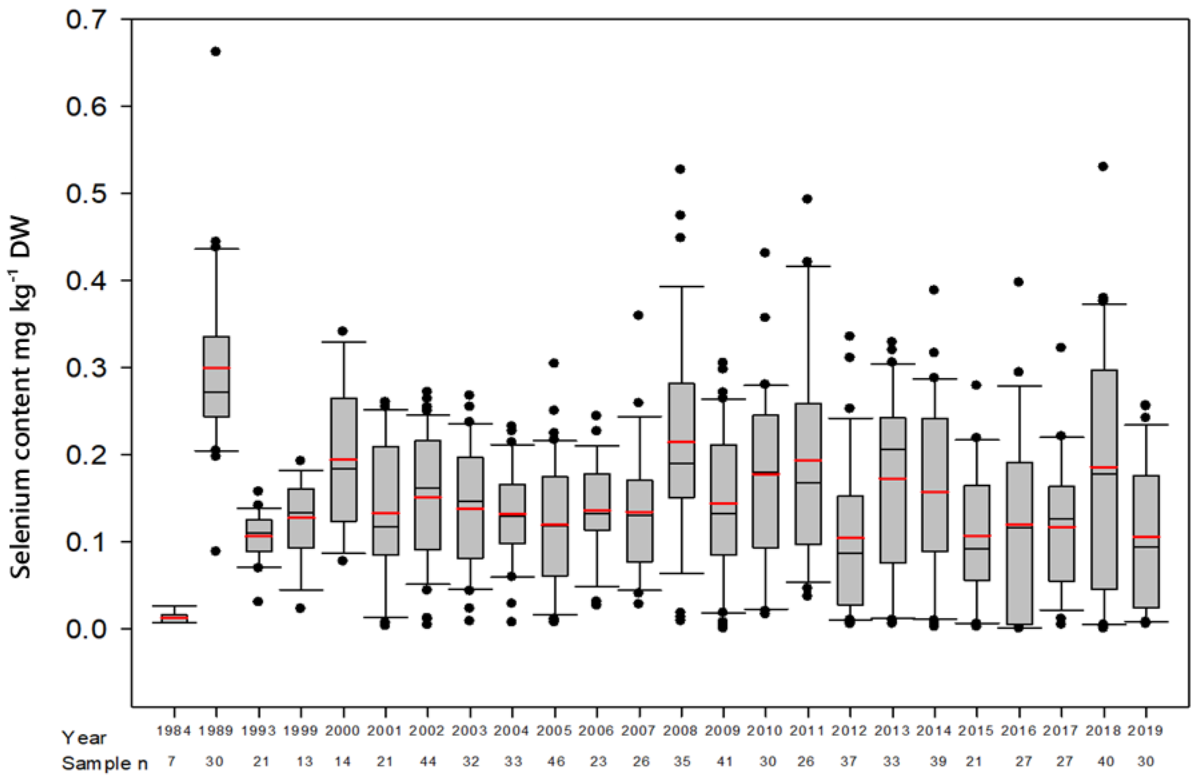

Figure 8. Selenium content of spring wheat during 1984–2019.

Spring wheat (Fig. 8) has the highest selenium content of bread grains. The latest change in the selenium content of fertilizers in 2007 increased the mean selenium content of spring wheat to 0.150 ± 0.110 mg kg^{-1} DW. Also, the occurrence of higher values became more common. However, the annual variation is great and under less favorable conditions like in 2012 selenium concentrations are lower and the mean values are close to the original target value, 0.10 mg kg^{-1} DW. The quality of the grains can also affect the selenium concentrations as selenium in mostly bound to protein fraction in the grain.

In 1980's and 1990's selenium fertilization did not affect winter cereals as much as spring cereals. Winter cereals (Figs. 9 and 10) have about 30–40 % lower selenium contents than spring cereals due to different cultivation/fertilization practices. In the fall, wet and cold soil conditions selenium is reduced and immobilized faster. Also, fertilization practices differ from spring cereals. A common practice was to apply a small dose of selenium supplemented fertilizers in the fall and plain nitrogen fertilizer in spring. The increase in the selenium content of fertilizers in 1998 and 2008 together with the present fertilization recommendations where supplementary fertilization is often given for winter cereals during the growing season have increased the mean selenium content to 0.07–0.11 mg kg^{-1} DW.

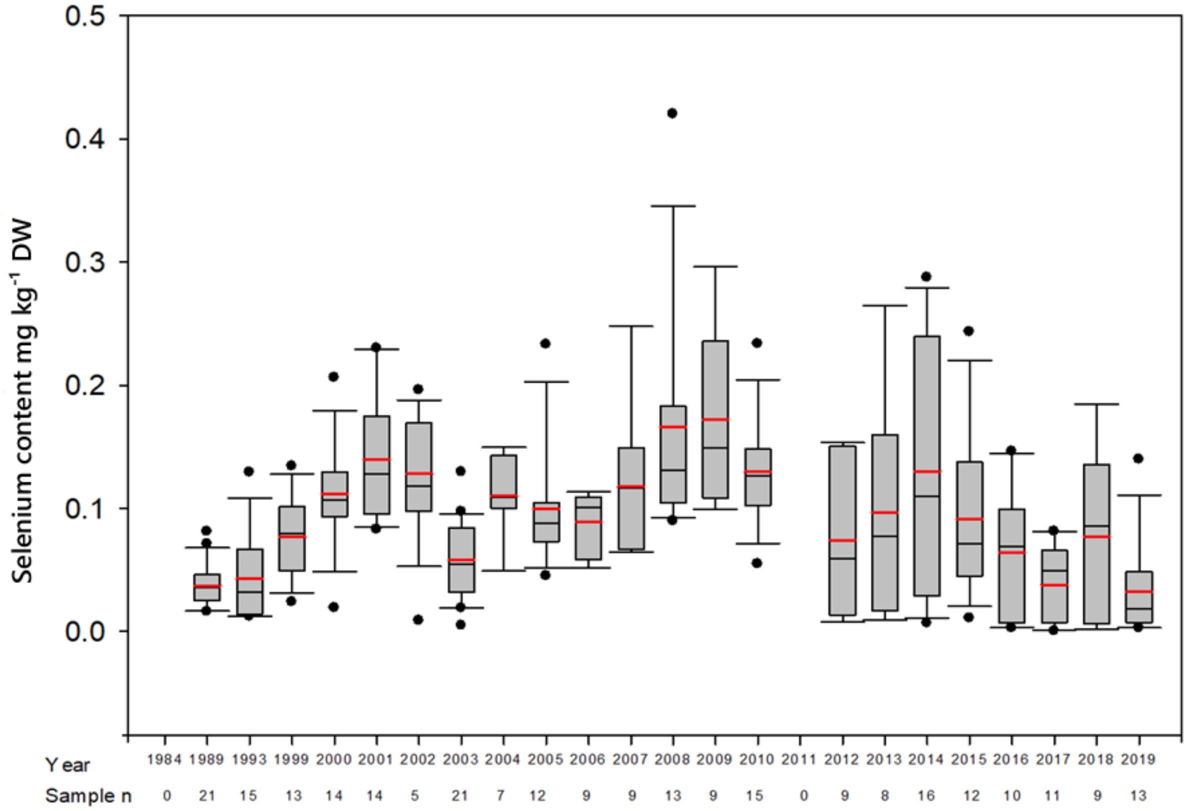

Figure 9. Selenium content of winter wheat during 1984–2019.

