

Selenium in soil–plant–food systems

F. Garousi

e-mail: farzaneh@agr.unideb.hu

University of Debrecen, Faculty of Agricultural and Food Sciences and
Environmental Management, Institute of Food Technology,
HU-4032 Debrecen, Böszörményi út 138., Hungary

Abstract. Humans and animals require a multitude of nutrients in order to have a properly functioning body for purposes of growth, development and metabolism. Plant-based foods have represented one of the most important nutrient sources in human diet since the beginning of mankind. But nowadays the amount of arable land is being reduced and much of the natural resources already in use show signs of degradation. Also, staple crops (i.e. plants that constitute the main food in the diets of people in developing countries, e.g. wheat, rice, maize, and cassava) regrettably contain low amounts of micronutrients, making them insufficient to meet the minimum daily requirements. Shortages in mineral micronutrients, including iron (Fe), zinc (Zn), selenium (Se), and iodine (I), are affecting more than half of the world's population. In this case, it is fundamental to improve strategies that let us make plant foods more efficient and with higher micronutrient amounts and bioavailability concerning their edible textures. In this regard, in this review paper, we tried to summarize selenium availability and its application in the soil, plant and food systems to understand the place of selenium in plant-based foods.

Keywords and phrases: selenium, soil–plant–food systems, mineral micronutrients, selenium cycling

1 History of selenium research

The first interest in Se related to its toxicity and the early work on Se was summarized by *Moxon & Rhian* in 1943, and Se research began in 1817. That year, Berzelius discovered this element and published his first detailed description about the research in 1818. He named the element Selenium. The history of Se research could be considered an attempt and it is made to take a “bird’s-eye” view at the development of this research field from 1817 till today (*Arnér*, 2012). The tool chosen is an analysis of the scientific literature on Se research, thereby attempting to give an unbiased assessment of this research field. Lastly, as in all investigations of historic trends, we should also ask where the future of Se research might take us. By necessity, the answer to that question is uncertain. However, it could be concluded that never before has Se research been as intense and expanding as it is today, which also holds major promises for the future (*Arnér*, 2012). Although as early as from 1842 a document was retrieved on the toxicity of Se, the first authentic written record of Se toxicity in livestock was apparently the report by Madison in 1856, who was a military surgeon stationed at Fort Randall, which was then in the Nebraska territory. He described a deadly disease among horses grazing in certain areas near the castle (*Whanger*, 2002). Many reviews have explained the development of Se research, and several findings have shaped today’s knowledge in the field, containing personal recollections by some of the pioneers of Se research. I could simply repeat information that have been given in previous reviews on the Se research field.

Hence, the reader is referred to other papers on the history of selenium research for debates on specific details or topics of that research (*Arnér*, 2012).

The first year covered by the ISI Web of Science database (1945) includes eight articles using the keyword selenium. These articles covered the topics of Se poisoning (three articles), Se amounts in soil, plants, or animals (two articles), or the photodynamic exclusivities of Se, its spectral virtues, or the oxidizing valence of dioxide of selenium (one article each). The subjects of those eight papers from 1945 that centred on the agricultural, physical, or chemical properties of Se are for the most part the very same subjects that have made “selenium” a much hotter topic in research than the issue of the more special “selenocysteine” or “selenoprotein” (*Arnér*, 2012).

With the industrial application of Se in ceramics, solar cells, glass, photocopyers, rectifiers, and many more and because of its properties as a catalyst in non-organic chemistry, a great number of research publications on Se are not related to biology or biochemistry at all (*Arnér*, 2012).

It somehow stands to reason to look back and discuss how the history of Se research has evolved. What results will the same analysis give if performed 10 years from now or in 50 or 200 years? Indeed, we cannot know how the future of selenium research will turn out, but we may be sure it will be an exciting one. With this topic of research presently being under quick development, it is clear that the potential of new Se-related discoveries of major importance awaits around the corner, as suggested by *Arnér* (2012).

