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Selenium in soil and winter wheat – analysis of soil-crop-inventory data

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Selen i mark och höstvetete – analys av mark-gröd-inventeringsdata

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Abstract

This study examined what variables that affect selenium (Se) concentrations in Swedish soils and winter wheat grains. The possibility and necessity of a Swedish Se-fortification program is also discussed. Analysis of data from the Swedish environmental monitoring program on arable land showed that Se concentrations in soils were significantly positively correlated with the organic matter in soil, more specifically with carbon ($R=0.56$; $p < 0.001$ $n=287$), nitrogen ($R=0.47$; $p < 0.001$; $n=287$) and sulphur $R=0.58$; $p < 0.001$; $n=287$). There was also a positive correlation with the cadmium concentrations in soil ($R=0.32$; $p < 0.01$; $n=287$). Weaker relationships were found between selenium concentrations in soil and texture, negative correlation with sand content ($R=-0.23$; $p < 0.05$; $n=286$) and positive correlation with clay content ($R=0.26$; $p < 0.05$; $n=286$). For selenium in the grain, a strongly significant positive relationship was found with pH in the soil ($R=0.41$; $p < 0.001$; $n=285$) and with the total concentrations of selenium ($R=0.31$; $p < 0.01$; $n=285$) and cadmium ($R=0.32$; $p < 0.01$; $n=287$) in the soil. There were no evidence for anion competition between selenium and other oxyanions. There was a strong negative correlation between Se/Cd ratios and cadmium concentrations in grain ($R=-0.20$; $p < 0.001$; $n=285$), suggesting that more selenium in relation to cadmium in the soil affects cadmium concentrations in crops. This implies that selenium fertilization may be a possibility to decrease cadmium concentrations in crops. The mean concentration of selenium in winter wheat grains in Sweden is 0.02 mg/kg. Dietary selenium intake among adults in Sweden today is below the recommended amount. Desirable selenium concentrations in grain were calculated if all cereal crops were to be fertilized amounting to 0.085 mg/kg and if only wheat were to be fertilized to be 0.145 mg/kg. Selenium deficiency in the diet is an overlooked problem in Sweden today and needs further attention.

Sammanfattning

Denna studie undersökte vilka variabler som påverkar selenkoncentrationerna (Se) i svensk mark och höstvetete och diskuterade möjligheten och nödvändigheten för ett svenskt Selen-gödslingsprogram. Analys av data från det svenska miljö-övervakningsprogrammet på åkermark visade att selenkoncentrationerna i marken var signifikant positivt korrelerade med organiskt material i mark, mer specifikt kol ($R=0.56$; $p < 0.001$; $n=287$), kväve ($R=0.47$; $p < 0.001$; $n=287$) och svavel ($R=0.58$; $p < 0.001$; $n=287$). En positiv korrelation mellan kadmiumkoncentrationerna i mark ($R=0.32$; $p < 0.01$; $n=287$) kunde också påvisas. Svaga korrelationer fanns mellan selenkoncentrationer i marken och texturen, en negativ korrelation med sandinnehållet i mark ($R=-0.23$; $p < 0.05$; $n=286$) och en positiv korrelation med lerinnehållet ($R=0.26$; $p < 0.05$; $n=286$). Selen i höstvetekärnor var positiv och stark signifikant korrelerat med pH i marken ($R=0.41$; $p < 0.001$; $n=285$), den totala koncentrationen av selen ($R=0.31$; $p < 0.01$; $n=285$) och kadmium i marken ($R=0.32$; $p < 0.01$; $n=287$). Selen i kärnan testades mot andra anioner och det visade sig inte finnas någon signifikant konkurrens. Det var en stark negativ korrelation mellan Se/Cd-ratio i marken och kadmiumkoncentrationen i höstvetekärnor ($R=-0.20$; $p < 0.001$; $n = 285$), vilket visar att selenhalten i förhållande till kadmium i marken påverkar kadmiumhalten i grödan. Detta indikerar att selengödsling skulle kunna minska kadmiumkoncentrationerna i grödor. Medelkoncentrationen av selen i höstvetekärnor i Sverige är 0.02 mg/kg. Intaget av selen med kosten bland vuxna i Sverige idag är dock mycket lägre än den rekommenderade mängden. Önskvärda koncentrationer i spannmålskärnor beräknades om alla spannmålsgrödor skulle gödslas med selen (0.085 mg / kg) och om bara vete skulle gödslas med selen (0.145 mg/kg). Selenbrist i kosten är ett förbiset problem i Sverige idag och behöver ytterligare uppmärksamhet.

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1 Introduction

1.1 General

Selenium (Se) is named after the Greek moon goddess Selene, even though the parent material of the moon is more depleted in Se than in the earth crust. However, similar Se concentrations are found in lunar rocks and on earth (Ringwood, 1979). Selenium was considered being a toxic element to humans and animals until 1957, when it was found out that Se was essential for human health. It can be toxic at relatively low intake, for example parts of China, India and the USA have soils with relatively high selenium levels (Christophersen et al., 2013; Feng et al., 2012). The concentration of selenium in soil is usually very low, on a global scale, average soil content is 4 mg/kg (Sieprawska et al., 2015). In many countries like China, Egypt, Thailand (Feng et al., 2012), USA and New Zealand there are areas with very low contents of selenium, resulting in a deficiency in the diet (Feng et al., 2012; Sieprawska et al., 2015). The content of selenium in the soil varies due to a result of different geological structures of certain areas. In Europe, the levels of selenium in certain countries are considered poor compared to the global average. In Sweden, Finland, Germany, Hungary and Scotland, levels of selenium in parent material are around 0.05 mg/kg soil (Sieprawska et al., 2015).

Selenium is so far not considered being essential for higher plants but deficiency of the element in animal and human diet has been associated with a number of diseases; some processes in the body are mediated by enzymes depending on selenium. It is estimated that around 0.5 to 1 billion people worldwide suffer from selenium deficiency. Known diseases associated with selenium deficiency is for example Keshan disease, cardiovascu-

lar diseases, cancer, Kashin-Beck disease, myxedema, cataracts and liver disease, HIV and increased risk of heavy metal toxicity. Diseases like Keshan disease, Kashin-Beck disease and myxoedema are rare, but the other examples are more common and may occur if human selenium demand is not met (Christophersen et al., 2013; Feng et al., 2012).

Ways to increase selenium in food has been tested in various ways. In Sweden selenium has been added to forage in livestock production since 1980, but only minor changes in the food has been noticed (Bruce, 1986). A large portion of added Se is ending up in manure and could potentially lead to crops being indirectly enriched with selenium.

In Finland mandatory addition of selenium to mineral fertilizers has been used since 1985 (Varo et al., 1994). The concentration of selenium added to NPK fertilizer in Finland is 10 mg/kg (Hartikainen, 2005; Christophersen et al., 2013). The effect of the addition of selenium proved to be very effective and safe way to increase the content of selenium in the whole food chain. Since the national selenium fortification program in Finland started, there has been a significant decrease of cancer and cardiovascular disease, but it is unclear if this can exclusively be ascribed to selenium (Hartikainen, 2005; Varo et al., 1994). Since the start of the Finnish Se-fortification program selenium concentrations in spring wheat have increased tremendously, a 25-fold increase of selenium levels with peak concentrations of 0.3 mg/kg dry matter have been observed. Selenium levels in milk and meat have increased 10-fold and 13-fold, respectively. In human, selenium serum levels have increased from approximately 0.055 mg/l to 0.103 mg/l between 1985 and 1991 (Christophersen et al., 2013).

2 Purpose and questions

2.1 General

The purpose of this study is to give the reader an overview of selenium in general but also to examine important variables about selenium in soil and how these affect plant uptake, specifically selenium in winter wheat grains. Additionally, this work also includes dietary aspects of selenium intake among humans. The study is aimed to whomever interested. The following questions were addressed in this study:

- Is the selenium in the grain correlated with the selenium in the soil?
- Is the pH in the soil correlated with the selenium in the soil or grain?
- Is the CaCO_3 in the soil correlated with the selenium in the soil or grain?
- Is the carbon, nitrogen or sulphur content in soil correlated with selenium in the soil or grain?
- Is the C/N ratio in soil correlated with selenium in the soil or grain?
- Is the texture correlated with the selenium in the soil or grain?
- Is the cadmium in the soil or grain correlated with the selenium in the soil or grain?
- Is there competition among anions affecting grain concentration of selenium?
- How much of the daily food intake of selenium comes from cereals in Sweden?

- Which mean selenium concentration in the grain is needed to meet the adequate daily intake of selenium in the Swedish population?
- How much selenium would be necessary in fertilizers to raise cereal selenium concentrations to adequate levels?

3 Selenium theory

3.1 Origin of selenium

Selenium is more common in sedimentary materials such as coal and shale, rather than in igneous rocks such as basalt, andesite and granite (Andren et al., 1975; Krauskopf (Ed.), 1982). The reason igneous rocks could have lower concentrations is because Se probably was volatilized during formation of igneous rocks. Usually, the selenium concentration of top soils is higher than of bedrock material. This is due to vertical plant transportation and Se-deposition from the atmosphere. Selenium concentrations in the soil vary globally and locally. Plant-available selenium in the soil is poorly correlated with the total selenium in the soil (Combs & Combs, 1986; Oldfield, 1999) and affected by factors such as adsorption, desorption, formation of organic and inorganic complexes, dissolution, precipitation, microbial activity and methylation to volatile compounds (Benjamin, 1983; Broadley et al., 2006; Hartikainen, 2005; Neal, 1995).

Sewage sludge, which can be used as a fertilizer, contains phosphorus and nitrogen, but also unwanted elements like cadmium and lead (Neal, 1995; Reilly, 1996). Selenium is also present in sewage sludge, due to removal from municipal water during the cleaning process. Even though selenium is present in sewage sludge, it is generally at lower concentrations than lead, cadmium, nickel and zinc (Neal, 1995) and low bioavailability for plants (Johnson et al., 1994). Studies from 16 metropolitan areas in the USA showed out that selenium concentrations in sewage sludge ranged between 1.7-8.7 mg/kg (Neal, 1995). The predominant form of selenium in sewage sludge differed; selenite was the main form in one study from Ja-

pan (Surerus et al., 1989) and selenate in another study (Jackson & Miller, 1999).

3.2 Selenium deposition

As mentioned above, deposition plays an important part in the supply of selenium to the top soil. Deposition of selenium is both due to anthropogenic but also natural processes. The biggest part of anthropogenic deposition comes from combustion of fossil fuels (Nriagu & Pacyna, 1988). Combustion of biomass, for example coal, is one major source for selenium deposition; this is due to the on-going natural deposition of selenium taken up by plants and leading to selenium-rich emissions when combusted. Additional anthropogenic reasons for selenium deposition come from metal production from sulphide ores and garbage combustion. Total emissions of selenium are estimated to be 5780 tons yearly on a global scale. When selenium emits into the atmosphere through high-temperature sources, it is emitted as selenium dioxide (SeO_2) equivalent to sulphur dioxide, and often condensed onto small particles making long-distance transport possible (Gladney et al., 1974).

Natural deposition of selenium is regarded to be more important than anthropogenic deposition. This is because natural deposition has been occurring for thousands of years and is quantitatively larger than anthropogenic deposition, even though anthropogenic deposition may be more important locally at some places. For example in Norway, areas closer to the Atlantic Ocean had much higher concentrations of selenium in the soil compared to areas on the inland. In other places, like in some parts of the USA, the soil has become seleniferous due to natural deposition from the sea and acidic rain (Låg & Steinnes, 1974; Låg & Steinnes, 1978; Steinnes et al., 1997). Natural mean global emission of selenium to the atmosphere has been estimated to be between 6000-13000 tons annually. Of these emissions, 60-80% is believed to be caused by biological methylation in aquatic environments (Amouroux et al., 2001). Another natural source of selenium emission is from forest fires.

3.3 Inorganic selenium compounds

Selenium can exist in the soil as selenide, selenite or selenate, a lot similar to sulphur. Sieprawska et al. (2015) and Broadley et al. (2011) mentioned that the concentration of selenium in the soil usually ranges from 0.01- 2 mg/kg. Concentrations over 0.5 mg/kg are regarded as high concentrations (Broadley et al., 2011).

In well aerated soils with low organic matter, high pH, moderate to high temperature and absent of waterlogging conditions, selenate tends to be predominant over selenite (Elrashidi et al., 1987; Neal, 1995). Selenide is predominant in reduced soil environments (Broadley et al., 2011). Selenate is not as strongly adsorbed to minerals as selenite, making selenate more plant available and easier for roots to take up. The downside of this is that selenate is easily leached out and may become not available for roots (Elrashidi et al., 1987; Neal, 1995). Selenite is adsorbed strongly to iron and aluminium oxides and hydroxides, allophane and to a certain degree also to clay (Benjamin, 1983; Neal, 1995). In the UK, selenite was found to be the predominant form available for root uptake in aerobic soils, even though selenate is considered to be the predominant form. This could possibly be explained by biological reduction of selenate to selenite (Li et al., 2008). In reduced environments such as water saturated soils with a high organic matter concentration and high pH, selenide and elemental selenium is more common but these compounds are generally unavailable for crops (Elrashidi et al., 1987; Neal, 1995).

At high selenium levels in soil, the concentration of selenium anions can be controlled by the solubility of minerals in soil (Elrashidi et al., 1987). One study suggests that selenate and selenite compounds are too reactive to remain in soil rather forming metal selenides such as Cu_2Se , PbSe and SnSe under temporarily reduced conditions probably hindering the precipitation of elemental selenium. In a similar study, selenium solubility was found to be controlled by elemental selenium and formation of FeSe and FeSe_2 under reducing conditions (Masscheleyn et al., 1990). Even though there are various reasons why selenium not easily forms Se-bearing minerals, the main reason are a low total concentration of selenium in soils and the fact that inorganic compounds of selenium tend to adsorb to non-selenium minerals entering the lattices of these minerals (Neal, 1995).