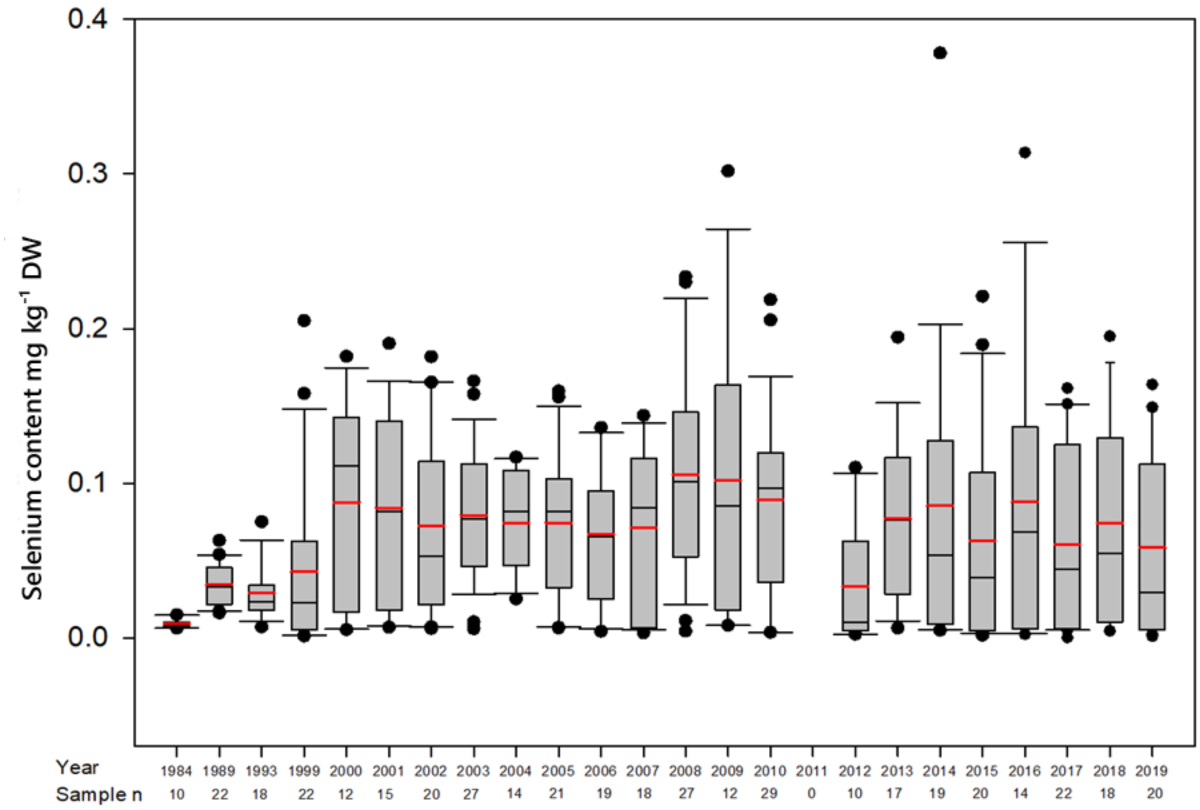

Figure 10. Selenium content of rye during 1984–2019.

Oats and barley (Figs. 11-12) are mainly used for feed purposes, but presently 8–10 % of oats are used for human consumption. Mean selenium contents have stayed near the level of 0.1 mg kg^{-1} DW, but the variation has increased slightly when the amount of selenium in fertilizers was increased to 15 mg kg^{-1}.

Generally, the selenium levels in cereals have been rather stable the in 2000th century even if annual and local variation exist. Changes in selenium concentrations in fertilizers have compensated the changes in fertilizing practices as environmental rules restrict the use of nitrogen and phosphorus. Also, the use of organic fertilizers has increased.

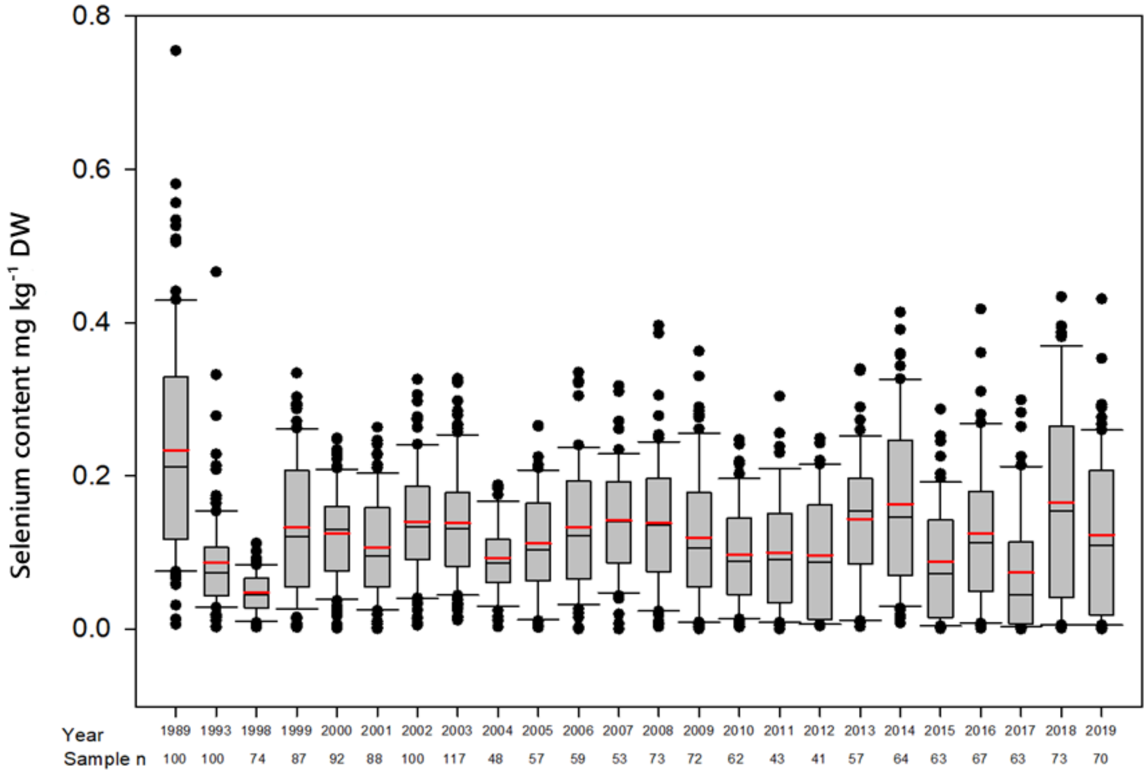

Figure 11. Selenium content of oats during 1989–2019.

