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Twenty Years of Selenium Fertilization

September 8-9, 2005, Helsinki, Finland

Merja Eurola (ed.)



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Authors

MTT Agrifood Research Finland, FIN-31600 Jokioinen, Finland

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Phone + 358 3 4188 2327, Fax + 358 3 4188 2339

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Summary










Merja Eurola, Veli Hietaniemi

Agrifood Research Finland, Research Services, Chemistry Laboratory, FIN-31600 Jokioinen, Finland, firstname.lastname@mtt.fi

With the workshop theme “Twenty years of selenium fertilization” the organizers wanted to summarize the 20-year research period of Finnish selenium supplemented fertilization and bring together people interested in selenium. The main areas of the program and proceedings are: selenium fertilization, selenium in foods and diets and selenium and health. The proceedings include 13 short papers written by the speakers, and 26 abstracts of poster presentations.

Key words: selenium, fertilization, food, feed, soil, nutrition

Organizers and sponsors

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	Plant Production Inspection Centre
	Ministry of Agriculture and Forestry
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History of selenium supplemented fertilization in Finland

Pentti Aspila

MTT Agrifood Research Finland, FIN-31600 Jokioinen, pentti.aspila@mtt.fi

Background

History of active research on selenium can be regarded to be started in 1957 when Schwartz and Foltz demonstrated importance of selenium in rats. Coinciding with this Mills detected preventing nature of GSH-Px in erythrocytes. Nevertheless, it took years before function of selenium was elucidated. In 1973 Rotruck et al. were able to demonstrate the role of Se in GSH-Px enzyme and later in 1979 Ladenstein et al. described the structure of GSH-Px.

Finnish soils are naturally poor in selenium, even though not exceptionally poor. In addition, availability of selenium from soil to plants is poor due to soil properties, e.g. low soil pH and oxidation-reduction potential of soil. Therefore foods and feeds naturally grown in Finland are extremely low in selenium as was shown by Oksanen and Sandholm in 1970. Low selenium intake in animals results in high incidence of diseases related to selenium deficiency, especially in fast growing and young animals. To overcome this obstacle various treatments against selenium deficiency diseases were experienced after the role of selenium in nutrition was demonstrated.

Early selenium supplementation in Finland

Selenium has been successfully used as a treatment in preventing nutritional muscular degeneration already since early 1960's. In Finland a decision to allow supplementing of mineral mixtures with inorganic selenium sources for feed purpose was made in 1969. This resulted in supplementing all commercial feeds with selenium, mainly sodium selenite, at the maximum allowed level of 0.1 mg Se/kg in total ration. This decreased in animals incidence of diseases related to selenium deficiency. However, in animals not commonly given commercial feed mixtures there were no impact.

In human dietary selenium intake inorganic Se supplementation had only minor effect, because transfer of inorganic feed selenium into animal products is poor. In 1970's daily selenium intake of Finnish population was mainly around 30 µg per day per capita, far below recommended safe daily allowance of 50 – 200 µg. Low selenium content in domestic food products also resulted in speculations on healthiness of locally produced food. In the

years when grain was imported due to low domestic crop yield, human selenium intake increased near to level of recommended daily allowance as Varo and Koivistoinen calculated in 1981. The Finnish authorities also considered the risk that low selenium content in Finnish food products could come as a trade barrier for food exports.

Rationale to increase selenium content in Finnish food

After the role of selenium in physiology became better understood, several studies in humans, e.g. studies of the group lead by Salonen in 1982 and 1984, were initiated in late 1970's to study potential health effects of low selenium intake. These studies brought up evidence of increased risk of cardiovascular diseases and cancer at low selenium intake level. This information resulted in excessive discussions in Finnish media and further to dramatic increase of sales in selenium tablets and other special selenium preparations. From the point of view of public health this was not a sustainable solution, because selenium intake was distributed extremely unevenly among the different population groups. Those people not taking extra preparations were still subject to selenium deficiency, and on the contrary some of those using these preparations in excess were facing a risk of overdosing, because the margin between the daily need and overdose is exceptionally narrow with selenium.

Along with increased awareness of the role of selenium, and as various studies proved necessity of selenium in nutrition, it became obvious that serious actions should be taken to convince the Finnish population of high quality of Finnish food and to remove obvious risks in the public health. There were naturally several paths to take to conclude the solution. The basic principle in defining the solution was to make it as comprehensive and safe as possible so that the whole population would have sufficient selenium intake and there would not be any risks of overdosing.

Research activities for selenium fortification in fertilizers

As the result of careful analysis, professor Koivistoinen being the key driving person, fortification of fertilizers used in food production chain was chosen in 1984 as the most reliable mean to raise selenium intake to sufficient and safe level for the whole population of Finland. Before this decision could be made, an extensive programme was launched to find proper means and levels for selenium fortification. This programme consisted mainly of two parts. In one part Yläranta (1985) investigated selenium transfer to plants through various means of selenium application in his extensive experiments carried

out in 1979-1983. Second part explored transfer of selenium from feeds to animal products in various experiments launched in 1982 and continuing to late 1980's. (e.g. Aspila 1991, Ekholm et al. 1991, Syrjälä-Qvist and Aspila 1993).

Transfer of fertilizer selenium to plants

Even though foliar application of selenium, either as sodium selenate or sodium selenite, turned to be taken up even several times more efficiently by the plants than respective selenium application in fertilizers, there are several risks with foliar application. In foliar application selenium uptake by the crop is depending on spraying conditions, stage of growth of the plants as well as climate condition during and after the spraying. To apply selenium through spraying needs normally an extra operation in the field, and consequently results in extra costs, and therefore could result in that not all the crops would be applied with selenium. Accurate dosing of such small quantities as selenium is needed in foliar application can not be guaranteed under the farm conditions.

In contrast to foliar application, fertilizer application is rather safe method for selenium supplementation, because selenium is mixed into the commercial fertilizers under controlled industrial conditions and the level of fertilizers applied to the crops under the farming conditions is well controlled. In acid soil conditions, common in Finland, selenium from sodium selenate is more readily taken up by the plants than selenium from sodium selenite. Based on this, it was obvious that sodium selenate is the most appropriate form of selenium to be used in fertilizers. In the soil selenium is rapidly reduced to insoluble form and therefore risk for leaching of selenium into environment is negligible.

Transfer of plant selenium to animal products

The most important selenium sources in Finnish human diet are milk and meat products accounting altogether nearly 70 % of the total selenium intake, both before and after starting applying selenium in fertilizers, as calculated by Eurola et al. in 2003. Therefore it was important to study the transfer of selenium from feeds to animal products. It was clear from the studies made in 1970's that inorganic forms of selenium are inefficient in raising selenium content in milk and meat. Therefore it was natural to choose organic plant incorporated selenium as the major target for the research. Due to practical reasons, foliar application of sodium selenite on growing grass or barley was chosen to produce experimental feeds used as the source of organic selenium. Target estimated by the research group, to have in fresh milk 20 µg of Se per liter, can be reached either supplementing the ration of cattle by approxi-

mately 1 mg Se / kg of feed DM as sodium selenite or 0.1 mg Se / kg of feed DM as selenium fertilized feed. The latter nicely equalling with the dietary requirement of cattle. Similar pattern between inorganic and organic selenium sources occurs also in transfer of feed selenium to meat. At high organic selenium intake level milk selenium content tends to plateau at the level of 43 µg of Se per liter of milk, i.e. only at the level of twice of the desired level in milk (Aspila 1991). Therefore it is unlikely that there would be a risk of detrimentally high level of Se in milk.

Fortification of selenium in fertilizers

To define the proper level of selenium in fertilizers different efficiency in uptake between the various crops needs to be considered. Selenate selenium from fertilizers is several times more efficient in increasing selenium content in grasses than in cereal crops. In Finland the common practise is to use multi-nutrient (NPK) fertilizers for the all field and horticultural crops, many of the crops having specifically formulated fertilizers. Based on this, in 1984 the proper level of selenium in fertilizers was concluded to be 6 mg/kg in fertilizers formulated for grasses and 16 mg/kg for those formulated for cereal and horticultural crops. The Ministry of Agriculture and Forestry also appointed a working group to monitor selenium content and intake in feeds and foods. Results from monitoring demonstrated nicely predicted changes in human selenium intake. Nevertheless, obviously due to applying the fertilizers formulated for the cereal crops for grasses, levels above the requirement were found in some feeds and animal products. Therefore, to avoid any risk of unnecessary high selenium intake and any environmental risk, the level of selenium in all fertilizers was reduced down to 6 mg/kg in 1990. This, on the contrary, resulted soon in reduced dietary intake, and in 1998 the level of selenium in all fertilizers was increased to present level of 10 mg/kg.

Future challenges in selenium supplementation

At the moment selenium intake in Finland in animals and in humans is within safe and sufficient level. Only exception is production and products from organic farms. The regulations in organic farming do not allow use of such fertilizers which would be fortified with selenium. Because organic products in general are regarded as safe and healthy products, low selenium content is affecting their image adversely. This constraint still remains to be solved.

Key words: selenium, fertilization, foods, feeds, intake

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Increasing the selenium content of agricultural crops: decisions and monitoring

Pirjo Salminen

Ministry of Agriculture and Forestry, Food and Health Department, P.O.Box 30, FI-00023 Government, Finland, pirjo.salminen@mmm.fi

Abstract

In Finland selenium has been added to fertilisers for 20 years. This has been founded on comprehensive, long-term research and monitoring as well as measures undertaken because of the results. The addition of selenium to fertilisers in Finland may be considered an excellent example of good collaboration between companies, research and authorities which has improved the quality of Finnish food and raised the selenium intake from food to a sufficient level in view of human and animal health.

In Finland the shortage of selenium in the nutrition of domestic animals was detected as early as the 1950s and 1960s. The issue became topical again in the 1970s, when the low selenium content in Finnish food had been proven in extensive scientific studies. The selenium intake of the Finnish population was below all recommendations. In December 1983 the Ministry of Agriculture and Forestry set up a Selenium Working Group to draft a proposal concerning the addition of selenium to the general fertilisers. Another task of the Working Group was to draw up a research and monitoring plan for observing the impacts of the added selenium on the soil, plants, feedingstuffs and foodstuffs of plant and animal origin. The selenium intake of humans and animals was also to be studied and monitored. The work group assessed the impacts of the added selenium and, where necessary, gave proposals for revising the selenium quantities to be added.

In accordance with the proposal of the Selenium Working Group, selenium has been added to multinutrient fertilisers used in agriculture and horticulture. At first the quantity added was 16 mg of selenium per kilo of fertiliser for cereals and 6 mg/kg for grasses. In spring 1990 the Ministry of Agriculture and Forestry decided, based on a proposal of the Selenium Working Group, to lower the quantity of selenium to be added to solid multinutrient fertilisers to 6 mg per kilo of fertiliser, and the addition of selenium to other fertilisers was prohibited. This was done because the increase in the selenium content in cereals and selenium intake was higher than expected. There was also some uncertainty as to the possible environmental impacts of the added selenium in fertilisers. The reduction led to a considerable decrease in the selenium content of feedingstuffs, fodder cereals and domestic foodstuffs.

The Finnish Fertiliser Act was amended in 1993, and the Decision of the Ministry of Agriculture and Forestry issued under the Fertiliser Act in 1994 also adjusted the maximum allowable quantity of selenium in fertilisers. Now 6 mg of selenium as selenite could be added to multinutrient and inorganic compound fertilisers intended for agriculture and horticulture. However, the decision did not concern EC fertilisers.

In 1998 the Ministry of Agriculture and Forestry decided to commission the Agricultural Research Centre of Finland (later MTT Agrifood Research Finland) to carry out the selenium monitoring. The legislation on fertilisers was last amended on the basis of a proposal of the Selenium Working Group in 1998, when the quantity of selenium to be added to inorganic compound fertilisers for agriculture and horticulture was raised by a Decision of the Ministry of Agriculture and Forestry from 6 mg to 10 mg of selenite per kilo of fertiliser. Again this decision did not concern EC fertilisers. The decision was based on observations which showed that the selenium intake of domestic animals and humans had decreased, first as a result of the reduction in the selenium quantity in 1990, and then due to the decrease in the use of multinutrient fertilisers. The conditions for environmental support and restrictions on the use of phosphorus had already clearly reduced the use of multinutrient fertilisers so that the selenium quantity per hectare of arable land has been decreasing.

The monitoring of selenium continues in Finland, but so far the Selenium Working Group has given no indications to the Ministry of Agriculture and Forestry of any need to adjust the selenium quantities in inorganic fertilisers in the upcoming Fertiliser Product Act.

Key words: selenium, monitoring, legislation

Technical solution adding selenium to fertilizers

Heikki Hero

Kemira GrowHow Oyj, Mechelininkatu 1a, 00180 HELSINKI, Finland, heikki.hero@kemira-growhow.com

Selenium is an essential microelement for animals and humans. After thorough research, there was a move to add selenium to fertilizers as a selenate. This is the form which plants can take in selenium from fertilizers through the soil. The most suitable selenate is sodium salt, Na_2SeO_4 , which contains 41% selenium.

Safe handling of selenates

A selenate is an oxidized form of selenium and metal selenium is used as a raw material. There are only a few selenate producers in the world.

A sodium selenate is highly toxic - its LD₅₀ values are 1.6 mg/kg or 7 mg/kg (oral dose). In this case, when two different values are shown, the lower is used. This means, if an 80 kg man takes in 130 mg of selenate, there is a 50% chance of death.

Sodium selenate is delivered as a solid salt, and is dissolved automatically in a secure location to a 10% solution, which is the storage concentration. This solution is stored where it will be mixed and/or transported to other plants in 1000-liter stainless steel containers. The containers are heavy-duty, and can fall from the trailer without resulting in leaks. Sodium selenate and its solutions are always stored in a safe, locked place. Only authorized persons should have access to the storage area and handle these materials. For final use, this 10% solution is further diluted to a 1% (Se) solution and pumped in precise quantities into the fertilizer process.

Fertilizers are produced on a large scale (up to 90 tons/h) and 10g of selenium is added to each ton of fertilizer. In the process, fertilizers are in slurry form and the selenium solution is added to 33 m³ mixing tank-type reactors. Selenium is distributed in the fertilizers homogeneously, with its original oxidized form remaining stable.

Critical point

The selenate must be kept in its original form. When used in a normal fertilizer process, the conditions are safe, without any unwanted chemical reactions. Reactions with some reducing agents and acids can be extremely dangerous. Any reactions that may produce H₂Se shall be prevented. H₂Se is even more dangerous than HCN.

Quality control

At Kemira GrowHow all fertilizers are analyzed. During the manufacturing process chemical quality is controlled every 30 minutes. In order to ensure quality, the quality is tested once more before delivery.

Selenium is analyzed as total Se from final products. The analysis is accurate: The target value is 10 mg/kg fertilizer, the annual mean value is 9.8 mg/kg by Kemira GrowHow's analysis and 9.9 mg/kg according to official analysis made by the Plant Production Inspection Center (KTTK) . All values range between 9-11 mg/kg.

Conclusion

Adding selenium as a selenate into fertilizer is an effective, natural way to correct the selenium balance in the human diet. The only safe and accurate way to add selenium into fertilizers is to observe Finnish fertilizer legislation, where this is specified: it is possible to add selenium as a selenate to multnutrients, inorganic compounds, garden and field fertilizers, 10 mg Se/kg fertilizer. This does not apply to EC FERTILIZERS.

The only safe way is to add selenates into the chemical process so that selenium is homogeneously distributed throughout the fertilizer.

Key words: selenium, selenate, fertilizer

Occurrence and chemistry of selenium in Finnish soils

Helinä Hartikainen

University of Helsinki, Department of Applied Chemistry and Microbiology, Box 27, 00014
University of Helsinki, Finland, helina.hartikainen@helsinki.fi

Abstract

Soil selenium is ultimately derived from the parent material in the bedrock, wherefore its content is markedly dependent on the origin and geological history of soil and dictated by the mineralogical characteristics of the parent material, weathering degree of mineral constituents and soil formation processes. In Finland, the bedrock is characterized by an abundance of plutonic and metamorphic rocks that are typically low in selenium. However, mineral soils of contrasting texture can be expected to differ in their element concentrations, because the various particle-size classes differ in the mineralogy. Generally, the clay fraction consists of minerals higher in selenium than minerals in the coarse fractions. Furthermore, the clay fraction is also rich in aluminium and iron oxides that decrease the mobility of selenium through their high sorption tendency. In organogenic soils, the native selenium content varies depending on the origin of the soil.

The chemical characteristics explain the low bioavailability of selenium in Finnish soils irrespective of their total selenium content. Selenide in rocks is oxidized during weathering predominantly to selenite. Only in arid regions under very oxic condition it can be oxidized up to selenate. These two species decisively differ in their reaction mechanisms and mobility. Selenate is retained very weakly and is easily leached. Selenite, in turn, is specifically retained on oxide surfaces by ligand exchange, which reduces its mobility and bioavailability. Furthermore, our soils are high in organic matter, an efficient electron source, wherefore selenate added in fertilizers will be easily reduced to selenite and retained. This reaction pattern diminishes the plant-availability but, on the other hand, the leaching losses. Thus, we can conclude that, similarly as with phosphorus, the main selenium losses from fields take place with eroded soil particles transferred with surface runoff water. The chemical retention in peaty soils is limited by the low amount of binding metals and minerals. Selenium losses from our soils as volatile compounds have been reported to be small.

Key words: selenium, bedrock, soil type, sorption reaction

Introduction

The main source of selenium (Se) in biological systems and food chain is soil. An important impetus to studies on occurrence of selenium and its geochemical behaviour has been the double-edged role of this element in biological systems: it is essential to animals and humans but it is toxic at high intake. Geochemical information is needed to overcome serious risks attributable to insufficient or excess intake. Furthermore, recently it has been shown that, against the prevailing concept, at proper level selenium exerts positive effects also on plants and can promote their growth (e.g. Hartikainen et al. 2000, Xue et al. 2001, Turakainen et al. 2004). Because soil selenium is ultimately derived from the parent material in the bedrock, its content is markedly dependent on the origin and geological history of soil and dictated by the mineralogical characteristics of the parent material, weathering degree of mineral constituents and soil formation processes.

A worldwide atlas compiled by Oldfield (2002) shows that the geographical selenium distribution in soils and rocks is very uneven, ranging from almost zero up to 1250 ppm in some seleniferous soils in Ireland. Even though the toxic levels in some areas originate from industrial operations including the combustion of fossil fuels and sulphide ore mining, more often they occur naturally. Experience with selenium in animal production has led to the recognition that on a worldwide scale, vast land areas do not supply enough of this element for optimum animal nutrition. On global scale, selenium-deficient areas seem to be far more common than toxic ones. Finland belongs to these problem areas. However, no systematic mapping of selenium in our bedrock and soils has been carried out. Therefore, this overview is a synthesis of rather sparse published data and conclusions based on general biogeochemical and chemical principles.

Origin of selenium in parent material

The mode of occurrence of selenium is dictated by its close relationship with sulphur. The association of these elements in unweathered rocks and minerals is attributable to the fact in the Periodical Table of Elements they belong to the same (oxygen) group. Because their ionic radii are rather similar (17.4 nm for S^{2-} and 19.1 nm for Se^{2-}) selenium can replace sulphur in sulphides commonly formed with transition metals such as Fe, Zn, Cu, Ni etc. Much of the selenium in the crust of the earth occurs in pyrite and other sulphide minerals (Berrow and Ure 1989, ref. Seiler 1998). It should be noticed that in rock-forming minerals selenium is not present in their structures but rather in the accessory sulphide phase (Koljonen 1973a).

Even though selenium often is volcanic by origin, in sedimentary deposits it can be biogenic. Presser (1994) concluded that, in old sedimentary deposits, the primary mechanism of selenium enrichment might have been the bioaccumulation in biota and biomagnification in food chain, followed by deposition and diagenesis of high-Se organic matter. Already in 1935 Byers (ref. Seiler 1998) noticed the importance of reduced sulphur compounds and marine sedimentary rocks of Cretaceous age as sources of selenium in the western United States. Generally speaking, the high selenium soils largely come from sedimentary deposits whereas the low selenium soils are typically derived from igneous rocks (Tamari 1998).

Bedrock of Finland and soils derived from it

In Finland, the bedrock represents a deeply denuded section of the Pre-Cambrian belts characterized by an abundance of plutonic and metamorphic rocks (Simonen 1960). They are typically low in selenium. Scattered geochemical studies on ores and minerals (Nurmi et al. 1991, Koljonen 1973a,b,c; 1974) indicate, however, that spotlike areas of moderate or rather high concentrations may be found. Certainly, some regional variation in the occurrence of selenium can be expected, because also the magmatic rocks can markedly differ in this element. There is a tendency that the selenium concentration decreases when passing from mafic to felsic and silicium richer minerals, because also the concentration of sulphide forming metals simultaneously decreases. A positive correlation between selenium and the colour index of the rock (see e.g. Koljonen 1973b) is attributable to the relationship with selenium and heavy metals in minerals. As a rule of thumb, the dark minerals are higher in selenium than the light ones.