3.4 Organic selenium compounds

Production of organic selenium compounds is affected by pH, oxygen partial pressure, organic matter content, microbial activity, mineralogical composition and adsorbing surfaces. In soils characterized by high organic matter concentrations, selenite is the most common form of inorganic selenium. Areas where these circumstances are met have a cold climate or suffer from waterlogging (Haug et al., 2007). Inorganic selenium compounds can be reduced. Soil organisms like fungi and bacteria can reduce inorganic forms of selenium to various volatile and non-volatile compounds (Reamer & Zoller, 1980). Forms of organic selenium compounds formed by fungi are amongst others dimethylselenide, dimethyldiselenide and dimethylselenone (Frankenberger & Karlson, 1989; Thompsom-Eagle et al., 1989). Bacteria can methylate these compounds rather quickly forming hydrogen selenide (Oremland et al., 1989). Aside from this, biological reduction processes can form other organoselenium compounds analogous to compounds with sulphur, for example various proteins and amino acids (Abrams et al., 1990; Van Dorst & Peterson, 1984).

Plants can take up simple organic selenium compounds in the form of amino acids. Some studies showed that selenium is incorporated into organic compounds in soil. One study showed that if selenite was added to forest soils, most of it was fixed to soil organic matter (Gustafsson & Johnsson, 1992). One other study showed that 60% of the selenium in soils was bound to organic matter if the organic matter content exceeded 1.6% (Kang et al., 1993). From a study on soils with less than 1% carbon, 40% of the selenium was bound to organic matter (Yamada et al., 1983). In a selenium-iron-rich soil about 50% of the extracted selenium was organically bound (Séby et al., 1997).

Yet, still little is known about the chemical aspects of the formation of different organic selenium compounds. Most research is concerning the microbial activity for forming organic selenium components. In one study selenate and selenite was added to reaction vessels without oxygen or microbes. Selenate remained unchanged but selenite was transformed into colloidal species associated with humic substances (Bruggeman et al., 2007). Results from one study indicated a strong correlation between selenium and iron in samples, suggesting that instead of direct association with humic substances, selenium might be bound via metal impurities to organic matter. Furthermore, it was speculated that selenium is attached

to organic complexes with highly charged metal ions such as iron, aluminium and manganese (Coppin et al., 2006). In some studies, selenium availability to plant decreased with higher organic matter content (Singh et al., 1981; Yang et al., 1983) and in other studies selenium availability increased instead (Davies & Watkinson, 1966).

3.5 Selenium adsorption

As mentioned earlier, adsorption to soil compounds differs between selenate and selenite, where selenite attaches more strongly than selenate. In humid climates such as in Scandinavian countries, a higher selenite over selenate content in soil is most probable since leaching of selenate is favoured (Benjamin, 1983; Hingston et al., 1968; Parfitt & Smart, 1968).

Selenite adsorbs to solid surfaces through ligand exchange substituting a negatively charged surface ligand. The negatively charged ligands can be hydroxyl groups from clay minerals or metal hydrous oxides (Benjamin, 1983; Hingston et al., 1968; Parfitt & Smart, 1968). The factors involved in adsorption of selenite are similar to those controlling phosphate and arsenate adsorption. The main factor is the pH in soil, since the amount of hydrogen anions in the soil regulates the affinity to surfaces. With increasing pH, selenite adsorption to surfaces decreases (Christophersen et al., 2013)

Selenate is less strongly and non-specifically adsorbed similar to nitrate or sulphate. It is believed that selenate forms an outer-sphere complex, with a water molecule in between the surface and the selenate anion (Sposito, 1984).

One study concluded that weathering of the soil increased selenite adsorption (John et al., 1976). In some studies, ionic strength seems to have a larger effect on selenate than selenite adsorption (Hayes et al., 1987; Hingston et al., 1968; Neal & Sposito, 1989). Sulphate is a strong competitor to selenate regarding adsorption and even though chloride does not compete as strongly as sulphate, competition by chloride cannot be ignored (Schulthess & Hu, 2001).

3.6 Plant uptake

Selenium taken up by plants is usually poorly correlated with the total amount of selenium in soil although there is some variation. The availability of selenium in the soil is highly dependent on in which forms selenium are present and soil characteristics such as adsorption components, redox status and pH value. Another aspects is the presence of anions such as sulphates, phosphates and organic anions that compete with selenium for the same adsorption surfaces and can make selenium more plant-available (Christophersen et al., 2013).

Selenate and sulphate are analogues, thus competing during plant uptake. Both use the same transporters during root uptake. This means the uptake of selenate can be strongly restricted by the amount of sulphate (Mikkelsen & Wan, 1990; Zayed & Terry 1992). The affinity constant (K_m) for selenate and sulphate uptake was found to be similar in barley roots (Leggett & Epstein, 1956). In theory it can also be the other way around, that selenate inhibits the uptake of sulphate as shown in nutrient solutions. However, in soil solution concentrations of selenate are lower than of sulphate and not have such an effect on plants (Broadley et al., 2011).

In *Arabidopsis thaliana*, the main transporter responsible for uptake of sulphate and selenate is Sultr1;2 located in the root. Deficiency of sulphate is compensated by the expression of the sulphate transporter genes, thus increasing sulphate and selenate uptake (Shibagaki et al., 2002; El Kassis et al., 2007; Barberon et al., 2007). This means not only are sulphate and selenate competing with each other through membrane transporters, sulphate also regulates the expression of sulphate transporter genes, determining the possible uptake of selenate (Li et al., 2008; Shinmachi et al. 2010).

Different plant species differ in their ability to take up selenium and their tolerance to high selenium concentrations. According to this, plants can be categorized into *Se-accumulators* and *non-accumulators*. Intermediate species are categorized as *Se-indicators*. For example, some species from the *Stanleya* genera are typical Se-accumulators (Rosenfield & Beath, 1964), *Stanleya pinnata* that had grown in a soil with a selenium concentration of 2-4 mg/kg, contained selenium at a concentration of 300 mg/kg dw in the shoots. What characterizes Se-accumulators is their ability to

grow on selenium-rich soils without damaging impact on the growth of the plant and the accumulation of selenium in the plant (Broadley et al., 2011).

Some members of the *Brassicaceae* family are also accumulators, generally due to their ability to accumulate sulphur and can accumulate and tolerate up to several hundred mg/kg dw of selenium in the shoot (Zayed & Terry, 1992). Even though there are some examples of agricultural and horticultural plants that are Se-accumulators, most of them are not (Shrift, 1981). Selenium toxicity for plants can even occur at concentrations below 100 mg/kg (Mikkelsen & Wan, 1990). In a study, 39 plant species grown under the same condition in hydroponic culture were analysed; a close positive correlation between sulphur and selenium in the leaves was found for 37 non-accumulators and for the 2 Se-accumulators (*Stanleya* and *Astragalus racemosus*) higher selenium than sulphur concentrations were found in the leaves (White et al., 2007a). The selenate/sulphate discrimination index is a measure of the accumulation of selenate in relation to sulphate and is calculated using molar ratios in leaves and in soil solution: [leaf Se/leaf S]/[solution selenate/solution sulphate]. A selenate/sulphate discrimination index of 1 indicates that there are no clear discrimination between selenate and sulphate. A selenate/sulphate discrimination index below 1 indicates that transporters in roots have a higher affinity for sulphate than for selenate and an index above 1 indicates a higher affinity for selenate than sulphate (Broadley et al., 2011).

Our understanding of selenite uptake by plants is still arbitrary, some studies suggest selenite passively passing through root cells by diffusion (Terry et al., 2000) and mass transport, but an active uptake is also suggested (Arvy, 1993; Li et al., 2008C). Phosphate in soil solution inhibits selenite uptake and phosphorus deficiency increases Se uptake (Hopper & Parker, 1989; Li et al., 2008c) showing that phosphate transporters are involved in root uptake of selenite. At pH levels below 4.0, a large proportion of selenite in soil is dissociated as H_2SeO_3 and can be transported through the aquaporin channel (NIP2;1) in rice (Zhao et al.; 2010). One major difference between translocation of selenate and selenite in plants is that selenate is quickly transported from the roots to the shoots whereas selenite mainly assimilates in organic forms in the root (Asher et al., 1977; de Souza et al., 1998; Li et al., 2008c). With this said, it is clear why fertilization with selenate is more efficient when trying to increase selenium concentration in crops (especially cereals). Selenium has shown to be taken up by wheat

seedlings as seleno-amino acids, for example seleno-methionine (Abrams et al., 1990). Still, it is unclear how important this is for plant uptake (Broadley et al., 2011).

3.7 Selenium metabolism

In plants, selenate is reduced to selenite after uptake first by activation of ATP sulphurylase to adenosine 5'-phosphoselenate (APSe) and thereafter by APS reductase to selenite. The rate limiting process in this step is the part with ATP sulphurylase, which is needed to reduce selenate (Pilon-Smits et al., 1999). This is one reason why selenite is more easily assimilated within plants in comparison with selenate (de Souza et al., 1998; Li et al., 2008c). Increasing the metabolic pathway for selenite in crops could be by overexpressing ATP sulphurylase in transgenic plants (Pilon-Smits et al., 1999).

After the initial reduction of selenate to selenite in plants, the next step is a further reduction to selenide by glutathione (GSH) (Sors et al., 2005b). Thereafter the cysteine synthase complex is used to assimilate selenide into seleno-cysteine. After this step, seleno-cysteine is assimilated into seleno-methionine through the methionine biosynthetic pathway. Seleno-cysteine and -methionine are easily incorporated into plant proteins by substitution. Se-containing proteins are non-functioning or less efficient (Eustice et al., 1981).

Non Se-accumulators can suffer from a high selenium uptake and high contents of Se-proteins (Broadley et al., 2011) whereas Se-accumulators can reduce Se contents by methylating seleno-cysteine and seleno-methionine and prohibiting these amino acids to be used in protein synthesis. Two examples of methylated compounds by Se-accumulators are Se-methylcysteine and γ -glutamyl-Se-methylcysteine. The methylation of seleno-cysteine is catalysed by selenocysteine methyltransferase (Neuhierl & Bock, 1996). In eight species of the genera *Astragalus*, the activity of seleno-cysteine methyltransferase showed to be correlating closely with the ability to accumulate selenium (Sors et al., 2005b). In *Astragalus bisulatus* and *Stanleya pinnata*, accumulation of selenium in young leaves was over 70% in the form of Se-methylcysteine (Pickering et al., 2003; Freeman et al., 2006). Se-methylcysteine and γ -glutamyl-Se-methylcysteine were found in edible plants of *Brassica* and *Allium* species especially when grown in areas with high contents of selenium. In non-

accumulators such as cereals, seleno-methionine was the main form present (Whanger, 2002; Rayman et al., 2008).

The chemical similarities between sulphur and selenium metabolism were also present in aerial parts of plants, both producing volatile compounds. The main volatile compound found is dimethylselenide (DMSe) metabolized from seleno-methionine, but also dimethyldiselenide (DMDSe), produced through methylation and latter oxidation of seleno-cysteine. Rates of Se volatilization differ between crops, with highest rates found for Se-accumulators. Release of volatile Se-compounds is affected by the sulphur supply by the soil. For example in broccoli, during conditions of sulphur deficiency approximately seven times higher rates of Se-emissions occurred than under sufficient sulphur supply (Zayed & Terry, 1992). In Indian mustard it was found out that more selenium was volatilized when supplied with selenite instead of selenate (de Souza et al., 1998). Bacteria in the rhizosphere seem to have an important role on Se accumulation and volatilization by plants Terry et al., 2000).

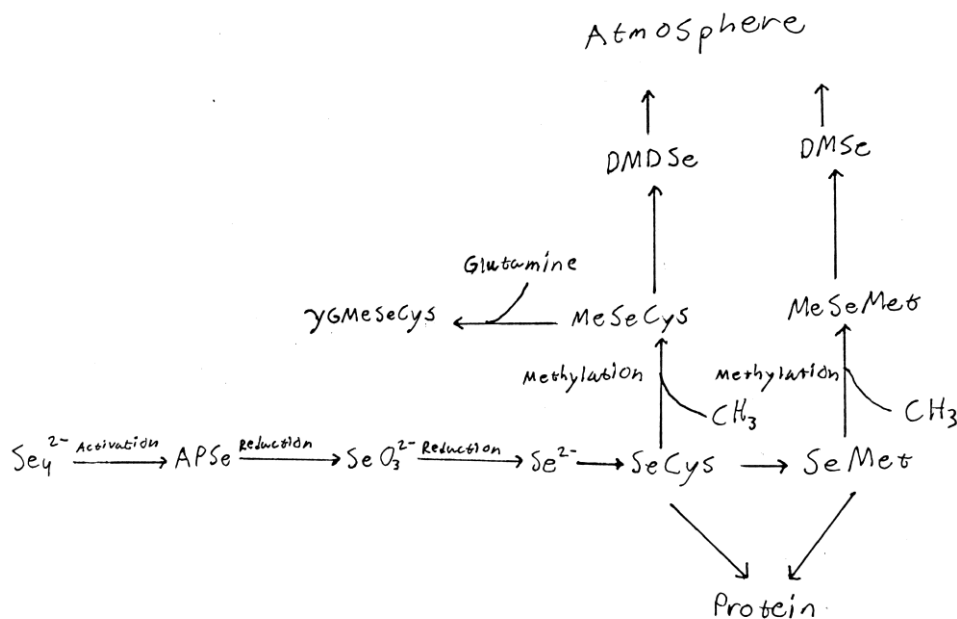


Figure 1. Metabolic pathways of selenium assimilation in plants. Based on Broadley et al. (2011).