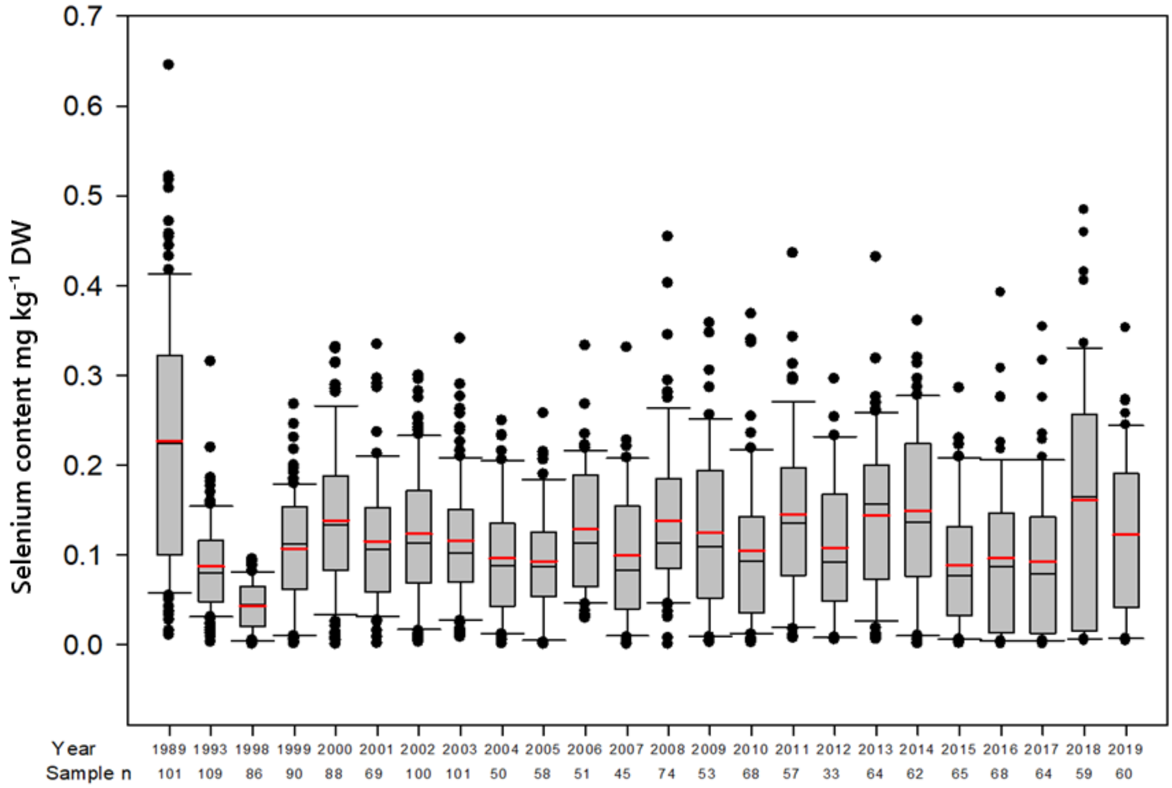

Figure 12. Selenium content of barley during 1989–2019.

3.5. Foods

3.5.1. Cereal products

When selenium fertilization was started the target was particularly to raise the selenium content of domestic cereal grains to about 0.1 mg kg^{-1} DW. This was considered sufficient to raise the selenium status of the Finnish population. The mean selenium contents of flours and bread meet well this target (Table 4 and Figs. 13-14). However, the variation is large due to the different fertilization practices. Low selenium concentrations in conventional cultivation indicate the use of non-selenium fertilizers or manure and other organic fertilizers or low fertilization doses. In Finnish soils selenium is reduced and immobilized during the growing season. Normally spring cereals are fertilized only when sowing, but if necessary additional fertilization is possible. Winter cereals often get phosphorus and potassium fertilization in fall and nitrogen fertilizations during the summer. If nitrogen fertilizers do not contain selenium levels of grain will be low.

In bad harvest years, when the domestic grain production does not cover the need, the selenium levels in cereal products are also affected by the proportion and origin of imported grain in milling. North American grain contains often more selenium than European grain, increasing the selenium levels of cereal products, whereas imports from Europe tend to decrease the selenium contents. The lower selenium contents in winter cereals reflect to the selenium contents of rye products. Also, the cultivation area of winter cereals is smaller. In many years the production of rye has not been able to cover domestic consumption.

Table 4. Selenium content (mg kg^{-1} DW) of wheat and rye flours and bread and oatmeal during 1984–2020.

Year	Selenium concentration of fertilizers for cereals	Wheat flour	Wheat bread	Rye flour	Rye bread	Oatmeal
	mg kg^{-1}	Mean ± Std Range	Mean ± Std Range	Mean ± Std Range	Mean ± Std Range	Mean ± Std Range
1984	0	0.06 ± 0.03 <0.01–0.12	0.05 ± 0.04 <0.01–0.13	0.09 ± 0.05 <0.01–0.02	0.07 ± 0.05 0.01–0.08	
1985–1990	16	0.17 ± 0.07 0.01–0.33	0.17 ± 0.06 0.01–0.30	0.05 ± 0.04 0.01–0.024	0.04 ± 0.03 0.01–0.14	
1993–1998	6	0.14 ± 0.05 0.05–0.27	0.14 ± 0.05 0.06–0.37	0.05 ± 0.03 0.01–0.25	0.06 ± 0.03 0.01–0.15	
1999–2007	10	0.10 ± 0.03 0.03–0.15	0.11 ± 0.03 0.03–0.21	0.05 ± 0.03 0.01–0.14	0.06 ± 0.03 <0.01–0.13	0.14 ± 0.05 <0.01–0.20
2008–2020 2013-	15 (25) 15 (25) 0.0015% liquid	0.12 ± 0.04 0.01–0.40	0.13 ± 0.05 0.05–0.46	0.07 ± 0.04 <0.01–0.17	0.06 ± 0.02 0.01–0.15	0.19 ± 0,02 0.17–0.20

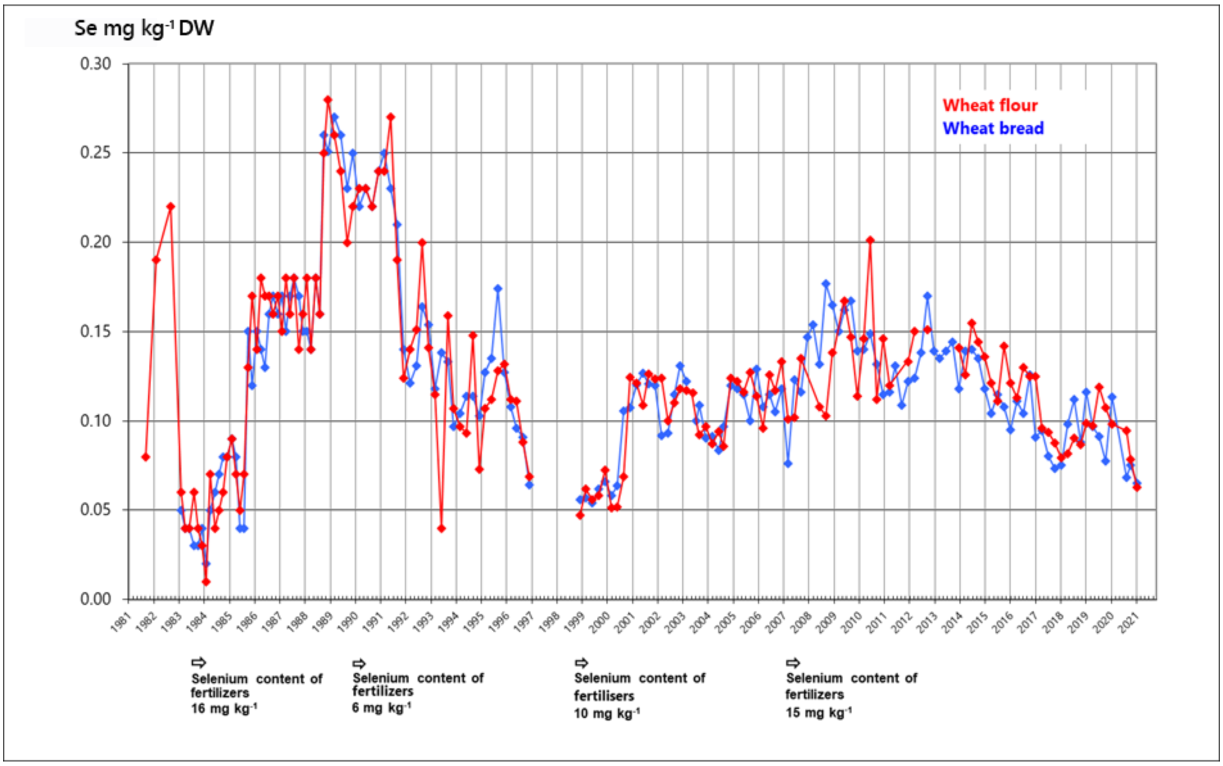

Figure 13. Selenium content of wheat flour and bread during 1981–2020.