In Finland, bedrock is covered by a thin layer of glacial till and, in places, by glaciofluvial deposits. On coastal areas the late- and postglacial marine and brackish-water clay and silt deposits are common. In inland, fine-textured sediments are mainly of lacustrine origin. A typical feature also is the abundance of peatlands: they cover about one third of our land area. These facts form a general frame for the occurrence of selenium in our soils.

Distribution of selenium in Finnish soils

Soils of contrasting texture differ in their element concentrations. This is attributable to the fact that the various particle size classes differ in the mineralogical composition and sorption components. As expected, a general finding is that the clay fraction is higher in selenium than the coarse ones. The clay fraction consists markedly of micas, e.g. biotite, and related clay minerals. Biotite is a black mineral relatively high in selenium (Koljonen 1973b). The coarser fractions are dominated by quartz and feldspars light by

colour and, consequently, low in selenium. Furthermore, the clay fraction is also much richer in aluminium and iron oxides than are the coarse particles. These oxides are the main components for selenium sorption. That is why the clay soils can be expected to contain more selenium added or released in weathering processes than do the coarse-textured soils. This distribution pattern in Finnish mineral soils has been confirmed by Sippola (1979) and Ylärinta (1983). In organogenic soils the native selenium content varies depending on the origin of the soil. According to Koljonen (1974) and Sippola (1979) peat soils are very poor in selenium. Similarly, gytjas formed in calcareous environment are low in selenium obviously because of shortage of adsorbing metals.

Bioavailable selenium

As with many other soil-borne elements, total selenium is not a useful index of plant-available selenium and cannot be used as a reliable parameter in risk assessment or in determination of selenium supplementation need. This was seen in the study of Oksanen and Sandholm (1970) who did not find any correlation between forage crops and soil type in various part of Finland. On the contrary, correlations between selenium in plant and soil can be found if the relationship is investigated within various types of soils as done by Sippola (1979). In organic soils, total selenium correlated much better with selenium in plant than did acid ammonium-acetate- Na_2EDTA extractable selenium. A smaller difference in the correlation coefficients was found in clay soils. The mobility and plant-availability of selenium in soil is controlled by a number of chemical and biochemical processes: sorption, desorption, formation of inorganic and organic complexes, precipitation, dissolution and methylation to volatile compounds.

In theory, Se exhibits a broad range of oxidation states: +6 in selenates, +4 in selenites, 0 in elemental Se, and -2 in inorganic and organic selenides. It also forms catenated species, such as volatile diselenides (RSeSeR). Interestingly, during weathering of minerals the behaviour of sulphur and selenium is dissimilar. Sulphide is readily oxidized into sulphate (SO_4^{2-}), whereas selenide normally remains to a lower oxidation stage, often elemental Se(0) or can be further oxidized to selenite (SeO_3^{2-}). The oxidation up to selenate (SeO_4^{2-}) presupposes that the environment is highly oxidative such as prevailing e.g. in arid regions.

The main sorption components for anions in soils are hydrated aluminium and iron oxides. Organic matter in soil does not retain anions directly even though some retention to humic compounds can take place through their organometallic complexes possibly present. However, selenite and selenate decisively differ in their reaction mechanisms. A general rule is that the anions of strong acids have a conservative behaviour and they are not sorbed on

oxide surfaces. The anions of weak acids, in turn, tend to be sorbed on oxide surfaces by a specific chemical mechanism, ligand exchange, where the anion forms an inner-sphere complex with the oxide surface. Selenic acid is much stronger than selenous acid, wherefore selenate is easily transported in the soil profile, whereas selenite is efficiently retained to oxide surfaces and therefore less available to plants. A low pH (rendering the surface charge of oxides more positive) enhances the sorption reactions. That is why liming increases the mobility of selenite as shown experimentally by Gissel-Nielsen and Hamdy (1977). Also a high salt concentration in the soil solution favours the sorption reactions.

At low redox potential, selenate is reduced to selenite, which decreases the mobility of this element. Finnish soils provide a good environment for the reduction reactions, because our soils are high in organic matter, an effective source of electrons. Furthermore, especially in the fine-textured soils the gas exchange between soil pores and atmosphere is often limited, which contributes to formation of reductive conditions. This means that selenate added with fertilizers will be reduced to selenite and retained to soil particles. The findings made in practice agree with the theory: selenium fertilization should be repeated every growing season, because the plant-availability cannot be maintained long. On the other hand, the reduction tendency of selenate diminishes the risk of selenium leaching. However, selenium may be transported to surface waters with the eroded soil particles. Thus, chemistry of selenite resembles that of phosphate. According to Ylärinta (1982) the volatile losses of selenium from Finnish soils are very small. However, he noticed that liming and addition of organic matter enhanced the selenium volatilization obviously through enhanced microbiological activity.

Acid sulphate soils –special problem areas

Even though detailed maps on selenium in our soils are not available, veterinary reports about the spread of nutritional muscular degeneration (NMD) in Finland since 1933 provides indirect information about *bioavailable* selenium. Isolated cases of disease occurred in 1950's throughout the country, but it was most frequently observed in the coastal areas of Gulf of Bothnia and especially in Ostrobothnia (Oksanen 1965). In these areas, acid sulphate soils are common. They are bottom sediments of Baltic Sea deposited during the Littorina stage when the water was salty and warm, and the primary production in sea water was high. When the large biomass settled down to the sea bottom and decomposed, it used up the free O₂ in the hypolimnion, and the reduced conditions allowed the formation of iron sulphide and pyrite. From this we could conclude that, as being marine by origin and high in sulphide precipitates, they are relatively high also in selenium. Thus, the most frequent occurrence of selenium problems in domestic animals found on these soils seems to disagree with their geological history. Similarly, the vet-

erinary reports are inconsistent with the later finding by Lahermo et al. (1998) that elevated concentrations of total selenium in stream sediments were found on Vaasa area in Ostrobothnia.

It is likely, however, that this contradiction is apparent and attributable to chemistry of selenium dictating its bioavailability. Littorina soils are typically very acid, high in soluble electrolytes and iron. All these edaphic factors are known to increase the retention tendency of selenium. However, an additional factor contributing to the deficiency symptoms in these soils could be the high sulphate concentration found to depress the uptake of selenium by plants in salt-affected soils (Wu and Huang 1991). Thus, numerous environmental factors control the availability of selenium to plants and, consequently, the selenium intake by animals and humans.

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Influence of selenium fertilization on soil selenium status

Markku Yli-Halla

MTT Agrifood Research Finland, Environmental research, Soils and Environment, FIN-31600 Jokioinen, Finland, markku.yli-halla@mtt.fi

Abstract

Selenium (Se) has been applied to Finnish agricultural soils in mineral fertilizers as sodium selenate since 1985. Usually, less than 10% of applied Se is taken up by the crop. Previous studies indicate that the level of easily soluble (hot water extractable) Se has not been elevated during the period of Se fertilization. It is assumed that Se not taken up by the crop is mostly retained by the acidic soil. In this study, Se balance over the period of 13 years (1992-2004) was calculated on the basis of crops grown and fertilizers used in 48 fields of 10 research stations at different parts of Finland. The material consisted of 10 organogenic soils, 18 coarse mineral soils and 20 clay and silt soils. The pH(H₂O) of the soils was 4.6 – 6.9 (mean 5.9). The soil samples taken from these fields in 1992 and 2004 were analysed for *aqua regia* (AR) extractable Se, which indicates the semi-total Se concentration. These results were also converted to grams per hectare by multiplying the AR extractable results with the volume weight of the soil in order to compare them with the Se balance of the respective fields.

The cumulative Se application was on average 37 g/ha (range 3 – 78 g/ha) during the 13-year period. Highest applications took place in intensive grassland cultivation. Se applications resulted in the estimated balance of 31 g Se/ha (range 2 – 67 g/ha). The average concentrations of AR extractable Se in the samples taken in 1992 were 0.393 mg/kg in organogenic soils, 0.148 mg/kg in coarse mineral soils and 0.211 mg/kg in clay and silt soils. These results corresponded to 516, 363 and 470 g/ha in the three soil groups, respectively. According to soil analyses, the Se content of a 23-cm deep plough layer was on average 23 g/ha higher in 2004 but the difference was not statistically significant. It was concluded that the possible accumulation of Se in soil occurring during the 13-year period was masked by the heterogeneity of the sampled fields and could not yet be detected by soil analyses. – The balance, calculated from fertilizer use and estimated crop uptake, corresponded to 8% (range 0.7 – 22%) of the Se content of the plough layer.

Key words: soil, selenium, fertilization, soil monitoring, aqua regia extraction

Introduction

In order to elevate selenium (Se) concentration of crops, sodium selenate (Na_2SeO_4) has been applied to agricultural soils of Finland in mineral fertilizers since 1985. The results of Ylärinta (1990) and Ekholm et al. (1995) indicate that more than 90% of applied Se is not taken up by the crop. Annual application of Se in cereal cultivation has varied between 3 and 8 g/ha, which during 20 years has resulted in the cumulative addition of about 100 g Se/ha. In intensive grassland cultivation, application of fertilizers is more abundant, having resulted in the cumulative addition of 150 g Se/ha. According to soil surveys, water-extractable Se has remained unchanged in spite of Se fertilization. In samples collected before the Se application, a concentration of 0.011 mg/l (N=250) was reported (Sippola 1979), and in another material collected after 14 years of Se fertilization the concentration was 0.010 mg/l (N=705, Mäkelä-Kurtto and Sippola 2002). Neither did soil test results (Ylärinta 1990) indicate any trend in the water-extractable Se concentration (1982-1984: 0.0074 mg/l, N=2300) and after (1985-1989: 0.0077 mg/l, N=1300). Se concentration in surface waters has not increased either (Wang et al. 1994). It is likely that Se is not leached or volatilized from the acidic mineral soils of Finland (Ylärinta 1982) but it is reduced to selenite and adsorbed in the soil. Supporting the sorption hypothesis, the impact of Se application on plant Se concentration has diminished quickly in pot experiments (Ylärinta 1983b, Yli-Halla et al. 1996) where leaching has been prevented. Only in organogenic soils has leaching of Se and, to some extent, volatilization been reported (Ylärinta 1982)

According to Sippola (1979), concentrations of total Se in soil amounts to about 0.2 mg/kg, corresponding to about 460 g Se/ha in a 23-cm deep plough layer. However, the concentration in organogenic and coarse mineral soils has been lower, corresponding only to 200 and 380 g Se/ha, respectively. In clay soils, the Se content has been about 750 g/ha (Sippola 1979). The theoretical accumulation of fertilizer Se during 20 years implies a substantial increase to the total Se content of some soils: 90 g Se/ha in cereal cultivation and 130 g/ha in intensively managed grasslands if about 90% of applied Se is retained in the soil. The purpose of this preliminary study was to estimate the Se balance of 48 fields, the crops and fertilization history of which were known and to investigate whether the residual Se can be recovered in the soil using samples, which had been subjected to Se applications for several years.

Material and methods

The soil samples of this study originated from ten research stations (Jokioinen, Laukaa, Maaninka, Mietoinen, Mikkeli, Pälkäne, Rovaniemen mlk, Ruukki, Sotkamo, Ylistaro) of MTT. The first set of samples had been collected in 1992 for soil monitoring (Urvas 1995) and had been stored air-dry in cardboard boxes. The same fields were sampled again in autumn of 2004 for this study. The material consisted of 10 organogenic soils, 18 coarse mineral soils and 20 clay and silt soils. The pH(H₂O), organic carbon concentration and clay content of these soils (Table 1), measured in the samples of 1992, was obtained from Urvas (1995). Se-containing fertilizers were predominantly applied during the 13-year period to these fields, even though there were a few fields, which were fallowed for a number of years or were in organic cultivation with no Se application. The crops grown and fertilization applied were collected from the records of the research stations. On this basis, Se application in mineral fertilizers was calculated. Se balance was estimated using average yields and Se concentrations of the crops, obtained from the records of Se monitoring programme.

Table 1. Mean values and ranges (in parentheses) of organic carbon (C) concentration, clay content and pH(H₂O) in the soil samples collected from the different research stations of MTT in 1992 and 2004. Data from Urvas (1995). N = number of samples. Not determined = n.d.

Soil group	N	Organic C, %	Clay content, %	pH(H ₂ O)
Organogenic	10	24.9 (14.6-39.7)	n.d.	5.3 (4.6-5.8)
Coarse	18	2.9 (1.6-5.3)	5 (0-14)	6.2 (5.3-6.9)
Clay and silt	20	3.6 (1.7-11.3)	44 (14-85)	5.9 (4.7-6.7)

The soil samples were analysed for *aqua regia* (AR) extractable Se (ISO 11455). In that method, soil samples are boiled with a mixture of concentrated HCl and HNO₃ for 2 hours using a reflux condenser. Se was measured according to a hydride method with Varian SpectraAA-300 Plus atomic absorption spectrophotometer. All determinations were made in February 2005. The detection limit corresponded to 0.017 mg Se/kg and the mean deviation for the results of replicated determinations was 6.8%. The AR extractable Se reflects the semi-total concentration of Se in soil. In order to relate the AR extractable Se concentra-

tions to the results of earlier studies, 26 soil samples were also digested with HNO₃-HClO₄-HF (HHH method), which has been used for the determination of total Se in larger soil materials (Sippola 1978, Ylärinta 1983a). To convert the results obtained as mg/kg to mg/l of soil, the volume weight of the soil was determined by weighing 25 ml of each soil sample. Expression of results as mg Se per litre of soil allows calculation of the Se content of the approximately 23-cm deep plough layer and a comparison between the Se content of soil and the Se balance, which was calculated from the crops grown and fertilizers used.

Results and discussion

The results in Table 2 show that AR dissolved practically equal amounts of Se from organogenic soils (range 87-113%) and from coarse mineral soils (range 85-115%) than did HNO₃-HClO₄-HF, while only 77% (range 69-85%) of Se in the clay and fine silt soils was extracted with AR. It is likely that the clay and silt soils had more Se incorporated in the mineral interiors, not attacked by AR.

Table 2. Concentrations of Se (mg/kg) extracted from soil samples with HNO₃-HClO₄-HF (HHH) and *aqua regia* (AR). N = number of samples.

Soil group	N	HHH	AR	t-value
Organogenic	10	0.30	0.29	n.s.
Coarse mineral	10	0.16	0.17	n.s.
Clay and silt	6	0.30	0.23	5.33*

The average concentrations of AR extractable Se in the samples taken in 1992 were 0.393 mg/kg in organogenic soils, 0.148 mg/kg in coarse mineral soils and 0.211 mg/kg in clay and silt soils (Table 3). The Se concentrations of the present coarse mineral soils of 1992 were close to the average of 0.166 mg Se/kg reported by Sippola (1979). In turn, the present organogenic soils had more than double the concentration published by Sippola (1979)(0.169 mg/kg, N= 55). However, the average of 19 organogenic soils published by Ylärinta (1983a)(mean 0.464 mg/kg) was even higher than the value obtained now. Organogenic soils thus seem to be highly variable in AR extractable Se. If it is assumed that in clay and silt soils AR extracts 77% of Se which is dissolved by the HHH method, the present clay and silt soils of 1992 compare well with

the value (0.276 mg Se/kg) calculated from the results of Sippola (1979).

Table 3. Mean concentrations and ranges (in parentheses) of Se extracted from soil samples with *aqua regia*, and Se contents in a 23-cm deep plough layer. N = number of samples.

Soil group	N	Se, mg/kg		Se, g/ha		Difference, g/ha
		1992	2004	1992	2004	2004 – 1992
Organo-genic	10	0.393 (0.200 – 1.120)	0.411 (0.170 – 1.110)	516	536	20 (-132 – 257)
Coarse mineral	18	0.148 (0.060 – 0.280)	0.149 (0.040 – 0.245)	363	388	25 (-106 – 178)
Clay and silt	20	0.211 (0.070 – 0.420)	0.225 (0.070 – 0.445)	470	492	22 (-127 – 159)
All	48	0.229	0.235	440	463	23

The difference of the Se concentrations in 1992 and 2004 was converted to g/ha using the volume weights of the soil samples and assuming that the volume of the plough layer is 2,300,000 dm³. The average difference (Table 3), corresponding to 23 g/ha (median 10 g/ha), was quite similar in all soil classes. Se application was on average 37 g/ha during the 13-year period (Table 4) and it resulted in the estimated balance of 31 g Se/ha (median 28 g/ha). The highest applications took place in intensive grassland cultivation, usually with several applications of mineral fertilizers annually. The balance corresponded to 8% of Se content, measured in the soil samples of 1992. According to the balance, the highest relative additions of soil Se was 22%, taking place in a silt low in Se. There were also 5 other results, all in mineral soils, where the balance was 15% or more of the original Se content.

The relatively close agreement between the mean difference of AR extractable Se concentrations (23 g/ha, Table 3) and 2004 and the calculated balance (31 g/ha, Table 4) seems to be coincidental. The average of the differences (2004-1992) consists of a range of -132 g/ha to +257 g/ha, and as many as 16 of the results were beyond ± 100 g/ha. The difference calculated from the measured Se concentrations was not in a statistically significant correlation with the calculated Se balance. The Se addition to soil in farmyard manure doesn't explain this result, since lower Se concentrations in 2004 than in 1992 occurred equally frequently in soils receiving manure and in other soils.

Table 4. Mean values and ranges (in parentheses) of Se application in mineral fertilizers in 1992-2004 and Se balances, estimated from the amounts of fertilizer Se, yields and Se concentrations of the crops. The balance is also related to the Se content of the plough layer in 1992. N = number of samples.

Soil group	N	Se applied g/ha	Se balance g/ha	Balance/ Se in 1992, %
Organogenic	10	46 (25 – 67)	37 (21 – 53)	8.0 (1.8 – 11.3)
Coarse	18	29 (3 – 78)	24 (2 – 67)	7.3 (0.7 – 16.8)
Clay and silt	20	39 (12 – 71)	33 (11 – 58)	8.4 (3.3 – 22.4)
All	48	37	31	8.1

The inconsistent difference of the AR extractable Se contents of the plough layer between 1992 and 2004 is at least partly attributable to the fact that, in spite of maps of the monitoring sites, the sampling locations have not been exactly the same in the two years. This can be concluded from the volume weights of quite a few samples. Even though the volume weights correlated strongly in 1992 and 2004 ($r=0.934$), there were 12 sites, out of the 48 sites, where the volume weight had changed by more than $\pm 10\%$. Particularly, in six organogenic soils, large changes (-23%, -22%, -21%, -18%, -12%, +31%) took place, suggesting different location sampled in 1992 and 2004. However, discarding these sample pairs most deviating in volume weight did not improve the correlation between the difference of the AR extractable Se concentrations and the calculated Se balance.

Conclusions

The Se balance over 13 years, calculated from fertilizer use and estimated crop uptake, corresponded to 8% (range 0.7 – 22%) of the Se content of the plough layer. On the basis of the present soil analyses, accumulation of residual fertilizer Se, applied as sodium selenate, could not be confirmed in any of the soil groups. This result is most likely attributable to the fields not being homogeneous enough to allow a reliable detection of residual Se at this level of accumulation. This outcome also demonstrates that Se application as selenate has, at least in a short time, a relatively small impact on AR extractable Se concentration of soil. *Aqua regia*, as a strong extractant, dissolves a major part of the native Se incorporated in unweathered soil minerals, therefore, allowing the spatial variability of parent material to have a major impact on the results. Other extractants, such as ammonium oxalate, may be worth testing in the determination of residual Se, associated with the surfaces of soil particles and thus being more selective for added Se. This solution has extracted on an average 26% and 13% of total Se of mineral and organogenic soils, respectively (Ylärinta 1983a). Reducing the impact of the native heterogeneity of soil is crucial in the further studies on the recovery of residual fertilizer Se.

Table 5. Volume weights (kg/l) of the soil samples collected in 1992 and 2004. Mean values and ranges, presented in parentheses, are given. N = number of samples.

Soil group	N	Volume weight		Change in volume weight %
		1992	2004	
Organo-genic	10	0.60 (0.38-0.88)	0.58 (0.29 -0.76)	-4 (-23 – 31)
Coarse mineral	18	1.08 (0.96-1.26)	1.15 (0.89 -1.33)	6 (-13 – 19)
Clay and silt	20	0.95 (0.73 - 1.10)	0.96 (0.75 -1.10)	2 (-12 – 10)
All	48	0.92	0.94	2

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Environmental effects of selenium fertilization - Is there a potential risk?