3.8 Benefits of selenium

Compared to humans and animals, selenium has so far not been proven to be essential for higher plants although there are indications. In humans and animals, selenium is essential for the production of functional enzymes such as glutathione peroxidase, where seleno-cysteine is the catalytic site. Higher plants also got similar enzymes like glutathione peroxidase, however, the catalytic site for these enzymes are cysteine instead of seleno-cystein (Terry et al., 2000), showing that selenium is not essential for this pathway in higher plants. However, selenium has been observed to boost plant growth and reproduction. Selenium is believed to reduce lipid peroxidation and enhance the activity of glutathione peroxidase, thus giving reported effects such as that selenium biofortification increased growth and UV resistance for ryegrass and reduced senescence and increased UV resistance for lettuce (Hartikainen, 2005). Enriching oil seed rape with selenite has greatly increased seed production (Lyons et al., 2009). High amounts of selenium in Se-accumulators are also suggested to protect against herbivores (e.g., Galeas et al., 2008), because of the resulting diseases from animals grazing on seleniferous soils (Brown & Shrift, 1982; Miller et al., 1991), thus maybe also explaining the evolutionary path for this trait amongst accumulator plants (Boyd, 2007).

3.9 Selenium fertilization and genetic modifications

As stated above, the amount of selenium in soils differs tremendously in various parts of the world. People can suffer from selenium deficiency. The main source of selenium in many diets is through consumption of crops (Combs, 2001; Rayman, 2008). The minimum daily intake of selenium recommended for humans is 70 µg Se per person (EFSA, 2017). The ways to increase selenium concentrations in crops could either be by so called agronomic biofortification (fertilization) or genetic methods that increase the Se-accumulation in crops (Broadley et al., 2011).

Biofortification through various genetic improvement methods needs to aim at possible genetic variation in uptake and assimilation of selenium. In bread wheat, tests of genotypes showed that environmental conditions had a much larger impact than genetic variation regarding selenium accumulation (Lyons et al., 2005; Zhao et al., 2009). Also the genetic variance was found to be larger between species rather than within species (Broad-

ley et al., 2011). Reports has been showing greatly increased selenium uptake in transgenic plants through the overexpression of genes controlling S/Se assimilation. Although this is a good indicator for selenium biofortification, these studies are usually aimed for Se-accumulators on seleniferous soils and the traits of these Se-accumulators have not been tested on selenium deficient soils (Pilon-Smits & Leduc, 2009)

Since agronomic biofortification has been mandatory in Finland since 1985 through small amounts of Na-selenate added to mineral fertilizers, higher selenium concentrations were achieved in cereals, vegetables and products from animals. Thanks to the Se-fortification program in Finland, the Finnish population has doubled the intake of selenium from foods. Even though mineral Se-suppliants could be used in the diet, organically bound Se in form of seleno-cysteine and –methionine is far more bioavailable for humans than inorganic Se-additions. Additionally, plants work as a buffer for supplying selenium, making it harder for humans to excess the intake of the important element (Hartikainen, 2005).

Fertilization with selenate is a very useful option for increasing selenium concentrations in the food chain because selenate is actively transported from roots to shoots and incorporated into various organic forms. A field study with increasing selenium supply showed that concentrations in winter wheat grains also increased linearly from 0.03 Se mg/kg in the control, to 2.6 mg/kg in the treatment fertilized with 100 g Se/ha as selenate (Broadley et al., 2010). Furthermore, a study from Canada showed promising results from fertilization of durum wheat. Fertilization through granular seed coating or foliar spray (all containing sodium selenate) raised selenium concentrations in the grain at all test sites (Grant et al., 2007).

The main Se-compound found in wheat flour is seleno-methionine corresponding to around 80% of all Se-compounds and Se-methylseleno-cysteine and inorganic selenium making up the rest (Hart et al. 2011). The uptake of applied Se by wheat was about 20-35%. The residual part was leached out or became unavailable for crops. Crops grown the following season showed little effect of the previous selenium fertilization (Broadley et al., 2010; Stroud et al., 2010). Concerning fertilization, although selenate is more efficient compared to selenite (Mikkelsen & Wan, 1990; Hawkesford & Zhao, 2007), there may be possibilities to make selenate fertilization more efficient in future.

4 Material and Methods

The material used for this study comes from inventory data of soils and crops in Sweden. The data include soil properties and concentrations of elements in cereal grain mainly winter wheat. The data were analysed with focus on selenium and complemented with information from the literature. Significant correlations are presented in the results and other non-significant correlations are presented in the Appendix.

4.1 Inventory data

The inventory data were previously analysed, see "*Tillståndet i svensk åkermark och gröda: Data från 2001-2007*" by Eriksson et al. (2010). In this work, emphasis was put on selenium and a comprehensive analysis was done. Firstly, the inventory data were log-transformed to gain a normally distribution. After this, scatter plots were conducted from all relevant variables. Lastly, Pearson correlation tests were conducted in JMP software (JMP® Pro 13. SAS Institute Inc., Cary, NC) to determine the correlation coefficient and the significance of the correlation. To describe the level of significance for each parameter from this study asterisks was used, "*" = $p < 0.05$ ", "**" = $p < 0.01$ ", "***" = $p < 0.001$, "ns" = $p > 0.05$). Results were discussed with help of relevant sources. Non-relevant data were excluded.

5 Results & discussion

5.1 Selenium in cereal grain and soil

A positive correlation was found between total selenium concentrations in soil and concentrations in plants, $R=0.31^{**}$; $n=285$ (Figure 2). This was expected as a larger pool of selenium in soil could also result in a higher uptake by plants. According to Christophersen et al. (2013), usually there is only a poor correlation between plant available selenium and total selenium in soil, although they mention that this may vary. Although a strong correlation was found in this study, the effect on selenium in grains cannot be exclusively ascribed to the total amount of selenium in the soil.

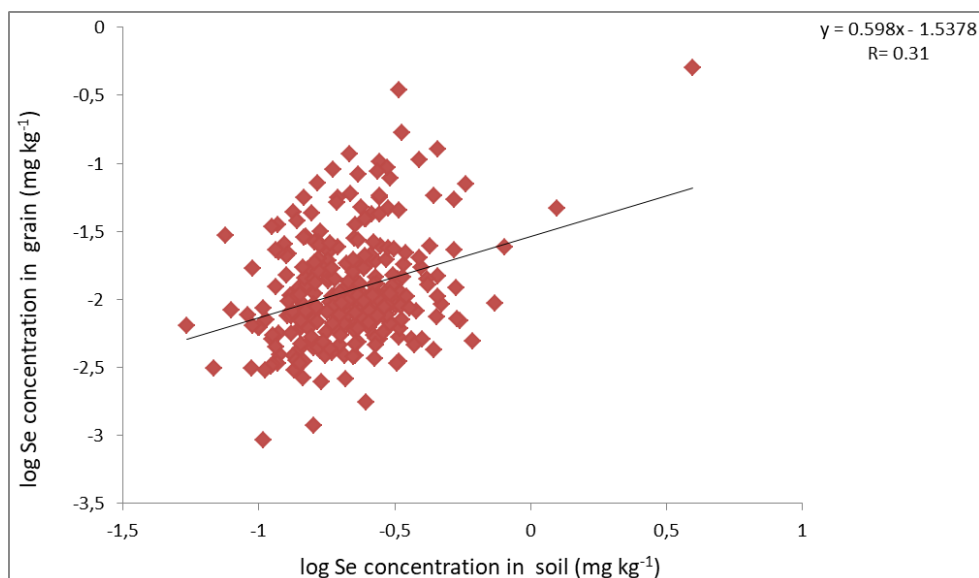


Figure 2. Selenium (Se) concentrations in grains as a function of selenium concentrations in soils (n=285).

5.2 Selenium and soil pH

No significant correlation was found between selenium in soil and soil pH values, $R=-0.034$ ns; $n=287$ (see Appendix, Figure 16). Even though this analysis showed no correlation, one could speculate that a higher pH reduces the amount of selenium in the soil since a higher pH value reduces the adsorption strength of selenite (Christophersen et al., 2013) and increases the amount of selenate present in the soil, which is not adsorbed as strongly as selenite, thus making it easier for roots to take up, but is also more prone to leaching (Elrashidi et al., 1987; Neal, 1995). However, it seems not to be important processes for the amount of Se in soil.

On the other hand, the concentration of selenium in grain and the pH in the soil had a statistically significant strong positive correlation, $R=0.41^{***}$; $n=285$ (Figure 3). One study from South Australia showed a higher concentration of selenium in wheat grains when grown on a calcareous sandy loam with a pH of 8.6 (0.720 mg Se/kg) compared to wheat grown on clay loam with a pH of 6.6 (0.063 mg Se/kg) (Lyons et al., 2004). Other studies have also shown similar results as this one and selenium concentrations have been higher in crops grown on soils with a higher pH (Cary & Allaway, 1969; Johnsson, 1991).

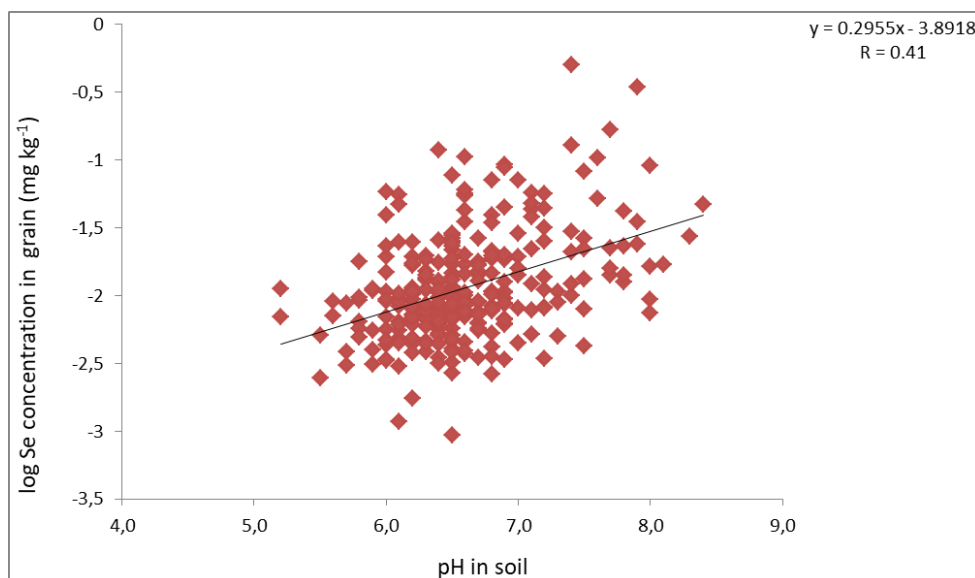


Figure 3. Selenium (Se) concentrations in grains as a function of the pH in soils (n=285).

With this in regard, the result can be explained by the fact that selenate becomes more predominant over selenite at higher soil pH (Elrashidi et al., 1987; Neal, 1995). Furthermore, selenate is more quickly translocated to the shoot than selenite, which mainly accumulates in the roots (Asher et al., 1977; de Souza et al., 1998; Li et al., 2008c). In addition, selenite adsorption is weakened at higher pH making it easier for roots to take up (Christoffersen et al., 2013). Thus, higher soil pH values should lead to higher selenium concentrations in cereal grains.

5.3 Selenium and CaCO₃ in soil

No significant correlation was shown between calcium carbonate and selenium in soil, $R=0.016$ ns; $n=95$ (see Appendix, Figure 17) and neither for selenium in grains, $R=0.19$ ns; $n=95$ (see Appendix, Figure 28).

Since a strong positive correlation was found for pH in soil and selenium in grain, one could expect to also find a positive correlation between calcium carbonate and selenium in the grain since calcium carbonate is only present in soils at pH values of 8.1 and above (Eriksson et al., 2015). Still, this was not the case and no explanation can be given. Other parameters might play a larger role for this outcome.

5.4 Selenium and carbon, nitrogen and sulphur in soil

There was a very strong positive correlation between selenium in the soil, $R=0.56^{***}$; $n=287$ (Figure 4) and soil carbon contents. On the other hand, carbon in soil showed not to be significantly correlated with selenium in the grain, $R=0.049$ ns; $n=285$ (see Appendix, Figure 24).

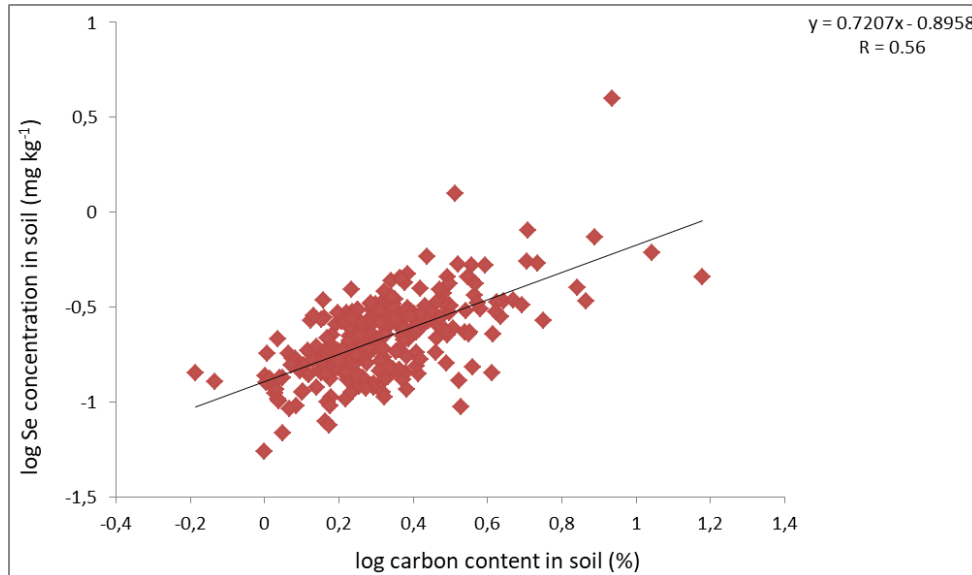


Figure 4. Selenium (Se) concentrations in soils as a function of the carbon content in soils ($n=287$).

Nitrogen in the soil was also strongly positive correlated with selenium in soil, $R=0.47^{***}$; $n=287$ (Figure 5) but no correlation was found for nitrogen in soil and selenium in grain, $R=0.14$ ns; $n=285$ (see Appendix, Figure 25).

