

Selenium content of Belgian cultivated soils and its uptake by field crops and vegetables.

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Abstract

A series of 695 food crops were collected on 539 soils throughout Belgium. All samples were collected on commercial production fields, omitting private gardens. All crops were analyzed for their selenium (Se) concentration. The soils represent different soil types occurring in Belgium, with soil textures ranging from sand to silt loam, and including a few clay soils. They were analyzed for Se concentration, organic carbon content, cation exchange capacity and extractable sulphur (S) concentration. The Se concentrations in the soils were low (range 0.14-0.70 mg kg⁻¹ dw), but increasing soil Se concentrations were observed with increasing clay content. Stepwise multiple regressions were applied to determine relations between Se concentrations in crops and soil characteristics.

Among field crops, wheat is the most important accumulator of selenium but the concentration remains rather low on the Belgian low-Se soils. Based on dry weight, leafy vegetables contain more Se than wheat. The soil is the most important source of Se and the element is transported with the water stream to the leaves, where it is accumulated. Vegetables rich in S, e.g. some Brassica and Allium species, have a higher capacity to accumulate Se as it can replace S in the proteins, although this accumulation is still limited at low soil Se concentrations.

In loamy soils, weak correlations were found between the soil Se concentration and its concentration in wheat and potato. The uptake of Se increased with increasing pH. The Se concentrations in Belgian soils are far too low to generate a driving force on Se uptake. General climatic conditions such as temperature, air humidity and soil moisture are also important for the transfer of Se within the plant, and plant linked factors such as cultivar, growth stage and edible part are important as well, although their influence remains limited at low soil Se concentrations.

Keywords: selenium, soil uptake, field crops, vegetables, soil-plant regressions

1. Introduction

Selenium (Se) is an essential micronutrient for humans and animals. Besides its well-known protective action against oxidative stress in body tissues, Se also plays a role in the maintenance of defenses against infection, modulation of growth and development, and there is a reduction in cancer risk at supranutritional levels (Combs 2001). The main source of Se in the soil is the geological parent material. The crustal abundance of Se is low ($<0.05 \text{ mg kg}^{-1}$) (Kabata-Pendias and Pendias 1984). Selenium is found often manifold its crustal abundance in black organic-rich shales, coal, and to a lesser extent in petroleum. Seleniferous black shales are the parent material of the widespread seleniferous soils in the United States (Lakin 1973), in Wales and in Ireland (Davies and Houghton 2005). The geographical distribution of Se in soils is very uneven, ranging from almost zero to up to 1250 mg kg^{-1} in some seleniferous soils in Ireland (Oldfield 2002). Selenium concentrations are particularly high in soils derived from cretaceous shales in semi-arid and arid regions (Rosenfeld and Beath 1964 in Spadoni et al. 2007).

Selenium is associated with volcanic sulphur and has been found in volcanic sulphur deposits leading to high Se concentrations in soils of volcanic regions (Lakin 1973). The melting and boiling points of like forms of selenium and sulphur differ markedly and selenium is largely less volatile than sulphur. At ambient temperatures selenium dioxide is a solid and sulphur dioxide is a gas. This means that selenium dioxide is carried down by rain nearer to the source of emission than sulphur dioxide (Lakin 1973), and the impact of volcanic emissions is mainly of local importance. Burning of coal and petroleum are more important as sources of atmospheric selenium than volcanic activities. The quantity of deposition is, however, far too low to generate Se accumulation in the top soil, and a resulting increase of Se in plants is unlikely. Atmospheric

deposition of selenium species on crops is probably a direct source of selenium to crops. Indeed, there is a net input of airborne Se to herbage, even in remote areas but the inputs are generally low (Haygarth et al. 1991). Foliar application of selenite or selenate is able to enrich the Se status of plants (Kapolna et al. 2009). Soil applications of commercial fertilizers enriched with Se appear to be a safe method to increase the selenium uptake in low-Se soils (Hartikainen 2005). As the selenium concentration in atmospheric deposition remains rather low, the soil Se concentration is apparently the most important source of selenium in crops. In Belgium the soil Se-concentrations are moderately low with a reported concentration of only 0.11 mg kg^{-1} as an average value for the most representative agricultural soils (Robberecht et al. 1982). The concentration of Se in most soils lies within the range of 0.01 to 2 mg kg^{-1} (Kabata-Pendias and Pendias 1984). In uncultivated soils on Quaternary parent material, De Temmerman et al. (1984), found total selenium concentrations ranging 0.2 - 0.5 mg kg^{-1} in sandy and sandy-loam soils and 0.3 - 0.7 mg kg^{-1} in loam and polder clay soils. Excessive soil concentrations ($> 3 \text{ mg kg}^{-1}$) occur in areas of North America, China and Ireland,