2 The chemistry of selenium

Selenium is one of the rarest elements on the surface of earth (0.05 mg kg^{-1}), whereas it is the 69th among the 88 elements (*Shriver and Atkins*, 1999). Se is named the two-faced element (like the moon, where its name originates from) as it has both a dark and a bright side. It is also known as the “necessary poison or the double-edged blade element” based on its poisonous and beneficial effect on human health (*El-Ramady et al.*, 2014). As it is reported, this duality of Se comes from the way to reconcile its apparently inconsistent properties and roles. Nevertheless, these gaps in our knowledge of Se are rapidly being filled by great efforts of an extraordinary array of researchers, working in a range of disciplines, helped by powerful new research techniques and tools (*Reilly*, 2006). It is clear that Se has a 78.96 atomic weight and 34 as atomic number. It is chemically related to other members of the chalcogen group (Group 16/VIA), which includes oxygen (O), sulphur (S), tellurium (Te), and polonium (Po). Therefore, it is classified as a metal-like element, a “metalloid”, but elemental Se has several different allotropes (*Chapman et al.*, 2010). This puts Se in an important group of metalloids, elements that are neither completely metals nor non-metals but have chemical and physical properties of both (*Reilly*, 2006). This position accounts for many of its biological interactions with some main elements containing sulphur as well as with arsenic and its neighbour, phosphorus (*Frost*, 1972). As for the external electronic configuration of this element, it is $3d^{10} 4s^2 4p^4$, with three fully filled inside shells.

Selenium has four capacity states: -2 state, which predominates in organic Se composite besides 2, 4, and 6 states. There are nearly 50 Se minerals. The most important and relatively usual ones include: clausthalite (PbSe), klockmanite (CuSe), tiemannite (HgSe), berzelianite (Cu_2Se), crookesite (Cu , Tl , Ag) $_2\text{Se}$, and ferroselenite (FeSe_2) (*Kabata-Pendias*, 2011). Therefore, the union of this element with host minerals, such as chalcopyrite, pyrite, and

sphalerite, is relatively common. On the other hand, this element has a major dependency on different substances resulted in a large number of organic compounds that are analogous to those of S-organic compounds and are quickly accumulated in some biolithes (*Kabata-Pendias*, 2011). As mentioned before, the average content of Se in the Earth's crust is estimated at 0.05 mg kg^{-1} ; however, a higher amount (up to 0.5 mg kg^{-1}) is also given. This element is slightly more concentrated in mafic rocks (rarely trespasses 0.1 mg kg^{-1}), while Se is related to clay fractions, and thus, its abundance in argillaceous sediments ranged from 0.3 to 0.6 mg kg^{-1} in sedimentary rocks. This concentration is higher than in sandstones and limestones ($0.01\text{--}0.1 \text{ mg kg}^{-1}$).

On the other hand, due to the fact that Se contains some amino acids (SeMet and SeCys), it is a completely special trace element and therefore involved in very special biological roles. These main roles include conservation against oxidative injuries, defences against infection, and modulation of growth and improvement. Hence, the main exposure to Se occurs through the food chain, and its distribution in natural environments has a specific effect on its content in soils and crops and on human health (*Marmiroli and Maestri*, 2008). In agriculture, Se is used especially as sodium selenite (Na_2SeO_3) as a supplier to fertilizers, insecticides, and foliar sprays. In small doses, Se is widely used in vitamins, other dietary supplements, and some ruminant feeds (as a fortifying element). Moreover, it is a relatively usual component of different cosmetics and medications as a remedial agent (e.g. in cardiology as an antioxidant) (*Kabata-Pendias*, 2011).

2.1 Selenium on earth and selenium cycling

Se is rarely recovered in a free state and exists in different oxidation states with 6 (VI), 4 (IV), 0 (Se^0), and -2. The oxidized water-soluble forms that have selenate Se(VI) and selenite Se(IV) can be found in both natural water and soil solution (*Kabata-Pendias*, 2011). High stable elemental selenium (Se^0) can again be found in soils, but in aqueous solutions it is not same because it is insoluble (*El-Ramady et al.*, 2014). This elemental selenium (Se^0) can exist in distinct allotropic forms, including rhombohedra Se (containing Se_6 molecules), three deep-red monoclinic shapes, α -, β -, and γ -Se (containing Se_8 molecules), trigonal grey Se (containing Se_n helical chain polymers), black, vitreous Se, and amorphous red Se. The grey (trigonal) Se is thermodynamically the most stable form, which has countless helical chains of Se atoms, and it is the only allotropic form that conducts electricity (*El-Ramady et al.*, 2014). The most presumably amorphous allotrope forms that occur in soils involve

both red and black. Furthermore, red amorphous Se can gradually return to the black amorphous form at temperatures above 30 °C. This black form can then slowly transform into the much more stable grey hexagonal allotrope or, depending on the pH and redox conditions of the soil, it will be re-oxidized (*Di Gregorio*, 2008).