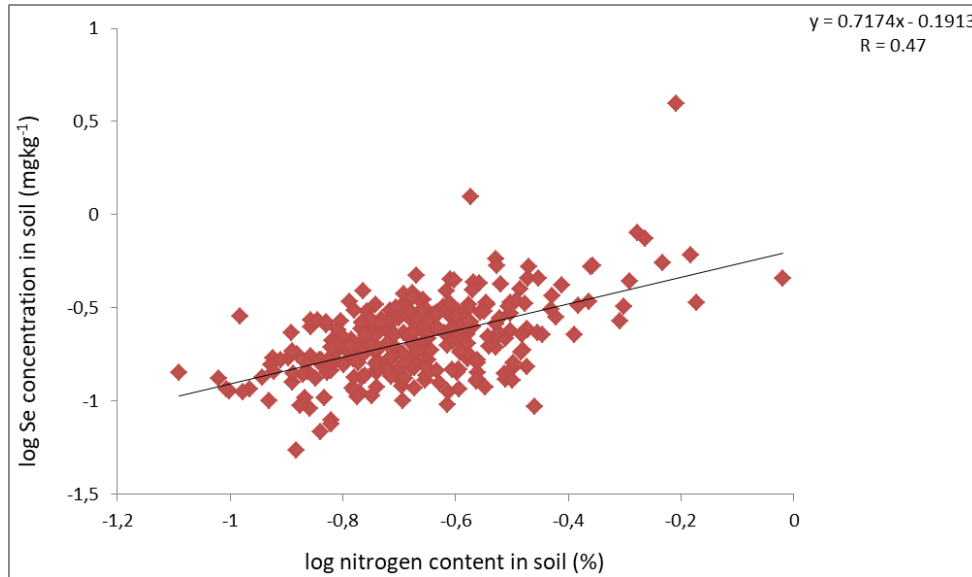


Figure 5. Selenium (Se) concentrations in soils as a function of the nitrogen content in soils ($n=287$).

Sulphur in soil was most strongly correlated with the content of selenium in soil, $R=0.58^{***}$; $n=287$ (Figure 6). However, no correlation between sulphur in soil and selenium in grain was found, $R=0.17$ ns; $n=285$ (see Appendix, Figure 26).

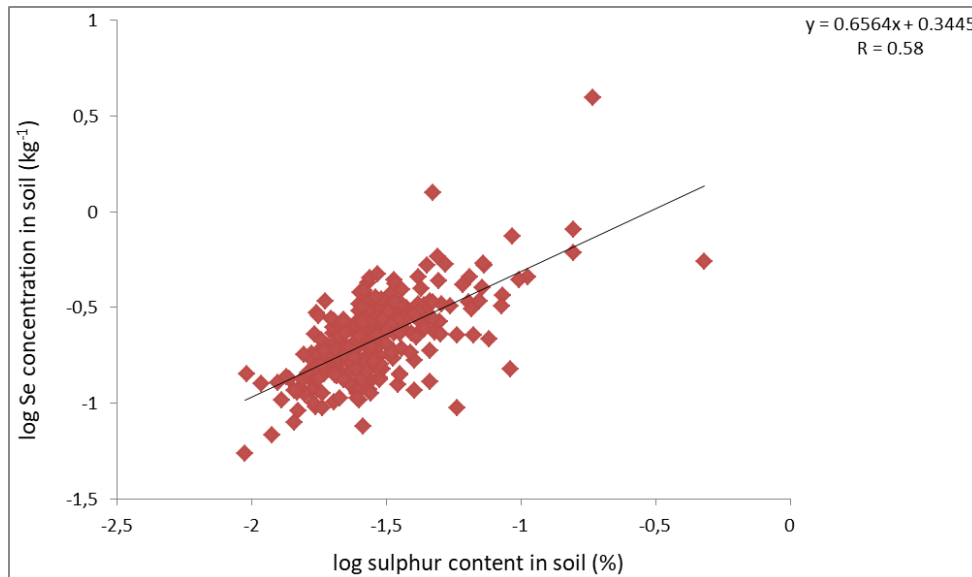


Figure 6. Selenium (Se) concentrations in soils as a function of the sulphur content in soils ($n=287$).

The positive correlations between selenium in soil and carbon, nitrogen and sulphur in soil were expected since a large amount of selenium in soil is bound to organic matter consisting of carbon, nitrogen and sulphur. Studies have shown that between 40-60% of selenium is bound to organic compounds in soil, even in soils with carbon contents less than 1% (Gustafsson & Johnsson, 1992; Kang et al., 1993; Yamada et al., 1983; Séby et al., 1997).

The lacking correlation between organic matter (carbon, nitrogen and sulphur) and selenium in grain is difficult to explain since one would expect to also find more selenium in grain at higher soil organic matter since it contains selenium. This may indicate that selenium bound to soil organic matter is not mineralized and therefore not plant available. Another explanation could be that soils with high organic content tend to have lower pH which partly explains the non-significant result between organic matter and selenium in grain, since there is a positive correlation between pH and selenium in grain. Concerning sulphur in soil, a negative correlation to selenium in grain was expected since selenate and sulphate compete for root uptake and since sulphur is present at larger amounts than selenium in soil. Uptake of selenium should be inhibited by sulphur (Li et al., 2008; Shinmachi et al. 2010). Results from one study showed a 10-fold increase in selenate uptake from sulphur-starved wheat plants treated in nutrient solutions (Li et al., 2008).

5.5 Selenium and C/N ratio in soil

A statistical significance was found between the C/N ratio and selenium in soil, $R=0.27^{**}$; $n=287$ (Figure 7) which was weaker than those for carbon or nitrogen in soil. This could possibly be explained by a stronger correlation for carbon and selenium in soil than nitrogen and selenium in the soil. For the grain part, no correlation was found between C/N and Se in grain, $R=0.14$ ns; $n=285$ (see Appendix, Figure 27) which was expected since neither carbon nor nitrogen seems to have a significant impact on selenium uptake.

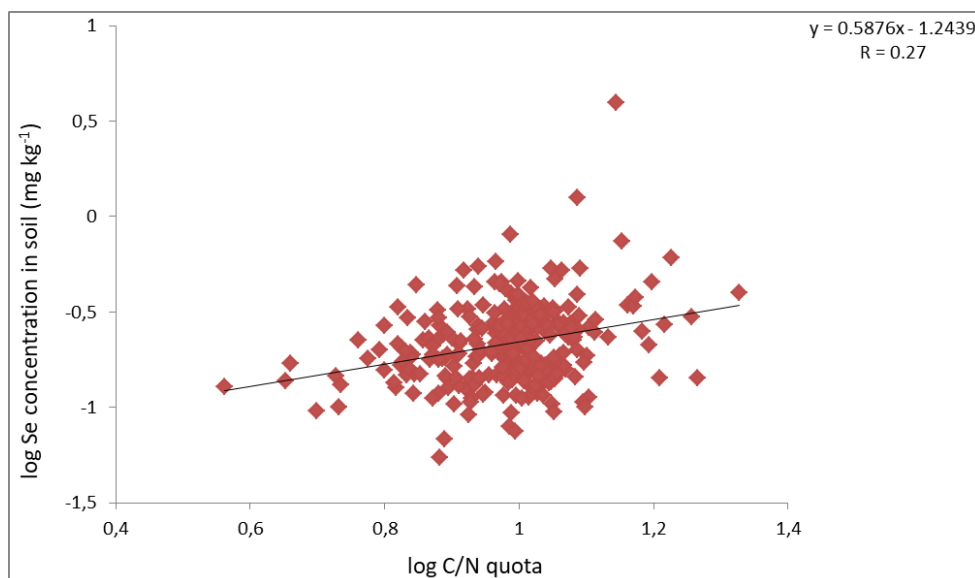


Figure 7. Selenium (Se) concentrations in soils as a function of the C/N ratio in soils (n=287).

5.6 Selenium and soil texture

Correlations between Se in soil and texture were tested using total clay content, sand plus silt content, but also for sand only and clay plus silt content. There were significant correlations between texture and selenium content in soil, but no significant correlations were found between selenium in grain and the different soil texture classes (see Appendix, Figures 20-23).

The clay content in soil showed the highest positive correlation with selenium in soil, $R=0.26^*$; $n=286$ (Figure 8). For sand plus silt a negative correlation was found to selenium, $R=-0.24^*$; $n=286$ (Figure 9).

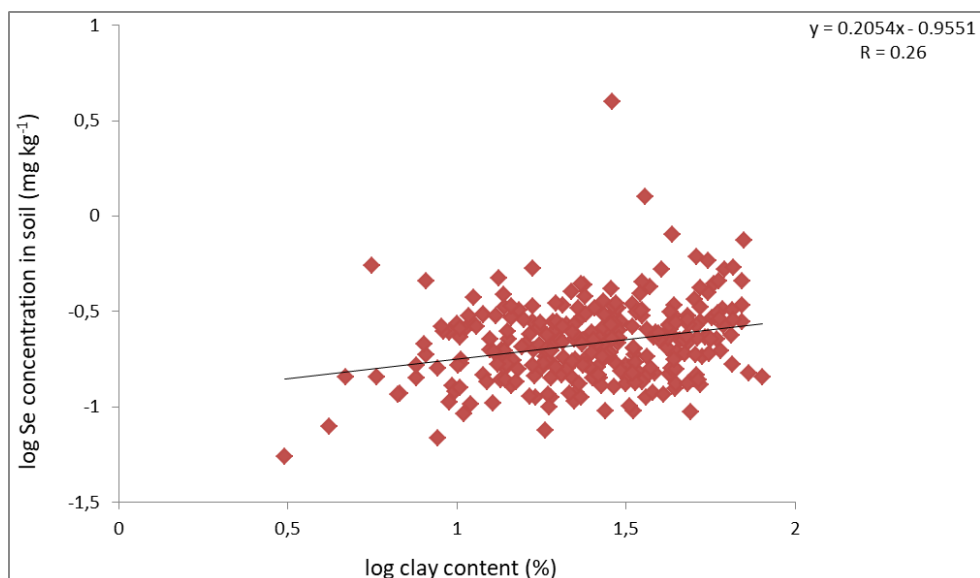


Figure 8. Selenium (Se) concentrations in soils as a function of the clay content in soils (n=286).

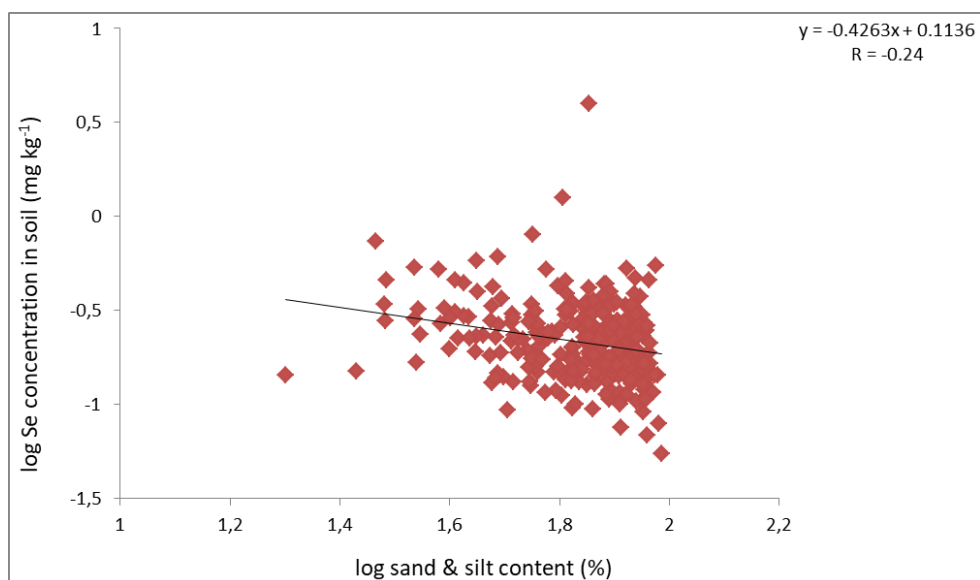


Figure 9. Selenium (Se) concentrations in soils as a function of the sand & silt content in soils (n=286).

For sand only, a clear negative correlation was found to selenium in soil, $R = -0.23^*$; $n = 286$ (Figure 10) for the clay plus silt content against selenium in soil, a positive correlation was found, $R = 0.24^*$; $n = 286$ (Figure 11) which, however, was not stronger than for clay only.

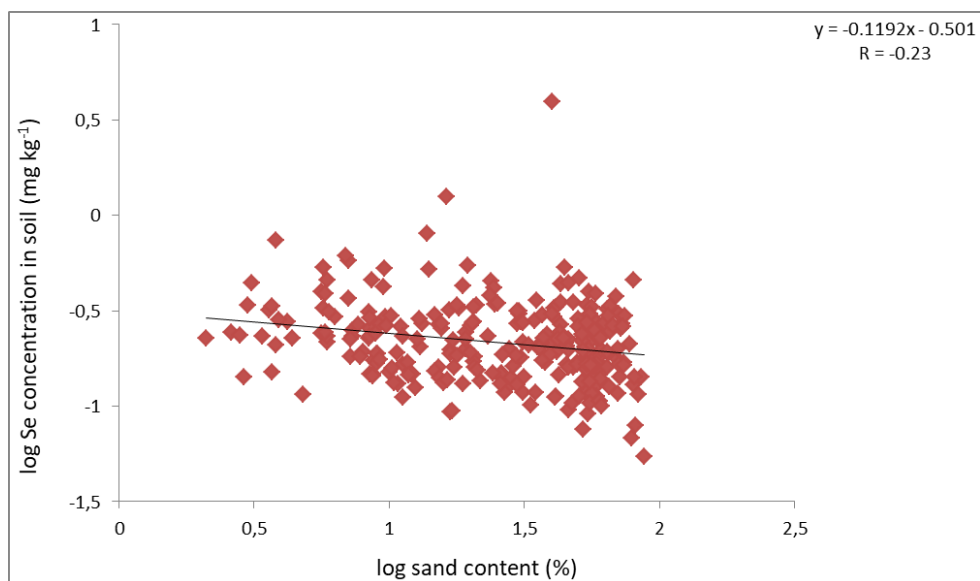


Figure 10. Selenium (Se) concentrations in soils as a function of the sand content in soils (n=286).