The accumulation of selenium in plants is primarily depending on the availability of Se in soil. The availability of Se to plants is a function of the pH and the redox potential (Eh) of the soil as well as of the total Se content (Lakin 1973). Selenium can be present in soils under various forms, but mostly selenate or selenite. Selenate is the major species in well aerated, neutral to alkaline soils (Kabata-Pendias and Pendias 1984). As plants do not discriminate between sulphate and selenate, selenate is taken up and transported from the root to the shoot (Terry et al. 2000). Selenite is the major inorganic Se species in well-drained mineral soils with a pH from acidic to neutral (Li et al. 2008). It is still not sure whether there is an active or passive transport

into the root and the root-to-shoot transport for selenite is both lower and slower than for selenate (Terry et al. 2000; Zhu et al. 2009). In soils, selenite is less bioavailable than selenate because it is strongly absorbed by iron oxides and/or hydroxides (Barrow and Whelan, 1989). In acid soils (pH 4.5-6.5) Se is usually bound as a basic ferric selenite of extremely low solubility and it is essentially unavailable to plants. In alkaline soils (pH 7.5 – 8.5) Se may be oxidized to selenate ions and become water soluble. This form is readily available to plants (Lakin 1973). As such, bio-availability of soil borne Se is depending on the geochemical nature, pedoclimatic variables (temperature and rain intensity) and related to fluctuations of soil moisture and pH (Spadoni et al. 2007). Plant availability of Se decreases also at an increased content of organic matter, clay minerals and iron hydroxides (Gissel-Nielsen et al. 1984). In a pot experiment, Johnsson (1991) found that increasing the proportion of clay and peat in the soil substrate largely decreased selenium uptake for wheat and oilseed rape at pH 5 as well as at pH 7. The sulphur concentration in the soil also interacts with the Se-uptake as wheat grain Se concentrations could be predicted from soil Se concentration and soil extractable sulphur (Stroud et al. 2010). Adams et al. (2002) did not find correlations between grain selenium and grain sulphur concentrations in a national survey in the UK, but in a field experiment they found that at an increasing rate of sulphur addition, grain selenium concentrations were significantly decreased. Phosphate also competes with Se for plant uptake, although to a lower extent (Hopper and Parker 1999). In solution cultures, where the availability of sulphate and phosphate is larger than in soils, they found that sulphate-selenate antagonisms are stronger than phosphate-selenite antagonisms. Öborn et al. (1995) found a correlation between soil and plant selenium for potato, taking into account soil pH and organic matter, but not for wheat.

The aims of the present study were (a) to obtain insight into the Se concentrations in field crops and in vegetables grown on Belgian soils because of their contribution to the human Se intake, and (b) to determine whether there is a relation between Se concentrations in crops and Se concentrations in corresponding soils, taking into account other soil parameters such as pH, organic carbon and the extractable sulphur content. This study focused on the actual situation in the main production areas for food crops in Belgium. This means that besides normal agricultural practices, no other practices were applied for experimental purposes. Fertilizers enriched with selenium are not yet a common practice in Belgium and there was no extra liming in order to alter the uptake of Se. The Se concentrations in Belgian soils are representative for large parts of Europe and topical in dealing with the intake of Se by human populations.

2. Materials and methods

2.1 Soil and plant sampling

Plant and corresponding soil samples were taken on commercial fields for crops and vegetable production. Samples were collected all over Belgium covering the main agricultural and horticultural regions. Soil and plant sampling took place in the period 2001-2012. Soil samples of the plough layer were taken with a gouge auger (Eykelkamp) within the rooting zone of the sampled crops (25 cm). The soil samples were grouped in general soil texture classes according to a study of the Soil Service of Belgium (Vanongeval et al. 1992)

2.2 Sample preparation

The vegetable and crop samples were cleaned (removal of dirty, damaged and dead leaves) and separated from their non-edible parts following current kitchen practices. Wheat and other grains

were threshed, dried and analyzed after grinding in a hammer mill (Culatti AG). Root, tuber and bulb crops were cleaned (removal of soil and roots), washed and peeled. The fresh edible part was cut, homogenized and dried. Leafy vegetables were washed (3 times in tap water), cut, homogenized and dried. All the samples were dried in an oven at 70 °C, ground with a hammer mill (Culatti, AG) and again homogenized. Dry products were stored in polyethylene pots at room temperature. The results were recalculated on a fresh weight basis by using the dry weight of an unwashed subsample.

The soil samples were air dried and sieved (2 mm) to remove stones and plant materials.