In various environments and due to different processes, selenium spreads e.g. through volcanic activities and hot springs, soil and rock weathering, inflammation of fossil fuels, soil leaching, sea salt spray, forest wildfires, groundwater motions, chemical and biological redox reactions, and mineral shaping, burning of municipal waste, Zn and Pb smelting, Cu/Ni, Fe and steel production, crop growth and irrigation practices, and plant and animal uptake and release (*Di Gregorio*, 2008). As a general law, Se concentration in soils or ground and fresh waters depends upon the source material, mapping, age of the soil, climate, and agricultural or industrial usage. Elemental Se and selenides are two prevailing species under acidic, reducing conditions in soils that are likely waterlogged and rich in organic matter (*Di Gregorio*, 2008; *El-Ramady et al.*, 2014).

2.2 Production, sources, and uses of selenium

At the global level, there are no mines that particularly extract Se; in contrast, it is a by-product of the production of other metals such as the refining of Pb and Cu or is recovered from the sludge accumulated in H₂SO₄ factories (*Johnson et al.*, 2010). The supply of Se is affected by the supply of the materials whose direct by-product it is – Cu, and, to a lesser extent, Ni. The estimated domestic Se production was slightly higher in 2012 in comparison with 2011 owing to a slight increase in Cu production (1,980 and 2,000 metric tons in 2011 and 2012 respectively; USGS, 2013). On a global level, Japan, Canada, and the USA produce great amounts of selenium, while smaller amounts are coming from Australia, Finland, Peru, Zambia, Belgium, Russia, China, and countries that have industry of Cu refining. Lots of Se compounds, such as cadmium sulfoselenide, ferro- and nickel selenide, selenium dioxide, and selenium diethyldithiocarbamate, are available commercially, as well as sodium selenate and sodium selenite (*El-Ramady et al.*, 2014).

Globally speaking, Se is continually recycled in the environment via the marine, atmospheric, and terrestrial systems. Estimates of Se flux specified that anthropogenic activity (76,000–88,000 tons per year) is a main source of Se release in the cycle, while the marine system (38,250 tons per year) offers the main natural pathway. Because of the rapidity of transport, Se

cycling via the atmosphere (15,300 tons per year) is considerable, but the terrestrial system (15,380 tons per year) is the most important in the case of human and animal health because of the direct relationship with the food chain and the agricultural processes. Although Se is a derivative of both natural and man-made sources, understanding the relationship between environmental geochemistry and health is of particular importance as rocks are the basic source of this element in agroecosystems (*El-Ramady et al.*, 2014).

There are several important agricultural and horticultural applications for Se. These applications involve the use of sodium selenite and selenate as additives and dietary complements in animal forages. Soil deficiencies could be supplemented by addition of Se compounds to fertilizers and top-dressings. On the other hand, in the 1930s, potassium ammonium sulfoselenide, which was used as a pesticidal substrate and was one of the first systemic insecticides to be regarded, became the centre of attention. This compound is still in use, but it is limited to non-food crops because of its poisonous character. In commercial greenhouses growing flowers for cutting, sodium selenate (Na_2SeO_4) was also used for similar purposes. This selenate (Na_2SeO_4) could be added to irrigation water, and the plant roots can take it up. Then, it is transformed in the leaves into volatile selenide (Se^{2-}), which is produced by the plant against aphids, to repel red spiders and similar pests (*El-Ramady et al.*, 2014).

3 Selenium in the soil–plant–food systems

It is clear that Se content in soils is inherited from source material and its distribution completely reflects soil-shaping processes and atmospheric deposition. Sandy soils, which developed under humid climate, especially in podzols, have the lowest amounts of Se, whereas the highest amounts are often to be found in organic and calcareous soils (*Kabata-Pendias*, 2011; *Ramady et al.*, 2014). Generally, the concentrations of Se in soils range from 0.05 to 1.5 mg kg⁻¹ worldwide, with a calculated average value of 0.44 mg kg⁻¹. However, we can also observe higher amounts of Se in the surface layer of volcanic soils, forest soils, organic rich soils, and calcareous soils. In general, the main factors controlling Se forms and behaviour in soils are Eh, or redox potential, and pH; however, a number of other parameters, such as organic ligands, clay content, and hydroxides, also play very significant roles (*Kabata-Pendias*, 2011; *Ramady et al.*, 2014). It has been reported about different inorganic species of Se, which were associated with defined soil parameters, that they reveal variable properties as follows: (1) selenates (mobile in inorganic forms