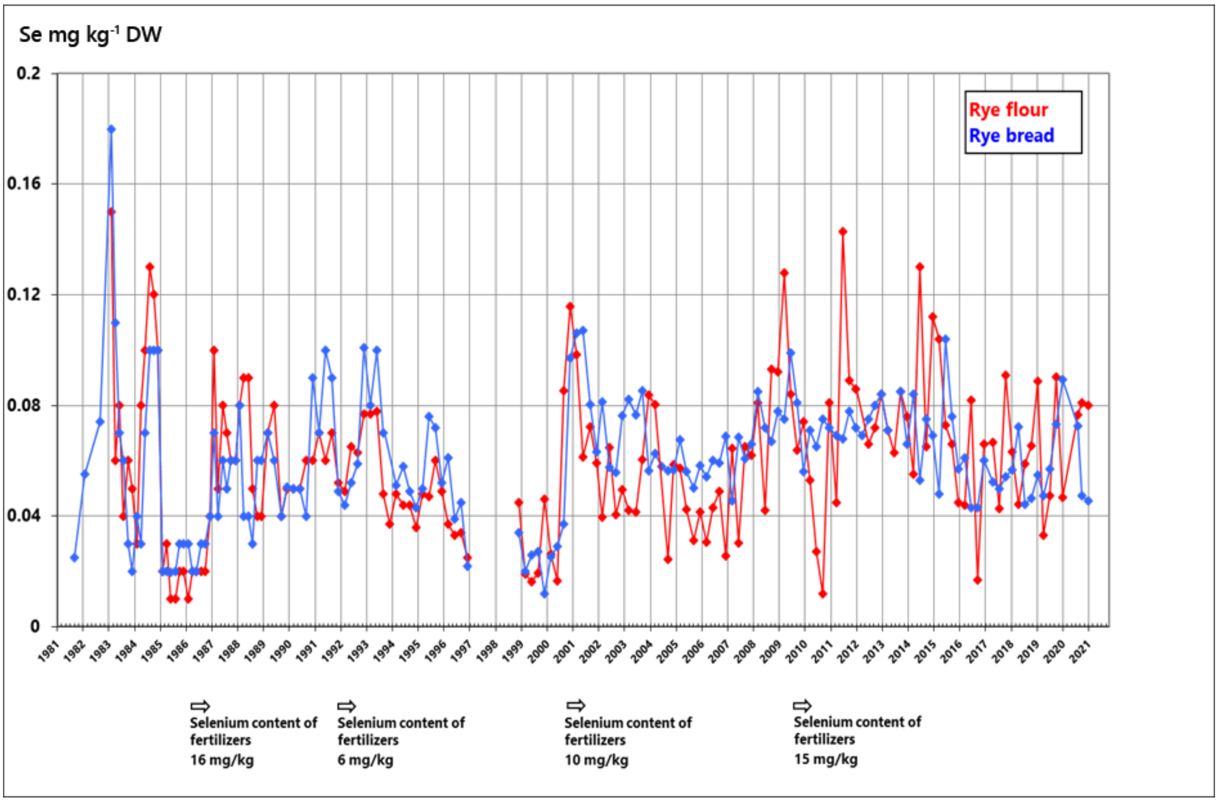

Figure 14. Selenium content of rye flour and bread during 1981–2020.

3.5.2. Milk products and eggs

Animal based products are most important sources of selenium (Fig. 21). Between 1999-2016 selenium concentration of milk has been stable but after 2016 concentrations of selenium in milk, milk products and eggs increased about 25 % (Figs. 15-17). In 2016, sodium selenate was dropped from the register of feed additives. However, it was restored as feed additive for ruminants. The use of organic selenium compounds in commercial feeds are more readily absorbed and this may increase selenium levels in foods of animal origin. Today producers are well informed of the health effects of selenium and know how to promote animal welfare.

Selenium concentrations in organic milk have been about half lower than in conventionally produced milk. According to the EU legislation selenium supplement is not allowed in organic fertilizers, but inorganic selenate can be added in feed products. This meant that the selenium content of organic forages was very low and feed selenium was not enough to cover the need. Symptoms of selenium deficiency appeared in livestock. In 2014 Ministry of Agriculture and Forestry allowed organic selenium to be added also in organic commercial feeds to promote animal welfare. This has raised the selenium level of organic animal-based foods to the same level as in conventional production.

Occasionally some other milk products have been analysed like non-fat quark 0.65 mg kg^{-1} DW Se, yogurt 2.5 % fat 0.41 mg kg^{-1} DW Se. The higher the concentration of protein the more Se milk products contain.

Table 5. Selenium content (mg kg^{-1} DW) of milk, milk products and eggs during 1984–2020.

Year	Selenium concentration of fertilizers for cereals	Standard milk 3,5 % fat	Low fat milk 1,5 % fat	Cheese, Edam 40 % fat	Eggs
	mg kg^{-1}	Mean ± Std Range	Mean ± Std Range	Mean ± Std Range	Mean ± Std Range
1984	0	0.06 ± 0.01 0.04–0.07		0.09 ± 0,02 0.06–0.12	0.07 ± 0,15 0.35–0.94
1985–1990	16 and 6	0.15 ± 0.07 0.04–0.26		0.28 ± 0,14 0.06–0.53	1.13 ± 0,03 0.42–1.16
1993–1998	6	0.15 ± 0.03 0.11–0.26		0.27 ± 0.06 0.06–0.53	0.97 ± 0.18 0.71–1.70
1999–2007	10	0.20 ± 0.03 0.15–0.28	0.23 ± 0.03 0.18–0.33	0.37 ± 0.05 0.22–0.53	1.02 ± 0.13 0.07–1.45
2008–2016 2013-	15 (25) 15 (25) + 0.0015% liquid	0.23 ± 0.02 0.18–0.27	0.26 ± 0.02 0.22–0.32	0.40 ± 0.05 0.33–0.53	0.93 ± 0.08 0.68–1.09
2017–2020	15(25) + 0.0015% liquid	0.31 ± 0.02 0.23–0.35	0.36 ± 0.03 0.31–0.41	0.52 ± 0.04 0.46–0.60	1.25 ± 0.17 0.93–1.50