2.3 Chemical analysis

2.3.1 Plants

Selenium analyses in plant material were performed in duplicate. Each batch of samples was accompanied by an appropriate standard reference material (SRM) to validate Se quantification. The reference samples used were NIST-1568a (rice flour) for cereals and potato, and NIST-1570a (spinach leaves) for the other vegetables (NIST, Gaithersburg, MD, USA). Amounts of 250 mg homogenized plant samples and 150 mg of CRM were microwave digested (MarsXpress, CEM, NC, USA) in PTFE tubes in presence of 8 ml of a mixture of HNO₃ (SpA grade, ROMIL Ltd, Cambridge, UK) - bi-distilled H₂O (1:1, v/v). Digested samples were appropriately diluted with bi-distilled water before ICP-MS analysis (Varian 820-MS, Mulgrave, AU). Hydrogen was used as reaction gas on the skimmer cone at a rate of 90 ml min⁻¹ to minimize ⁴⁰Ar based polyatomic interferences. Table 1 shows a summary of the ICP-MS parameters. Both ⁷⁷Se and ⁷⁸Se isotopes were measured. In NIST 1570a and in most vegetables,

however, ^{78}Se values were systematically higher than ^{77}Se values and tended to be overestimated, possibly due to a remaining influence of the $^{38}\text{Ar}^{40}\text{Ca}$ interference at these low Se concentrations or to ^{77}Se hydride formation. All plant data are therefore only based on ^{77}Se results. The limit of quantification of Se was calculated as six times the standard deviation of 20 procedure blanks, and was equal to $0.12\ \mu\text{g L}^{-1}$ in the measurement solution.

2.3.2 Soils

Soil samples were extracted with HNO_3 (4 ml; SpA grade, ROMIL Ltd, Cambridge, UK) under reflux and selenium was determined with ICP-MS (Varian 820-MS, Mulgrave, AU), identically as for the plant analyses. Certified reference materials HISS-1 and MESS-2 (NRC, National Research Council Canada) were used for quality control of the soil Se data. The ^{77}Se and ^{78}Se isotopes were measured. In both reference materials and in all soil samples, however, ^{77}Se values were systematically higher than ^{78}Se values and tended to be overestimated likely due to matrix induced $^{40}\text{Ca}^{37}\text{Cl}$ interferences which can't be removed by use of H_2 gas (removal is thermodynamically impossible). All soil data are therefore only based on ^{78}Se results. Extractable S concentrations were determined using KH_2PO_4 (0.016 mM, pH 4.8) extractions (ratio 10 g air dry soil: 30 ml KH_2PO_4 w/v) (Zhao and McGrath 1994) and the concentrations of S were determined by ICP-AES (Varian 830 ES Mulgrave, AU). A standard soil analysis was carried out to determine the pH in a 1M KCl solution (with glass electrode) and the organic carbon content (%) by means of a modified Walkley and Black method (Jackson 1958). The cation exchange capacity (CEC) was measured by percolation of 150 ml 1 M NH_4OAc through a percolation tube filled with a mixture of 5 g soil and 35 g quartz sand, followed by washing through the excess with 300 mL denatured ethanol. The exchangeable ammonium ions were then

eluted with 500 mL 1 M KCl and analysed in the percolate by means of a steam distillation (Tecator Kjeltec System 1002 Distilling Unit).

2.3.3 Statistical analysis

Statistical analyses of soil and plant data were performed with UNISTAT Statistical package, Version 5.6 (UNISTAT Ltd, London, UK). The normal distribution of data was verified by the Kolmogorov-Smirnov test with Lilliefors correction. Data that were log-normally distributed were \log_{10} -transformed before further analysis. Soil Se concentrations were analyzed by one-way analysis of variance (ANOVA) followed by the Tukey HSD multiple range test ($\alpha = 0.05$). Basic statistics were calculated on untransformed data.

Soil-plant regression models were derived to determine the relation between Se concentrations in crops and soil characteristics (Se concentration in soil, pH, organic carbon content, extractable sulphur content). The regression model used is presented in the following equation:

$$\text{Log}_{10}(\text{Se-plant}) = a + b \cdot \text{pH} + c \cdot \text{Log}_{10}(\text{Se-soil}) + d \cdot \text{Log}_{10}(\text{organic carbon}) + f \cdot \text{Log}_{10}(\text{extractable S})$$

with Se-plant expressed in mg kg^{-1} on a fresh weight basis, Se-soil and extractable S expressed in mg kg^{-1} on an air-dry weight basis, and organic carbon expressed in percentage. A logarithmic transformation of data was necessary to obtain a normal distribution for some crops. The regression parameters were derived by stepwise multiple regression (UNISTAT 5.6; $\alpha = 0.05$ to enter a variable and $\alpha = 0.10$ to remove a variable).