Georg Alfthan, Antti Aro

Biomarker Laboratory, National Public Health Institute, Mannerheimintie 166, 00300 Helsinki, georg.alfthan@ktl.fi, antti.aro@ktl.fi

Various components of artificial fertilizers may leach into natural waters and cause harmful effects for the environment like eutrophication. Selenium in the form of sodium selenate has been added to artificial fertilizers in Finland since 1985. The amounts of Se used annually in fertilizers during 1985-1990, 20 tons and during 1991-1998, 7.6 tons, are comparable with the total fallout of Se from precipitation, estimated to be 18 tons in 1989 (Wang et al. 1993). Concern about possible bioaccumulation of selenium in the water ecosystem gave rise to monitoring of waters in Finland. Studies on selenium in waters commenced in 1990, and thus had not been done before the selenium fertilization started.

Selenium concentrations of tap water, groundwater, lake and river waters and lake and river sediments collected during 1990-1992 disclosed no obvious environmental effects that could be ascribed to selenium fertilization (Alfthan et al. 1995, Wang et al. 1991; 1994; 1995). Comparison of the total selenium levels in environmental samples showed them to be generally lower than in other European countries. A follow-up study was done in 1997-1999 on the seasonal variation of water selenium from 14 rivers and lake sediments from seven lakes (Eurola and Hietaniemi 2000). During 1997, the mean Se concentration of river waters was lowest in June (92 ng/l) and highest in August (119 ng/l). The mean values were similar to those measured in 1990 to 1992. The results for both water and sediment Se concentrations are shown for samples taken in 1992 and 1999, Table. The mean water Se concentration did not differ between the two sampling years. The mean selenium concentrations of the sediment top layers sampled in 1999 were only slightly lower than in 1992. In five of the lakes, the Se concentration in sediments was higher in the top layers than the bottom layers, approximately corresponding to the time after and before fertilization started, but the Se concentration had already started to increase during the first half of the 1900s (Wang et al. 1995).

Table 1. Lakewater and sediment selenium in the 20th century.

Lake	Trophic level	Water 1999 ng/l	Water 1992 ng/l	Sediment Bottom 1999 mg/kg	Sediment Top 1999 mg/kg	Sediment Top 1992 mg/kg
Pyhäjärvi	+	115	81	0.18	0.23	0.23
Villikkalanjärvi	+	162	113	0.23	0.16	0.27
Kyöliönjärvi	+	116	59	0.31	0.45	0.35
Onkivesi	+	91	58	0.26	0.37	0.26
Pääjärvi	±	99	143	0.71	0.49	1.05
Iso-Hietajärvi	-	40	34	1.16	2.06	2.03
Pesosjärvi	-	52	89	2.95	2.82	3.64
Mean		96	82	0.82	0.94	1.12

mg/kg = dry weight

Bottom sediment 1999 is mean of sediment layers below 20 cm representing the 19th century.

Xenobiotics accumulate in aquatic organisms and especially in predatory fish. We studied the relationships between selenium in perch, water and sediments according to the trophic state of 26 lakes (Wang et al. 1995). The selenium concentrations of perch and surfacial and preindustrial sediments were strongly interrelated and associated with trophic state of the lakes, Figure. The total water selenium concentration was not associated with any of the other factors.

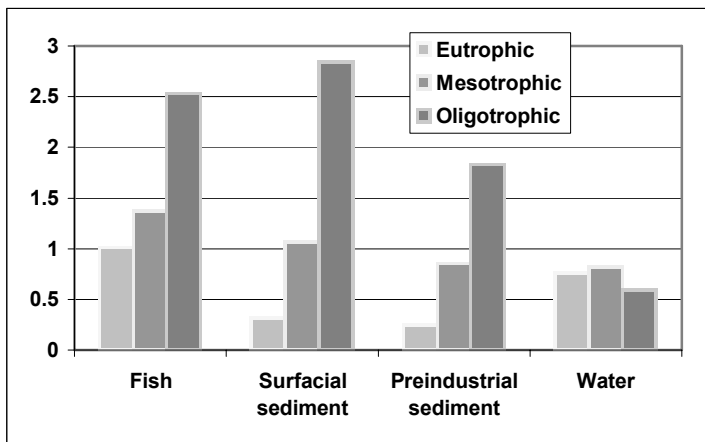


Fig. 1. Selenium concentration of perch and lake water and sediments according to trophic state of lakes.

In conclusion, obvious effects on the water ecosystem from Se supplementation of fertilizers have not been observed to date. Transport and distribution of selenium in the aqueous environment is complex and data should be interpreted with caution.

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Selenium requirements and recommendations

Raymond F. Burk

Division of Gastroenterology, Hepatology, and Nutrition and Center in Molecular Toxicology, Vanderbilt University School of Medicine, Nashville, Tennessee 37232, USA; raymond.burk@vanderbilt.edu

Interest in selenium as an essential micronutrient for human beings arose in the 1960s after it had been found to protect against several diet-related conditions in animals. In early human studies, blood and plasma levels of the element were determined in attempts to assess selenium status (Allaway et al. 1968, Burk et al. 1967). However, no reference values were available, so interpretation of those results was difficult.

Functional measurement of selenium became possible when, in 1973, the element was discovered to be an essential constituent of liver glutathione peroxidase (GPX) in the rat (Rotruck et al. 1973). GPX activity was also present in plasma so measurement of it there was used as an accessible biomarker of selenium status in human beings (Yang et al. 1987). Plasma activity has been shown to be due to the extracellular GPX, which was designated as GPX-3. The major tissue form of GPX is a different gene product, GPX-1.

In addition to GPX-3, selenoprotein P is present in plasma (Burk and Hill 2005). Thus, 2 selenoproteins are available in plasma for measurement. They serve as 'functional' forms of selenium and, together with measurement of selenium, have been used as indexes of selenium nutritional status. GPX activities in the red blood cells and platelets have also been used as markers of selenium status but are employed infrequently.

In 1979 Chinese scientists reported that administration of selenium to children in a low-selenium area prevented the development of Keshan disease, a cardiomyopathy (Keshan Disease Research Group 1979). Following this the U.S. National Research Council listed selenium as essential and indicated that an intake of 50-200 μg per day was safe and adequate (National Research Council 1980).

Based on another study in China carried out in 1983 (Yang et al. 1987), the National Research Council set recommended dietary intake values of 70 μg per day for men and 55 μg per day for women in 1989 (Na-

tional Research Council 1989). These figures were revised in 2000 to 55 µg per day for men and women (Institute of Medicine 2000).

In 2001 we carried out a selenium supplementation study in a low-selenium area of China (Xia et al. 2005). Two forms of selenium, selenite and selenomethionine, were supplemented at levels up to 66 µg selenium per day for 20 weeks. Both plasma selenoproteins were measured to assess selenium nutritional status.

Plasma GPX activity became optimized with supplementation of 37 µg selenium as selenomethionine. Dietary selenium intake was 10 µg per day so a total intake of 47 µg per day optimized this selenoenzyme, confirming the results of the study done in China in 1983. Selenoprotein P did not become optimized with supplements of selenomethionine as high as 61 µg selenium per day, however. The effect of selenite was approximately half that of selenomethionine for a given dose of selenium.

These results indicate that a higher selenium intake is needed to optimize selenoprotein P than is needed to optimize plasma GPX activity. Because these plasma selenoproteins are surrogates for selenoproteins in tissues, the failure to optimize selenoprotein P suggests that some tissue selenoproteins were not optimized by the supplements given. Thus, a higher selenium intake than was given in this study will be needed to optimize all selenoproteins. An additional study will be needed to determine how much selenium is required to optimize selenoprotein P.

In conclusion, it appears from the study published this year that the recommended dietary allowance for selenium will need to be increased. Also, selenium in selenomethionine appears to be more bioavailable than selenium in selenite.

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Selenium content of foods and diets in Finland

Päivi Ekholm¹⁾, Merja Eurola²⁾, Eija-Riitta Venäläinen³⁾

¹⁾Department of Applied Chemistry and Microbiology, University of Helsinki, P.Box 27, 00014 University of Helsinki, Finland, paivi.ekholm@helsinki.fi

²⁾MTT Agrifood Research Finland, 31600 Jokioinen, Finland.

³⁾National Veterinary and Food Research Institute, P.Box 45, 00581 Helsinki, Finland.

Abstract

The selenium (Se) content of 13 basic Finnish food items has monitored regularly since the beginning of the use of Se supplemented fertilizers 20 years ago. This operation was found to increase the Se contents of all foods, and the average daily intake increased also to an adequate level. The fertilization practice is found to be safe, because the plants act as effective buffers against too high Se contents. The fertilization practice is also found to be adjustable, because the Se contents of food respond to the amount of Se in the fertilizers.

Key words: selenium, food, intake

Introduction

In 1984 the Ministry of Agriculture and Forestry made a decision that nutrient element fertilizers should be supplemented with sodium selenate. The supplementation was made to all granular NPK-fertilizers; 16 mg Se/kg fertilizer for the grain production, and to 6 mg Se/kg for grassland crops. The supplementation practice was simplified at the beginning of 1991 by lowering the Se supplementation level to 6 mg/kg in all fertilizers. The amount of Se was then added to 10 mg/kg since 1998. The original target was to increase the Se content of Finnish cereal grains to 0.1 mg/kg dry matter (DM) and also the average daily Se intake to the range considered as safe and adequate; 0.05-0.2 mg/day (Food and Nutrition Board, 1980). Together with the Se supplementation of fertilizers an extensive monitoring of the Se content of 13 Finnish basic food items was begun.

The decision of Se supplementation was made, because in the 1970's it was shown that all Finnish agricultural products contained exceptionally low amounts of Se (Koivistoinen, 1980). The average daily Se intake varied somewhat according to the extent of grain imports in Finland, but

in general it was as low as 0.025 mg/10 MJ. The inadequate Se intake was also a serious problem in animal husbandry (Oksanen, 1980). Severe nutritional disorders were common and they could be effectively treated with Se and vitamin E. Therefore, all commercial animal feeds had been supplemented with selenite since 1969 in Finland.

Effect of Se supplementation on food Se

Grain: The effect of Se-supplemented fertilization on cereal grains was distinct. The Se contents of spring cereals (spring wheat, oats, and barley) increased 20-30-fold during the years when two supplementation levels were in use. After using only the lower of the original supplementation levels since 1991, the Se contents of spring cereals decreased to about 10-fold higher compared with the level common before the Se fertilization. Since the raising the Se supplementation level to 10 mg/kg fertilizers increased the Se level of spring cereals to the level, which is 15-fold higher than before the Se fertilization practice (Fig 1.).

The increase in winter cereals (rye and winter wheat) was considerably less, the contents varying between 0.02 and 0.07 mg/kg during the years 1985-1995, this was 2-7-fold higher compared with the level common before the Se fertilization. The reason for this difference is, that winter cereals are usually given only light Se supplemented multimineral fertilization in the fall during sowing, while nitrogen fertilizers without Se was applied in the spring. Selenate reduced to selenite during the winter and thus bound to the soil. The Se content of winter cereals has increased to the average 0.1 mg/kg DM since the nitrogen fertilizers are supplemented with Se (Fig 1.).

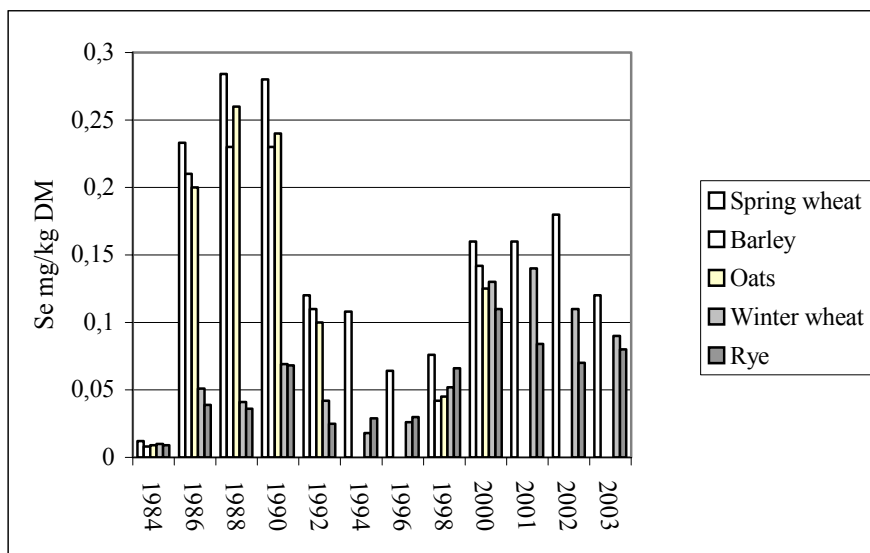


Fig. 1. Se content of cereal grains in Finland.

The Se content of flour and bread are quite similar. Finland occasionally imports grain because of an inadequate or low-quality harvest, and domestic grain and imported grain are mixed for milling. Because of that, the Se content of grains differs sometimes from that of flours and breads. The Se content of European cereals varies usually between 0.02 and 0.050 $\mu\text{g}/\text{kg DM}$ and that of North American cereals between 0.2 and 0.5 mg/kg (Varo and Koivistoinen, 1981).

In 1985-1990 cereal products contributed about 20% of the total daily Se intake of the population. The adjusting the Se supplementation amount has affected the Se content of grains, and the contribution of cereals to the Se intake has decreased to 16% in the year 2004.

Meat: The se content of beef produced in Finland in the mid-1970's was low. An average content of about 0.05 $\text{mg}/\text{kg DM}$. Pork contains more Se. In Finland the average level in the 1970's was about 0.2 $\text{mg}/\text{kg DM}$. Even this level was low compared to the reported values from other countries.

The effect of Se fertilization on the Se contents of beef and pork was very clear. During 1985-1990, beef contained an average of 0.51 $\text{mg Se}/\text{kg DM}$, which was about 13-fold higher than the figure for 1975/77. The average Se content of pork during 1985-1990 was about 4-fold

higher than during 1975/77. Reduction of the amount of Se in the fertilizers decreased the Se contents of beef and pork meat significantly. The Se content of beef and pork in 2004 was about 6-fold and 2-fold, respectively, compared to the common level before the beginning of the Se fertilization (Fig 2).

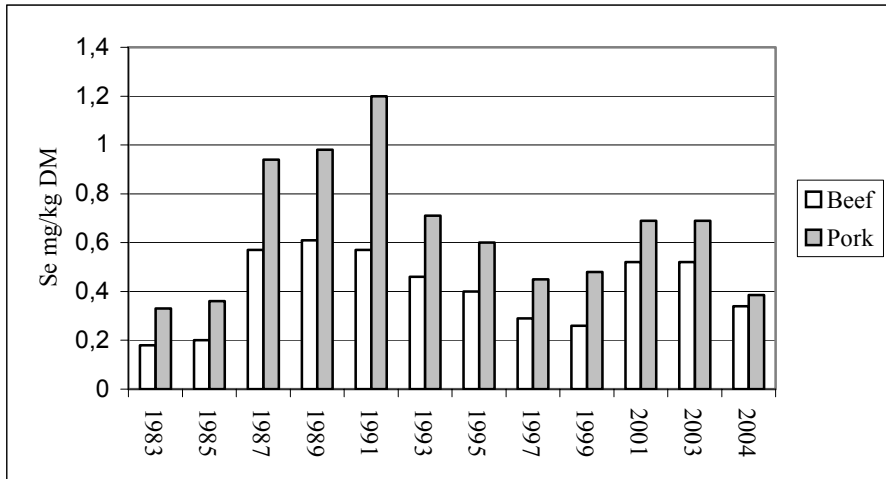


Fig. 2. Se content of beef and pork in Finland.

Meat and meat products are an important dietary source of Se in Finland. The contribution to the total Se intake was about 40% in the beginning of the 1990's and it was about 35% in the year 2004.

Dairy products and eggs: In the mid-1970's the selenium concentration of milk was very low, about 0.003-0.004 mg/l. It slowly increased in the early 1980's, probably because of increasing use of selenite-containing commercial feeds and mineral concentrates and Se medication of cattle. The effect of Se-supplemented fertilizers on milk composition was rapid and substantial. Se-supplemented fertilizers were used for the first time in May 1985. The milk samples collected in June 1985 already contained nearly 2-fold higher Se content. During the first years of Se fertilization the Se content of milk fluctuated with the season, being about 15% lower in the outdoor season than in winter. The seasonal variation became smaller in later years, and in 1990 it was almost undetectable. During the last years the about 20% seasonal variation is seen again. After the adjusting the Se-

supplementation levels the changes in the Se content of milk were also seen very quickly (Fig 3).

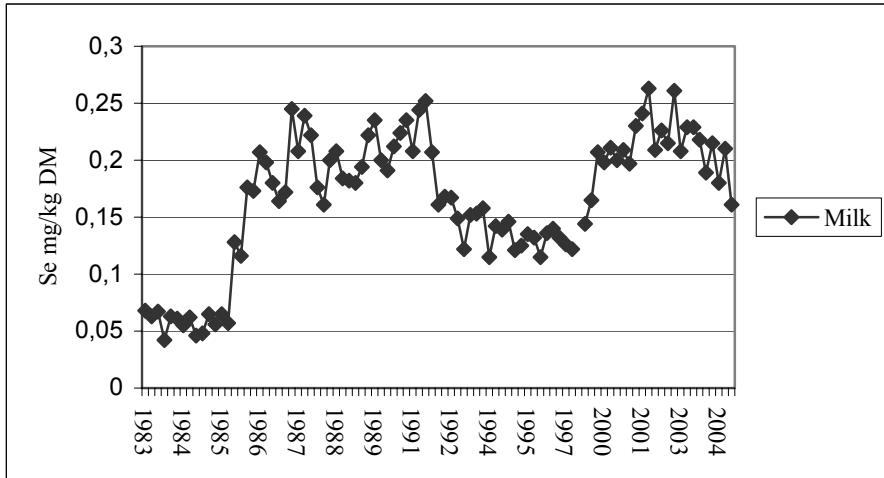


Fig. 3. Se content of milk in Finland.

The Se content of eggs was relatively high, about 0.45 mg/kg DM, already in the middle of the 1970's because of the use of Se-enriched feeds. After 1985 the content gradually rose to the level of 1.2 mg/kg DM, and decreased again to 0.8 mg/kg. The contribution of dairy products and eggs to the total Se intake was over 25% when the Se content of cereals was higher. The present contribution to the total Se intake is about 30%. The foods of animal origin contribute over 70% of the total Se daily intake. The significance of animal foods from the Se intake has increased remarkably.

Dietary intake: The average daily Se intake in the middle of the 1970's, when grain was not imported, was as low as 0.025 mg/person. In the early 1980's, when grain was imported, the intake was 0.04-0.05 mg/day. However most of the time the Se intake was below the lower limit considered as safe and adequate. The Se supplementation of fertilizers affected the average intake substantially. A plateau during the years 1986-1990 was 0.11-0.12 mg/day. During the years 1992-1997 the Se intake was 0.079 mg/10 MJ in average, and the trend was decreasing. In the year 1998 the Se amount in the fertilizers was increased and that increased also the average daily Se intake. In the 2000's the average daily Se intake has been about 0.07-0.08 mg/10 MJ. The present trend of the intake is still decreasing because of the decreasing of

the Se content of all foodstuffs. The estimated Se intake is calculated for a diet where all used foods are domestic. The use of imported foods decreases the Se intake. The daily Se intake meets well the recommendations (National Nutrition Council, 1998; States Food and Nutrition Board and Institute of Medicine, 2000,).

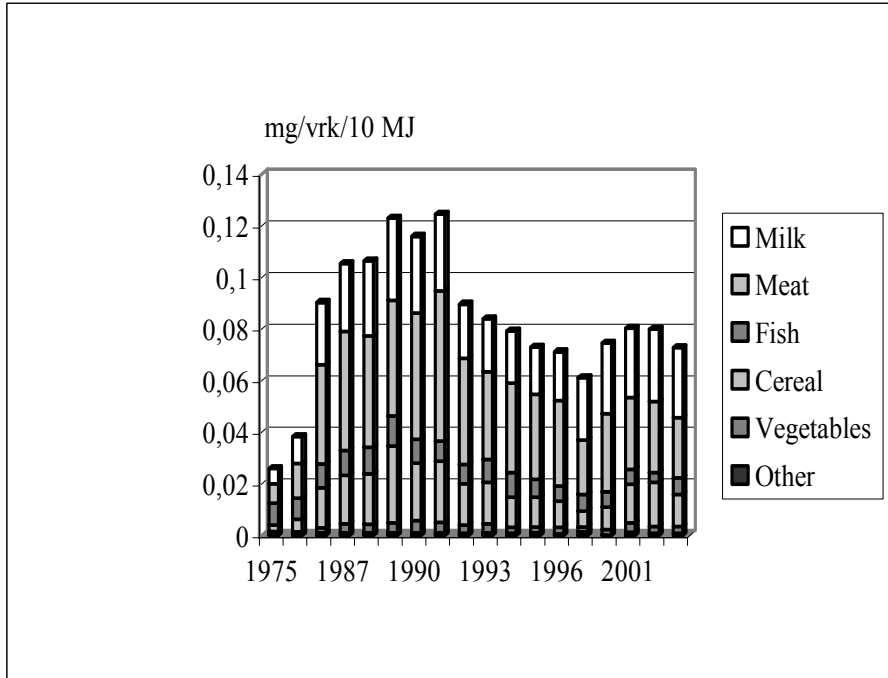


Fig. 4. The average daily Se intake in Finland.