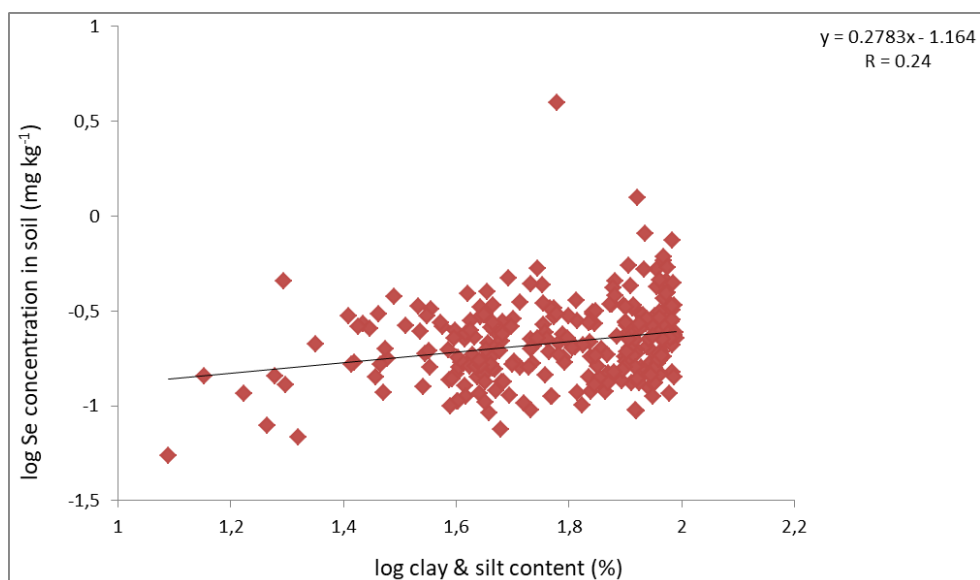


Figure 11. Selenium (Se) concentrations in soils as a function of the clay & silt content in soils (n=286).

Thus, total selenium in soil in this study increased with increasing clay content and decreased with increasing sand content. Since every correlation of selenium and texture class in soil was statistically significant, it is obvious that total selenium in soil is dependent on particle size, which is in agreement with a study by Sippola (1979). On the other hand, texture seemed to have no statistically significance on plant uptake of selenium in

this inventory. However, highest selenium contents were found in timothy grown on clay soils according to Sippola (1979).

5.7 Selenium and cadmium in soil and crop

The data showed a significant positive correlation between selenium and cadmium in soil, $R=0.32^{**}$; $n=287$ (Figure 12). Concerning crops, only one positive correlation was found. Selenium in grain and cadmium in soil were positively correlation, $R=0.32^{**}$; $n=287$ (Figure 13). Other correlations between selenium in soil and cadmium in grain, selenium in grain and cadmium in grain were not significantly correlated (see Appendix, Figures 18 and 29).

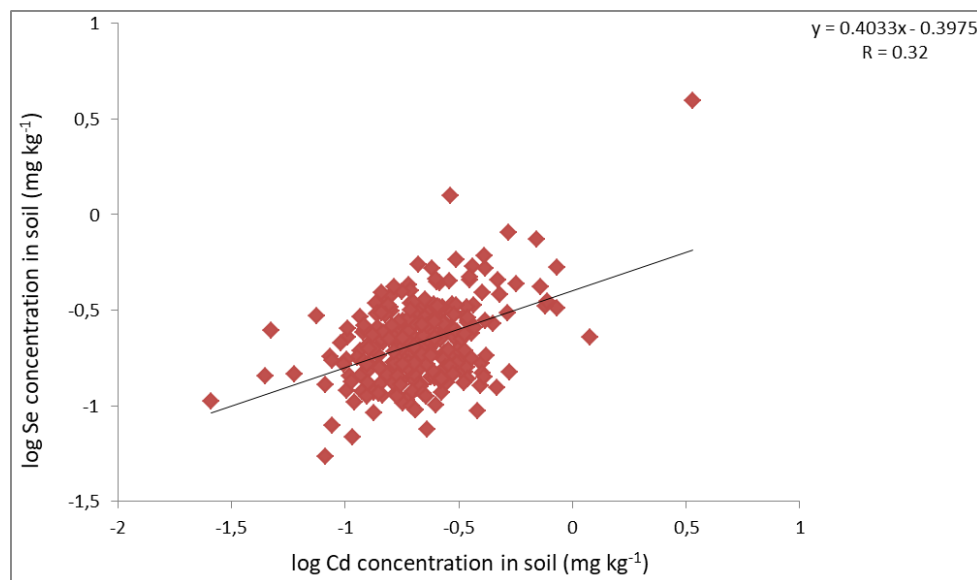


Figure 12. Selenium (Se) concentrations in soils as a function of the cadmium (Cd) concentrations in soils ($n=287$).

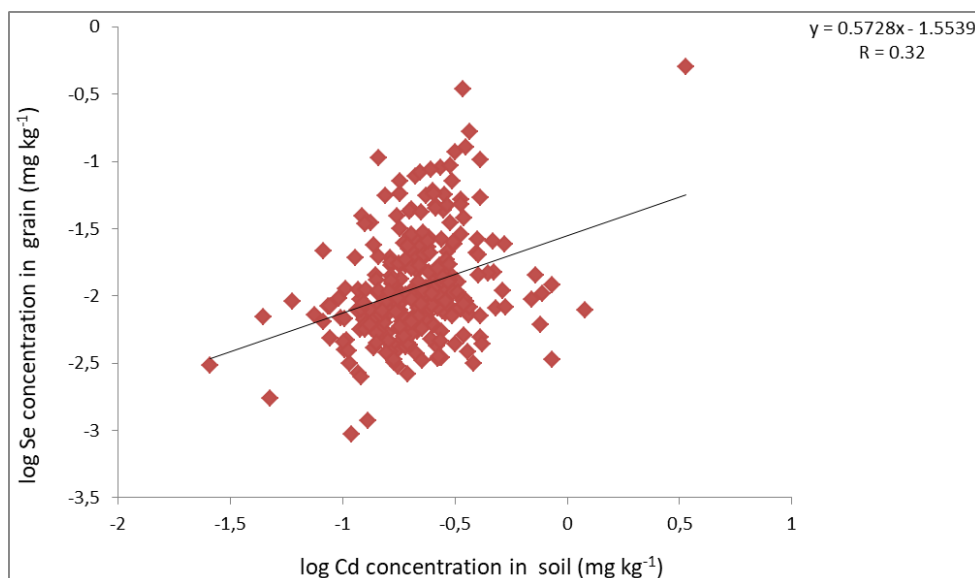


Figure 13. Selenium (Se) concentrations in grains as a function of the cadmium (Cd) concentrations in soils (n=287).

The correlations found in this study can partly be explained by contents in parent material. Cadmium is more common in sedimentary than in igneous rocks (Smolders & Mertens, 2013). Concentrations in sedimentary can vary between 0.01-2.60 mg/kg and 0.07-0.25 mg/kg in igneous rocks (Traina, 1999). Highest concentrations of cadmium are found in Cambrian-Silurian areas with sedimentary rocks such as alum shale and Cambrian sandstone. Alum shale is commonly found in regions such as Skåne, Västergötland, Östergötland, Närke and Öland. Cambrian sandrock is found in regions such as Skåne, Västergötland, Östergötland and Närke. Worth mentioning is that no correlation in cadmium-rich regions between cadmium in soils and crops has been proven so far (Carlsson, 1995).

As also selenium is more common in sedimentary than igneous rocks (Andren et al., 1975; Krauskopf (Ed.), 1982), the composition of the parent material can explain the positive correlation between selenium and cadmium in soil. Simply, the origin of cadmium and selenium is from the same source.

5.8 Anion competition during crop uptake

As selenium is taken up as an anion, this analysis aims to evaluate if competition of other anions during crop uptake of selenium may affect the concentration of selenium in the grain of winter wheat. The analysis showed that the sum of molar concentrations of phosphorus, molybdenum and boron in grain did not correlate with the selenium concentration in grain (see Appendix, Figure 30). On the other hand, correlating molybdenum and boron to selenium in grain showed a significant positive correlation, $R=0.28^{***}$; $n=285$ (Figure 14), whereas considering phosphorus only, showed no significant correlation to selenium in grain (see Appendix, Figure 31).

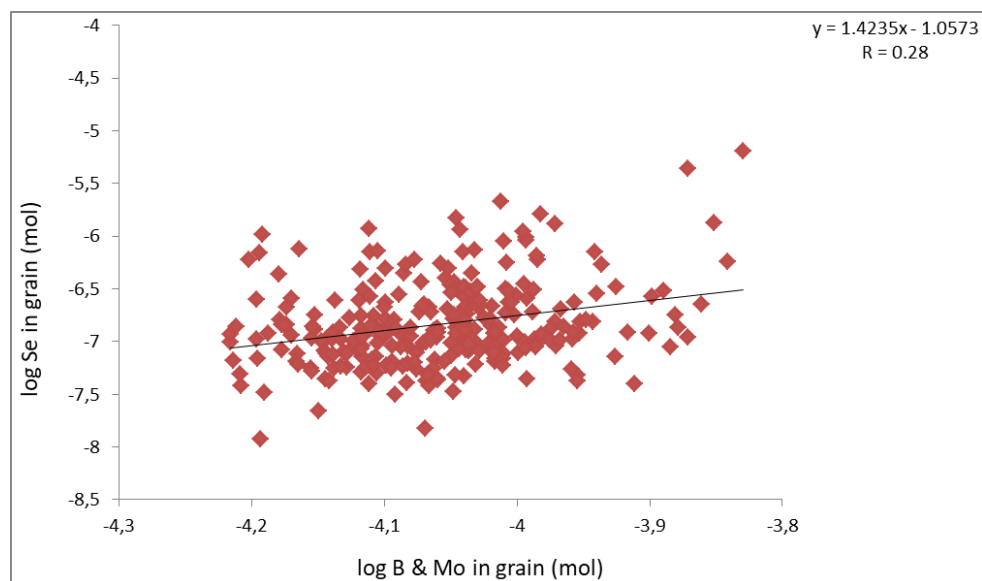


Figure 14. Selenium (Se) content in grains as a function of boron (B) and molybdenum (Mo) in grains ($n=285$).

The results indicate that phosphorus, molybdenum and boron anions have no significant negative impact on plant uptake of selenium and thus do not compete. Selenite can compete with phosphate during root uptake whereas selenate uptake uses the same transport molecules as sulphur. As phosphate inhibits selenite uptake and is enhanced by phosphorus deficiency in the plant (Arvy, 1993; Hopper & Parker, 1989; Li et al., 2008c), one could expect a negative impact of phosphorus on selenium in crops. However, selenite is mainly accumulated in the roots and therefore the effect of phosphorus surplus or deficiency may not affect the grain concentration of selenium as much. Unfortunately, no data for sulphur in grain are available, which are supposed to be a major competitive anion for selenate. The positive correlation between selenium and molybdenum plus boron cannot be explained.

The presence of anions such as sulphate and phosphate in soil solution determines to what extent selenium is adsorbed in the soil and becomes available to plants (Neal, 1995). One hypothesis why selenium may become more unavailable when using phosphorus fertilizers is that selenite is precipitated when non-soluble phosphates are formed, (Dhillon & Dhillon, 2000; Hopper & Parker, 1999; Liu et al., 2004). On the other hand, fertilization with phosphate may increase the availability of selenium since it could desorb selenite from minerals in the soil as phosphate is more strongly bound to trivalent iron and aluminium (Dhillon & Dhillon, 2000; Nakamaru et al., 2006).

5.9 Se/Cd ratio in soil and Cd and Se in winter wheat

The question whether it is possible to decrease concentrations of cadmium in crops through fertilization with selenium came up during the project. By fertilizing soils, the Se/Cd ratio increases since more selenium is added to soil. Correlations between the Se/Cd ratio in soil and selenium and cadmium concentrations in grain can be an indication for if any interactions may exist. Of course only natural occurring ratios in soils were tested in this case as no data from fertilization experiments are part of the inventory data used for this evaluation.

The correlation between selenium in grain and the Se/Cd ratio in soil was not significant (see Appendix, Figure 15) indicating that selenium in crops

is not affected by the ratio in soil. However, the correlation between cadmium in grain and the Se/Cd ratio in soil proved to be significant, $R = -0.20^{***}$; $n = 285$ (Figure 15).

This suggests higher selenium over cadmium contents in soil have an impact on the cadmium content in grain. Since an increasing Se/Cd ratio in the soil seems to decrease cadmium concentrations in the grains under natural conditions, fertilization of soils with selenium can be a possible way to decrease cadmium uptake by crops.

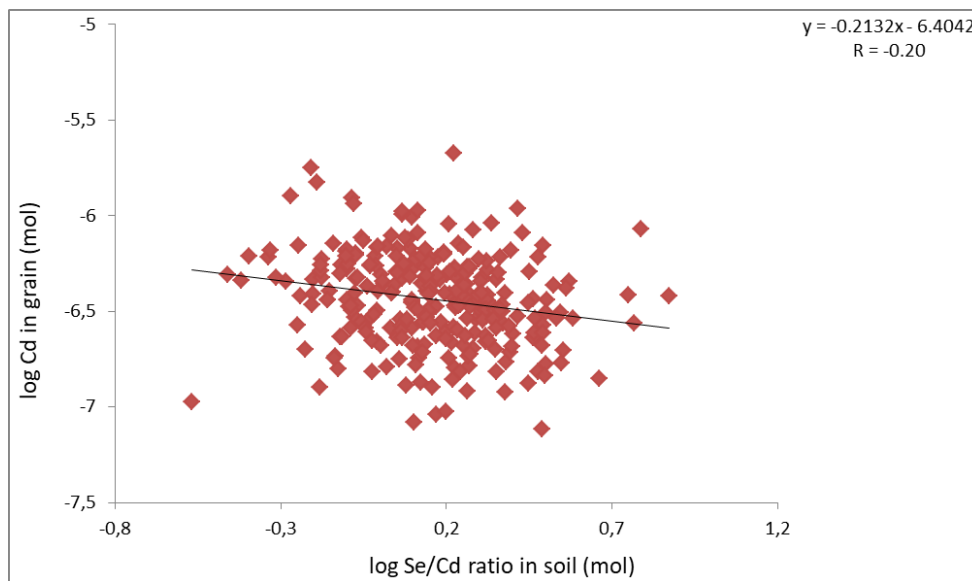


Figure 15. Correlation between Se/Cd ratios in soil and cadmium (Cd) contents in grains ($n = 285$).