3 Results and discussion

3.1 Se in Belgian agricultural soils

In total 539 agricultural soils were sampled all over Belgium. The major agricultural areas in Belgium mainly developed on Quaternary parent material. Only a limited number of soils were sampled on other parent materials in the south of Belgium. Table 2 summarizes the total Se concentrations measured in agricultural soils. The concentrations are in agreement with the ranges of total selenium found earlier in uncultivated Belgian soils: 0.2 - 0.5 mg kg⁻¹ in sandy and sandy-loam soils and 0.3 - 0.7 mg kg⁻¹ in loam and polder clay soils (De Temmerman et al. 1984). The average concentrations are, however, higher than the average concentration of 0.11 mg kg⁻¹ (range 0.04-0.27 mg kg⁻¹) in 10 Belgian soils with textures ranging from sand to clay, as determined by Robberecht et al. (1982). The Se concentration furthermore increases significantly with increasing clay content (Table 2).

The total Se concentrations in UK soils range between 0.1 and 4 mg kg⁻¹ with 95 % of the samples containing < 1.0 mg kg⁻¹ (Broadley et al. 2006). A low Se level in soils is a rather general phenomenon in Europe. In Italy several Se-marginal and Se-deficient areas were identified based on Se concentrations in wheat grain (Spadoni et al. 2007). The large majority of the Belgian agricultural soils can be considered as low in selenium.

3.2 Se in crops

Among important food crops, wheat appears to be an important source of selenium due to the high consumption of wheat derived products (Waegeneers et al. 2013). However, based on dry weight, the concentrations are only half as high as those for e.g. leafy vegetables (Table 3 and 4). Moreover, wheat and more precisely durum wheat (Triticum turgidum var. durum), used for

many applications such as for pasta, has probably a potential to accumulate Se and as such it could accumulate much higher concentrations if cultivated on soils with a higher Se-concentration than those generally found in Europe (Cubadda et al. 2010). Wheat Se concentrations range from $<20 \mu\text{g kg}^{-1}$ in Se-deficient areas up to $30000 \mu\text{g kg}^{-1}$ in seleniferous regions (Cubadda et al. 2010). As shown in Table 3, our results are at the lower end of that range which is typical for soils with low Se concentrations in Europe. The results for the spelt samples (Triticum spelta) are similar to wheat (mean $40\text{-}50 \mu\text{g kg}^{-1}_{\text{fw}}$). On the contrary, the average Se concentration in the edible parts of potato (Solanum tuberosum), $6 \mu\text{g kg}^{-1}_{\text{fw}}$, is much lower than in wheat, even on a dry weight basis (30 versus $50 \mu\text{g kg}^{-1}_{\text{dw}}$). The fresh weight concentrations in potato are in agreement with those reported in Portugal (3 to $4 \mu\text{g kg}^{-1}_{\text{fw}}$; Ventura et al. 2009) but they are lower than those from Croatia ($9.5 \mu\text{g kg}^{-1}_{\text{fw}}$; Klapac et al. 2004) and higher than those for Slovenia ($1.5 \mu\text{g kg}^{-1}_{\text{fw}}$; Smrkolj 2005). Carrot (Daucus carota), celeriac (Apium graveolens) and black salsify (Scorzonera hispanica) have concentrations that are similar to or slightly lower than those of potato ($3\text{-}6 \mu\text{g kg}^{-1}_{\text{fw}}$), while radish (Raphanus sativus) and Fennel (Foeniculum vulgare) have much lower concentrations ($< 1 \mu\text{g kg}^{-1}_{\text{fw}}$). The carrot data are in agreement with those from Portugal ($3 \mu\text{g kg}^{-1}_{\text{fw}}$; Ventura et al. 2009) but lower than those from Croatia ($20 \mu\text{g kg}^{-1}_{\text{fw}}$; Klapac et al. 2004). The distribution pattern in the plants follows the pattern that is generally observed for elements taken up by the roots and transported with the water stream. Plant parts evaporating large amounts of water have a higher Se concentration when expressed on a dry matter content. The Se concentrations in the corresponding soils are rather low. As the differences in soil concentrations are small among the different crops, it can be concluded that, in this survey, the total soil Se concentration is not the main driving force to create differences in Se concentration in the edible parts of crops. If there are differences, they are linked to the plant

species, to the plant part used for consumption i.e. seeds versus roots or tubers or leaves, and to several other parameters (cultivars, fertilization, climatic parameters, soil drainage, etc.).