Summary

The Se fertilization has proven an effective, safe, and adjustable method to increase the Se content of foods and also the average Daily Se intake in Finland.

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Selenium in animal feeds and nutrition

Tarja Root

Plant Production Inspection Centre, Department of Agricultural Chemistry P. O. Box 83, 01301 Vantaa, Finland, tarja.root@kttk.fi

Abstract

Selenium (Se) is an essential nutritional trace element, which is needed for growth and reproduction in all living animals. At the same time it is a highly toxic substance, and therefore the Se content of animal diets should be monitored constantly. The dietary requirement of Se differs between the animal species and is affected by the form of selenium ingested and dietary composition, especially its content of vitamin E. The Finnish recommendation of Se for cattle is 0.1 mg/kg feed DM, for pigs 0.2 mg/kg DM, for poultry 0.1-0.2 mg/kg DM and fur animals 0.6-0.9 mg/kg DM. The level of Se in feeds of plant origin varies depending on plant species, part of the plant, growing season and soil which the plants grow on. In Finnish soils the selenium availability to plants is limited, and Se addition to fertilizers has increased the overall Se content of feed materials from 0.02 mg/kg dry matter (DM) to 0.2 mg/kg DM. The best Se sources of the feeds of animal origin are fish products. The main form of selenium in plant and animal origin feed materials is organic protein-bound selenomethionine, together with small amounts of selenocysteine and selenite. Animal feeds and diets can also be supplemented with inorganic selenium (sodium selenite, sodium selenate). However, at present the organic selenium sources are not accepted as feed additives. The maximum permitted amount of Se in compound feeds or daily rations is 0.5 mg/kg DM.

Key words: selenium, animal nutrition, feed

Introduction

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 chicks could be prevented by adding selenium or vitamin E in the diet (McDonald et al. 1985). Selenium is a component of the glutathione peroxidase molecule, which explains its interactive role with vitamin E and the sulphur-containing amino acids. Selenium deficiencies are well known in the form of white (nutritional) muscular disease in ruminants and other animals (Van

Soest, 1994). However, the line between the requirement and harmfulness of Se is narrow since selenium is a highly toxic element. Therefore the total amount of selenium in animal diets has to be monitored constantly.

The amount of selenium in feeds of plant origin is very variable depending on the plant species, the part of the plant sampled, the growing season and soil which they grow on (Underwood and Suttle, 1999). The selenium content in Finnish soils is known to be low, but in addition, for climatic and geochemical reasons selenium availability to plants is limited (Yläranta, 1985). This reflects directly to feeds (and foods). Since 1984 the fertilizers produced in Finland have been supplemented with sodium selenate, which has increased the overall Se content of feed materials grown in Finland on average from 0.02 mg/kg dry matter (DM) to 0.2 mg/kg DM (Eurola et al., 2003). Consequently this has increased the level of selenium in foods of animal origin and helped the human population to meet their Se requirements.

Selenium requirement of animals

Selenium takes part in essential functions in living organisms and is necessary for growth and fertility in all animals. The dietary requirement of selenium differs between the animal species depending on their digestive system and type of production. For given species the minimum requirement of selenium varies mainly with the form of selenium ingested and dietary composition, especially its content of vitamin E (Underwood and Suttle, 1999).

In spite of the fact that the nutritional bioavailability of selenium varies according to criteria chosen, population and individuals, it is shown that in general the bioavailability of inorganic selenium, mostly as selenite, is lower than the organic form of selenium (Mutanen, 1986). When assessing the selenium requirement of animals, the vitamin E supply should be assumed to be normal, because vitamin E deficiency enhances the selenium requirement.

Ruminants seem to absorb selenium less efficiently and more variably than non-ruminants. Rumen micro-organisms reduce selenium to unavailable forms (McDowell, 1992), and only one third of inorganic selenium is absorbed. The apparent absorption of selenium has been shown to be greater from concentrate than from a lucerne hay diet (52.8 vs. 41.8%) (Koenig et al., 1997).

Feed intake of sheep is greater per unit body weight compared to cattle, which may create a higher burden on antioxidant defences and therefore lead to greater need of selenium. Wool production in sheep affects selenium requirement (Wilkins et al, 1982) and high milk yield of dairy cows increases the selenium requirement (Underwood and Suttle, 1999).

The Finnish recommendation of selenium for cattle is 0.1 mg/kg feed DM, for pigs 0.2 mg/kg DM, for poultry 0.1-0.2 mg/kg DM and fur animals 0.6-0.9 mg/kg DM (MTT, 2004). In Norway the dietary selenium requirement for Rainbow trout is shown to be 0.15-0.38 mg/kg DM.

Selenium content of feeds

Soils containing less than 0.5 mg Se/kg are likely to lead to crops and pastures with inadequate selenium concentrations (< 0.05 mg/kg DM). The main form of selenium in plant and animal origin feed materials is organic protein-bound selenomethionine, together with small amounts of selenocysteine and selenite (Underwood and Suttle, 1999).

Natural concentration of selenium in forages varies mainly according to the soil selenium status. According to the Finnish monitoring programme grass silages contained on average 0.37 mg Se/kg DM during the years 2000-2001. Grass silages from the organic production system contained nearly ten times less selenium than conventionally produced grasses (Eurola et al., 2003). Silages from the spring harvest seemed to have higher selenium content than the summer and autumn harvests. Legumes tend to contain less selenium than grasses (Underwood and Suttle, 1999).

Wheat can be higher in selenium than barley and oat grains (Miltimore et al. 1975). In Finland the Se content of feed oats and barley has been stabilizing to a mean level of 0.10-0.14 mg/kg DM (Eurola et al., 2003).

The best selenium sources of the animal protein feeds are those of marine origin. Salmon and herring meals has been shown to be rich in Se (1.9 mg Se/kg DM) (Miltimore et al. 1975). Tuna fish-meal can, however, contain even higher amounts of Se (5.1 and 6.2 mg Se/kg DM) (Scott and Thompson, 1971). In the European Union based on the Commission Regulation (EY) N:o 1234/2003 fish meal is not allowed in the feeding of ruminants, but it still provides good protein and selenium source for pigs and poultry as well as fish and fur animals.

Animal diets can be supplemented with inorganic selenium (sodium selenite, sodium selenate) added to feeds. However, at present organic selenium sources are not accepted as feed additives. Feed manufacturers aim to have the selenium content of compound feeds close to the maximum permitted selenium level, which is 0,5 mg/kg DM (Ministry of Agriculture and Forestry Regulation N:o 43/2005).

In Finland the Plant Production Inspection Centre monitors commercial feeds, and during the years 2000-2001 36% of the analysed samples exceeded the permitted Se value (Eurola et al., 2003). 35% of these samples were feeds for fish, which did not contain added selenium.

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Selenium and animal health

Kristiina Dredge

University of Helsinki, Faculty of Veterinary Medicine, ELKE – Development of Animal Health Service, Saari Unit, Pohjoinen pikatie 800, 04920 Saarentaus, kristiina.dredge@helsinki.fi

Abstract

Selenium is an essential nutrient for all animals. It is a biochemical component of glutathione peroxidase enzyme (GSH-PX) as well as of thyroid gland hormone and of several other proteins. GSH-PX protects cellular membranes and organelles together with vitamin E.

Selenium deficiency occurs worldwide. Deficiency of selenium and/or vitamin E can lead to several different subclinical or clinical forms of diseases, of which enzootic muscular dystrophy (NMD), and mulberry heart disease are the most common ones. Development of a clinical disease is often predisposed by other factors, such as rapid growth, sudden increase in physical exercise, and excessive amounts of polyunsaturated fatty acids in diet.

NMD occurs in all farm animals. It is relatively common in Scandinavia, and in some European and Northern American countries. It most often affects young calves, lambs, goat kids and foals, being an important cause of mortality. NMD has acute and subacute forms, of which the former causes dystrophy of myocardium and the latter of skeletal muscles. Mulberry heart disease is the most common form of vitamin E – selenium deficiency (VESD) syndrome in pigs. Outbreaks can affect 25% of a herd, and mortality rate among the diseased can level up to 90%.

Selenium deficiency has also been associated with decreased resistance to infectious diseases, impaired reproductive performance, and retained placenta. The association, even though, is partly unclear and the research results in some cases contradictory.

Adding selenium to fertilizer and animal feedstuffs has fortunately decreased the incidence of selenium and vitamin E responsive diseases markedly, but has still not been able to eliminate the conditions completely. Organic farms and farms that use fertilizers that do not include selenium have to plan selenium supplementation more carefully than the others.

Adequate selenium and vitamin E supplementation is necessary, not only for animal health, but also for the quality of the animal products received from food animals. Recommendation for dietary requirements for selenium varies between different countries. In Finland the norm, 0.1 mg/kg dry matter of feed, is half of that by the Swedes, and only third of the British recommendations, which seems confusing. The source and form of the supplement can also affect the utilization. Selenium is poisonous in big amounts, and the safety marginal is not very wide. These things have to be kept in mind while planning the supplementation for a herd.

Key words: selenium, diseases, animal health

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Selenium in plant nutrition

Marja Turakainen¹⁾, Helinä Hartikainen²⁾, Mervi Seppänen¹⁾

University of Helsinki, ¹⁾Department of Applied Biology, ²⁾Department of Applied Chemistry and Microbiology, P. O. Box 27, FIN-00014, marja.turakainen@helsinki.fi

Abstract

Selenium (Se) is not classified as an essential element for plants although its role for animal and human health is well established. Though higher plants have been considered not to require this element, the experience with low-Se soils in Finland has provided evidence that when added at low concentrations, Se exerts a beneficial effect on plant growth via several mechanisms. Similarly as in humans and animals, it strengthens the capacity of plants to counteract the oxidative stress caused by oxygen radicals produced by internal metabolic or external factors. At proper levels it also delays senescence and may improve the utilization of short-wavelength light by plants. High additions, in turn, are toxic and may trigger pro-oxidative reactions and enhance lipid peroxidation. Plants defend themselves against Se excess by producing volatile Se compounds. In food chain, plants act as effective buffers, because their growth is reduced at high Se levels.

In our experiments, added Se also improved the quality of plant products. It counteracted the decrease of tocopherols (vitamin E) during senescence of lettuce and, thus, the impairment of its nutritive value. The recent results showed that at very high level Se diminished total glycoalkaloid content in young potato tubers. At low levels it increased starch concentration of leaves and tubers. Furthermore, the yield was higher in Se-supplied plants than in the control plants. The yield was composed of relatively few but larger tubers. During storage Se concentration remained constant, and applied Se was transferred from seed tubers to the next potato generation. Low Se supplementations delayed enzymatic discoloration of tubers measured 1 and 8 months after harvesting. The result suggests that Se increased tolerance of raw tubers to browning maybe through its antioxidative function.

Key words: selenium, potato, lettuce, ryegrass, antioxidants, yield, starch, storage quality

Introduction

The advantage of se fertilization compared to a direct supplementation of food and feed with selenium (Se) has been questioned, because the higher plants are generally considered not to require this element. However, the prevailing view has placed the scientific community before a dilemma, for plants play a key role in cycling Se from soil to animals and humans. Are plants only conveyers in this system, or do they derive some direct, as not yet unknown, benefit from Se for themselves? We still do not know for sure. Nevertheless, when considering this question we have to recall two facts. Firstly, some plants have developed a remarkable ability to take up Se from soil (Terry and Zayed 1998). This means that they have metabolic systems to treat and accumulate this element. Secondly, it has been shown repeatedly that Se is more bioavailable to animals and humans in organic forms than in inorganic forms (Ortman & Pehrson 1998). Plants have an important role in synthesizing organic Se, including amino acids, and providing it to animals and humans. In wheat, soybean, and Se-enriched yeast, Se is found predominantly as selenomethionine (Fishbein 1991 and references therein). Thus, it can be hypothesized that protein-bound Se can have similar roles in animal and plant cells.

We have studied the effects of Se supplementation on plants from physiological and agronomical point of view. The work hypotheses have risen from findings in medical and veterinary sciences. We have focused on the impact of various Se addition levels on the growth and antioxidative capacity of plants as well as on nutritive and storage quality of plant products. The ability of Se to enhance the tolerance of plants against detrimental effects of internal and external stressors such as senescence and UV-B –radiation has been investigated. The main experimental plants represent species of importance in animal feeding and human nutrition: ryegrass (*Lolium perenne*), lettuce (*Lactuca sativa*) and potato (*Solanum tuberosum* L.)

Material and methods

In greenhouse experiments, the experimental plants were cultivated in soils never amended with Se-containing fertilizers or in quartz sand. In all experiments, Se was added in increasing concentrations as H₂SeO₄ (Fluka Chemie AG product, analytical grade) and all treatments had four replicates. The fresh weight (FW) and dry weight (DW) yields were taken to indicate the growth response. Lipid peroxidation in the plant tissues was assayed by measuring thiobarbituric acid reactive sub-

stances (TBARS) according to a modified method of Yagi (1982). With respect to antioxidants, attention was focused on GSH-Px (EC1.11.1.9) whose activity was measured by a modified method of Flohe and Gunzler (described by Hartikainen et al. 2000), and on α - and γ -tocopherols (vitamin E) determined by a small-scale HPLC method of Xue et al. (1997). Selenium in dry plant material was analysed according to Kummulainen et al. (1983) and Ekholm (1997).

In recent experiments with potato, tubers were harvested 16 weeks after planting. The yield, the mean tuber weight and their mean number per pot were determined after harvest. The starch concentration of leaves were analysed from leaves collected 4 and 8 weeks after planting, and from tubers 16 weeks after planting as described earlier by Palonen (1999). Tubers were stored 4 °C at 75 % humidity until analysis. After 1- and 8-month storage, susceptibility of tubers to enzymatic discoloration was evaluated visually 30 and 60 min after cleavage in two halves. The Se concentration was analysed from freeze-dried tubers after 1-, 6-, and 12- month storage periods. In the following year, the tubers were used as seeds, and the harvested tubers were analysed for the Se concentration.

Results and discussion

The experiments have provided evidence that Se is able to enhance their antioxidative capacity and to defend plants against oxidative stress caused by oxygen radicals produced in metabolic processes or by irradiation. There are indications that Se may improve the utilization of short-wavelength light by plants. High additions of Se showed to be toxic and enhanced the lipid peroxidation. Pro-oxidative reactions may be one of the toxicity mechanisms of Se excess (Hartikainen et al. 2000, Xue et al. 2001, Seppänen et al. 2003, Turakainen et al. 2004a).

Studies with lettuce showed that at low concentrations Se can promote growth, slow down senescence (Hartikainen et al. 2000), and increase starch accumulation in chloroplasts (Pennanen et al. 2003). Total tocopherols diminished during senescence, but the added Se counteracted their decrease and, thus, the impairment of the nutritive value of lettuce. The most recent experiments have indicated also positive effects of Se on quality of potato tubers. Very high selenium supplementation decreased total glycoalkaloid content in young tubers (Turakainen et al. 2004b). Furthermore, our experiments showed that the tuber yield of Se-supplied potato plants was higher and composed of relatively few but larger tubers than that of the control plants. Four weeks after plant-

ing the starch concentration in the upper leaves was significantly higher in the Se-supplied plants than in the control plants. Eight weeks after planting this beneficial effect was not found any more. In the tubers supplied with a moderate Se dosage (0.075 mg kg^{-1} soil), starch concentrations was about 10 % higher than in the control plants. The higher accumulation of starch in the upper leaves in the Se-supplied plants indicates enhanced starch synthesis, reduced carbohydrate transport from the chloroplasts, or increased efficiency of photosynthesis. Carbohydrate transport was probably not affected, because photoassimilates were efficiently transported to potato tubers.

Pilon-Smith et al. (1998) have shown that plants tend to synthesize volatile compounds in order to reduce excess Se. In our studies, lettuce seemed to produce volatile Se compounds as a defending mechanism against Se excess. However, in potato tubers the Se concentration did not change during storage. This indicates that no Se losses from harvested tubers took place during storage. It is noteworthy, that in the tubers produced by the Se-supplied seed tubers, the Se concentration increased with increasing Se dosage given to the previous potato generation. Thus, Se can be transferred from the seed tubers to the next potato generation.

Low Se supplementations (0.0035 and 0.01 mg kg^{-1}) delayed enzymatic discoloration of tubers evaluated visually 30 and 60 min after cleavage of tubers stored for 1 or 8 months. Even though the tubers of the experimental cultivar Satu are quite resistant to enzymatic discoloration, low Se supplementation further delayed this reaction. The result suggests that Se increased tolerance of raw tubers to browning maybe through its antioxidative function.

Summary

Our systematic experiments have shown that at proper addition levels Se exerts beneficial effects on plants through multiple mechanisms and promotes their growth. Similarly as in humans and animals, Se increases in plants the antioxidative capacity needed to counteract the oxidative stress caused oxygen radicals produced by internal metabolic or external factors. At proper level it is also able to delay senescence. There are also indications that Se enhances the utilization of short-wavelength light. In potato cultivation, the Se supplementation has positive effect on potato carbohydrate accumulation and possibly on yield formation. At low supplementation level it may improve the processing quality of potato tubers. Furthermore, the Se concentration remains constant during storage, and Se can be transferred to the next potato

generation. Thus, Se fertilization can affect positively not only the quantity of the yield but can exert beneficial effects on the quality of plant products. In food chain, the plants act as effective buffers against too high concentrations by showing distinct toxicity symptoms.

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Yagi, K. 1982 Lipid peroxides in biology and medicine. pp. 223-230. Academic Press, New Health Implications of Low Selenium Intakes

Importance of selenium in human nutrition

Gerald F. Combs, Jr.

Grand Forks Human Nutrition Research Center, United States Department of Agriculture-Agricultural Research Service, USA

Five Decades of Selenium research

Nearly 50 years of research have established that selenium (Se), once known only as a sulfur-like element with toxic potential, is in fact an essential nutrient. This was first shown in rats and chicks in the late 1950's and then, over the next two decades, in a range of animal species. Because those findings showed Se to correct pathologies in vitamin E-deficient animals, they prompted a debate concerning the nutritional importance of Se per se – a debate in which the relevance to humans was unclear because morbidities associated with low Se status had not been reported.

In the early 1970's, the discovery of Se as an essential cofactor of glutathione peroxidase (GPX) answered the twin questions of whether Se was a nutritional essential and how it functioned in concert with vitamin E to effect cellular antioxidant protection. Less than a decade later, the reports of efficacy of Se in preventing a juvenile cardiomyopathy endemic in parts of rural China with severe endemic Se deficiency drew international attention to Se as being relevant to human health.

During this time, the studies of eminent scientists in two countries, Finland and New Zealand, drew special scientific attention. These showed that each country had soils of low available Se content; each had a population with fairly low blood Se levels compared to other western countries while neither had significant malnutrition; each had a history of health problems in livestock that responded to Se-supplementation. These countries took different tacks in addressing these findings: New Zealand allowed the use an array of Se treatments for livestock (prills, drenches, dietary supplements) or pastures (sprays); Finland approved the use of Se-supplements to some livestock feeds and undertook to increase Se throughout the food system by implementing the addition of Se to its agricultural fertilizers.

The nutritional essentiality of Se is now unquestioned, as the element has been recognized as an essential constituent of at least a dozen en-

zymes, and genomic analyses have indicated 25 selenoprotein genes suggesting still uncharacterized SeCys-enzymes (see Kryukov et al, 2003). The discovery of the Se-dependent GPX led, over the next three decades, to Se being found in the form of selenocysteine (SeCys) in: four GPX isoforms; two isoforms of thioredoxine reductase; three isoforms of the iodothyronine 5'-deiodinases; selenophosphate synthase; and selenoproteins P, W and Sep15. Allelic variants of GPX1 and Sep15 have been linked to cancer risk (see Diwadkar-Navsariwala and Diamond, 2004).

That Se might also be anti-carcinogenic was suggested in the 1960's based on an inverse relationship of cancer mortality rates and forage crop Se contents in the US. Evidence developed since that observation has shown that Se can, indeed, play a role in cancer prevention: some epidemiological studies have found Se status to be inversely associated with cancer risk; hundreds of animal studies have shown that Se-treatment can reduce tumor yields; Se has been shown to inhibit growth and stimulate programmed cell death in a variety of cell culture systems. It is now clear that both inorganic and organic Se-compounds can be anti-tumorigenic at doses greater than required to support the maximal expression of the SeCys-enzymes regarded as discharging the nutritional effects of the element (see Combs and Lü, 2001). Evidence points to methylated Se-metabolites being active in anti-carcinogenesis (see Ip, 1998).