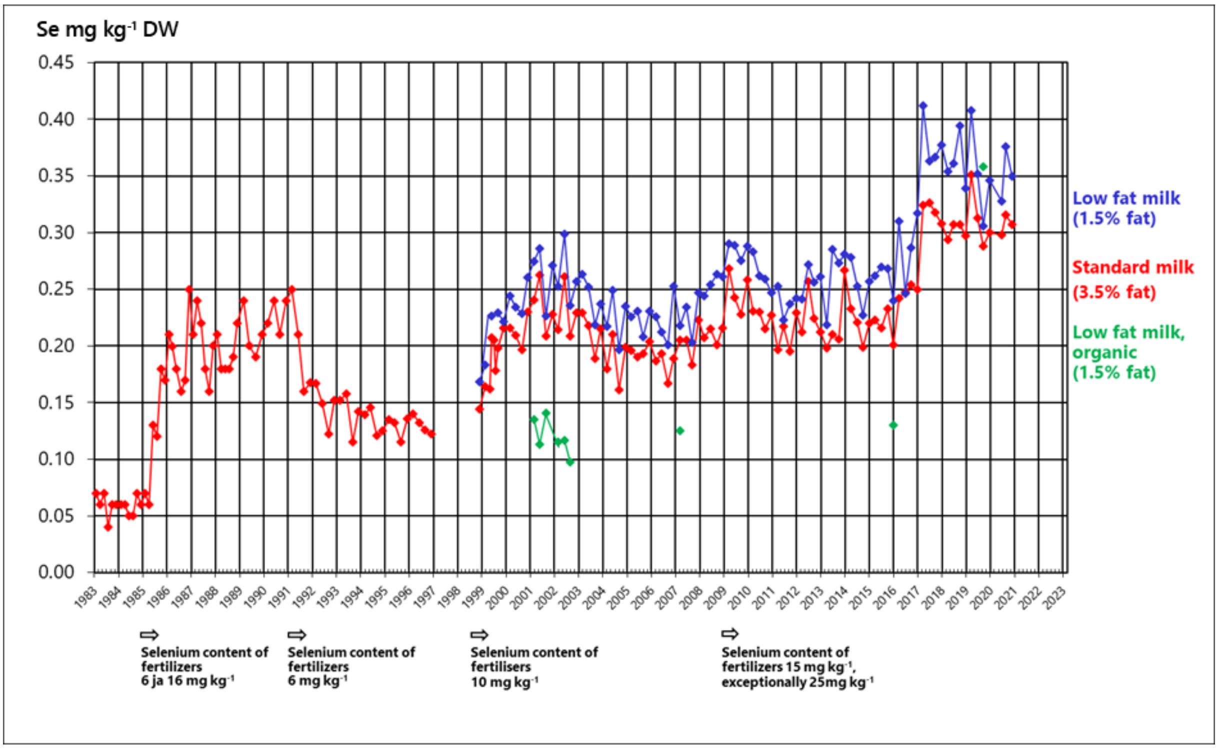

Figure 15. Selenium content of milk during 1983–2020.

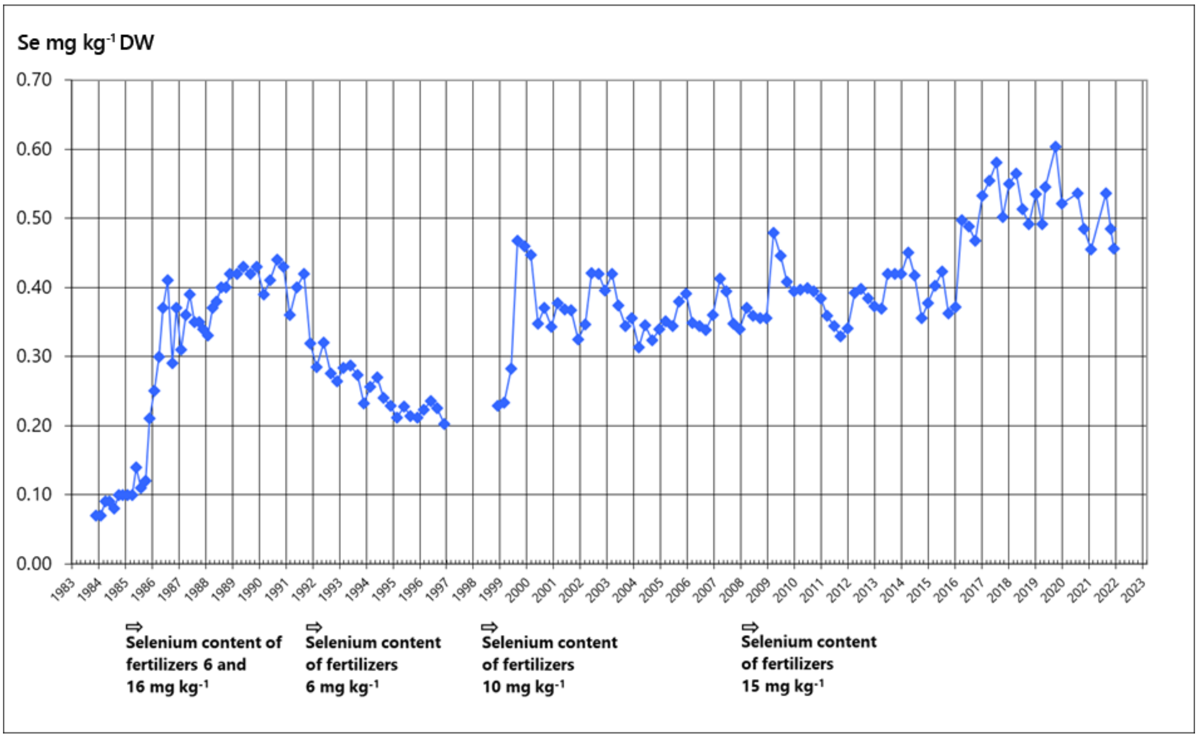

Figure 16. Selenium content of cheese during 1984–2020.

In 2019 Se content of some industrial baby milk and milk-based baby food products were studied to ensure that the present Se level of domestic milk has not caused too high Se intake for infants. However, there is only one manufacturer in Finland for these products and others were imported from the EU region. The products information of Se contents was reliable and used according to the instructions these products are safe and wholesome for infants in case breastfeeding is not sufficient.

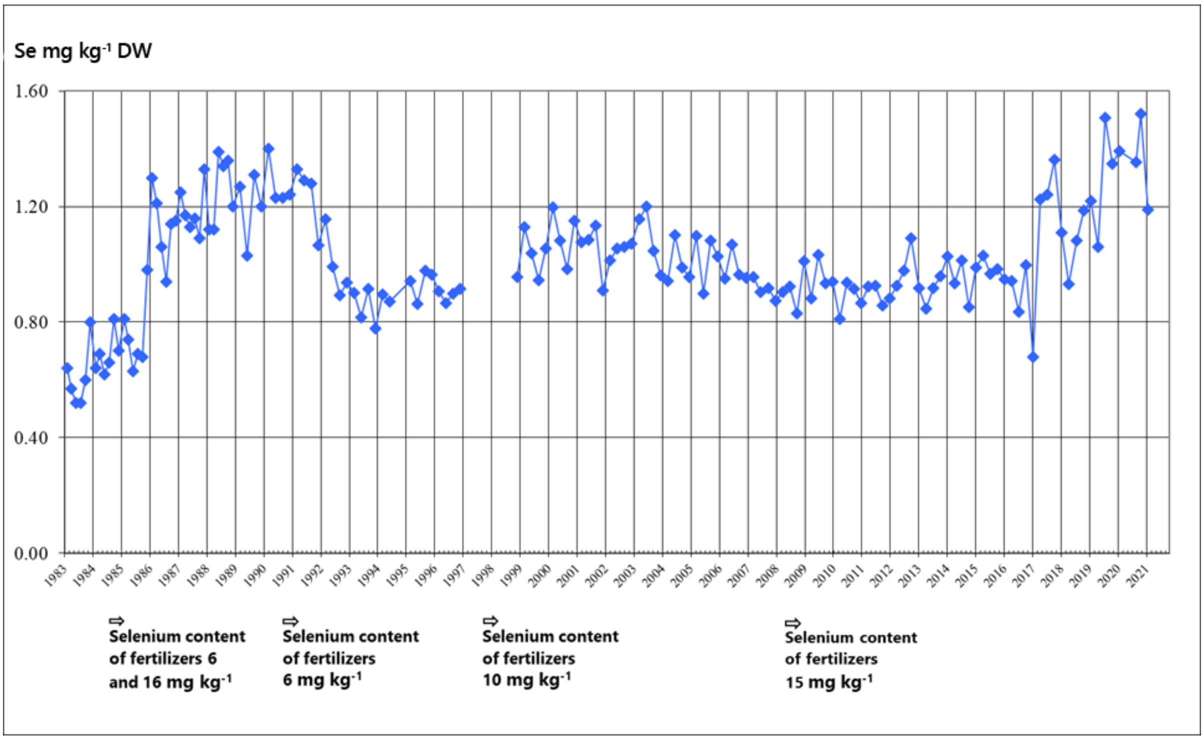

Figure 17. Selenium content of eggs during 1984–2020.