Among leafy vegetables, spinach (Spinacia oleracea), celery (Apium graveolens) and celeriac (Apium graveolens var. rapaceum) (mean Se concentrations: 12-27 $\mu\text{g kg}^{-1}_{\text{fw}}$) tend to accumulate more Se than parsley (Petroselinum crispum), endive (Cichorium endivia), Belgian endive (Cichorium intybus var. foliosum), chard (Beta vulgaris subsp. cicla), lamb's lettuce (Valerianella locusta) and lettuce (Lactuca sativa) (mean < 10 $\mu\text{g kg}^{-1}_{\text{fw}}$), although there is only a significant difference between Belgian endive (mean 4.2 $\mu\text{g kg}^{-1}_{\text{fw}}$) and celeriac leaves (27 $\mu\text{g kg}^{-1}_{\text{fw}}$). On a dry weight basis Se concentrations are higher in leafy vegetables (> 60 $\mu\text{g kg}^{-1}_{\text{dw}}$) than in grains, bulbs and roots ($\leq 50 \mu\text{g kg}^{-1}_{\text{dw}}$). This indicates that Se is primarily taken up by the roots and transported to the leaves where the water is evaporated and Se remains in the leaves. As the soil concentration is rather similar for all leafy vegetables, the differences between the crops can be explained by plant specific differences in uptake and accumulation.

Selenium concentrations in vegetable fruits (Table 5) such as zucchini (Cucurbita pepo), pumpkin (Cucurbita maxima), cucumber (Cucumis sativus), tomato (Solanum lycopersicum), red pepper (Capsicum annuum) and bean (Phaseolus vulgaris) are low and similar to each other on a fresh weight basis ($\sim 2 \mu\text{g kg}^{-1}_{\text{fw}}$). The Se concentration in tomato corresponds with Greek data (2.3 $\mu\text{g kg}^{-1}_{\text{fw}}$; Pappa et al. 2006).

Allium species such as leek (Allium porrum), onion (Allium cepa), shallot (Allium ascalonicum) and garlic (Allium sativum) are known to be able to accumulate high levels of Se (Yadav et al. 2007). From Table 6 it can be concluded that Allium bulbs have slightly higher Se concentrations than vegetable fruits (5-10 $\mu\text{g kg}^{-1}_{\text{fw}}$ versus 2 $\mu\text{g kg}^{-1}_{\text{fw}}$) but these concentrations are not high at all. These results demonstrate that even crops that are known to be able to

accumulate Se to a higher extent because of their higher sulphur concentration compared to other crops, are not able to do that on low-Se soils. The results obtained are of the same order of magnitude than those of garlic and onion from Greece (14 and 7 $\mu\text{g kg}^{-1}_{\text{fw}}$ respectively; Pappa et al. 2006) but lower than those from Croatia (34 and 15 $\mu\text{g kg}^{-1}_{\text{fw}}$ respectively; Klapac et al. 2004).

Cabbages (*Brassica oleracea*) such as white and red cabbage (var. Capitata), savoy cabbage (var. Bulatta), Brussels sprouts (var. Gemmifera), green cabbage (var. Sabellica), cauliflower (var. Botrytis) and broccoli (var. Italica) also have the potential to accumulate Se to a higher extent, as they also accumulate a lot of sulphur for their development and plants do not discriminate between sulphur and selenium (Kabata-Pendias and Pendias, 1984). Kohlrabi (var. Gongylodes) and turnip (*Brassica napus* var. Napus) belong to the same family but they tended to accumulate less Se in their storage organ. From Table 7 it can be concluded that, depending on the soil conditions, *Brassica* species are able to reach relatively high concentrations on soils even with rather low Se concentrations. The results for broccoli (mean 18 $\mu\text{g kg}^{-1}_{\text{fw}}$) are in agreement with those from Portugal (10 $\mu\text{g kg}^{-1}_{\text{fw}}$; Ventura et al. 2009) but the Se concentrations in cabbages are much higher in Croatia (Klapac et al. 2004) (66 versus 10 $\mu\text{g kg}^{-1}_{\text{fw}}$).

3.3 Soil-plant relationship

Soil data for some major crops are presented in Table 8. Due to the very limited variability of Se concentrations in the soils sampled, it is not easy to find relations between Se concentrations in the soils and in crops. Other soil characteristics such as pH, the extractable sulphur content and the organic carbon content, were able to explain part of the variation in Se concentrations

observed in wheat, potato, carrot and celeriac even though the relations were weak for all these crops (Table 9). No significant relations between the soil characteristics and crop Se concentrations could be found for salsify, leek, brassica species and leafy vegetables. The variability in soil Se and in pH could be enlarged by an experimental design including fertilizing with selenite and liming. From that kind of studies it is easier to find relations between Se in crops and soil characteristics than in the current survey. It was, however, our aim to study the actual non-modified crop production as these data are representative for the current human Se intake and used for a dietary intake study (Waegeneers et al. 2013).