Global Variation in Selenium Status

In most diets, the dominant food sources of Se are cereals, meats and fish. For example, in American diets five foods (beef, white bread, pork, chicken and eggs) contribute half of the total Se, and 80% of total dietary Se is provided by only 22 foods (Schubert et al, 1987). The dominance of cereal-based foods as core sources of Se means that, in many countries, Se intakes can be affected by the importation of grain from relatively Se-rich areas in the USA, Canada and Australia. Indeed, changes in wheat importation have been linked to corresponding changes in Se intakes Finland and other countries, and reductions in North American imports have been cited as causing general reductions in Se intakes in Europe in recent years.

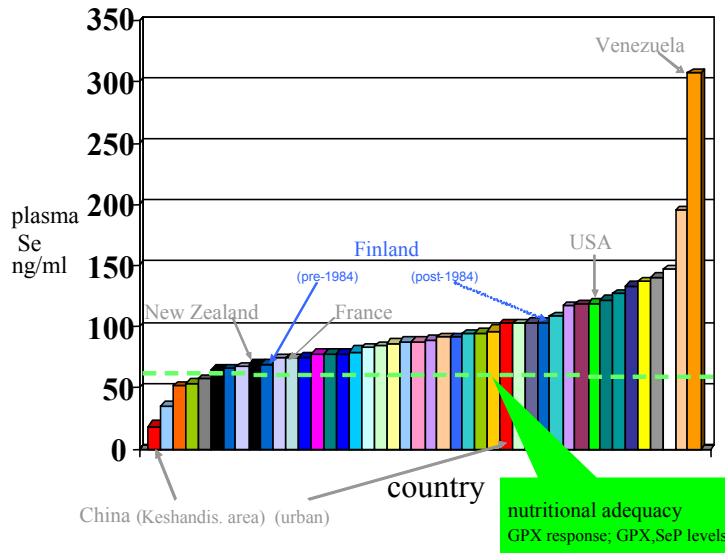


Fig. 1. Global variation in Se status

A comparison of the Se contents of different food systems (Combs, 2001) suggested that millions of people may be unable to consume enough of the element to support maximal expressions of GPX1, i.e., at least 40 ug Se per day (Yang et al, 1987). The best described Se-deficient areas are New Zealand, Finland (pre-1984), and a long belt of mountainous terrain extending from the northeast to south-central portions of mainland China; but low Se intakes have also been reported in parts of eastern Europe. A comparison of plasma/serum Se levels from 68 countries (Fig. 1) with the minimum reported level for which further Se-supplementation does not increase plasma GPX1 activities, 70 ng/ml (Nève, 1995), suggests that sub-clinical Se deficiency may affect at least 10% of residents in most countries for which data are available, and >50% of the populations in half of those countries (Combs, 2001). Only in Canada, Japan, Norway and the US does low Se status appear not to affect many people.

Health Implications of Low Selenium Intakes

Two diseases have been associated with severe endemic Se deficiency in humans: a juvenile cardiomyopathy (Keshan disease), and a chondrodystrophy (Kaschin-Beck disease). Each occurs in rural areas of China and Russia (eastern Siberia) in food systems with exceedingly low Se supplies. Keshan disease has been noted in mountainous areas where the soil Se levels are very low (<125 ppb Se) and grains gener-

ally contain <40 ppb Se. In these areas humans have shown the lowest reported blood Se levels e.g., <25 ppb. Dramatic reductions in Keshan disease incidence have been achieved by the use of oral sodium selenite (0.5-1 mg Se/child/week) or selenite-fortified table salt (10-15 ppm Se) (Keshan Disease Res. Group, 1979). Recent findings suggest that the disease may actually be caused by RNA-viruses the virulence of which can be potentiated by severe Se deficiency (Beck et al, 2001). Kaschin-Beck disease is an osteoarthropathy affecting the epiphyseal and articular cartilage and the epiphyseal growth plates of growing bones and manifested as enlarged joints (especially of the fingers, toes and knees), shortened fingers, toes and extremities, and, in severe cases, dwarfism. While that severe endemic Se deficiency appears to be a pre-disposing factor, it is not clear that Se deficiency is a primary cause of the disease.

It is likely that Se deficiency may also be a factor in some other diseases (see Combs, 2001). That Se-dependent GPX is important in protecting proliferating keratinocytes in wounded tissues suggests that Se-deficient individuals may have compromised wound healing, although there have been no clinical reports of such effects. Studies in central Africa found that the prevalences of the iodine-deficiency diseases, goiter and myxedematous cretinism, were greater among populations of relatively low Se status than among those of greater Se status. Because Se is essential for the metabolic production of thyroid hormone (which requires a Se-containing deiodinase to convert thyroxine to the active thyroid hormone), such a relationship suggests that the efficacy of iodine supplementation may be limited in Se-deficient populations, in which cases treatment with both Se and iodine would be indicated. Low Se status has been linked to increased risks of pre-eclampsia, spontaneous abortions, and male infertility. Recent findings have shown that severe Se-deficiency in vitamin E-deficient hosts can increase the mutation rates of RNA-viruses, suggesting that Se deficiency may increase risks of measles, influenza, hepatitis and acquired immune deficiency syndrome - all global problems.

Low blood Se levels have been measured in patients with several other diseases (see Combs, 2001). Children with protein-deficiency diseases, Kwashiorkor or Marasmus, tend to be low in Se as Se occurs in food proteins. Malnourished children also appear to have increased needs for Se and other antioxidant nutrients, due to the pro-oxidative effects of malnutrition and inflammation. Neonates typically have lower blood Se levels than their mothers, and low plasma Se levels have been associated with increased risks to respiratory morbidity among low birth weight newborns. Low blood Se levels have been observed in infants

with PKU, but these effects have been due to the use of parenteral feeding solutions containing negligible amounts of Se.

Health Implications of Supranutritional Selenium Intakes

Several clinical trials have been conducted to determine the anti-cancer efficacy of Se in humans. This body of research includes a few trials that were not evaluated with appropriate statistical methods or were not subjected to appropriate scientific review, and a few trials that employed fairly low doses of Se (50 µg/day) or mixed treatments of biologically active substances (see Combs, 2005). The Nutritional Prevention of Cancer (NPC) Trial (Clark et al, 1995) remains the most useful one conducted to date in considering the role of Se in cancer prevention.

The first report from that trial included data for its first 10 years (1983–1993) which showed no significant effects of Se-treatment on the incidences of either of the primary endpoints of the study: basal (BCC) or squamous cell carcinoma (SCC) of the skin. They also showed significant risk reductions for several secondary endpoints: total cancer incidence (RR=0.63), total cancer deaths (RR=0.50), incidences of carcinomas of the lung (RR=0.54), prostate (RR=0.37), colon-rectum (RR=0.42), and total non-skin (RR=0.55). More recently, the results for the full 13 yrs of the trial (Reid et al, 2002; Duffield-Lillico et al, 2003a, 2003b) showed Se-treatment associated with reduced risks to total cancer incidence (RR=0.63) and incidences of carcinomas of the prostate (RR=0.51) and colon-rectum (RR=0.46), but not lung cancer incidence (RR=0.70, P=0.18). While the complete data seemed to suggest an increase in non-melanoma skin cancer risk, the analysis of 1250 validated subjects (of a total of 1312) revealed that Se-treatment did not affect risk of either BCCs (and may have delayed the diagnosis of the first BCC), or SCCs diagnosed after two years of treatment (RR=1.21, P>0.05).

Subgroup analyses of the NPC Trial data show that Se (200 mcg/d) was effective in reducing cancer risks only among subjects who entered the trial with plasma Se levels in the lower tertiles of the study population (Fig. 1). Those with baseline plasma Se levels above ca. 120 ng/ml showed the lowest cancer risks and no risk reductions in response to supplemental Se. This suggests that cancer risk reduction was achieved by raising plasma Se level to at least 120 ng/ml. Clearly, the amount of supplemental Se necessary to reach that threshold was greater for the low Se subjects (e.g., those with base-line Se levels less than 100 ng/ml)

than it was for those with greater baseline Se levels. Thus, smaller supplements may be effective for subjects with more moderate plasma Se levels, e.g., in the 80-120 ng/ml range.

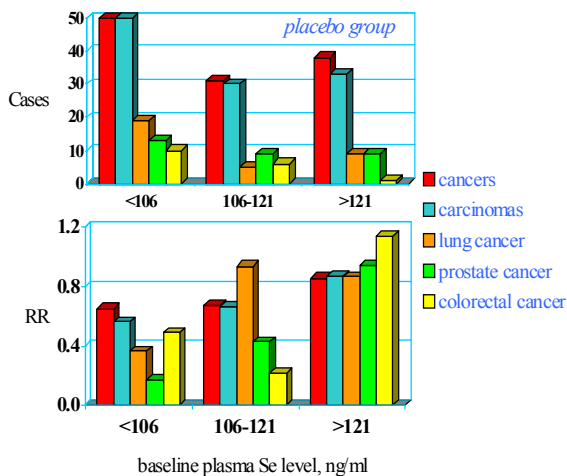


Fig. 2. Sub-group comparisons from NPC Trial.

Safety of Selenium

Chronic selenosis was identified in the 1960's among residents of Enshi County, Hubei Province, China, apparently resulting from exceedingly high concentrations of Se in the local food supplies and, in fact, throughout the local environment (Yang et al, 1989a, 1989b). Local soils were found to contain nearly 8 ppm Se, coal (ash was put on soils) contained as much as 84,000 ppm Se, and locally produced foods contained the highest concentrations of Se ever reported. Drinking water, leaching through seleni-ferous coal seams, contained >50 ppb Se. In affected villages, residents consumed an estimated 3.2-6.7 mg Se/person/day and showed losses of hair and nails, and some also showed skin lesions, hepatomegaly, polyneuritis and gastrointestinal disturbances. Both WHO (1996) and Institute of Medicine (2000) set the upper safe limit of Se intake at 400 mcg/day for an adult. This level may be too conservative, as it was derived arbitrarily by using one-half the estimate made by Yang et al (1989b) for the same purpose. A review by the US EPA (Poirier, 1994) set a no adverse effect level for an adult of 853 mcg Se/day.

Assessing Se Status

Absent a parameter of Se status reflecting both medium-term (days to weeks) Se intake and metabolic function, the clinical assessment of Se status has relied upon measurements of blood Se to indicate intake and of blood GPX activity to indicate function. Each has significant limitations. The Se contents of blood cells, serum or plasma are affected not only by the amount but also by the chemical species of dietary Se. For example, because selenomethionine (SeMet, e.g., in plant foods) can replace methionine in protein synthesis as well as be converted to Se-Cys, sources of SeMet enter non-specifically into blood proteins as well as specifically into SeCys-proteins, thus supporting greater blood Se values than will sources of SeCys (e.g., in animal products) at equivalent Se intakes. While almost all serum/plasma Se is protein-bound, most is present in two SeCys-proteins, SeP and GPX1. Hill et al (1996) calculated that maximal expression of these proteins contributed 80 ng/ml to plasma Se, indicating that those parameters are useful only in populations with relatively low Se intakes. Nève (1995) noted that subjects with plasma/serum Se levels above 70 ng/ml show no further GPX responses to Se supplementation. On the basis of these observations, the plasma/serum level of 80 ng/ml would appear to be a useful criterion of nutritional adequacy.

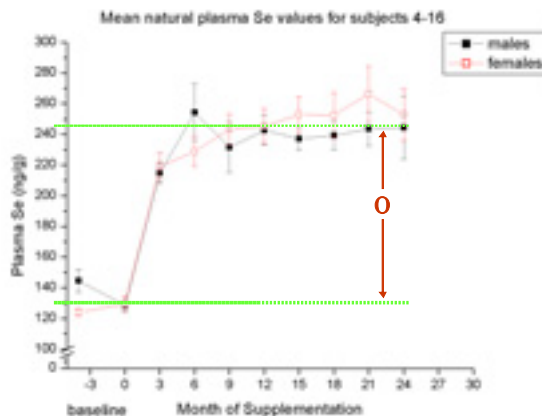


Fig. 3. Plasma Se responses of SePK trial subjects.

Because that is less than the plasma Se level associated with minimal cancer risk in the NPC trial, 120 ng/ml, it is appropriate to ask how much Se may be required for a given individual to reach the latter, apparently protective level. Results of our Se pharmacokinetics (SePK) study show that plasma Se moves from one plateau level to another

within 9-12 mos. of Se-supplementation at 200 mcg/d (Fig. 3). NPC Trial subjects showed similar responses (Fig 4).

An analysis of data from the NPC trial indicated that Se dose adjusted for metabolic body size (D , $\text{ng/kg}^{0.75}$) was related to the 12 mo. increase in plasma Se (Δ , ng/ml) according to the following function: $\Delta = 10.52 D$ (Fig. 5). From this relationship, the dose (D) required to reach a target plasma Se level (T , e.g., 120 ng/ml) within 12 mos. of supplementation for a person with a known baseline plasma Se level (B , ng/ml) can be predicted: $D = (T - B)/10.52$. This would suggest, for example, that a 70 kg person could move from a base plasma Se level of 106 ng/ml to a level of 120 ng/ml with a daily dose of 32 mcg Se for 9+ mos.

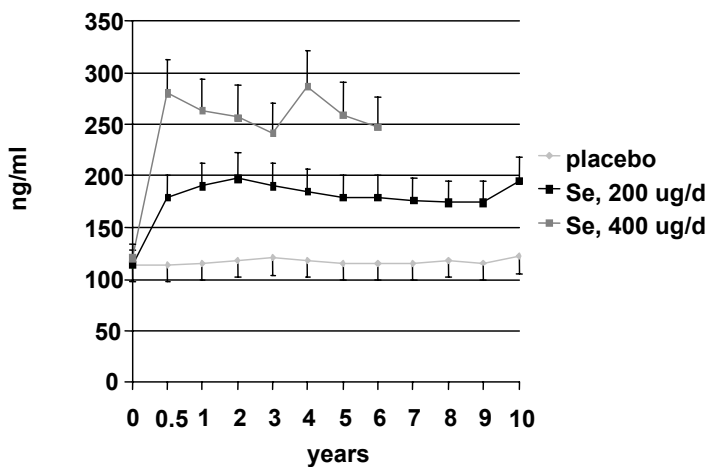


Fig. 4. Plasma Se responses of NPC Trial subjects to 200 or 400 MCG Se/d.

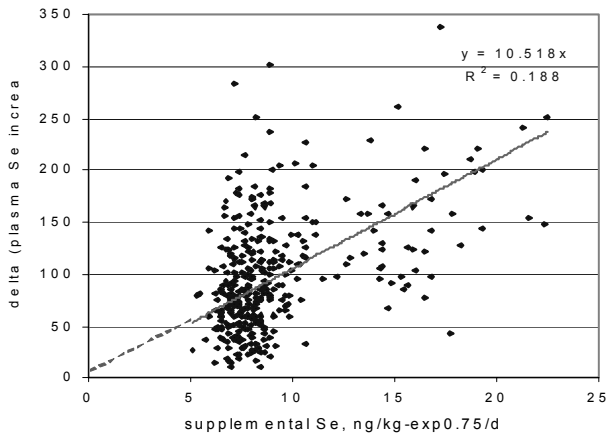


Fig. 5. 12 mo. plasma Se responses of NPC trial subjects.

Conclusion

In the span of five decades, Se has moved from being thought of as a toxicant to being considered essential nutrient. The elucidation of its role in nutrition has led to fundamental discoveries in metabolic biochemistry (the unique metabolism of SeCys), virology (the destabilization of RNA viruses due to oxidative stress), and public health (the role in cancer risk reduction). Unlike most other nutrients, which were recognized due to the fatal outcomes of their deficiencies, the consequences of Se deprivation appear to be largely sub-clinical in nature, requiring other precipitating factors (e.g., vitamin E deficiency, viral exposure, etc.) to reveal the effects of compromised Se-enzymes and/or essential Se-metabolites. Even after a half-century of research, much remains to learn about the metabolic bases of the roles of Se in nutrition and health.

Key words: selenium, nutrition, food, diet, intake, plasma, selenium deficiency

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Trends in blood and tissue selenium levels in Finland 1984-2004

Georg Alfthan

Biomarker Laboratory, National Public Health Institute, Mannerheimintie 166, 00300 Helsinki, georg.alfthan@ktl.fi

Trends in blood and tissue selenium levels in Finland

The supplementation of fertilizers with sodium selenate in Finland is a nationwide experiment aimed at increasing the selenium status of both animals and humans. The window for optimal intake of selenium is narrow with risk for deficiency at very low and toxicity at excessive levels. Therefore systematic monitoring of the selenium status of the population is necessary for safety reasons and also for research purposes.

Serum selenium

Serum selenium concentrations in healthy Finnish urban and rural adults have been monitored regularly since the 1970s. During the 1970s, the low dietary intake of Se, 25 µg/d (Mutanen and Koivistoinen 1983), corresponded to a serum Se level of 0.63-0.76 µmol/l (Alfthan 1988) being among the lowest values reported in the world (Alfthan and Neve 1996). Since 1985, the serum Se concentration of the same healthy adults have been monitored systematically, in urban Helsinki (n=30-35) and rural Leppävirta (n=35-45). The intake of Se has been ascertained to be solely from foods and not supplements.

Before supplementation of selenium to fertilizers became effective in 1985, the mean serum Se concentration ranged between 0.75 µmol/l and 1.23 µmol/l in the 1st half of the 1980s. The large variation was due to the import of high-selenium wheat (Alfthan 1988). One year before Se supplementation of fertilizers was started, the mean serum Se concentration was 0.89 µmol/l and, it reached its highest level four years later at 1.5 µmol/l, one of the highest values in Europe, Fig. 1. After the decrease in the amount of fertilizer Se in 1990 from 16 to 6 mg Se/kg fertilizer, serum Se decreased to a new stable level of 1.10 µmol/l in 1999. This serum Se level was still above the mean serum Se value for Europe, but lower than is generally found in Canada or USA (Alfthan and Neve 1996). After the second change in the amount of fertilizer Se

in 1998 to 10 mg Se/kg fertilizer, a new serum Se plateau at about 1.4 $\mu\text{mol/l}$ has been reached in 2004.

Serum Se concentrations in subpopulations thought to be at risk of sub-optimal Se intake have also been studied before and during the fertilization (Varo et al. 1994). The mean serum Se concentrations of mothers giving birth and their neonates during 1983 to 1996 have followed the trend of adult serum Se levels at a lower level. Neither exceptionally low nor exceptionally high individual values have been observed during this period.

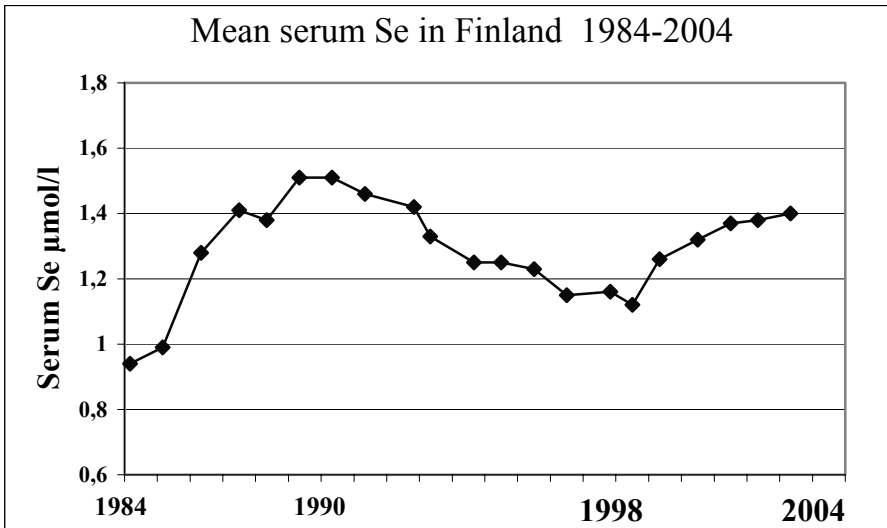


Fig. 1. Mean annual serum Se concentration in healthy Finns before and during the Se fertilization.

Since 1985, whole blood Se has been monitored systematically only in the rural group. Whole blood Se reached its peak mean value approximately one year later than serum Se. Before supplementation of fertilizers with Se the mean value was 1.15 $\mu\text{mol/l}$, and in 1990 a maximal value was reached, 2.62 $\mu\text{mol/l}$, Fig. 2. After 1992, the decrease paralleled that of serum Se, leveling off at 1.85 $\mu\text{mol/l}$ by 1999. As a consequence of the second change in the amount of fertilizer Se, the mean whole blood Se seems to have reached a stable level of 2.25 $\mu\text{mol/l}$.

Tissue selenium

Toenails reflect the integrated intake of Se over a period of six months to a year (Longnecker et al. 1993). Toenail Se concentrations have not been studied systematically on an annual basis. Toenail data for the

period 1984 to 1995 has been compiled from different Finnish studies on healthy subjects (Ovaskainen et al. 1993, Alfthan et al. 1991a, Michaud DS et al. 2002). Before supplementation of fertilizers with Se started, the mean toenail Se concentration was 0.45 mg/kg. The maximum level, 0.91 mg/kg, was observed in 1992 about two years later than for whole blood Se. In accordance with serum and whole blood Se, a clear downward trend was seen after the first change in the amount of fertilizer Se and the latest value, from 1995, is 0.72 mg/kg. The inter-individual variation in toenail Se was typically 10-12%. In a European multicenter study comprising eight countries, the toenail Se concentration of 59 middle-aged Finnish men sampled during 1990-1992 was the highest, 0.84 mg/kg (Virtanen et al. 1996).