5.10 Selenium fortification of cereals – a Swedish scenario

Recommended daily intakes of selenium through food vary between 50-200 µg (Aspila, 2005). According to EFSA (2017) the adequate daily intake of selenium is 70 µg, which is higher than data provided by the Swedish Food Administration (National Food Administration, 2017) suggesting 60 µg of selenium daily intake. The mean intake amongst men and women in Sweden (Riksmaten, 2012) was 46 µg of selenium daily and does not meet the needs of humans. The question whether agronomic fortification in Sweden is a viable alternative to rise selenium concentrations in cereals to meet the recommended dietary intake is highly relevant.

In the Finnish selenium fortification program, where sodium selenate is used, fertilizer application on cereal fields is approximately 500 kg/ha with 16 mg Se/kg fertilizer. This gives about 8 g/ha of selenium for each crop. The desirable selenium concentration in the plants was 0.1 mg/kg dry matter. This concentration was exceeded greatly during the program, thus indicating agronomic fortification of selenium in crops is a promising way to increase the amount of selenium passing through the food chain (Ylä-ranta, 1990).

The same article showed that the mean selenium concentration of barley that was 0.16 mg/kg dry matter, a 20 fold increase in concentration in 1985 as compared to 1984 when no selenium-enriched fertilizer was applied. Results for oats were similar as for barley. In the following three years, mean selenium concentration in crops remained above the desirable concentrations amounting to 0.21 mg/kg and 0.20 mg/kg dry matter in barley and oats (Ylä-ranta, 1990).

Average selenium concentration in spring wheat grain was 0.23 mg/kg dry matter in 1985 and 1986. In winter wheat and rye, concentrations varied between 0.02 to 0.05 mg/kg dry matter. The lower concentrations of selenium in winter crops were most likely due to less application of selenium on winter crops, possibly reduction of selenate, and risk of selenium leaching during autumn and spring months (Ylä-ranta, 1990).

According to the Swedish report Riksmaten (2012), 16 % of the selenium intake among men and women comes from products containing cereals. This means 7.36 µg of the mean daily selenium intake in Sweden for men and women comes from cereals. In the scenario where cereals are en-

riched to meet dietary needs, daily intake through cereals has to be increased with 24 μg to meet the EFSA recommendation of 70 μg . Daily selenium intake from cereals would need to be 31.36 μg in total, an increase of 426%. Mean selenium concentration in winter wheat in Sweden is 0.02 mg/kg (Eriksson et al., 2010). Assuming a similar selenium concentration in all cereals, concentration has to be raised to approximately 0.085 mg/kg to meet the adequate daily intake of selenium in the Swedish population (See calculations in Appendix).

In the scenario where only wheat would be selenium-enriched through fertilization, the concentration in grains would have to be increased further than in the previous example. The average daily intake of cereals in Sweden is 95.1 g/dry matter, of which 52 % consists of wheat (National Food Administration, 2012). This means that wheat is responsible for 3.83 μg of the daily intake of selenium. An increase of 727% in the selenium concentration in wheat grain is needed to meet the adequate daily intake among the Swedish population resulting in an approximate desirable selenium concentration of 0.145 mg/kg in wheat grains (See calculations in Appendix).

6 Conclusions

With the results from this study some conclusions can be made about selenium in Swedish soils and winter wheat grains. The first conclusion was that the variables that determine the total amount of selenium in soil are mostly different from those controlling selenium concentrations in the crop.

For the soil, the most important factor on selenium in soil was the organic matter content (carbon, nitrogen and sulphur). All three parameters reached the highest degree of significance in this study, followed by the content of cadmium in soil and lastly texture seemed to have a weak correlation with selenium in soil, although significant. Selenium concentrations decreased with coarser particles.

For the grain, pH in soil was of outmost importance, with higher pH values resulting in higher concentrations of selenium in grain. In addition to soil pH, the concentration of selenium and cadmium in soil were of equal importance for selenium concentrations in grain. With increasing concentrations of micronutrients in the grain (molybdenum and boron), selenium increased.

To increase selenium concentrations in the grain, the most reasonable alternative seems to be to raise the pH of the soil by liming of soils to reach higher pH values. As it is difficult to modify the origin of soils and since organic matter content did not affect selenium concentrations in grain, it seems pointless to increase organic matter contents in soil for the sake of increasing selenium concentrations in grain.

The most promising option mentioned in this study would be to raise grain concentrations through fertilization with selenium. The form of selenium that would be most suitable with regard to the mechanisms of selenium uptake and accumulation would be selenate. Selenate is more easily available than selenite and most likely to end up in cereal grains and not retarded in roots.

There was a strong indication that fertilization with selenium possibly can decrease cadmium concentrations in crops. As few viable agronomic measures to decrease cadmium in crops are known, this requires further investigations.

Considering the article by Ylä-ranta describing the Finnish selenium fortification program, it would make sense to add sodium selenate to fertilizers in future. As similar conditions prevail in Sweden as in Finland, the possibility for a similar successful Swedish program to increase selenium concentrations in Swedish crops should be initiated due to the fact that daily intake of selenium in the Swedish population is far below the recommended intake.

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Appendix (supplementary data)

Tables

Table 1. Soil pH, carbon, nitrogen, sulphur, C/N quota, CaCO₃ and soil texture in Swedish arable topsoils (0-30 cm)

	pH	Carbon (%)	Nitrogen (%)	Sulphur (%)	C/N	CaCO ₃ (%)	Clay (%)	Sand (%)	Silt (%)
Average	6,6	2,3	0,23	0,034	9,8	1,9	30	35	36
Median	6,5	2,0	0,21	0,027	9,8	1,4	27	32	35
Standard Deviation	0,55	1,4	0,10	0,034	2,3	2,1	16	23	13
Min	5,2	0,65	0,081	0,0094	3,7	0,0075	3,1	2	9
Max	8,4	15	0,96	0,48	21	10	80	88	75
25% Percentile	6,3	1,6	0,17	0,022	8,5	0,22	17	12	27
75% Percentile	6,9	2,5	0,27	0,034	11	2,7	41	55	45

Table 2. Selenium, cadmium, boron, molybdenum and phosphorus concentrations in grains of winter wheat

	Se grain (mg/kg dw)	Cd grain (mg/kg dw)	B grain (mg/kg dw)	Mo grain (mg/kg dw)	P grain (mg/kg dw)
Average	0,02	0,048	0,88	0,67	3695
Median	0,010	0,041	0,88	0,53	3716
Standard Deviation	0,041	0,029	0,16	0,54	567
Min	0,00093	0,0086	0,55	0,031	1936
Max	0,50	0,24	1,5	3,6	5646
25% Percentile	0,0064	0,029	0,77	0,34	3297
75% Percentile	0,019	0,059	0,97	0,80	4069

Table 3. Selenium and cadmium concentrations in Swedish arable soils (0-30 cm)

	Se soil (mg/kg dw)	Cd soil (mg/kg dw)
Average	0,25	0,25
Median	0,21	0,21
Standard Deviation	0,25	0,23
Min	0,0545	0,026
Max	3,96	3,4
25% Percentile	0,16	0,16
75% Percentile	0,28	0,28

Table 5. Significance level of soil regression analyses (p values)

	Se soil (mg/kg dw)
Se grain (mg/kg dw)	**
Clay (%)	*
Sand + silt (%)	*
Sand (%)	*
Clay + silt (%)	*
pH	ns
C (%)	***
N (%)	***
S (%)	***
C/N ratio	**
CaCO ₃ (%)	ns
Cd grain (mg/kg dw)	ns
Cd soil (mg/kg dw)	**

Table 6. Significance level of ratio regression analyses (p values)

	Se/Cd ratio soil (mol)
Se grain (mol)	ns
Cd grain (mol)	***

Table 4. Significance level of grain regression analyses (p values)

	Se grain (mg/kg dw)
Se soil (mg/kg dw)	**
Clay (%)	ns
Sand + silt (%)	ns
Sand (%)	ns
Clay + silt (%)	ns
pH	***
C (%)	ns
N (%)	ns
S (%)	ns
C/N ratio	ns
CaCO ₃ (%)	ns
Cd grain (mg/kg dw)	ns
Cd soil (mg/kg dw)	**
B, Mo & P grain (mol)	ns
P grain (mol)	ns
B & Mo grain (mol)	***

Soil

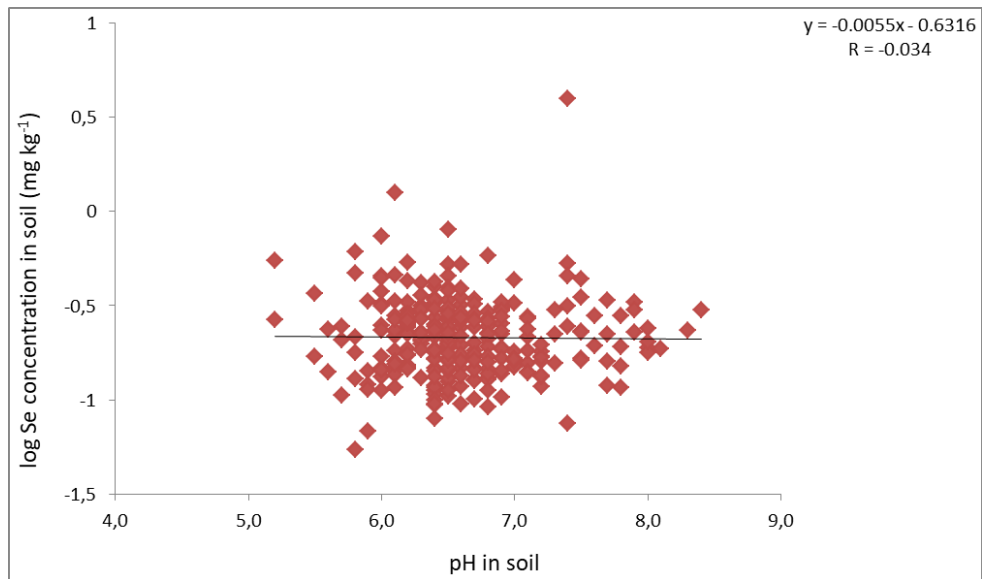


Figure 16. Selenium (Se) concentrations in soils as a function of the pH in soils (n=287).

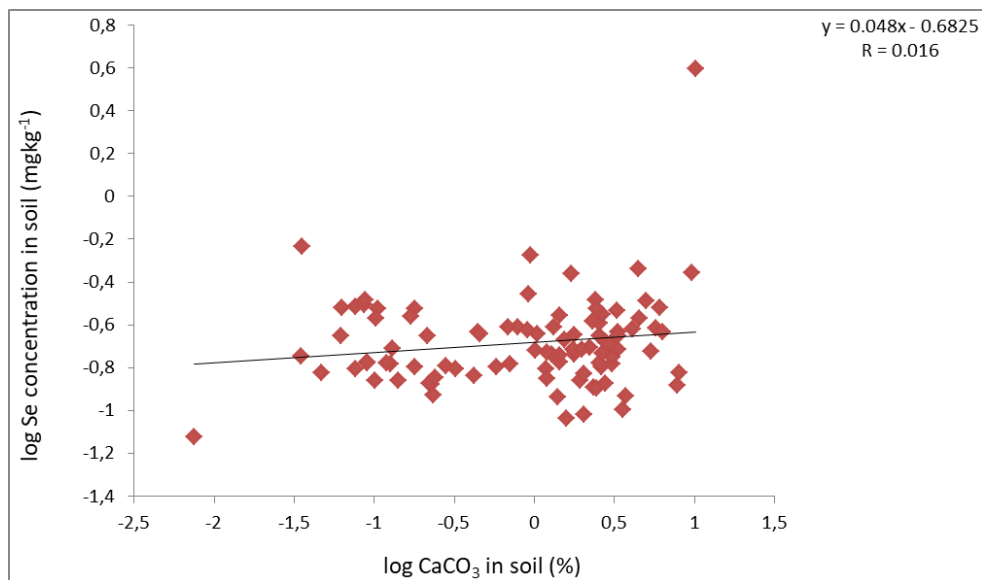


Figure 17. Selenium (Se) concentrations in soils as a function of CaCO₃ in soils (n=96).

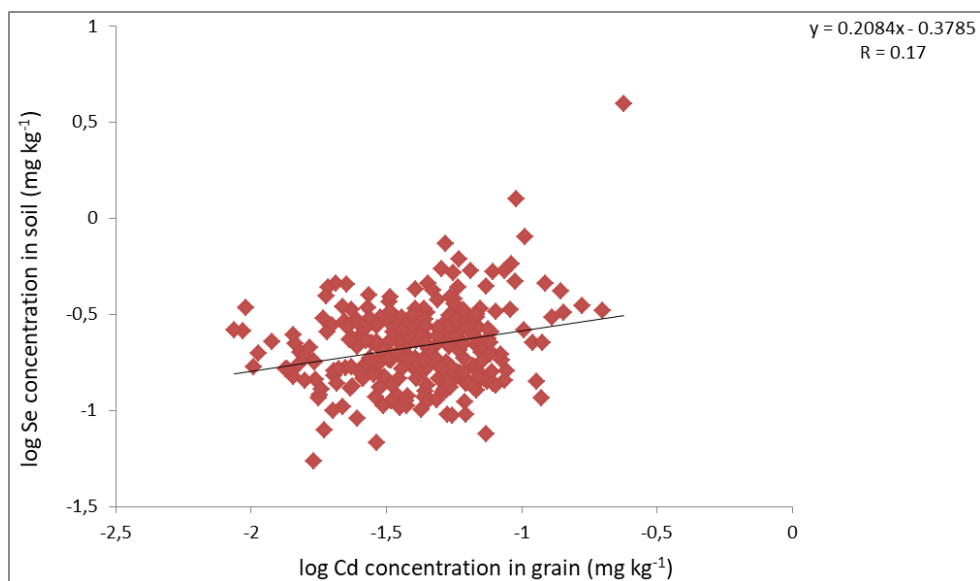


Figure 18. Selenium (Se) concentrations in soils as a function of the cadmium (Cd) concentrations in soils (n=287).