Soil pH is a recurrent soil characteristic that significantly affects the crop Se concentration. The impact of pH can, however, not be seen for all crops as Se uptake mainly increases at elevated pH values. Crops such as wheat and potato are primarily cultivated on heavier soils with a higher pH value. Vegetables are mostly cultivated on sandy-loam or sandy soils and such soils are in general more acidic. Liming is a normal practice but even then the optimal pH in sandy soils is still acidic. Chilimba et al. (2011) found a strong correlation between Se in maize grain and soil pH at $\text{pH}_{\text{H}_2\text{O}} > 6.5$, especially on calcareous Eutric Vertisols, but there was only a weak correlation in more acidic soils. Although the majority of the soils for wheat grain production in the current study are within a similar pH range, the pH effect was less pronounced, indicating the importance of not only pH but also mineralogy. The extractable S content in the soil significantly affected the Se content in wheat and carrot, while the soil Se content significantly affected the Se content in wheat and potato when grown on silt-loam soils, and in celeriac. Fan et al. (2008) found a negative correlation between the increase of soil Se concentration and Se in wheat grain over the last 160 years. The uptake was influenced by S inputs from fertilizers and atmospheric

deposition and the competition in uptake of both elements. The organic carbon content only affected the Se content in carrot.

Based on 10 field sites, Stroud et al. (2010), found a highly significant relation between the Se concentration in wheat grain, the total Se concentration in the soil and the extractable S concentration in the soil, explaining 70.5% of the variance in grain Se concentration. The inclusion of extractable Se even improved the relation ($R^2_{\text{adj}} = 0.86$). Extractable Se was not measured in the current study. The pH was not a significant parameter in the study of Stroud et al. (2010), but this might be due to the limited variation in soil pH between the experimental fields, as 9 out of 10 sites had a near-neutral pH.

Interactions with major and trace elements in the soil (Fe, Al, and Mn oxides and hydroxides) are also important for the uptake by the plant (Čuvarđić 2003). Plant linked factors such as species, cultivar, growth stage and edible plant parts are most likely very important but their influence is also limited by the relatively low soil concentrations. The general climatic conditions such as temperature, air humidity and soil moisture are of prime importance for the transfer of Se within the plant. Indeed, climate affects water availability in soils, controls redox conditions, influences the amount of organic matter content by regulating oxidation processes and is correlated with the atmospheric wet deposition of Se through the rainfall (Spadoni et al., 2007). A combination of all these parameters probably determines the Se concentration in crops cultivated in Belgium.

4 Conclusions

Based on literature data, worldwide observations show that a clear relation is observed between Se concentrations in the soils and the accumulation of this element in plants. In Belgium and in

large parts of Europe the Se concentrations in the soils are rather low, which generally leads to low crop Se concentrations. In the present study some weak relations were found between soil Se concentrations and its accumulation in crops (e.g. wheat and potato). Primarily in the heavier soil types (silt loam) such a relation could be found, but not in the sandy soil types. The most important parameter in Belgian soils is the pH, as the uptake of Se increases at higher pH levels (neutral and even alkaline soils). The calculated mean dietary Se intake by the general population in Belgium is sufficient but at the lower end of recommended values, which means that several groups of consumers have a too low Se intake due to the rather low Se concentrations in food from plant origin. From this study it can be concluded that the Se concentration in the soil and the pH of the soil are key parameters for the uptake of Se in Belgian food crops. As it is not easy to increase the pH of sandy soils extensively, fertilizers enriched with Se could be an option to increase crop selenium concentrations.

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Table 1: Summary of the parameters of the ICP-MS system used during selenium analysis.

ICP-MS instrument	VARIAN 820
Forward power	1.45 kW
Nebulizer gas flow	0.99 l min ⁻¹
Cool gas (plasma gas)	17 l min ⁻¹
Auxiliary gas	1.8 l min ⁻¹
Sheath gas	0.20 l min ⁻¹
Reaction gas	H ₂ 90 l min ⁻¹
Sample introduction	Micromist low flow nebulizer
Channel monitored	77 and 78

Table 2: Total selenium concentration in Belgian agricultural soils (n = 539) as a function of soil texture. The Se concentrations are expressed in mg kg⁻¹ air dried soil.

Soil type	n	Average	Median	Range
sand - loamy sand	93	0.25 ^a	0.25	0.14 – 0.40
sandy loam	145	0.27 ^b	0.26	0.17 – 0.45
silt loam	297	0.35 ^c	0.34	0.18 – 0.70
clay	4	0.46	0.46	0.29 – 0.61

Different superscripts indicate significant differences in Se concentrations at $p < 0.05$ following Tukeys HSD multiple range test on log-transformed data. The data were retransformed into natural numbers. The Se concentrations in clay soils were not included in the multiple range testing because of their low number (n = 4).

Table 3: Selenium concentrations in the edible parts of food crops, root- and tuber vegetables, and in the corresponding soils.