The largest fraction of body stores of Se is situated in the liver. Its Se is mobile and reflects dietary Se intake over a time span of weeks (Levander et al. 1983a). Se has been determined in human liver samples obtained at autopsy from men who had died in traffic accidents both before (1983-1985) and during (1988-1989) the Se supplementation of fertilizers. Initially, the mean value was 0.95 ± 0.27 mg/kg dw. The mean Se concentration of liver tissue obtained 3-4 years later had increased to 1.58 mg/kg (Varo et al. 1994).

Serum, red blood cell and platelet glutathione peroxidase activity

The activity of the Se-dependent glutathione peroxidase (GSHPx) is associated with Se intake only up to moderate intake levels. At higher Se intakes, the activity of the enzyme in serum and whole blood reaches a plateau and cannot be stimulated further. The plateau, in terms of serum Se, is below 50 µg/d, and for whole blood approximately 60-80 µg/d (Yang et al. 1987, Levander 1989, Alfthan et al. 1991b). Saturation of serum GSHPx activity has been regarded as a measure of optimal Se intake and has been the basis of the current US Recommended Dietary Allowance (Levander 1989).

Two placebo-controlled supplementation studies have been carried out in Central Finland on the same 50 middle-aged healthy male blood donors (Levander et al. 1983b; Alfthan et al. 1991a). The aim of the studies was to find out to what extent platelet GSHPx activity could be increased by Se supplementation and the qualitative effect of organic/inorganic Se supplementation on GSHPx activity. The first study was performed in 1981 and the second in 1987, i.e. before and during Se fertilization. Common to both studies, 10 men were supplemented with 200 µg of Se as organic Se in the form of Se-enriched yeast or with 200 µg Se as sodium selenate. The third group received a placebo. At base-

line in 1981, the mean plasma Se concentration was 0.89 $\mu\text{mol/l}$ and in 1987 1.40 $\mu\text{mol/l}$, which corresponded to mean dietary Se intakes of 39 $\mu\text{g/d}$ and 100 $\mu\text{g/d}$, respectively.

The percentage increase in platelet GSHPx activity for men supplemented with either selenate or yeast Se was calculated in relation to the activity of the placebo groups. Before the addition of Se to fertilizers, selenate and yeast-Se supplements increased the enzyme activity by 104% and 75%, respectively. During fertilization the effects of selenate and yeast-Se were much lower, 41% and 6%, respectively. The results suggested that an intake of 100 μg Se per day was still not sufficient to completely saturate GSHPx activity in platelets. Extrapolation of platelet data, including the two Finnish studies and six other studies with a similar design, suggests that maximal stimulation of platelet GSHPx activity would occur at a plasma Se level of 1.3 $\mu\text{mol/l}$ (Alfthan et al. 2000).

Key words: selenium, trend, serum, tissue, glutathione peroxidase

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Posters

Twenty years of Selenium Fertilization

Investigation of selenium using soil and plant samples from a long-term field experiment

Béla Kovács¹⁾, Imre Kádár²⁾, Éva Széles¹⁾, József Prokisch¹⁾, Zoltán Győri¹⁾ László Simon³⁾

¹⁾Debrecen University, Centre of Agricultural Sciences, Department of Food Science and Quality Assurance, 4032 Debrecen Böszörményi u. 138. Hungary, kovacsb@agr.unideb.hu

²⁾Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences, Department of Agrochemistry, 1022 Budapest, Herman Ottó u. 15. Hungary

³⁾College of Nyíregyháza, Department of Land and Environmental Management, 4401 Nyíregyháza, P.O.Box 166., Hungary

Abstract

The potentially dangerous chemical compounds and elements, eg. selenium in relatively high concentration can cause harmful influence and results in the environment. The fate of selenium must be followed in the soil-plant system. Slow or accumulative changes in environment may be captured only by long-term studies.

To monitor the dynamics of selenium, its transformation into different forms, retention and movement in the soil-plant system, a heavy-metal-load field experiment was set up in Nagyhörcsök (Hungary) in 1991. The aims of the research programme in the above experiment were to study the behaviour of different elements (eg. selenium) in soil, its effect on soil life, the uptake by and transport within the plants and effects on the quantity and quality of the crop.

Soil and plant samples from the above field experiment were analysed using an OPTIMA 3300DV inductively coupled plasma optical emission spectrometer (ICP-OES) and Thermo Elemental inductively coupled plasma mass spectrometer (ICP-MS).

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Key words: selenium, long-term field experiment, ICP-OES, ICP-MS

Increasing the selenium (Se) content of UK crop plants for human consumption

Sarah E. Johnson¹), Helen C. Bowen¹), Martin R. Broadley²), Rosie J. Bryson³), Miles Harriman⁴), Mark C. Meacham¹), Mark Tucker⁴), Philip J. White¹)

¹)Warwick HRI, Wellesbourne, Warwick CV35 9EF, UK

²)Plant Sciences Division, University of Nottingham, Sutton Bonington, Leicestershire LE12 5RD, UK

³)Velcourt Ltd, NIAB Annex, Huntingdon Road, Cambridge, CB3 0LE, UK

⁴)Yara UK, Immingham Dock, Lincolnshire DN40 2NS, UK

Abstract

Selenium (Se) is an essential element for humans. Dietary Se intakes in the UK have fallen from 60 $\mu\text{g d}^{-1}$ in 1974 to <39 $\mu\text{g d}^{-1}$ in recent years (reviewed by Rayman, 2002) and this is thought to be due to the replacement of bread wheat sourced from North American wheat (high in Se) with European wheat (low in Se). A concomitant decrease in the blood plasma Se concentrations of the UK population has been recorded. The effects of sub-optimal Se intakes on human health include impaired immune function, increased risk of cancers, increased oxidative stress and reduced fertility. One solution to this problem in the UK might be to adopt a fertilisation strategy based on the Finnish experience (Rayman, 2002). Thus, the primary aim of this (ongoing) study is to determine if the Se content of some commonly-grown UK crops can be increased to levels that would increase dietary Se intakes in the UK, using Se-containing fertilisers.

First, the effects of Se fertilisation level on the growth and Se content of crops under field conditions are being determined in three replicate experiments running from 2003 to 2005. Four arable crops (wheat, oilseed rape, maize and soya), and four vegetable crops (potato, carrot, onion and white cabbage) were selected for the experiment because they contribute significantly to the UK diet. Shoot Se contents are being determined by inductively-coupled emission spectrometry (ICP-ES). Preliminary data from 2003 and 2004 will be presented.

Second, we are exploring complementary approaches to using Se fertilisers to increase dietary Se intakes. For example, it may be possible to increase crop Se accumulation by manipulating the S supply and/or by selecting or breeding appropriate crop varieties. Thus, in a second series of experiments, a model plant specie *Arabidopsis thaliana* (Brassicaceae family) is being grown on a nutrient-replete agar supplemented with various concentrations of Na_2SeO_4 . Initially, the effects of interactions between external Se and S on the growth and shoot concentrations of Se and S were determined (White et al., 2004). These studies have indicated that several transport proteins, with contrasting selectivities, mediate the uptake of Se and S into plants, and that

the relative activities of these transporters are governed by plant nutritional status. They also indicate that Se toxicity is directly related to the Se:S concentration ratios in the shoot. In other experiments, the interaction between Se fertilisation (E) and genotype (G) is being studied in a population of recombinant inbred lines from an artificial cross between Landsberg *erecta* (*Ler*) x Columbia (Col) accessions of *A. thaliana*. This population was chosen as it has previously been shown to segregate for other mineral composition traits (Payne et al., 2004). Experiments are being conducted in a nutrient-replete agar of contrasting Se compositions, which thus allows E, G and E x G interactions components to be quantified. These experiments will also enable chromosomal loci that impact on shoot Se concentrations to be identified. The use of radiolabelled Na⁷⁵SeO₄ to determine shoot Se content in *A. thaliana* is facilitating the high-throughput of plant samples demanded by this work.

Payne, K.A., Bowen, H.C., Hammond, J.P., Hampton, C.R., Lynn, J.R., Mead, A., Swarup, K., Bennett, M.J., White & P.J., Broadley, M.R. 2004. Natural genetic variation in caesium (Cs) accumulation by *Arabidopsis thaliana*. *New Phytologist* 162: 535-548.

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Key words: selenium, food, intake

Can cereals be bred for increased selenium and iodine concentration in grain?

G Lyons¹⁾, I Ortiz-Monasterio²⁾, Y Genc³⁾, J Stangoulis¹⁾, R Graham¹⁾

¹⁾School of Agriculture and Wine, University of Adelaide, Waite Campus, PMB 1, Glen Osmond, South Australia 5064, Australia, graham.lyons@adelaide.edu.au

²⁾Centro Internacional de Mejoramiento de Maiz y Trigo (International Maize and Wheat Improvement Centre) (CIMMYT), Apdo. Postal 6-641, 06600, Mexico.

³⁾Molecular Plant Breeding CRC, Waite Campus, PMB 1, Glen Osmond South Australia 5064, Australia

Abstract

Selenium (Se) and iodine (I) are essential micronutrients for humans and animals, and deficient and marginal intakes are widespread. Staple cereals with superior ability to take up these elements from the soil and load them into grain have the potential to improve the Se and I status of whole populations. In this study, diverse cereal germplasm from surveys and field trials conducted in Australia, Mexico, Nigeria and the USA, was evaluated for genotypic variation in grain density of Se and I. Much of the variation in grain Se density was associated with spatial variation in soil available Se, particularly in South Australia. No significant genotypic variation was detected in grain Se density among modern commercial bread or durum wheat, maize, triticale or barley varieties. However, the diploid wheat, *Aegilops tauschii* L. and rye were higher than other cereals in field and hydroponic trials. No genotypic variation was detected in grain I concentration in the wheat or maize cultivars tested. Se was more evenly distributed throughout the grain of wheat than rice. Although concentrations of available Se and I in soil are the most important determinants of levels of these micronutrients in cereal grain, there may be sufficient genotypic variability in Se and I density in rice to enable selection for these traits. Further evaluation of diverse rice germplasm grown together on various soil types is needed to confirm this. Given that substantial Se and I (particularly I) are lost during polishing, screening programs should investigate possible genotypic differences in grain distribution of these micronutrients, with selection for greater concentration in the endosperm a primary criterion.

Key words: genotypic variation, iodine, maize (Zea mays L.), rice (Oryza sativa L.), rye (Secale cereale L.), selenium, wheat (Triticum aestivum)

Selenium increased growth and fertility in higher plants

G Lyons¹, J Stangoulis¹, Y Genc², R Graham¹

¹School of Agriculture and Wine, University of Adelaide, Waite Campus, PMB 1, Glen Osmond, South Australia 5064, Australia,
graham.lyons@adelaide.edu.au

²Molecular Plant Breeding CRC, Waite Campus, PMB 1, Glen Osmond South Australia 5064, Australia

Abstract

Selenium (Se) is not considered to be essential for higher plants. We evaluated diverse plant species for growth and fertility responses to applied Se. Trials included wheat field trials of randomised split-plot design, *in vitro* cereal germination and early growth studies, pot trials conducted in glasshouse and phytotron, and hydroponic trials using very pure nutrients conducted in glass cabinets with filtered air. Our findings include a 72% and 65% increase in seed pod number in *Arabidopsis thaliana* L. and vetch (*Astragalus sinicus* L), respectively, a 14% increase in whole top biomass in *A. sinicus*, and an 8% increase in seedling root growth in wheat (*Triticum aestivum* L.). No yield increases were observed in our field trials that investigated Se fertilisation of wheat. These studies contribute to mounting evidence of a beneficial role for Se in higher plants.

Key words: Arabidopsis thaliana L., fertility, growth, micronutrient, selenium, Astragalus sinicus L., wheat (Triticum aestivum L.)

Selenium uptake and species distribution in peas after foliar treatment with selenate

P. Smrkoj¹, I. Kreft², V. Stibilj¹

¹)Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia

²)Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, Ljubljana, Slovenia, ivan.kreft@guest.arnes.si

Abstract

Selenium fertilization of plants has been used to increase the nutritional selenium levels in humans and animals. The speciation of selenium in samples is necessary to understand selenium mobility, uptake and toxicity. The aim of this work was to check the ability of peas to accumulate Se by hydride generation atomic fluorescence spectrometry (HG-AFS) and to identify the selenium species in peas seeds by high performance liquid chromatography-UV photochemical digestion-hydride generation atomic fluorescence spectrometry (HPLC-UV-HG-AFS) using selenomethionine, selenocystine, selenate, selenite and Se-methylselenocysteine standards. In this study pea (*Pisum sativum* L.) was treated once or twice by spraying leaves with a water solution containing 15 mg Se/L in the form of sodium selenate at flowering time. The average total Se content in seeds was 21 ± 2 , 383 ± 19 and 743 ± 37 ng g⁻¹ in nontreated and once and twice foliarly treated plants, respectively. After water extraction 32 ± 3 % of Se was in soluble form and no selenium species were found in extracts under found optimal conditions of HPLC-UV-HG-AFS. After enzymatic hydrolysis 92 % of Se was soluble in seeds and a great part of added Se (VI) was converted to selenomethionine representing 49 and 67 % in once and twice treated plants, according to the total Se content. The other part of soluble selenium in supernatants after enzymatic hydrolysis was not detected.

Key words: Pisum, peas, HPLC, selenate, foliar fertilisation

Interference of sulfur with shoot accumulation and toxic effects of selenium in wheat

A. Yazici¹⁾, B. Torun²⁾, L.Ozturk² and I. Cakmak¹⁾

¹⁾Sabanci University, Faculty of Engineering and Natural Sciences, Istanbul, Turkey, cakmak@sabanciuniv.edu

²⁾Cukurova University, Faculty of Agriculture Department of Soil Science, Adana, Turkey

Abstract

Six bread wheat (*Triticum aestivum*) cultivars were grown under greenhouse conditions to study the role of increasing sulfur (S) application (0, 75 and 225 mg S kg⁻¹ soil) on dry matter production, shoot accumulation of selenium (Se) and development of Se toxicity symptoms. Plants were grown for 3 weeks in greenhouse under different Se (0, 0.2, 1 and 5 mg Se kg⁻¹ soil) and S treatments which were applied in forms of sodium selenate and CaSO₄, respectively. As the genotypic differences found for sensitivity to Se toxicity and Se accumulation in shoot were relatively small, the results obtained are presented as average of all cultivars. At the nil Se, growing plants without S application did not affect dry matter production of plants compared to the plants treated with increasing S application, indicating that the S status of the soil used in the experiments was not limited to plant growth. Increasing Se application to soil from 0 to 5 mg kg⁻¹ significantly reduced plant dry matter production only at the low S applications. As average of all cultivars, decreasing Se supply from 5 to 0 mg kg⁻¹ increased plant dry matter production 11-fold at the nil S treatment and only 1.2-fold at the a 225 mg kg⁻¹ S treatment.

When plants were grown at the highest Se application without S, very severe toxicity symptoms, such as whitish and chlorotic patches, developed on the older leaves, mainly on the leaf basis. The leaf parts affected particularly by Se toxicity were whitish and had an albino appearance, lacking chlorophyll. Application of S prevented development of these leaf symptoms. Severity of Se toxicity symptoms on leaves were not directly related to the tissue concentration of Se and greatly affected from the concentrations of S in leaves. In S-treated plants containing 398 mg Se per kg dry weight of leaves there was no or slight Se toxicity symptoms on leaves, while in plants with 213 mg Se per kg dry weight of leaves, but without S treatment, leaf symptoms were very severe, and there were marked decreases in dry matter production. This indicates importance of Se/S ratio in the tissue in development of Se injury in plants. Sulfur application caused marked decreases in Se concentration of plants. Increase in S application from 0 to 225 mg kg⁻¹ reduced Se concentration of plants from 28 to 3 mg kg⁻¹ at the Se rate of 0.2 mg kg⁻¹, from 213 to 22 at the Se rate of 1 mg kg⁻¹ and from 1542 to 398 mg kg⁻¹ at the Se rate of 5 mg kg⁻¹. By contrast, increasing Se applications generally increased S con-

centration of plants, in most cases by 2-fold. This increasing effect of Se on S accumulation was more pronounced in the case of total amount of Se per plant (S content).

The results obtained indicate that the toxic effects of Se in wheat plants can be markedly minimized by increasing S applications. Sulfur is highly effective in repressing uptake of Se by roots. Sulfur is also affective to interfere with the toxic actions of Se at cellular level. Therefore, the critical toxic Se concentrations in leaves are much greater in plants containing lower than the plants with higher S concentrations. In contrast to the S-induced decrease in Se uptake, increasing Se application stimulated S uptake of plants. It seems very likely that there is a common uptake system (sulphate transporter?) mediating uptake and transport of Se and S in wheat. The stimulating effect of Se on accumulation of S in plants suggests that Se possibly interferes with the action of sulphate to repress the activity of sulphate transporter.

Key words: wheat, selenium, sulphur

Selenium in the food chain of Buriatia

Nadegda Golubkina¹⁾, Sangidma Mnkueva²⁾, Georg Alftan³⁾

¹⁾Department of Food Toxicology, Institute of Nutrition, Russian Academy of Medical Sciences, Ustinsky pr. 2/14, 109240 Moscow, Russia

²⁾East Siberian State Technological University, Ulhan-Ude, Russia

³⁾Biomarker Laboratory, National Public Health Institute, Mannerheimintie 166, FIN-00300 Helsinki, Finland

Previous reports (Ermakov 2003) have shown that selenium concentrations in Buriatian foodstuffs are in the range of 20-280 µg/kg, revealing the possibility of local severe selenium deficiency similar to the Se deficiency in the Chita region, where the range of foodstuff selenium concentrations is much narrower and lower, 10-80 µg/kg. The selenium concentration in foods grown and consumed and in plasma and hair of people living in Buriatia were compared with that of the endemic Chita region of Russia. The mean (SD) results for the selenium concentration in cereals of Buriatia were in wheat 53±13 µg/kg (n=9, 31-78 µg/kg), barley 54 µg/kg (n=6), oats 49±24 µg/kg (n=4, 43-86 µg/kg) and rye 22-29 µg/kg (n=2). The selenium concentration of milk was 100 µg/kg dry matter and of meat of domestic animals, pork 18-173 µg/kg, beef 49-144 µg/kg, mutton 162-225 µg/kg and horse 148-152 µg/kg fresh matter (32-218 µg/kg dry matter for Chita region). The mean selenium concentration of bread was extremely high and similar to that of the Chita region, 202±149 µg/kg dry matter (54-433 µg/kg, n=14) indicating the utilization of imported high-selenium wheat in the republic. Fish of Baikal and other lakes of Buriatia seem also to be an important source of selenium for human beings. Values as high as 347 ±179 µg/kg fresh matter (10 species, range 84-687 µg/kg) were typical for small lakes of Buriatia and different parts of Lake Baikal.

The human selenium status of Buriatia residents were characterized by plasma selenium concentration 0.85±0.16 µmol/L (n=21, Ulan-Ude) and hair selenium content, 408±78 µg/kg (n=86, 297-531 µg/kg). According to meat and human hair selenium data, selenium deficiency is typical for a relatively narrow territory located in the South-East of Buriatia that includes Selenga, Ulan-Ude, Eravna and Mukhorshibirsk regions. Cereal selenium values were higher than values typical for the Chita region. Thus local selenium deficiency and utilization of imported wheat with high selenium content are the main characteristics of modern selenium status of Buriatia. Nevertheless the situation may be worsened in case selenium-rich wheat imports are discontinued.

Selenium-enriched eggs: from improvement of egg quality to improvement of human diet

Peter F. Surai¹⁾, Tigran A. Papazyan²⁾, Filiz Karadas³⁾ and Nick H.C. Sparks⁴⁾

¹⁾Alltech (UK) Ltd., Stamford, UK, psurai@alltech.com

²⁾Alltech Russia, Moscow

³⁾Department of Animal Science, Yuzuncu Yil University, Turkey

⁴⁾Avian Science Research Centre, SAC, Scotland

Abstract

Selenium deficiency is widespread across the globe. Recently we have come to a conclusion that Se-enriched eggs could be used as an important delivery system of this trace mineral for human. In particular, development and commercialisation of the organic form of selenium (Sel-Plex, Alltech, USA) opened a new era in production of selenium-enriched products. It was shown that egg selenium content could be easily increased when organic selenium is included in the diet at a level to provide 0.4-0.8 ppm Se. As a result, the technology for production of eggs delivering ~50% (30-35 µg) of selenium RDA was developed and successfully tested. Currently companies all over the world produce and market Se-enriched eggs. For example, in Russia there are 12 poultry farms in various regions producing se-enriched eggs, while in Ukraine RozDon poultry farm produces more than 1 million Se-enriched eggs daily. Prices for those eggs varied from country to country and are similar to those for free-range eggs. Clinical studies conducted with healthy volunteers in Ukraine showed that consumption of two Se-enriched eggs per day for 8 weeks significantly increased Se level in plasma. Therefore, Se-enriched eggs are considered to be an effective solution of the Se-deficiency in various countries all over the world.