in neutral and alkaline soils but not absorbed on hydrous sesquioxides, especially $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), (2) selenites (slightly mobile in neutral and acid soils of humid temperate regions and are quickly absorbed on hydrous sesquioxides and organic matter), and (3) selenides (rather immobile in acid soils because of the formation of stable mineral and organic compounds) (*Combs and Combs, 1986; Kabata-Pendias, 2011; Ramady et al., 2014*).

The most significant forms and concentrations of Se in soil solution are governed by different physical, chemical, and biological factors, and usual inorganic anions include HSeO_3^- , SeO_3^{2-} , H_2SeO_4^- , SeO_4^{2-} , and HSeO_4^- (*Kabata-Pendias and Sadurski, 2004*). Selenate anions (SeO_4^{2-}) are the favoured form under oxidizing conditions, whereas under mild reducing conditions SeO_3^{2-} is likely to dominate (*Kabata-Pendias, 2011*). SeO_3^{2-} is strongly sorbed on oxides and precipitates such as $\text{Fe}(\text{SeO}_3)_3$, whereas SeO_4^{2-} anion is very weakly sorbed, especially at high pH. Therefore, mobile and easily phyto-available (available to plants) Se occurs in well-aerated alkaline soils, which are common in arid and semi-arid regions. On the other hand, organic matter has a strong tendency to shape organometallic complexes to remove Se from the soil solution (*Kabata-Pendias & Mukherjee, 2007*). Also the phyto-availability of different Se species in soils declines in the following order: selenate > selenomethionine > selenocysteine > selenite > elemental selenium > selenide (*Kabata-Pendias & Mukherjee, 2007*). Moreover, a close relationship is reported between Se and organic carbon in most soils.

Microbial processes play a decisive role in Se cycling in both the formation and mineralization of organic Se such as selenomethionine and selenocysteine and especially in its volatilization from soils contaminated with Se (*Martens & Suarez, 1998; Ramady et al., 2014*). These processes are important for the reduction of Se, fundamentally through the reduction of selenate and selenite. Insoluble selenide composites can accumulate in cases of improperly drained soils. Se may volatilize in the form of $(\text{CH}_3)_2\text{Se}$, just as in the form of several other methane and sulphide Se compounds, due to methylation processes under anaerobic conditions (*Kabata-Pendias & Mukherjee, 2007*). A number of microorganisms, such as bacteria and fungi species, are included in the volatilization processes of Se. It is reported that organic corrections may considerably increase the rate of Se volatilization from soils (*Kabata-Pendias & Mukherjee, 2007; Ramady et al., 2014*).

Generally, Se content can be increased in plants in various ways, including foliar applications, hydroponics, or aeroponic cultivation in a nutrient solution containing Se and wetting seeds in Se solution before sowing (*Germ et al., 2007; El-Ramady et al., 2014*). Therefore, the Se uptake by plants (mainly as

SeO_4^{2-} or SeO_3^{2-} , when it is present in soluble forms) depends on a number of factors related to soil and plant characteristics, although differences between these plant species are very accentuated (Kabata-Pendias, 2011). Rayman *et al.* (2008) reported that there was no bioavailability data for either Se-methyl-selenocysteine or γ -glutamyl-Se-methyl-selenocysteine.

Although Se has not yet been classified as a necessary element for higher plants, its role has been remarked to be beneficial for plants that are able of uptake followed by large-scale accumulation (Shanker, 2006). There are various organic Se species, including selenocysteine, methylselenocysteine, selenomethionine, selenotaurine, seleniobetaine, seleniocholine, dimethylselenide, dimethyldiselenide, and trimethylselenonium (Pyrzynska, 1995). The necessity of these seleno-proteins in higher plants has not been proved, but syntheses of them in some plants, such as sugar beet, have been reported (Terry *et al.*, 2000). Furthermore, various seleno-amino acids containing selenomethionine (SeMet), selenocysteine (SeCys), and selenomethylocysteine (SeMC) in relationship with glutathione peroxidases have been found in both higher plants and bacteria (Kabata-Pendias, 2011; Ramady *et al.*, 2014).