Crop	n	Crops (edible part) $\mu\text{g kg}^{-1}$				Soils mg kg^{-1}		
		average $\mu\text{g kg}^{-1}$		median	range	average	median	range
		DW	FW	FW	FW	DW	DW	DW
Wheat	182	54.8	48.7*	42.9	3.5-303	0.33	0.30	0.17-0.70
Spelt	5	40.9	37.0*	34.1	17.8-51.2	0.25	0.20	0.18-0.35
Potato	80	28.4	5.8	5.4	0.98-14.7	0.31	0.31	0.21-0.53
Carrot	121	43.4	3.1	2.5	0.5-14.6	0.28	0.28	0.16-0.45
Celeriac	18	43.0	3.5	3.2	1.3-6.2	0.31	0.30	0.21-0.41
Salsify	54	32.4	6.0	4.3	0.9-54.7	0.25	0.23	0.14-0.40
Radish	1	18.0	0.87			0.39		
Fennel	1	22.2	0.97			0.25		

* On whole weight basis.

Table 4: Selenium concentrations in the edible parts of leafy vegetables and in the corresponding soils.

Leafy vegetables	n	Crops (edible part) $\mu\text{g kg}^{-1}$				Soils mg kg^{-1}		
		Average		median	range	average	median	range
		DW	FW	FW	FW	DW	DW	DW
Lettuce	4	101	5.8	4.0	3.7-11.7	0.28	0.27	0.21-0.38
Spinach	2	169	12.4	12.4	9.2-15.7	0.30	0.30	0.26-0.34
Celery	7	106	14.8	8.4	6.0-40.4	0.31	0.30	0.21-0.39
Celeriac leaves	6	168	27.0	27.5	9.4-49.0	0.29	0.30	0.21-0.36
Parsley	3	63	7.2	6.3	4.4-10.9	0.30	0.26	0.26-0.39
Endive	4	76	4.4	3.7	2.5-7.9	0.32	0.34	0.22-0.38
Belgian endive	5	62	4.2	3.1	0.9-12.1			
Chard	4	72	7.3	6.2	3.5-13.4	0.37	0.38	0.33-0.40
Lamb's lettuce	1	42	3.8					

Table 5: Selenium concentrations in the edible parts of vegetable fruits and in the corresponding soils.

	n	Crops (edible part) $\mu\text{g kg}^{-1}$				Soils mg kg^{-1}		
		Average		median	range	average	median	range
		DW	FW	FW	FW	DW	DW	DW
Zucchini	4	52.9	1.7	1.8	0.8-2.3	0.32	0.35	0.22-0.37
Pumpkin	3	11.9	1.3	0.5	0.3-3.1	0.29	0.30	0.20-0.37
Cucumber	1	72.2	1.8			0.37		
Tomato	1	36.2	1.8			0.37		
Red pepper	1	20.7	1.1			0.37		
Green bean	3	19.6	2.0	1.8	1.2-3.1	0.32	0.32	0.20-0.43

Table 6: Selenium concentrations in the edible parts of allium species and in the corresponding soils.

	n	Crops (edible part) $\mu\text{g kg}^{-1}$				Soils mg kg^{-1}		
		Average		median	range	average	median	range
		DW	FW	FW	FW	DW	DW	DW
Leek	25	82.9	8.2	7.4	2.6-33.8	0.31	0.32	0.23-0.39
Onion	6	40.9	5.4	5.1	1.9-8.3	0.33	0.31	0.30-0.39
Shallot	1	41.0	6.3			0.34		
Garlic	1	27.1	10.5					

Table 7: Selenium concentrations in the edible parts of Brassica species and in the corresponding soils.

	n	Crops (edible part) $\mu\text{g kg}^{-1}$				Soils mg kg^{-1}		
		Average		median	range	average	median	range
		DW	FW	FW	FW	DW	DW	DW
White cabbage	6	85	7.2	7.0	1.7-14.2	0.32	0.31	0.26-0.38
Red cabbage	3	91	8.5	5.5	5.4-14.4	0.33	0.32	0.30-0.38
Savoy cabbage	3	104	11.7	10.4	6.5-18.3	0.33	0.32	0.30-0.38
Brussels sprouts	4	247	33.4	32.4	4.9-63.9	0.29	0.29	0.26-0.34
Green cabbage	1	46	6.0			0.33		
Cauliflower	3	102	8.2	3.6	2.6-18.5	0.27	0.28	0.22-0.32
Broccoli	4	129	17.3	17.8	7.1-26.5	0.31	0.31	0.26-0.37
Kohlrabi	2	37	1.8	1.8	1.4-2.3	0.34	0.34	0.31-0.38
Turnip	2	29.1	2.2	2.2	1.7-2.7	0.34	0.34	0.30-0.39

Table 8: Chemical soil characteristics, of the soils on which the crops were sampled (results are expressed on an air-dry weight basis).