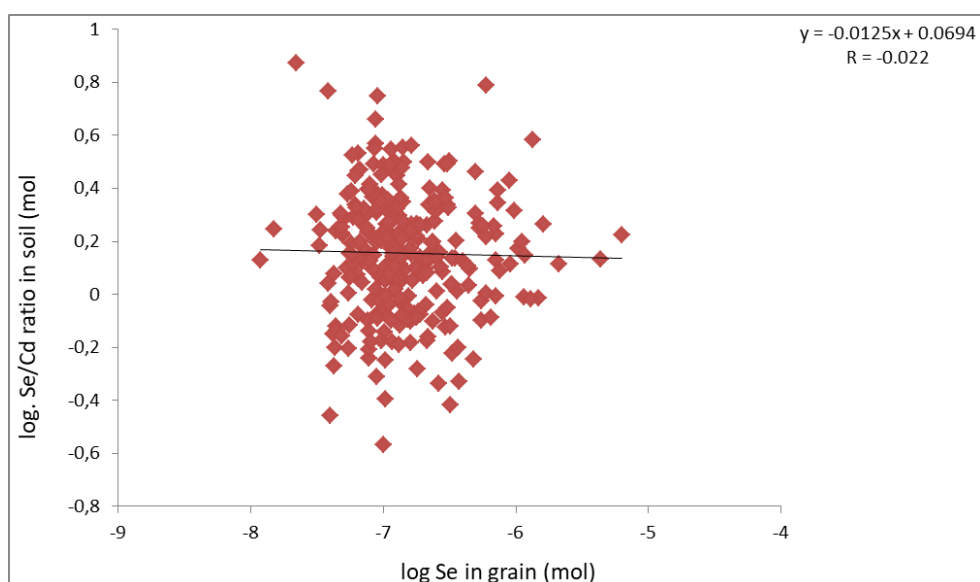


Figure 19. Se/Cd ratio (mol) in the soil as a function of selenium (Se) substance amount in the grains (n=285).

Grain

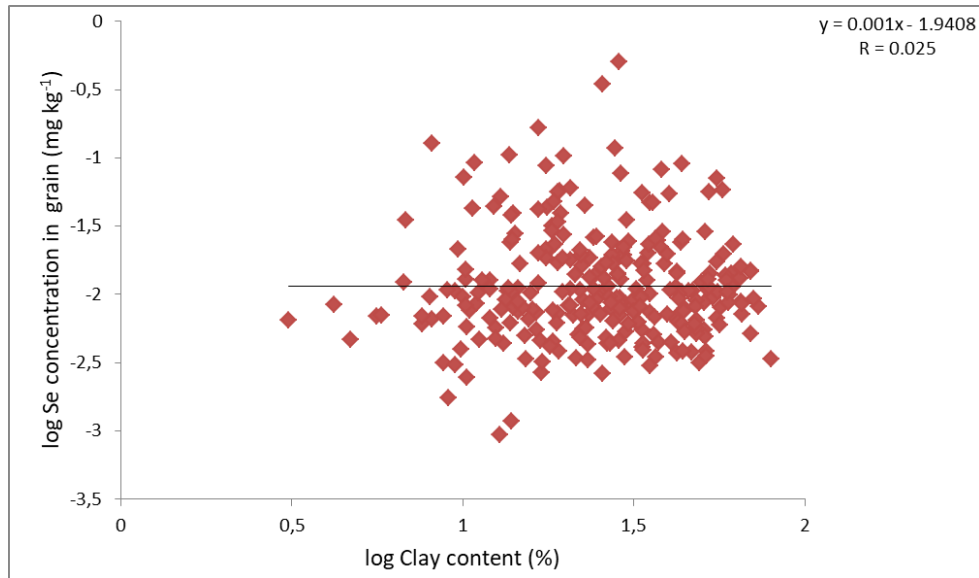


Figure 20. Selenium (Se) concentrations in grains as a function of the clay content in soils (n=284).

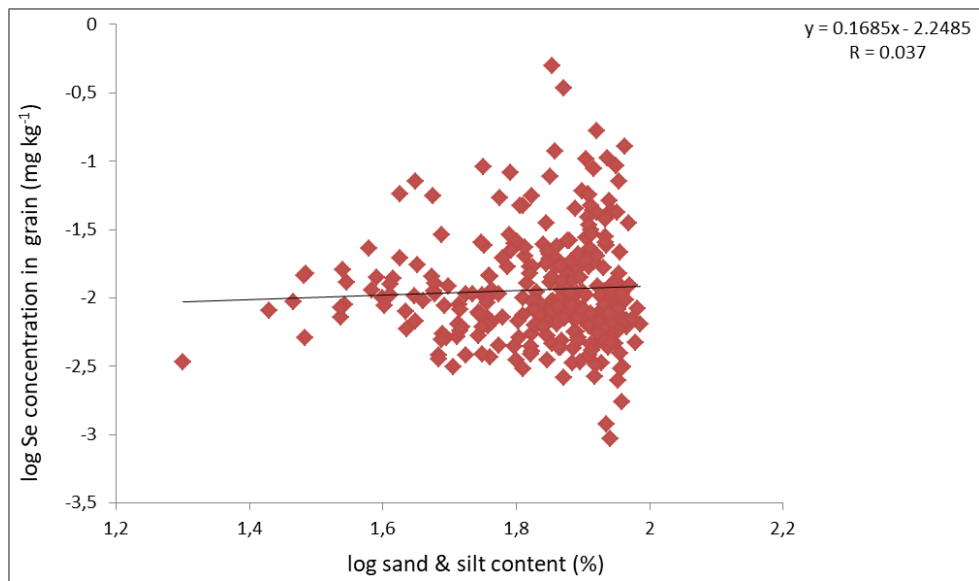


Figure 21. Selenium (Se) concentrations in grains as a function of the sand and silt content in soils (n=284).

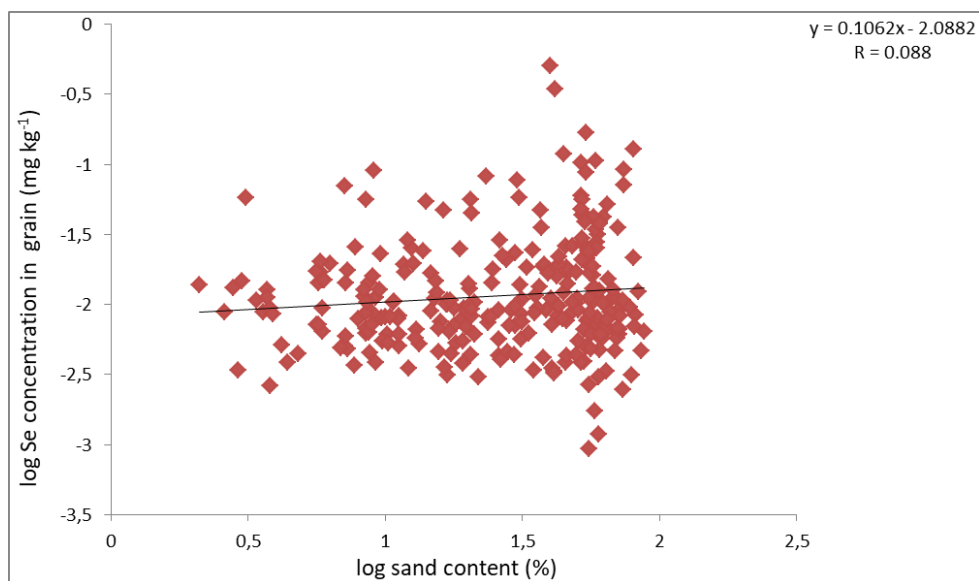


Figure 22. Selenium (Se) concentrations in grains as a function of the sand content in soils (n=284).

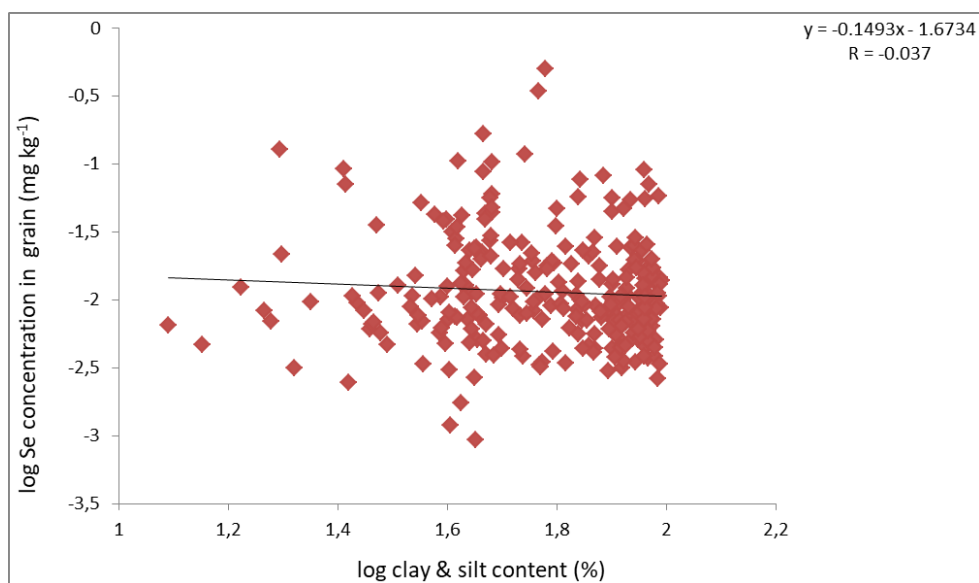


Figure 23. Selenium (Se) concentrations in grains as a function of the clay and silt content in soils (n=284).

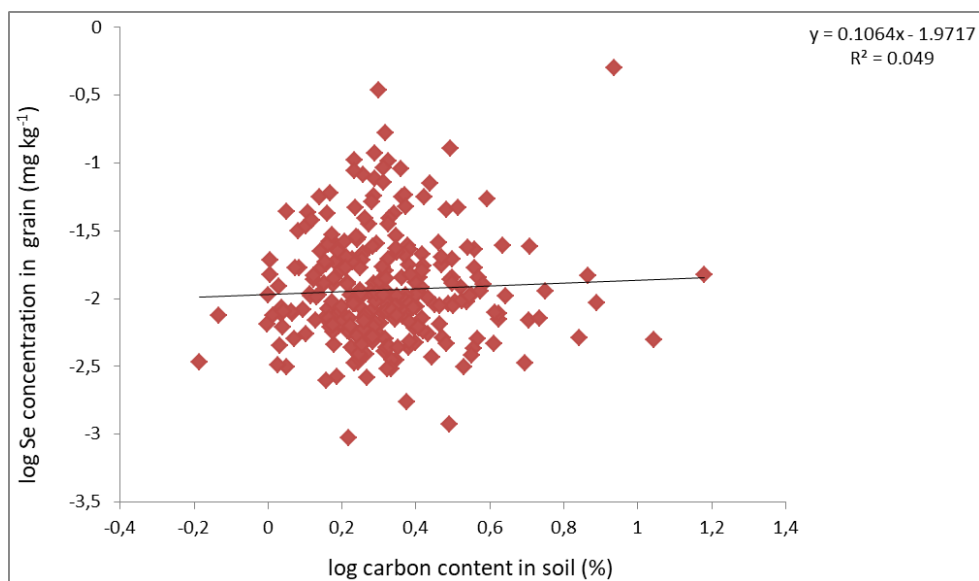


Figure 24. Selenium (Se) concentrations in grains as a function of the carbon content in soils (n=285).

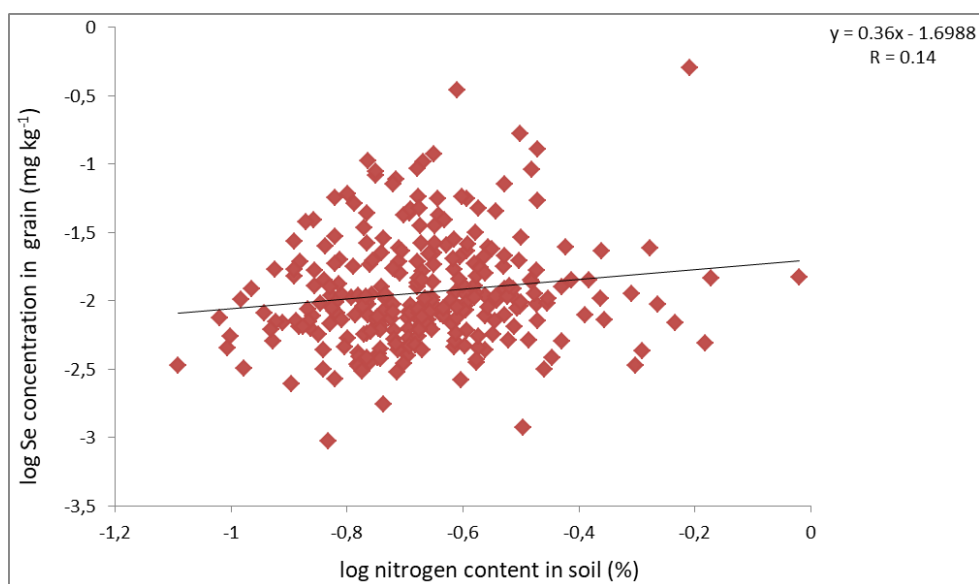


Figure 25. Selenium (Se) concentrations in grains as a function of the nitrogen content in soils (n=285).