3.5.3. Meat and liver

Meat and meat products are an import dietary source of selenium in Finland. The effect of selenium fertilization on selenium concentrations of cattle and pig has been very clear (Figs 18-19). In samples of 2019 the selenium content of cattle and pig meat was 0,21 and 0,26 mg kg^{-1} WW, respectively and in cattle and pig liver 0,59 and 0,65 mg kg^{-1} WW, respectively.

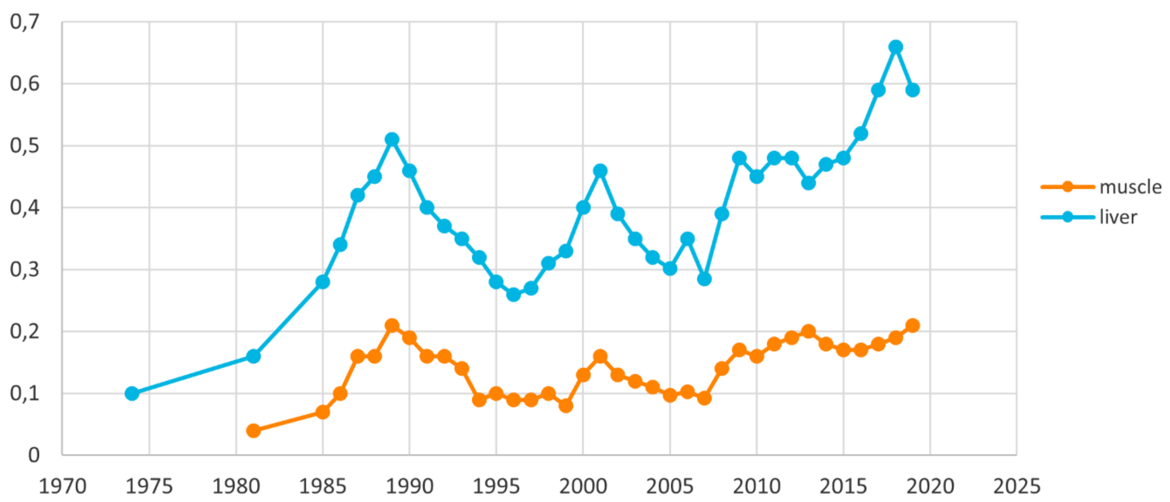

Figure 18. Levels of selenium in muscle and liver of cattle (mg kg^{-1} WW)

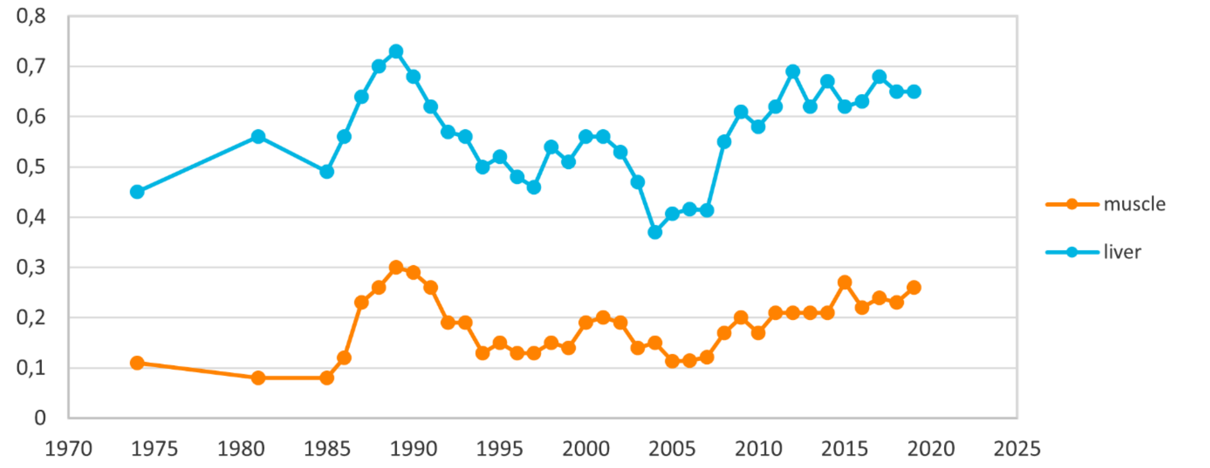

Figure 19. Levels of selenium in muscle and liver of pig (mg kg^{-1} WW)

3.5.4. Fish

The selenium contents of Baltic herring and cultivated rainbow trout has been followed regularly. Selenium fertilization does not affect the selenium content of these fishes. The fertilizer selenium is strongly bound to the soil constituent and leaching through rivers is small. In the cultivated fish the feeding determines the selenium levels. In 2017–2020 the mean selenium content of Baltic herring was 0.57 ± 0,11 mg kg^{-1} DW and rainbow trout 0.46 ± 0.09 mg kg^{-1} DW. The herring has some annual variation in the selenium concentrations according to the fat content of the fish. In the summer the protein content of herring is proportionally higher as the fat content of fish is smaller.

3.5.5. Vegetables

Plants are divided into three categories in relation their ability to accumulate selenium: hyperaccumulators, secondary accumulators and non-accumulators. Most agricultural food crops like cereals, root vegetables and many leaf vegetables belong into non-accumulators that contain <100 mg kg-1 of selenium. However, dome sulphur containing crop plants i.e. *Brassicaceae* and *Allium* species can contain higher amounts of selenium.

Vegetables generally contribute only a little to the selenium intake (Fig. 20). Therefore, only potatoes and white cabbage have been regularly analysed for selenium. Samples of other vegetables has been taken occasionally.

The mean selenium content of potatoes in 2000`s was 0.028 ± 0,016 mg kg^{-1} DW, range 0,002-0,056 mg kg^{-1} DW and of white cabbage 0,150 ± 0,072 mg kg^{-1} DW, range 0,041-0,0350 mg kg^{-1} DW. The sample quantity has been small, only 3–4 combined samples per year. In 2013–2018 the selenium contents were at the same level as before the selenium supplemented fertilization begun. Potatoes and other vegetables are usually fertilized with chlorine-free fertilizers that do not contain selenium. Variation between individual samples is large. Cabbages belon into *Cruciferae* -family, that take up sulphur and selenium readily. Thus, the selenium concentration in dry weight basis is higher.