Crop	Soil texture	n	Se mg kg ⁻¹	pH _{KCl}	% OC ^a	CEC ^b cmol ⁺ kg ⁻¹	Extr-S ^c mg kg ⁻¹
Wheat	Sandy	29	0.28	6.1	1.7	-	13.7
	loam		(0.17-0.38)	(4.6-7.0)	(1.2-2.9)		(8.8-21)
	Silt loam	149	0.33	6.2	1.8	-	12.9
			(0.17-0.70)	(4.0-7.4)	(1.1-5.4)		(6.2-43)
Potato	Sandy	14	0.25	6.3	1.5	-	25.5
	loam		(0.21-0.30)	(5.0-7.1)	(0.9-2.2)		(9.8-53)
	Silt loam	66	0.32	5.9	2.2	-	19.6
			(0.21-0.53)	(4.5-7.3)	(1.1-5.5)		(7.4-42)
Carrot	Sand-	30	0.25	5.4	2.4	-	27.1
	loamy-		(0.16-0.35)	(4.3-6.7)	(1.3-4.3)		(8.3-78)
	sand						
	Sandy	64	0.27	5.6	1.7	-	15.0
Salsify	loam		(0.18-0.44)	(4.3-6.6)	(0.3-3.8)		(6.2-62)
	Silt loam	34	0.34	6.1	2.0	-	15.8
			(0.18-0.45)	(4.6-7.6)	(1.1-4.2)		(5.6-49)
	Loamy	50	0.24	5.6	2.8	-	13.6
Celeriac	sand		(0.14-0.40)	(4.5-6.8)	(1.4-6.7)		(4.5-66)
	Sandy	8	0.27	5.6	2.3	-	19.0
	loam		(0.21-0.35)	(4.8-6.4)	(1.7-3.2)		(8.3-45)

Leek	Silt loam	9	0.35 (0.30-0.41)	6.1 (5.0-7.1)	4.2 (2.8-6.4)	-	24.0 (12.7-36)
		13	0.28 (0.23-0.37)	5.6 (5.1-6.2)	2.2 (1.1-3.7)	-	11.6 (7.2-22)
	Sandy loam	10	0.36 (0.30-0.39)	5.9 (4.8-7.2)	3.0 (1.2-4.0)	-	42 (9.6-91)
Brassica sp.	Sandy loam	13	0.28 (0.22-0.32)	6.2 (5-7)	3.0 (1.8-4.8)	10.8 (7.6-15)	33.3 (6.5-66)
	Silt loam	13	0.35 (0.29-0.38)	6.2 (5.7-6.9)	3.1 (1.8-5.9)	12.7 (7.9-17)	109 (15-388)
Leafy vegetables	Sandy loam	10	0.25 (0.21-0.35)	5.9 (5.1-6.5)	2.9 (2.1-4.1)	10.0 (7.0-15)	34.4 (8.3-84)
		18	0.35 (0.30-0.40)	6.0 (4.6-7.1)	3.0 (1.2-4.9)	13.4 (7.9-16)	50.3 (12.7-338)
	Silt loam	5	0.33 (0.30-0.39)	5.4 (5.0-6.0)	2.9 (1.9-4.9)	13.6 (10.1-17)	27.3 (12.6-52)
Onion	Silt loam						

^a OC is the organic carbon content; ^b CEC is the cation exchange capacity; ^c Extr-S is the extractable sulphur content.

Table 9: Regression parameters for significant Se soil-plant regression equations of the type

$$\text{Log}_{10}(\text{Se-plant}) = a + b \cdot \text{pH} + c \cdot \log_{10}(\text{Se-soil}) + d \cdot \log_{10}(\text{OC}) + f \cdot \log_{10}(\text{Extr-S}).$$

Crop	Soils	N	Intercept	pH	Se-soil	OC ^a	Extr-S ^b	R ² _{adj}	P
			a	b	c	d	f		
Wheat	All	182	-1.77	0.11	-	-	-0.27	0.09	< 0.001
	Silt-loam	149	-1.76	0.10	0.42	-	-0.27	0.13	< 0.001
Potato	All	80	-2.85	0.10	-	-	-	0.10	< 0.01
	Silt-loam	66	-0.78	0.11	-0.86	-	-	0.16	< 0.01
Carrot	All	121	-2.61	0.08	-	-0.31	-0.25	0.20	< 0.001
Celeriac	All	18	-3.63	-0.19	0.92	-	-	0.48	< 0.01

^a OC is the organic carbon content; ^b Extr-S is the extractable sulphur content.