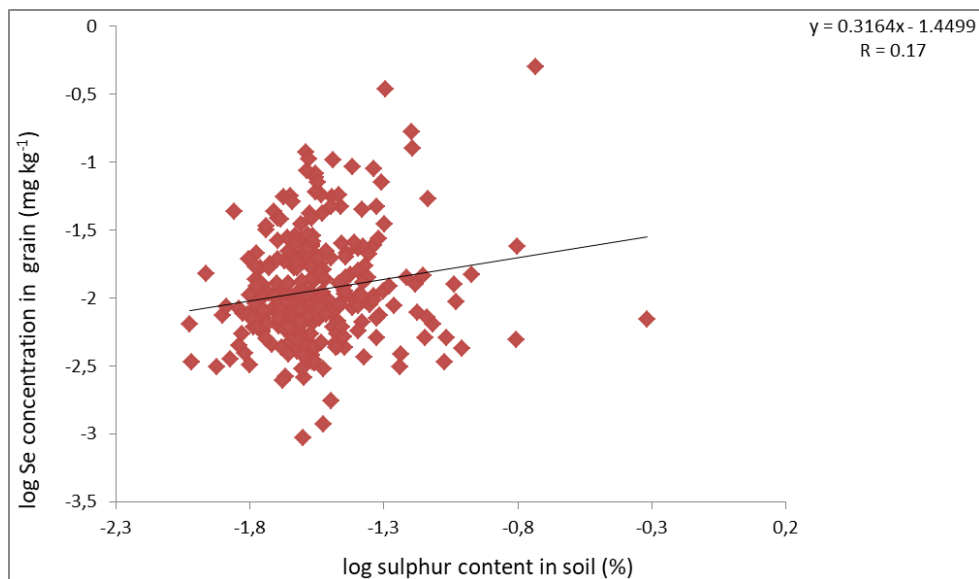


Figure 26. Selenium (Se) concentrations in grains as a function of the sulphur content in soils (n=285).

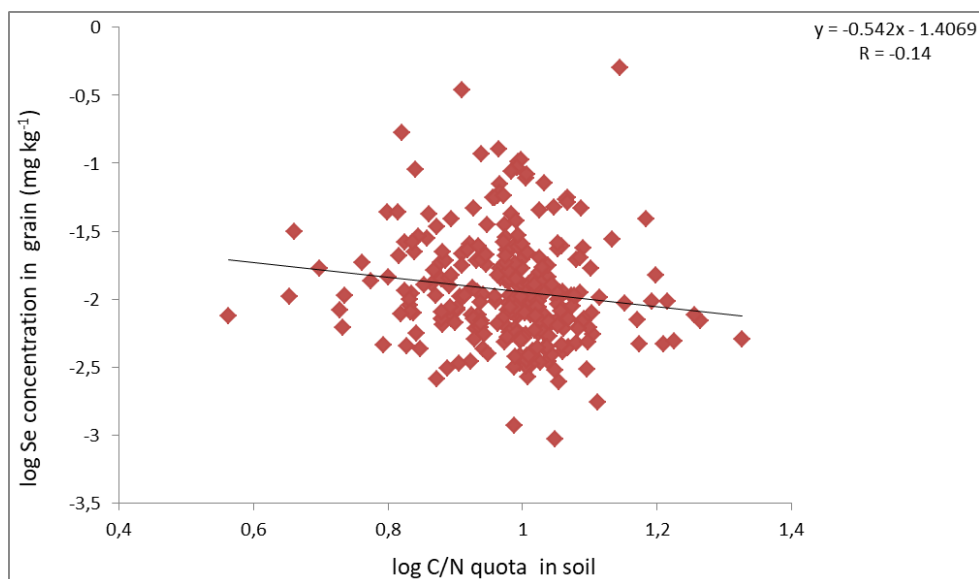


Figure 27. Selenium (Se) concentrations in grains as a function of the C/N ratio in soils (n=285).

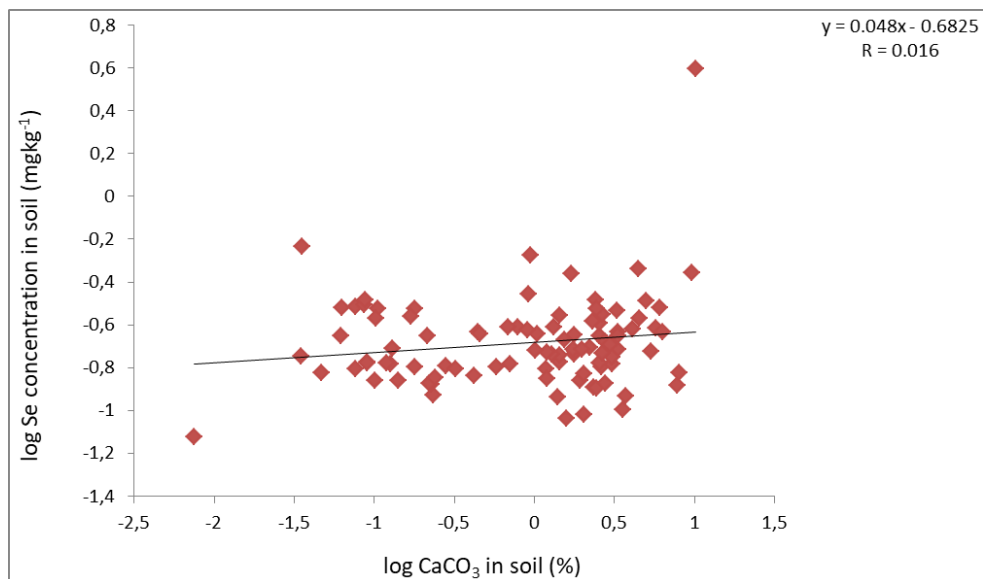


Figure 28. Selenium (Se) concentrations in grains as a function of the CaCO₃ content in soils (n=95).

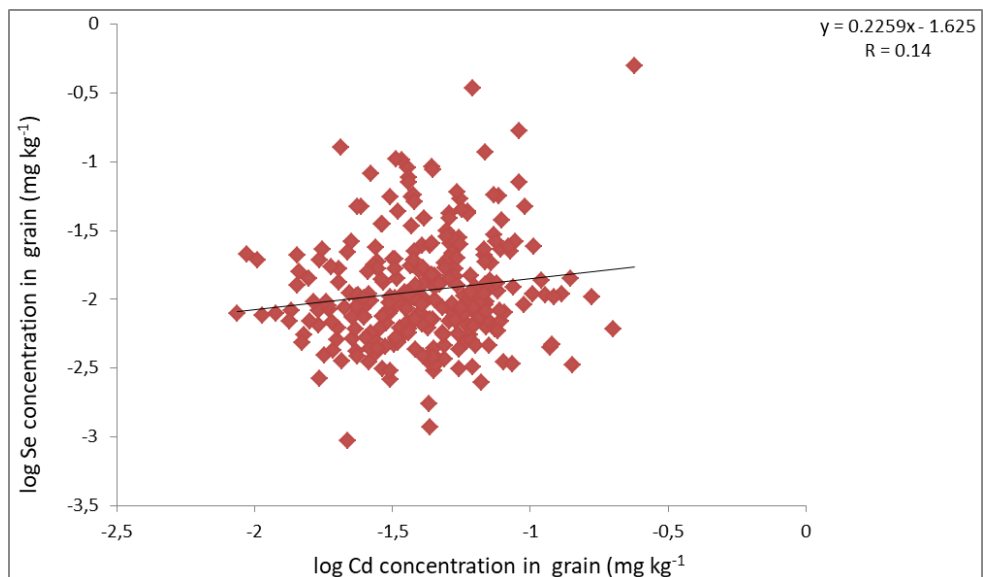


Figure 29. Selenium (Se) concentrations in grains as a function of the cadmium (Cd) concentrations in grains (n=285).

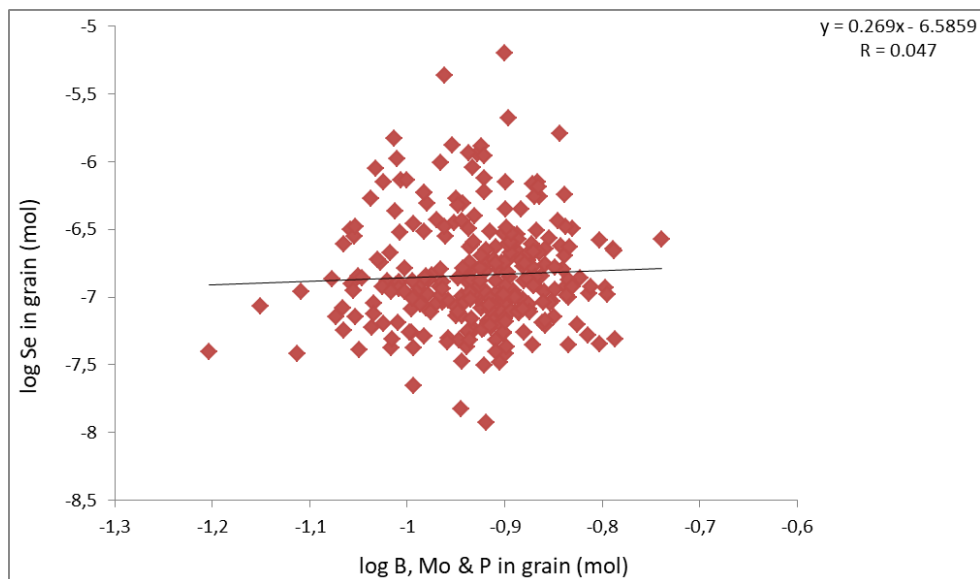


Figure 30. Selenium (Se) substance amount in grains as a function of the substance amount of boron (B), molybdenum (Mo) and phosphorus (P) in grains (n=285).

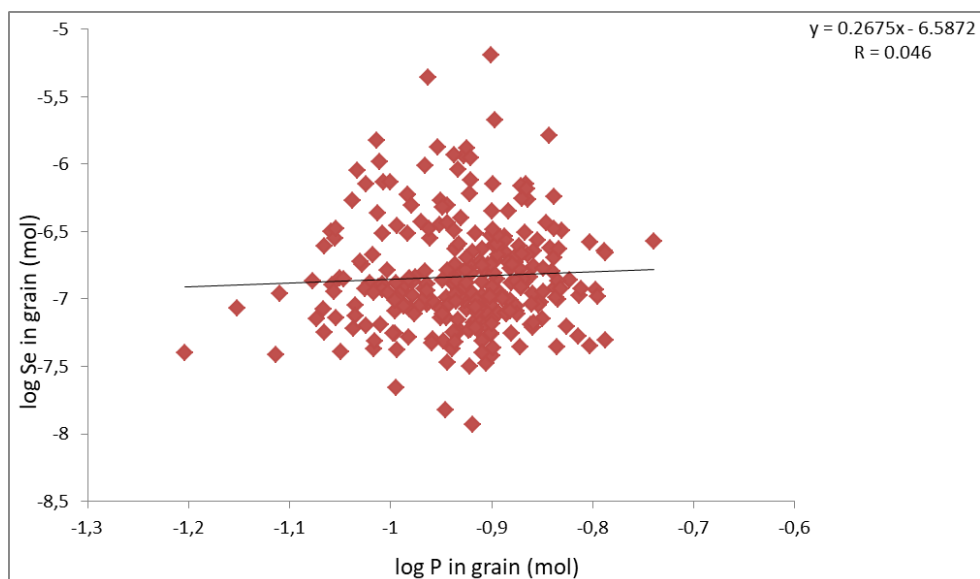


Figure 31. Selenium (Se) substance amount in grains as a function of the substance amount of phosphorus (P) in grains (n=285).

Calculations (Se-fortification scenarios)

Scenario 1: Fertilization of all cereal crops in Sweden

Assumptions:

- Se concentrations in all cereal crops are fairly similar.
- Intake of Se from cereal products are increasing proportionally with increasing Se concentrations in the grain.
- Mean intake of Se among adults in Sweden is 46 $\mu\text{g}/\text{day}$ (National Food Administration, 2012).
- Adequate intake is 70 $\mu\text{g Se}/\text{day}$ (EFSA, 2017)
- $70 - 46 = 24 \mu\text{g Se}/\text{day}$ missing.
- 16% of the daily Se intake comes from Cereals (National Food Administration, 2012):
 $0.16 \times 46 = 7.36 \mu\text{g Se}/\text{day}$ from cereal products.
- $24 + 7.36 = 31.36 \mu\text{g Se}/\text{day}$ needed from cereal products.
- Needed increase of cereal grain Se concentrations: $\frac{31.36}{7.36} = 4.26 = 426\%$.
- Mean concentration Se in winter wheat grains = $0.02 \text{ mg}/\text{kg}$.
- Desired concentration: $0.02 \times 4.26 = 0.085 \text{ mg Se}/\text{kg}$.

Scenario 2: Fertilization of wheat crops in Sweden

Assumptions:

- Intake of Se from cereal products are increasing proportionally with increasing Se concentrations in the grain.
- Mean intake of cereals among adults in Sweden is 95.1 g/day. Of this, wheat products are responsible for 49.5 g/day, this means wheat products are 52% of the daily cereal intake (National Food Administration, 2012).
- Just multiply the daily intake from cereals with the percentage of daily wheat cereal intake:
 $7.36 \times 0.52 = 3.83 \mu\text{g Se}/\text{day}$ from wheat products
- $24 + 3.83 = 27.83 \mu\text{g Se}/\text{day}$ needed from wheat products.
- Needed increase of cereal grain Se concentrations: $\frac{27.83}{3.83} = 7.27 = 727\%$.
- Desired concentration: $0.02 \times 7.27 = 0.145 \text{ mg Se}/\text{kg}$.