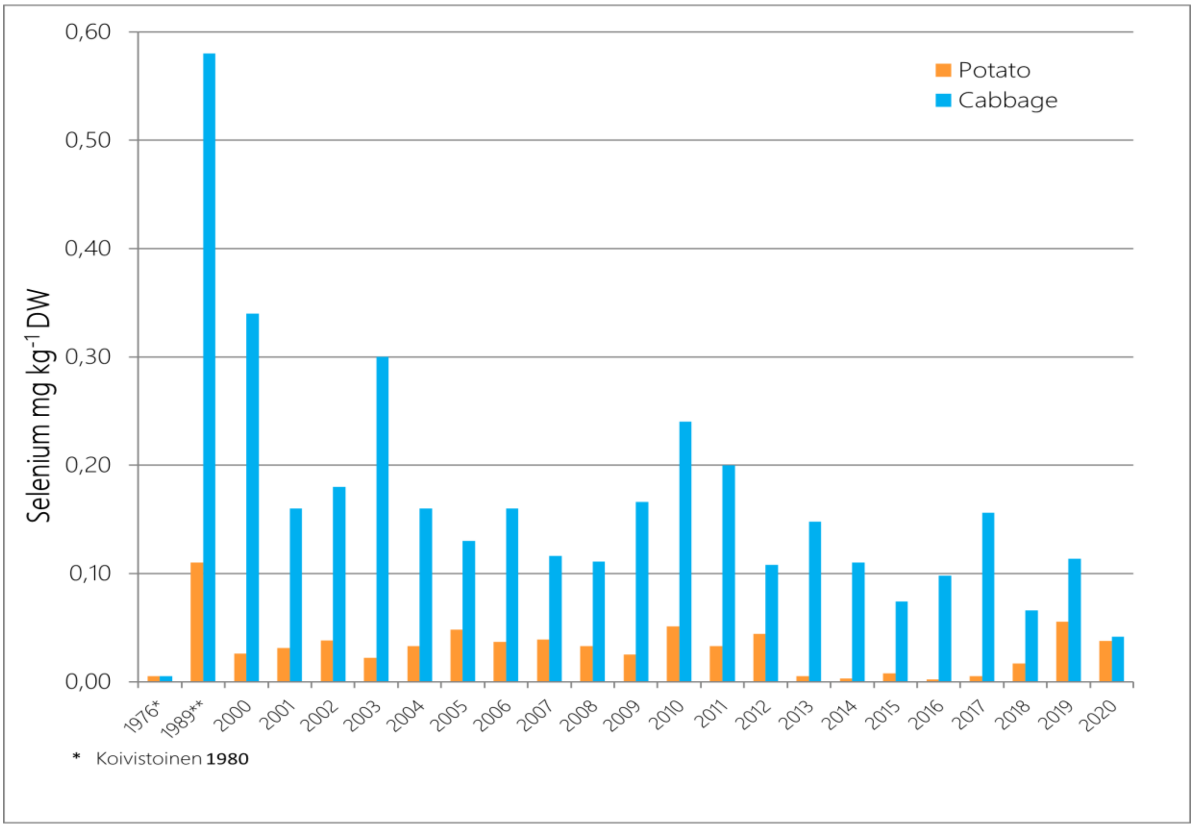

Figure 20. Selenium content of potato and white cabbage in 1976–2020.

3.6. Selenium intake

Selenium is an essential trace element for humans. It is a critical part of several enzymes like five different glutathioine peroxidases (Flohe et al. 1973, Flohe 1988), thioredoxine reductase and iodothyroninedeiodinase which have a function in antioxidant system protecting tissues from oxidative damage (Berry & Larsen 1992), in cell division and growth by participating the DNA synthesis. Selenium plays also a significant role in thyroid metabolism (Berry and Larsen 1992). The known biological functions of selenium include also regulation of the redox status of vitamin C and other molecules (May et al. 1998). A total more than 20 different seleno proteins are known, but the function of many of them is still unknown (Kryukov et al. 2003).

Serious selenium deficiency diseases are very rare and occur only in certain areas of China, Tibet, and Siberia (Yang et al. 1988). This consideration indicate that selenium deficiency seldom causes overt illness. However, inadequate selenium intake has been linked to an increased risk of cardiovascular diseases and cancer (Salonen & Huttunen 1986, Ip 1986). Low selenium intake has also found to increase the risk of cretinism in infants (Vanderpas et al. 1990). However, the use of a selenium supplement has not been conclusively shown to be beneficial in the prevention or treatment of cardiovascular disease or cancer (Rayman 2012).

The excess selenium intake causes nausea, vomiting, and garlic-like breath odour. Other symptoms of toxicity are nail and hair deformities and, in severe cases, peripheral nerve damage and liver damage. The poisoning of selenium is still rare by humans and is associated with supplementation or use of selenium medicines. The selenium intake which exceeds 300 µg per day during long period is considered to be unsafe (Rayman et al. 2018).

The Nordic and Finnish recommendation of daily selenium intake is based on the optimisation of the plasma selenoprotein P concentration in proportion to the body size. The recommendation for women is 50 µg per day and 60 µg for men (Nordic Council of Ministers 2014, VRN 2014). The average requirement is estimated to be 30 µg for women and 35 µg for men, lower limit is 20 µg. During the pregnancy and lactation the recommendation is 60 µg per day (Nordic Council of Ministers 2014). These recommendations are similar in the USA (Institution of Medicine 2000).

For geochemical and climatic reasons Finland belongs to low selenium area of the world. The selenium content of domestic cereals and other agricultural products were extremely low (Koivistoinen 1980). The selenium intake was also found to be one of the lowest ever reported (Mutanen 1984). The supplementation of the fertilizers since 1984 has clearly increased the selenium content on Finnish foods and the average selenium daily intake is nowadays at a very safe and adequate level. The average daily selenium intake was c. 80 µg/day at the energy level 10 MJ in the year 2020. The calculation is based on the food consumption statistics and the selenium contents of food (Luonnonvarakeskus 2021). This method is earlier considered to be satisfied method to estimate the average selenium intake in Finland. The present intake level is clearly higher than the average intake in other Nordic or European countries and slightly lower than typical intake in the USA (103 µg/day) (Food and Nutrition Board, 2000). The most important selenium sources in the diet are milk and eggs (c. 40 %) and meat (c. 37 %). The part of cereal and cereal products is c. 10 % (Fig. 21). It can be reasonable assumed that the selenium intake is adequate also in vegan and vegetarian diets and that too high intake without selenium supplementation is not possible. The supplementation of the fertilization has guaranteed safe and sufficient selenium intake in Finland.