The uptake and metabolism of Se is different because of the difference in growth stage, plant species, and plant organs. More Se accumulates in shoot and leaf than in root tissues in different plants, but there are some exceptions (Zayed *et al.*, 1998). Se concentrations in the up-ground parts, roots, stolons, and tubers of potato will increase with increasing Se supplementation, as reported by Turakainen (2007). Moreover, Se concentration declined during the growing time in the aerial parts, roots, and stolons of potato plants, while intensive accumulation took place in immature and mature tubers (Turakainen, 2007). In seleniferous soils, there are great changes in plants' capability to uptake Se from these soils. It is worth mentioning that most of the cultivated crop plants have a low level of tolerance to high Se levels and, in general, they contain less than $25 \mu\text{g Se g}^{-1} \text{DW}$ and are non-accumulators like potato (Ramady *et al.*, 2014). It was found that critical Se concentration in plant tissues, which reduced the yield in the case of Indian mustard, rice, maize, and wheat (in $\mu\text{g g}^{-1} \text{DW}$), was 105, 77, 42, and 19, when Se amounts (as selenite) were 5, 5, 4, and $10 \mu\text{g Se g}^{-1} \text{soil}$ respectively (Rani *et al.*, 2005).

There are a number of physiological functions or roles of Se in higher plants (Pilon-Smits & Colin, 2010; Hasanuzzaman *et al.*, 2010; Hajiboland, 2012; Ramady *et al.*, 2014). One of the beneficial effects of Se in plants exposed to stress situations is increasing antioxidant activity. It is reported that plants treated with selenate induced higher increases in plant enzymes that detoxify H_2O_2 , especially both ascorbate peroxidase and glutathione peroxidase. Application

of low rates of selenate is used to increase the induction of plant antioxidation system and then to facilitate stress resistance, as indicated by *Hasanuzzaman et al.* (2010). An excess of Se may reduce germination and growth rates of non-tolerant plant species and bring about chlorotic leaves and black spots. It is reported that the critical Se concentration in solid media for gain reed (*Arundo donax* L.) plant ranged from 20 to 50 mg kg⁻¹ for the American and Hungarian ecotypes respectively (*El-Ramady et al.*, 2014 b). In some plants, increased Se levels repress the concentrations of N, S, and P, just as several amino acids (*Kabata-Pendias*, 2011; *Ramady et al.*, 2014).

Blockage uptake of some metals (mainly Cu, Cd, Mn, and Zn) may happen under high Se concentrations. Hence, the application of N, S, and P is known to help in Se detoxification, which may lead to either suppressing the Se uptake by roots or to establishing a healthy ratio of Se for these previous elements (*Kabata-Pendias*, 2011; *Ramady et al.*, 2014).

At a global level, the range of Se in cereals is estimated at 100–800 µg kg⁻¹ FW (*Fordyce*, 2005). This Se range mean (in µg kg⁻¹) varies from 142 to 970 and from 14 to 90 for countries with high and low Se amounts in grains respectively (*Kabata-Pendias & Mukherjee*, 2007). Using soil application of 10 g Se ha⁻¹ rate, it is found that Se contents in grains of oats and barley (in µg kg⁻¹) ranged from 19 to 260 and from 32 to 440 respectively (*Gupta & Gupta*, 2000), while using two foliar application rates of Se (10 and 20 g Se ha⁻¹) increased Se contents of winter wheat grains from 0.094 to 0.192 mg kg⁻¹, and the first Se rate was sufficient for reaching the essential content in wheat grains (*Dusçay et al.*, 2006).

A number of feed and forage samples from China were analysed by *Ge & Yang* (1993). They found that these samples were from Se-defecient areas, which contain the following Se levels (in µg kg⁻¹): < 20, 30–50, 60–90, and > 100 for intensely deficient, deficient, moderately deficient, and adequate Se supply areas respectively (*Kabata-Pendias*, 2011). Thus, the agronomic biofortification with Se-supplemented fertilizers is a usual practice with cereal crops to increase the Se content and nutritional quality of grains (*Banuelos et al.*, 2005). However, the transformation of Se by bacteria and the efficacy of these bacteria regarding Se availability for plants are still not clarified (*Acuna et al.*, 2013).