Key words: selenium, egg, nutrition

On selenium supplementation of bread

V.I. Murakh, S.I. Matveyev, E.V. Savin

Tumen Center for Treatment and Prophylactic Nutrition of the Russian Academy of Medical Sciences, Tumen, Russian, val@biochem.unibel.by

Abstract

The problem of health maintenance has always been, and is still remaining to be, one of the most important and topical problems in biology and medicine. The results of epidemiologic observations and statistical analyses show slowing down of the progress in extending the life - span of the population of the Republic of Belarus and premature mortality of severe chronic infectious disease, such as heart diseases and malignant tumors.

The majority of premature death cases among men and women is caused by either unbalanced nutrition or excessive consumption of fat and salt, or dietary selenium, potassium, calcium, nutrition fibre and vitamin deficiencies which reduce bodily adaptation capacities and stability towards the action of xenobiotics.

The physiological antioxidant protection system, with selenium being a component, is stressed to the greatest extent. This is related to the fact that the population of many country's regions is exposed to low doses of ionizing radiation and dwells in areas characterized by increased heavy metal and other xenobiotic contents.

The situation is aggravated by the territory of the Republic of Belarus being a bio- and geochemical region where the selenium levels are lower than the critical ones in soil (0.1 mg/kg) and not more than 10 ug/l in drinking water. Therefore the content of selenium, as a natural antioxidant, in foodstuffs and methods for selenium status improvement are of pivotal interest for the country. The average daily consumption as recommended by FAO must be 50-200 ug per day.

Bread can be supplemented with selenium by adding the inorganic form (sodium selenite) directly during baking or by using bioselenium yeast, containing selenium as inorganic compounds (selenium methionine or selenium cysteine), in production of bread. Data are given on implementation of the selenium supplementation technology by different bakeries of the Republic of Belarus and Russian.

Key words: selenium supplementation, bread, bioselenium, sodium selenite, selenium methionine

Selenium and selenoproteins in milk and mammary tissue

Tien Hoac¹⁾, Jan Stagsted²⁾, Jacob H. Nielsen²⁾, Björn Åkesson¹⁾

¹⁾Biomedical Nutrition, Lund Institute of Technology, Lund University, Lund, Sweden

²⁾Department of Food Science, Research Centre Foulum, Danish Institute for Agricultural Sciences, Tjele, Denmark

Abstract

Deficiency of selenium has been associated with various disorders such as cancer, heart disease and Keshan disease. Milk is an important source of this nutrient, since it supplies about 20% of the daily intake selenium in Scandinavian countries. Thus, it may be possible to increase selenium intake by improving the content of selenium in milk. The aims of this study were to investigate the effect of selenium supplementation in cow feed on the properties of bovine milk and to study the relationship between selenium and different selenoproteins in mammary tissue.

Six cows were divided into two groups, which were fed with selenium fortified feed (25 mg organic Se/day) or control feed. Selenium contents in bovine serum and milk were measured with graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Selenium content in serum was increased more than three fold after two weeks' of supplementation in both groups, whereas the concentration of selenium in milk was increased approximately six fold during the same period. The rate at which selenium increased in milk was significantly higher than that in serum. The increased incorporation of selenomethionine into milk proteins conferred novel antioxidant properties and enhanced the oxidative stability of milk.

In another sub-project mammary tissue obtained at slaughter of nine cows with different age and lactation stage, was analysed for selenium content (ICP-MS) and enzyme activities of thioredoxin reductase (TR) and glutathione peroxidase (GSHPx). The results showed that the activities of TR and GSHPx varied six and fifteen fold between mammary tissues, respectively. There were positive correlations between the following variables: Se and TR ($p < 0.01$), TR and GSHPx ($p < 0.01$) and Se and protein content ($p < 0.01$). This indicated that selenium status regulated selenoprotein activities in bovine mammary gland but also other variables seemed to be of importance.

Key words: selenium supplementation, milk, mammary tissue, thioredoxin reductase, glutathione peroxidase

Selenium status in dairy cows and feed samples in Estonia

M. Malbe^{1,2)}, N. Oinus³⁾, K. Praakle²⁾, M. Roasto⁴⁾, A. Vuks⁴⁾, M. Attila²⁾, H. Saloniemi²⁾

¹⁾Faculty of Veterinary Medicine, Department of Clinical Veterinary Sciences, P.O. Box 57, Helsinki University, Finland, Phone: +358-9-19149643, Fax: +358-9-19149636, marge.malbe@helsinki.fi

²⁾Helsinki University, Faculty of Veterinary Medicine, Helsinki, Finland

³⁾Estonian Agricultural University, Institute of Agricultural and Environmental Sciences, Tartu, Estonia

⁴⁾Estonian Agricultural University, Institute of Veterinary Medicine and Animal Sciences, Tartu, Estonia

Abstract

Introduction: Knowledge about selenium content in Estonian food chain is limited as no systematic selenium study is ever done in Estonia. Aim of our study was to evaluate selenium status in dairy cows and feed samples.

Materials and methods: Altogether, 17 commercial dairy herds from 13 Estonian districts were studied. Blood samples from ten cows in each farm were collected. From each farm grain sample was taken. Information about feeding of selenium containing feed supplements and grain origin was asked. Selenium content in grain and glutathione peroxidase (GPx) activity in haemolysed whole blood was analysed.

Results and discussion: Mean GPx activity in cows was 92-1204 μ Kat/l. Dividing cows into selenium-deficient ($GPx \leq 472 \mu$ kat/L) and non-deficient ($GPx > 472 \mu$ kat/L) group, it came evident that 66% cows were selenium-deficient and only 34% of the cows belonged to the non-deficient group. Locally grown grain was used in 10 farms. Selenium content in local grain was below 0.02 mg/kg dw in 6 samples and 0.04-0.12 mg/kg dw in 4 samples. Selenium content in commercial grain was 0.37-0.90 mg/kg dw (n=7). Selenium containing mineral feed was used in 9 farms. Results of our study confirm the presence of selenium-deficiency in plant-animal chain in Estonia. Selenium status in Estonian food chain must be monitored to decide on the most effective way of selenium supplementation.

Key words: Selenium, glutathione peroxidase, dairy cow, bovine, grain, feed

Grass, barley, grass and maize silages produced with or without selenium enriched fertilizers and offered to Belgian Blue suckling cows: a 3 years survey

J.F. Cabaraux¹⁾, S. Paeffgen²⁾, J.L. Hornick¹⁾, N. Schoonheere¹⁾, L. Istasse¹⁾, I. Dufrasne³⁾

Liege University, Faculty of Veterinary Medicine, Department of Animal Production,

¹⁾Nutrition Unit, B43, ³⁾Experimental Station, B39, B 4000 Liege, Belgium.

²⁾Kemira GrowHow, B 1300, Wavre, Belgium.

Abstract

In Belgium, the selenium (Se) content in locally produced feedstuffs is low. Since October 2002, the Belgian Blue herd of the Experimental Station was divided in two groups (control and Se groups). Fertilizers enriched or not with Se were spread on pastures used for grazing or for the production of grass silage and on fields in which winter barley or maize were grown.

The use of Se enriched fertilizer increased the Se content in grass of grazed pastures by 4.8 times (248.3 vs. 51.8 μ g/kg DM), in grass silage by 3.5 times (186.9 vs. 53.4 μ g/kg DM), in winter barley by 6.5 times (286.3 vs. 43.7 μ g/kg DM) and in maize silage by 3.8 times (27.0 vs. 102.4 μ g/kg DM). The blood Se content measured by the activity of glutathione peroxidase remained low at 27.2 μ g/l in the cows of the control group. By contrast the blood Se content started to increase on the end of the first winter period in the Se group. During the first grazing period, the concentration sharply increased to reach a plateau at 80 μ g/l. The concentration decreased then during the winter period at an average concentration of about 55 μ g/l. The pattern of Se concentration was similar during the following two seasons. These lower concentrations during the winter period were associated to the relative contribution of Se enriched feedstuffs in the winter diet.

It appeared thus from the present trial that Belgian Blue cows responded to a large extent to a Se supplementation by feedstuffs grown with Se enriched fertilizers.

Key words: Belgian Blue herd, selenium fertilization, glutathione peroxidase

The use of the selenised yeast additive Sel-Plex® in dairy cow diets

Richard Phipps¹⁾, Andrew Jones¹⁾, Darren Juniper¹⁾, Gérard Bertin²⁾

¹⁾University of Reading, ASRG, School of Agriculture, Policy and Development, Reading RG6 6AR, UK

²⁾Alltech France, EU Regulatory Department, 2-4 Avenue du 6 Juin 1944, F-95190, Goussainville, France

Abstract

Twenty multi-parous Holstein Friesian cows were used to compare effects of an organic selenium (Se) supplement (Sel-Plex®, batch n° SEK-941, 2234 ± 198 mg Se/kg) with an inorganic Se supplement (Na₂SeO₃) on the performance and health of dairy cows. All cows received the same basal TMR comprising of maize silage (375 g/kg DM), grass silage (125 g/kg DM), cracked wheat (250 g/kg DM), soyabean meal (135 g/kg DM), rapeseed meal (100 g/kg DM) and mineral mixture (15 g/kg DM) providing dietary Se concentrations (mg/kg DM) of 0.15 (T1 control, no additional Se), 0.27, 0.33, 0.41 (T2-T4, Sel-Plex®) and 0.25 (T5, Na₂SeO₃). There were no significant treatment effects on DM intake, milk yield, milk composition, milk urea, SCC or many aspects of blood chemistry and haematology. Treatments T1 – T5 had whole blood Se concentrations of 211, 214, 235, 251 and 208 µg/l, respectively. Milk Se concentrations followed a similar trend with values of 19, 28, 40, 54 and 21 µg/l for treatments T1 to T5 respectively. Corresponding Se values for urine (mg/l) and faeces (mg/kg DM) were 0.02, 0.05, 0.08, 0.14 and 0.06 and 0.37, 0.51, 0.65, 0.78 and 0.58 for treatments T1 to T5, respectively. Subsequent regression analysis indicated a significant linear (P<0.001) response of increasing dietary Se concentration on the Se content of blood, milk, urine and faeces. Pairwise comparison of treatment means for T2 (Sel-Plex®) and T5 (Na₂SeO₃) showed significantly (P<0.05) higher total Se concentration in milk of Sel-Plex® supplemented cows (27.8 vs. 20.8 µg Se/l), of which a greater proportion of total selenium was in the form of selenomethionine. The results of this study indicate that the use of the organic selenium additive Sel-Plex® is an effective way of increasing the Se content of milk.

Key words: organic selenium, selenite, milk, blood, faeces, urine

Examination of selenium tolerance in dairy cows receiving a selenised yeast supplement – Sel-Plex®

Richard Phipps¹⁾, Andrew Jones¹⁾, Darren Juniper¹⁾, Gérard Bertin²⁾

¹⁾University of Reading, ASRG, School of Agriculture, Policy and Development, Reading RG6 6AR, UK

²⁾Alltech France, EU Regulatory Department, 2-4 Avenue du 6 Juin 1944, F-95190, Goussainville, France

Abstract

In order to comply with EU regulations (2001/79/EC) a tolerance study investigating the effects of feeding at least ten times the maximum recommended dietary concentration of selenium (Se), derived from selenized yeast (Sel-Plex®, batch n° SEK-941, 2234 ± 198 mg Se/kg), was undertaken with 28 multi-parous Holstein Friesian cows. Animals were allocated to one of two dietary treatments, Treated (T) or Control (C), on the basis of milk yield and parity. The study comprised one continuous 60 day period where both treatment groups received the same basal TMR (maize silage [375 g/kg DM], grass silage [125 g/kg DM], cracked wheat [250 g/kg DM], soya bean meal [135 g/kg DM], rapeseed meal [100 g/kg DM] and mineral mixture [15 g/kg DM]) that had been either supplemented with Sel-Plex® (mean Se content 6.25 ± 0.78 mg/kg DM) or fed as a control (mean Se content 0.15 ± 0.06 mg/kg DM). Blood and milk samples were taken on days 0, 20, 40 and 60 and subjected to a range of analyses. Although there was a trend towards lower DM intake in group T, there were no other significant treatment effects on either milk yield or milk composition, in terms of milk fat and protein. There were few significant treatment effects on many of the aspects of blood chemistry and haematology. Mean whole blood and milk Se concentrations in group T at days 0, 20, 40 and 60 were 142, 695, 805 and 1058; and 15, 456, 522 and 422 $\mu\text{g/l}$, respectively. Corresponding Se values for group C were significantly ($P < 0.001$) lower with whole blood and milk Se concentrations of 142, 213, 190 and 284; and 17, 33, 36 and 40 $\mu\text{g/l}$. Furthermore, the proportion of Se that comprised selenomethionine increased from 13 to 49% in blood and 28 to 96 % in milk for group T. Cow health was unaffected by treatment and there was no indication of adverse effects associated to high dose ($> 10x$) Sel-Plex® supplementation.

Key words: organic selenium, tolerance, dairy cows

Selenium in white clover grass pasture for grazing lambs

Riitta Sormunen-Cristian¹⁾, Päivi Nykänen-Kurki²⁾, Lauri Jauhiainen³⁾

MTT Agrifood Research Finland, ¹⁾Animal Production Research, 31600 Jokioinen, Finland
²⁾Ecological Production, 50600 Mikkeli, Finland, ³⁾Information Services, 31600 Jokioinen, Finland, first.name.surname@mtt.fi

Abstract

In Finland, the use of white clover has recently increased especially in organic farming. However, information on its mineral content is very sparse. Therefore, contents of Ca, P, Mg, K and Se of white clover grass without nitrogen (CG0) and grass-only pastures with annual nitrogen rates of 0 (G0), 120 (G120) and 250 (G250) kg ha⁻¹ were studied in organic soil. The pastures were grazed twice per season by growing lambs. Feed intake was determined by *n*-alkanes. The white clover contents averaged 36% and 42% in the first and the second grazing period.

At the beginning of grazing the Se content averaged 0.19, 0.16, 0.29 and 0.29 ppm in CG0, G0, G120 and G250 pastures ($p=0.01$), respectively. When the season progressed, the Se content decreased in all pastures and averaged 0.015 ppm in late August. There was no difference in Se content between fertilized G120 and G250 pastures (0.09 ppm), but Se contents of unfertilized CG0 (0.07 ppm) and G0 pastures (0.06 ppm) were significantly ($p<0.01$) lower. The Ca and Mg contents and the Ca/P ratio were higher, and the K/(Ca+Mg) equivalent ratio lower in white clover grass than in grass-only swards.

Daily Se supply was calculated according to herbage intake estimation and it averaged 0.09, 0.08, 0.11 and 0.12 mg per lamb in CG0, G0, G120 and G250 pastures, respectively. The daily Se requirement of sheep is 0.1-0.2 ppm and at minimum 0.06 ppm is needed for the prevention of white muscle disease. Except selenium the mineral composition was more balanced for growing lambs when white clover was added to grass pasture.

Key words: grazing, legume, mineral content, sheep, sward, Trifolium repens

Effect of organic selenium on goose reproduction

A.A. Tverdohlebov¹⁾, Tigran A. Papazyan²⁾, David A. Davtyan²⁾, Peter F. Surai³⁾

¹⁾Kurgan Agricultural Academy, Kurgan, Russia,

²⁾Alltech Russia, Moscow

³⁾Alltech (UK) Ltd., Stamford, UK, psurai@alltech.com

Abstract

For the last few years a great body of scientific information indicates that organic selenium is more effective in transferring to the egg and the developing embryo in comparison to sodium selenite. The aim of the study was to evaluate effects of the replacement of sodium selenite by organic selenium in the form of Sel-Plex (Altech, USA) in goose diets in commercial conditions. In the experiment 5672 Italian White Goose Breeders were divided into 3 groups. Control group was fed on the commercial diet without Se supplementation, second group was supplemented by sodium selenite (0.3 ppm Se) and third group was supplemented with the same amount of Se (0.3 ppm) in the form of Sel-Plex during the laying period. Fertility was shown to be 93.4, 96.7 and 97.1%, while hatchability of fertile eggs was 67.2, 71.3 and 75% in the control and experimental groups respectively. The weight of the day-old goslings was shown to be 93.9, 96.4 and 98.8 g respectively. Therefore, these data indicate that the replacement of the sodium selenite by Sel-Plex could improve reproductive performance of geese in commercial conditions.

Key words: selenium, egg, nutrition

Analytical approaches for selenium speciation in biological materials

Joanna Szpunar, Ryszard Lobinski

CNRS UMR5034, Hélioparc, 2, Av. Président Angot, 64053 Pau, FRANCE,
Joanna.Szpunar@univ-pau.fr

Abstract

There is substantial evidence on the complexity of selenium speciation in living organisms and on the importance of the selective determination of the particular species of this element in order to understand its metabolism in environmental and clinical chemistry, ecotoxicology and nutrition. The major fields of interest include: (i) characterization of selenium species in plant and animal organisms with a special focus on edible tissues, (ii) speciation of metabolite products (selenoaminoacids, selenopeptides and selenoproteins) in organisms growing in selenium rich environment, (iii) speciation of selenium metabolites in body fluids, (iv) characterization of selenium enriched food-stuffs, food supplements and fodders available on the market.

The myriad of selenium species with different physicochemical properties present in biological systems represents a challenge to the analyst. The most popular approach is the use of so called hyphenated techniques representing a unique analytical tool able to provide qualitative and quantitative information on element species at trace and ultratrace levels in complex matrices. The multiple areas of interest in the field selenium speciation require dedicated analytical approaches, both in terms of the separation technique and the element or molecule specific detection used. Since many selenium compounds have not been identified yet the role of molecular identification techniques such as GC MS for volatile species, ES MS/MS for selenopeptides and MALDI TOF for selenoproteins cannot be overestimated.

The presentation discusses analytical chemistry of selenium species related to biological materials on the basis of the practical experience gathered in a decade of research in the field.

Key words: selenium, speciation, selenoproteins, biological material

Selenium speciation in edible tissues of animal origin

Véronique Vacchina¹⁾, Sandra Mounicou²⁾, Gérard Bertin³⁾, Joanna Szpunar²⁾

¹⁾UT2A, Hélioparc, 2, Av. Président Angot, 64053 Pau, France,
Joanna.Szpunar@univ-pau.fr

²⁾CNRS UMR5034, Hélioparc, 2, Av. Président Angot, 64053 Pau, France

³⁾Alltech France, 2-4 Av. 6 Juin 1944, 95190 Goussainville, France

Abstract

Selenium is an essential element playing a vital role in many metabolic functions and showing some cancer preventive properties. The main source of Se intake is food. However, the concentration of food production in regions with low soil selenium content has led to decline in the amount of this element in human food supply which poses potential health risk. Among selenium food sources, particular attention is paid to edible animal tissues of animal origin such as meat and eggs due to their nutritional importance. Strategies of Se supplementation aimed at increasing its uptake by animals (broilers and layers) were proposed resulting in higher Se content in respective foodstuffs. The interest in species selective determination of selenocompounds results from their different bioavailability in humans and potential importance for the stability and quality of the marketed products.

The study presented concerned chicken meat (breast and leg) and eggs from animals fed with selenium enriched (both inorganic and organic) and control diets. Size-exclusion HPLC – ICP MS of sequential foodstuffs extracts (aqueous followed by SDS) was used to study selenium speciation. Additional information on the selenium incorporation into proteins was obtained by quantification of selenoaminoacids by RP HPLC-ICP MS after proteolytic digestion of meat and egg samples.

Significantly higher selenium content was observed in edible tissues of animals fed with organic selenium rich diet. The supplementation with organic selenium is accompanied by a relative increase in the high-molecular selenium species and an increase in the selenomethionine concentration with no change in the selenocysteine level. No such phenomenon was observed for the samples supplemented with inorganic selenium.

Key words: selenium, speciation, animal tissue, HPLC, ICP-MS

Selenium levels of Estonians

Marjatta Kantola¹⁾, Päivi Rauhamaa¹⁾, A. Viitak⁴⁾, T. Kaasik²⁾,
Helena Mussalo-Rauhamaa³⁾

¹⁾Finnish Forrest Research Institute, Central Laboratory, Jokiniemenk.1, P.O.X. 18,
01301 Vantaa, Finland, marjatta.kantola@metla.fi

²⁾Department of Public Health, University of Tartu, Estonia

³⁾Department of Public Health, University of Helsinki, Finland,
helena.mussalo-rauhamaa@eslh.intermin.fi

⁴⁾Tallinn Technical University, Chemistry Department, Tallinn, Estonia, anuv@edu.ttu.ee

Both Finland and Estonia belong to the Scandinavian area, surrounding the Baltic Sea, which is regarded to be selenium-deficient (Reimann et al. 2003). During the time when Finnish soil has been supplemented with selenium, the situation in Estonia, in our nearest neighbour in south, has been still 'untouched'. The objective of the present study is to sum up the dietary intake of selenium of Estonian people with the aid of serum selenium concentration.