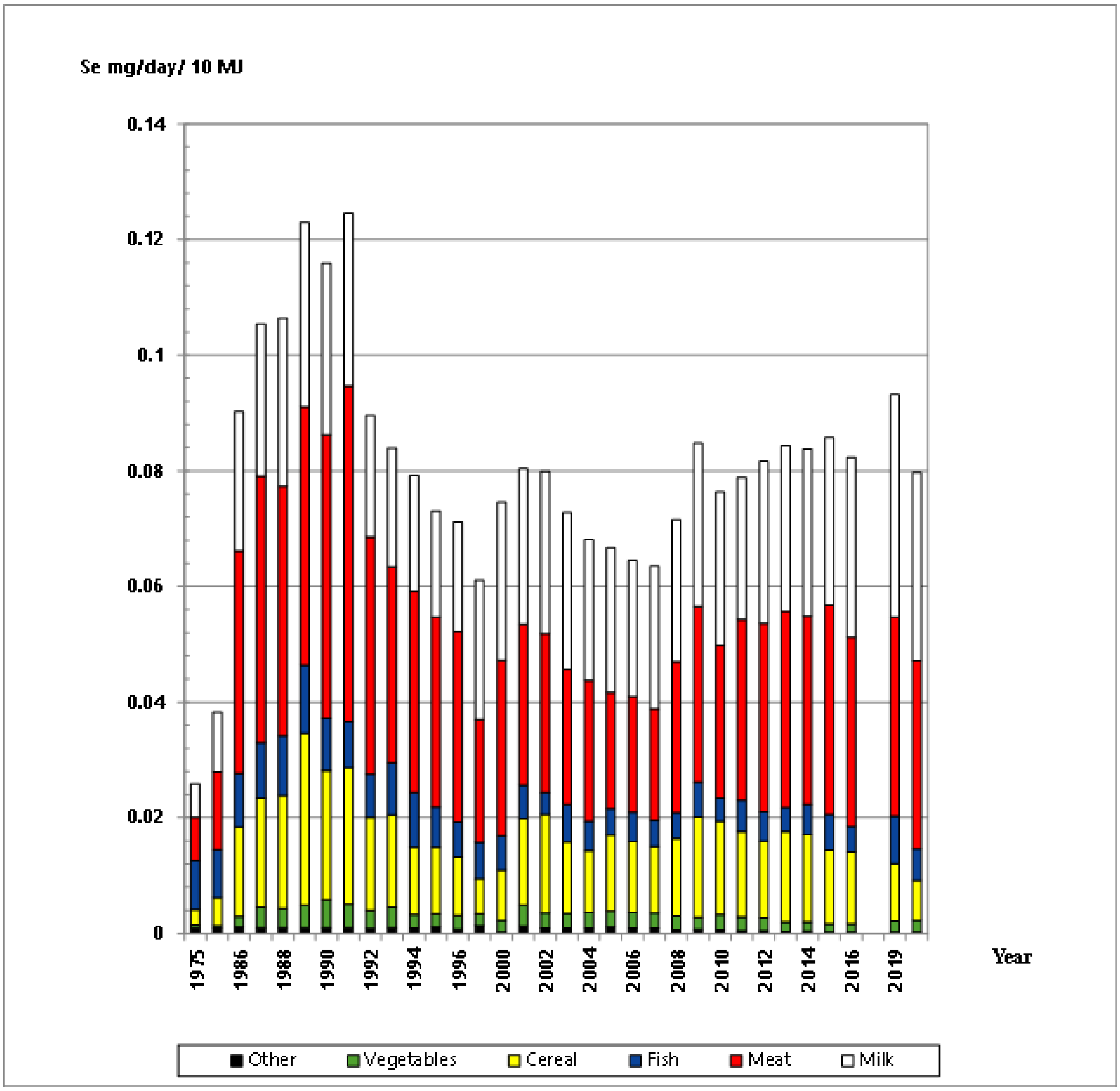

Figure 21. The average selenium intake in Finland 1975–2019.

3.7. Serum and blood selenium

Selenium concentrations in human serum and blood samples were measured regularly in Finland from year 1985 to 2012 from samples collected in Helsinki and Leppävirta municipalities. The results were combined because of their similarity in both areas. In 2017 samples (n=1530) from a representative health examination survey, the FinHealth 2017 Survey, was used.

Serum selenium concentration was 0.85 µmol l^{-1} before starting selenium supplementation. First the concentration was nearly doubled by the supplementation, but it decreased again in the late 1990's. In the 21st decade the selenium concentration has again been increasing, and in 2017 it was 1.5 µmol l^{-1} (Figure 22). Selenium concentrations were also analyzed in whole blood. Before the supplementation selenium concentration was 1.15 µmol l^{-1} on average, from 1989-1991 it was 2.6 µmol l^{-1} and in 2012 it was 1.6 µmol l^{-1} in whole blood.

The changes in selenium concentrations are explained by changes in selenium supplementation and with the amount of selenium used. From 1985 to 1990 two different amounts of sodium selenate were added to fertilizers: 6 mg of Se as sodium selenate per kg in fertilizers used in fodder and hay production and 16 mg/kg for cereal production. At this timepoint the practice was simplified to a single practice of 6 mg/kg in all fertilizer. In 1998 the amount of selenium used was increased to 10 mg/kg and in year 2007 it was increased from 10 mg/kg to 15 mg/kg.

The changes that were made to the selenium content of fertilizers resulted in analogous changes in serum selenium concentrations as seen in Figure 22. The changes show clearly that serum selenium concentration changes when intake changes and that serum selenium concentration is a very good biomarker of selenium intake. The results show that selenium concentration and intake were appropriate in year 2017, neither too high nor too low. For the sake of comparison, serum selenium concentration in Europe has ranged between 0.9-1.0 µmol l^{-1} (Rayman 2000).

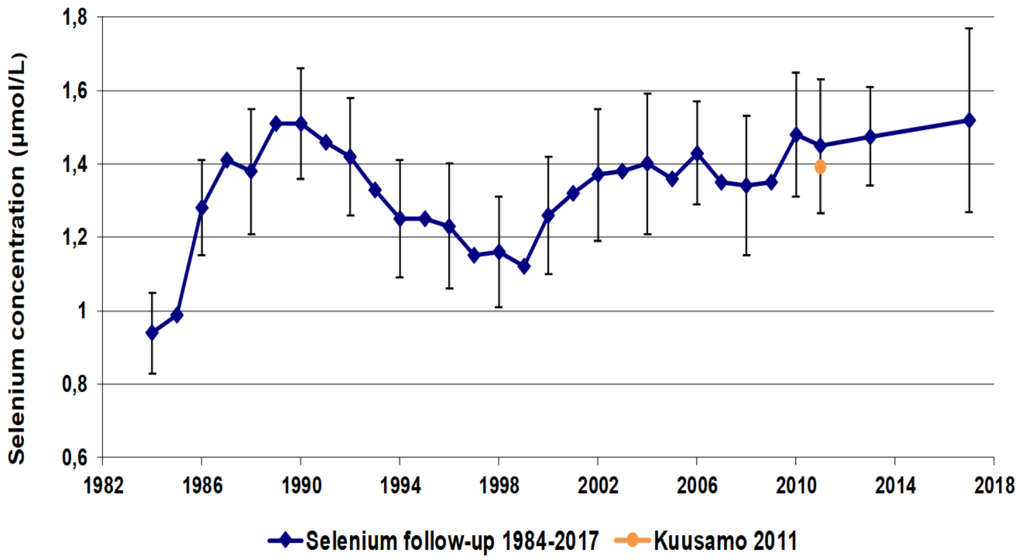

Figure 22. Serum selenium concentration 1984–2017 in Finnish men and women.

4. Conclusions

In Finland the biofortification of Finnish foods with selenium through selenium supplemented fertilization has been a long-term solution for improving selenium status of humans and domestic animals, thus preventing selenium deficiencies. It has been proven to be an efficient way to affect the whole agro-ecosystem and ensure the adequate selenium concentrations in foods and feed produced in Finland. However, the new Fertilising Products Regulation in the EU will increase the availability of bio-based fertilizers throughout the EU and may thus reduce the use of mineral fertilizers. Bioavailability of selenium from bio-based fertilizers was poor and follow-up of selenium concentrations in foods and feed need to be followed more closely if bio-based fertilizers reduce the use of selenium fortified mineral fertilizers.

The task and objective of the Selenium Working Group is to ensure that selenium levels in domestic foods, feeds and the population´s selenium intake are adequate. Selenium fertilization is part of the well-being of the Finnish population.

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