In the 1990's our research team collected several series of serum specimens from Estonians of different age and living in different geographical areas. In total, selenium concentration was analysed in 434 serum samples by the electro thermal atomic absorption spectrometry. First samples were collected in the beginning of 1990's, and the last ones during the years 2000 and 2001. The findings are gathered up in this study and they are compared to the results found in the literature, especially those of Finns.

It is well known that nutrition is the main determinant of serum selenium. We found that the dietary selenium intake among the Estonian people is scarce based on the concentration of selenium in the sera. The range was 31.5-131 µg/L (0.40- 1.66 µmol/l). The selenium contents of Estonians were at the similar level as reported for Finns before the selenium supplementation of fertilisers was carried out in Finland in 1985. Anyhow, the selenium concentrations were strongly dependent of the geographical location of living residences: the highest concentrations were found in the Eastern Estonia. A tentative reference value for omnivorous apparently healthy adults is suggested to range from 0.50 to 2.50 mol/l (Alfthan et al. 1996).

Reimann, et al. 2003. Agricultural soils in Northern Europe: A geochemical atlas. Hannover

Alfthan, G., Neve, J. J. 1996. Trace Elements in Med. Biol. 10: 77-78.

Key words: selenium, serum, Estonians

The association of Glutathione Peroxidase 1 codon 198 polymorphism with prostate cancer risk and progression

Matthew Cooper, Fiona R. Green, Margaret Rayman

School of Biomedical & Molecular Sciences, University of Surrey, UK GU2 4XH,
Ml.cooper@surrey.ac.uk

Abstract

Higher dietary selenium intake has been shown to reduce cancer incidence in numerous studies suggesting a possible role for selenoproteins in cancer incidence and progression. Glutathione peroxidase 1 (GPx1) is the cytosolic form of a larger family of selenium dependant, glutathione peroxidases. These enzymes detoxify hydrogen peroxide and its organic hydroperoxides and are a defence against cellular oxidative damage, a major factor in oncogenesis. A single nucleotide polymorphism (SNP) results in the substitution of proline with leucine at codon 198. Proline is known to cause a 'kink' in the secondary structure of polypeptides and therefore this SNP may affect the functionality of GPx1. The rare allele has been associated with an increase in risk of breast (OR 1.906 95% C.I. 1.016-3.576), lung (OR 2.3 95% C.I. 1.3-1.8) and bladder cancer (OR 2.63 95% C.I. 1.45-4.75). We determined genotypes for the Pro/Leu198 polymorphism using a TaqMan™ allelic discrimination assay in the CAPS study (CAncer Prostate in Sweden) of 1400 prostate cancer cases and 800 cancer-free controls. The control population was in Hardy Weinberg Equilibrium and data analysis was undertaken using SPSS, adjusting for age and geographical location. No association was found between the Leu allele and prostate cancer risk but we are investigating whether it has an affect on metastasis by assessing the impact on clinical markers of severity. Furthermore, in this population of relatively low selenium status (mean \pm SD plasma selenium $75\mu\text{g/L} \pm 15$ in 50 controls) the available selenium may be prioritised for the synthesis of more important selenoproteins, thus diminishing the effect of the Pro/Leu198 polymorphism.

Key words: GPx1, selenium, prostate cancer, SNP

Prevention by Se-cysteine precursors of disturbances in glutathione pool in simulating endogenous intoxication

A.G. Moiseenok¹⁾, G.V. Alfthan²⁾, V.S. Slyshenkov¹⁾, T.A. Pekhovskaya¹⁾,
A.A. Shevalye¹⁾

¹⁾Institute of Biochemistry, National Academy of Sciences of Belarus, Grodno, Belarus,
val@biochem.unibel.by

²⁾National Institute of Public Health, Helsinki, Finland

Abstract

Endogenous intoxication (EI) accompanied by oxidative stress (OS) is most frequently simulated by parenteral administration of bacterial lipopolysaccharide (LPS). The glutathione (G-SH) system impairments, which follow EI, are poly-organic and represent a characteristic manifestation of OS. Prevention of OS by modulation of Se-cysteine-containing proteins and antioxidant protection enzymes (glutathione peroxidase, thioredoxine reductase, selenoprotein P, etc) is a rational approach enabling to substantiate new technologies for prevention of oxidative stress and stress-induced pathology.

The experiments were carried out on 40 Wistar CRL:(WI) WUBR female albino adult rats subdivided into 5 groups and treated with Se-containing substances (intragastrically, 250 mikrog Se/kg body weight in a 2% starch solution) in the following order: group 1- control, 2- selenite, 3- dimethyldipyrasolylselenide, 4- Se-pyrane, 5- Se-methionine. The Se-consumption with feed was 0.14 ppm. On day 10, half of the animals from each group were administered subcutaneously with *E. coli* LPS (Sigma, L-2630) at a dose of 400 mikrog/kg body weight, and development of EI and OS was observed by measuring colonic temperature as well as OS product accumulation in blood plasma and erythrocytes.

EI was found to be followed by Se mobilization from blood plasma, decreased plasma and liver GSH level and glutathione-S-transferase (GT) activity, G-SH/G-SS-G ratio and total glutathione in liver, with liver glutathione reductase (GR) activity being unchanged. The 10-day selenite and Se-methionine administration caused selenemia enhancement, decreasing in group 2 and being unchanged in group 5 with EI. The administration of Se-substance (with the exception of Se-pyrane) prevented a reduction of plasma and liver G-SH (with the exception of selenite). The protective selenite effect was also absent in studying the G-SH/G-SS-G ratio and total glutathione. The highest liver glutathione redox state level was observed in experimental group 5 (Se-methionine administration) where it was above the control values, but was not followed by GR activation. The activity of the latter was diminished in selenite-treated animals. The group 2-5 animals had increased liver GT activity, and no LPS-caused decrease was observed after the dimethyldipyrasolylselenide and Se-methionine administration.

Key words: selenite, dimethyldipyrasolylselenide, Se-pyrane, Se-methionine, glutathione, glutathione-S-transferase, liver, selenemia, oxidative stress

Changes in glutathione peroxidase activities and glutathione system indices in rat liver and intestine in endogenous intoxication initiation under controlled selenium consumption

T.A. Pekhovskaya¹, V.S. Slyshenkov¹, V.A. Gurinovich¹, N.E. Petushok¹, A.A. Shevalye¹, V.A. Zaitsev², L.A. Zubarevich³, A.G. Moiseenok¹

¹Institute of Biochemistry, NAS of Belarus, Grodno, 230027, Belarus, val@biochem.unibel.by

²Republican Scientific-Practical Centre for Hygiene, Minsk, 220012, Belarus

³Selekor Ltd, Moscow, 109004, Russia

Abstract

We studied the content and the ratio of the glutathione oxidized and reduced forms (GSSG, GSH, total G) as well as glutathione reductase and glutathione peroxidase activities (t-BOOH and H₂O₂ substrates) in the liver, duodenal, small and large intestines of albino rats (Wistar CRL:(WI) WUBR) consuming a low selenium diet supplemented with sodium selenite (SS) in drinking water or the organic preparation Sedimethyldipyrasolyl selenide (DPS) (both at a dose of 0,1 mikrog Se/ml water). The Se-consumption with feed was 0,14 ppm. Some animals were administered intraperitoneally with E. coli lipopolysaccharide (Sigma, L-2630) at a dose of 400 mikrog LPS/kg body weight to provoke endogenous intoxication (EI, endotoxemia).

The development of hyperthermia was monitored by measuring colonic temperature, increasing blood plasma oxidative stress indices and their slackening in SS and DPS consumption. EI elevated the GSSG concentration and reduced the liver GSH/GSSG ratio, which was not found in the SS- and DPS - supplemented animals. Glutathione peroxidase activity turned out to be considerably increased in consuming Se-containing preparations, however, the greatest increase was after the SS administration.

The EI development in the duodenal, small and large intestinal mucosa was accompanied by an identical decrease of GSH amount, the GSH/GSSG ratio and total G. The SS consumption elevated the GSH/GSSG ratio in all the intestinal regions and the total G in the large intestine as well as activated glutathione reductase in the small intestine. Both the Se-containing compounds stabilized the mucosal G system (probably, synthesis of G) in EI, which was pronounced in the large intestine.

The results obtained indicate considerable variations in formation of Se-cysteine liver and intestinal stores in consumption of organic and inorganic selenium forms and enables to optimize the schemes for prevention and pathogenetic treatment of oxidative stress- induced pathologic processes in hepatology and gastroenterology.

Key words: selenite , dimethyldipyrasolyl selenide, glutathione peroxidase, glutathione reductase, glutathione, intestinal mucosa

Selenium supplementation and ischemia reperfusion injury in rats

Anthony Perkins, Kylie Venardos, Glenn Harrison, John Headrick

Heart Foundation Research Centre, Griffith University Gold Coast Campus, Southport, Queensland, Australia, A.Perkins@griffith.edu.au

Abstract

This study examined the effects of selenium supplementation on the activity of glutathione peroxidase and thioredoxin reductase and how this impacted on myocardial function post ischemia reperfusion. Methods: Male wistar rats were fed diets containing 0, 50, 100 and 1000 ug/kg sodium selenite for 5 weeks. Hearts were subjected to Langendorff ischemia and reperfusion, with functional recovery assessed. Heart tissues were assayed for thioredoxin reductase and glutathione peroxidase activity, mRNA expression and for lipid peroxides and protein carbonyls. Results: Hearts from selenium deficient animals were more susceptible to ischemia-reperfusion injury when compared to normal controls (38% recovery of RPP vs 47% RPP) whereas selenium supplementation resulted in improved recovery of cardiac function post ischemia-reperfusion (57% recovery of RPP). There were significantly less lipid peroxides and protein carbonyls in hearts from rats on high selenium diets. The endogenous activity of thioredoxin reductase and glutathione peroxidase and the expression of mRNA for these proteins was increased in selenium supplemented animals. Conclusions: Selenium supplementation reduces oxidative stress and improved cardiac function post ischemia reperfusion in rats.

Keywords: selenium, anti-oxidant enzyme, ischemia reperfusion injury

Study of the effect of Sep15 and GPx4 gene polymorphisms on prostate cancer risk

Indira Vishnubhatla¹⁾, Margaret Rayman¹⁾, Hans-Olov Adami²⁾,
Katarina Bälter²⁾, Henrik Grönberg³⁾, Fiona R Green¹⁾

¹⁾School of Biomedical and Molecular Sciences, University of Surrey, Guildford, UK GU2 7X8

²⁾Department of Medical Epidemiology, Karolinska University, Sweden

³⁾Department of Oncology, Umeå University, Sweden

Abstract

Recent studies have reported functional polymorphisms in several selenoprotein genes and association of these allelic variants with cancer risk. The model for chemoprevention by selenium suggests that reduced levels of one or more selenoproteins increase cancer risk, with these levels affected by reduced dietary intake and genetic polymorphisms that result in an increased Se requirement. In this study, we investigated the effect of single nucleotide polymorphisms (SNPs) in the selenocysteine insertion sequence (SECIS) element which is vital for efficient selenoprotein translation, in selenoprotein 15 [Sep15 811C/T] and glutathione peroxidase [GPx4 718T/C]. Our study was carried out in men from a low Se status population and powered to detect a low odds ratio of 1.5 to 1.9, as often found for this type of association. Using the TaqMan allelic discrimination assay, we genotyped DNA from 1400 prostate cancer cases and 800 cancer-free controls matched for age and location who took part in the CAncer Prostate Sweden (CAPS) study. The combined genotypic, clinical and demographic data were analysed statistically (SPSS 12.0). Overall, control allele frequencies were consistent with previous reports (Sep15 811T allele, 0.21 and GPx4 718C allele, 0.58) and observed genotype frequencies were in Hardy-Weinberg equilibrium. Although no direct association between prostate cancer risk and genotype was found in the case-control analyses, we are examining the relationship between genotype and clinical markers of disease severity. The outcome may be useful in identifying men who are genetically susceptible to advanced disease and could benefit from Se supplementation.

Key words: selenoproteins, Sep15, GPx4, SNP, genotyping, SECIS, CAPS study, prostate cancer risk, low Se status

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Selenium and antioxidant enzymes status in HCV/HIV patients supplemented with antioxidant cocktail

A. Skesters¹⁾, A. Silova¹⁾, G. Selga¹⁾, M. Sauka¹⁾, N. Rusakova¹⁾, T. Westermarck²⁾, Faik Atroshi³⁾.

¹⁾Laboratory of Biochemistry of Riga Stradins University, Dzirciema Str. 16, Riga, LV-1007, Latvia, Andrejs.Skesters@rsu.lv.

²⁾Rinnekeoti Research Centre, 02980, Espoo; ³⁾Pharmacology&Toxicology, ELTDK, University of Helsinki, Helsinki, Finland.

Abstract

Background. In Latvia about 100.000 cases have been diagnosed as positive HCV, with up to 30% as HIV positive. Micronutrient deficiencies are common in HIV, both in early and late stages of the disease. Micronutrient deficiencies are common in HIV/AIDS, resulting from both malabsorption and virally-caused depletion. Selenium deficiency has also been documented in both HIV and AIDS patients in both plasma and red blood cells and to correlate with progression and mortality of HIV. Low selenium levels correlate with low glutathione peroxidase activity in HIV and AIDS. Observational studies have linked higher levels of selenium in the blood with higher CD4+ counts and reduced risk of mortality from HIV disease. **Objective:** To investigate the association, if there will be, between selenium and antioxidant enzymes status in HCV/HIV patients after antioxidants cocktail supplementation. **Results:** Low plasma selenium levels were found in patients with increased risks of HIV transmission. Similar trend was also shown when antioxidants enzymes were considered in these patients. **Conclusion:** In the search for modifiable risk factors to improve outcomes among HIV-infected subjects, multivitamin and trace elements have been used as a supplement. Our study shows that the role of micronutrients in HIV disease indicates that selenium deficiency may be considered as a risk factor in HIV. Adequate selenium/or antioxidants status may be beneficial for some but not all outcomes. Further studies are needed to better understand the role of selenium and antioxidants enzymes after supplementation.

Keywords: selenium, HIV, deficiency, antioxidant supplementation

The problems of selenium compound (food additive) safety

Igor Sannotsky

RAMSc Institute of Industrial Medicine, 31 Prosp. Budennov, Moscow, Russia, husainova@horizon.ru

Abstract

The wide use of microelement preparations for treating microelement deficiency and prophylactic use may be dangerous due to overdosage. As protective measures monitoring of the health of the population and selection of Se-compounds with minimal cumulative activity are important.

Methods and results. Toxicity (DL_{50} , rats, per os) and cumulativity (Q_{cum} , method by Lim et al.) of some Se-compounds are as follows: Na_2SeO_3 , DL_{50} : 6-10 mg/kg body weight = very high; Q_{cum} : 1,6 = strong; Se-Met + SeCys: 1000 mg/kg = middle; 2 = middle; dimethyldipirosoliselenide (DMDPSe): 6000-8100 mg/kg = weak; 5 = weak, respectively.

The material cumulation (fluorometric method by Alfthan G., 1984) of DMDPSe after subchronic feeding (1.5 months daily with food in doses of 6 and 60 mg/kg = 1/1000 DL_{50} and 1/100 DL_{50}) was studied in rats. After the two doses the cumulation in the kidneys was 13 and 16%, respectively. There was some cumulation in the gonads, and no cumulation in other organs. In blood serum the cumulation was 15 and 24% compared to control level after subchronic feeding. No integral deviations were obtained. After 6 months of post-Se-feeding there were no differences compared to control.

Subchronic DMDPSe feeding resulted in some increase of non-protein SH-compounds in blood serum (photometric ultramicromethod by Folomeev V.F., 1989); a high **negative** correlation ($r=0.7$) between protein SH-compounds and serum Se after the dose of 60 mg/kg and a high **positive** correlation ($r=0.87$) between non-protein SH-compounds and serum Se level after the dose of 6 mg/kg. The hematological indexes did not change after 1.5 months of Se feeding or after 6 months postfeeding, but there was an inversion of the correlation coefficient between the different lymphocyte subpopulations (disturbance of regulation).

Conclusion. It is suggested that the most adequate Se-compound for use as food additive is DMDPSe (Se^{2+}). However, there is a further need to investigate the long term effects, in particular on the immune system. General use of mineral food additives needs monitoring of the health of the population.

The selenium content in soil and potato tubers affected by organic fertilization

K. Borowska, J.Koper

Department of Biochemistry, University of Technology and Agriculture, 6 Bernardynska St. 85-029 Bydgoszcz, Poland, kborowska56@o2.pl

Abstract

In trace amounts, selenium is an essential micronutrient and has important benefits for animal and human nutrition. In many low selenium countries the possibility of fertilizer or foliar application of selenium to plants has been studied. Many factors influence the plant uptake and metabolism of added selenium, such as clay and humus contents in soil, soil pH, other nutrients content, the chemical form of added Se and the climate. The aim of this study was to determine influence of organic fertilization on the selenium content in soil and potato tubers. Soil samples were taken from the long-term experiment established at the Experimental Station of the IUNG Pulawy. The soil was affected of organic fertilisation in a form of manure (0,20,40,60,80 t·ha⁻¹). Total selenium content was determined fluorometrically by the method of Warkinson. Forms of selenium available to plants were extracted with DTPA and then determined fluorometrically. The application of manure increased the organic carbon content in the investigated soil.

Table 1. The selenium content in soil and potato tubers (mean values)

Dose of manure [t·ha ⁻¹]	Total Se in soil [mg·kg ⁻¹]	Se-DTPA in soil [µg·kg ⁻¹]	Se in potato tubers [mg·kg ⁻¹ d.w.]
0	0.145	6.9	0.085
20	0.161	7.0	0.086
40	0.165	6.7	0.109
60	0.180	7.3	0.119
80	0.173	7.5	0.109

Statistical analyses confirmed that application of FYM resulted in the highest amounts of total selenium in soil. Total selenium content in the soil samples was statistically highly correlated with organic carbon content. Presence of DTPA-extractable forms of selenium in the total selenium content ranged from 4.0-4.4% in the samples fertilized with FYM to 4.8% in the control. This rate of contribution of Se-DTPA in the total selenium content indicated its low mobility and availability to plants.

Key words: selenium, soil, potato tubers

The selenium content and dehydrogenases activity in selected soil types of Central Poland

K. Borowska¹, J.Koper¹, H.Dąbkowska-Naskręci², A. Piotrowska¹

¹ Department of Biochemistry, ² Department of Soil Science and Soil Protection, University of Technology and Agriculture, 6 Bernardynska St. 85-029 Bydgoszcz, Poland
kborowska56@e2.pl

Abstract

Soils are considered to be an important source or stored of selenium for plants, crops and forage, and thus important to animal and human health. In soil, the processes of decomposition and synthesis of mineral and organic matter occur all the time, and they are monitored and activated by a variety of enzymes. All these processes form soil metabolism, which is crucial for soil fertility maintenance and preservation. The aim of this research was to determine the total and DTPA-extractable selenium content and dehydrogenases activity in black earths, brown and lessivé soils of Central Poland. Soil samples were taken from the depth of 0-20cm and 20-40cm. Total selenium content was determined by the method of Watkinson with 2,3-diaminonaphthalene (DAN) using a Hitachi F-2000 spectrofluorometer. Forms of selenium available to plants were extracted with DTPA and then determined fluorometrically. Dehydrogenases activity was assayed colorimetrically using TTC as a substrate. Total selenium content in black earths, brown and lessivé soils was in the range of 0,114-0,332 mg·kg⁻¹, 0,060-0,210 mg·kg⁻¹ and 0,035-0,252 mg·kg⁻¹, respectively. Mean values of DTPA-extractable forms of selenium in black earths was 6,6µg·kg⁻¹, in brown soils - 7,3µg·kg⁻¹ and in lessivé soils was 6,3µg·kg⁻¹. Presence of DTPA-extractable forms of selenium in the total selenium content ranged from 3.3-7.7%, what indicated low mobility of Se and availability to plants. Mean value of dehydrogenases activity in black earths was 816.6 µg TPF·kg⁻¹·24h⁻¹), in brown soils was 360.9 µg TPF·kg⁻¹·24h⁻¹ and in lessivé soils was 89.5 µg TPF·kg⁻¹·24h⁻¹. Total and DTPA-extractable selenium content in the soils was statistically highly correlated with pH, organic carbon content and clay and silt fractions content. We found a very significant correlation between total selenium content and dehydrogenases activity only in the investigated lessivé soils.

Key words: selenium, dehydrogenases, soil