There are several articles and books concerning the relationship between Se and plant-based foods and human health (*Combs*, 2005; *Hartikainen*, 2005; *Reilly*, 2006; *Rayman et al.*, 2008; *Fairweather-Tait et al.*, 2010, 2011; WHO, 2011; *Banuelos et al.*, 2014; *Ramady et al.*, 2014). In general, people can obtain their Se requirements almost entirely from foodstuffs, whereas Se often

occurs bound to proteins in both plant and animal tissues (WHO, 2011). Hence, seafood, meat, and cereals are considered to be the most significant food sources of Se because they have elevated protein content (for seafood and meat: 0.3–0.5 mg Se kg⁻¹) due to their consumption in great amounts (for cereals 0.1–10 mg Se kg⁻¹). Fruits and vegetables (foods with almost low protein levels) tend to have low Se content (< 0.01 mg Se kg⁻¹).

Generally, Se content in different food systems depends on and reflects the soil-available Se to produce those food systems (WHO, 2011). Global Se intakes (in $\mu\text{g day}^{-1}$) show significant changes among various countries, whereas the average intakes are usually low (10–20), temperate (40–90), and sufficient (85–150) in parts of China, North America, and Europe respectively (FAO/WHO, 1998; WHO, 2011). In more details, it is found that daily dietary Se intake ranges from 7 to 4.990 μg , with mean values of 40 μg in Europe and 93 to 134 μg for women and men in the USA respectively (Rayman, 2012). Finally, it is suggested that the average daily Se intake is 53 and 60 μg for women and men respectively (Rayman, 2004).

In the UK, it is reported that the main food groups providing Se in the diet or the contribution of each food group to total population dietary exposure include eggs (4%), vegetables and fruits (7%), fish (10%), milk or dairy products (21%), cereals and bread (26%), and meat (26%). On the other hand, certain types of nuts grown in Brazil are good sources of Se, with concentrations ranging from ~ 0.03 to 512 mg kg⁻¹ fresh weight (Rayman *et al.*, 2008; Ramady *et al.*, 2014). It is reported that Se concentrations in the heart, liver, and kidney of beef tissues are 0.55, 0.93, and 4.5 mg kg⁻¹ respectively, whereas values for muscle tissue were around 0.2 mg kg⁻¹. Juniper *et al.* (2008) found that supplementation of cattle with Se-enriched yeast increased muscle Se concentration up to ~ 0.6 mg kg⁻¹, while the average Se content in chicken was ~ 0.2 mg kg⁻¹ and in beef ~ 0.25 – 0.3 mg kg⁻¹ – in the USA (Fairweather-Tait *et al.*, 2011). The total Se content in fish is between 0.1 and ~ 5.0 mg kg⁻¹ (Fairweather-Tait *et al.*, 2010), but the Se content in some marine fish is considered relatively high for shark, cod, and canned tuna (~ 1.5 , 2.0, and 5.6 mg kg⁻¹ resp.; Reyes *et al.*, 2009).

It is worth mentioning that the main Se species in fish contain selenite/selenate (12–45%) and selenomethionine (29–70%), which depend on both the fish species and the whole Se content (Rayman *et al.*, 2008; Fairweather-Tait *et al.*, 2010; Ramady *et al.*, 2014). Lipiec *et al.* (2010) found that eggs of hens contain from 3 to 25 mg Se in every whole egg, whereas Se supplementation in the diet of hens may increase the Se content of eggs up to 0.34–0.58 mg kg⁻¹. Se-enriched eggs are widely produced in the entire world (Fisinin *et al.*,

2009). Eggs are sources of the major Se species containing selenomethionine, selenocysteine, and maybe selenite, where the predominant species (>50%) contain selenomethionine in the white of egg and selenocysteine in the yolk of egg (Lipiec *et al.*, 2010). Selenite and selenocysteine are the predominant Se species in cow's milk; moreover, the supplementation plan of dairy cows with Se-enriched yeast is already in use, and after applying this supplementation the main species will contain selenite, selenocysteine, and selenomethionine (Muniz-Naveiro *et al.*, 2007).

It has been found that both fruits and vegetables contain almost low Se amounts. In the case of unenriched vegetables with low Se levels, the main species contain selenite (4%), Se-methyl-selenocysteine (12%), γ -glutamyl-Se-methyl-selenocysteine (31%), and selenomethionine (53%) in garlic with a natural Se amount of 0.5 mg kg^{-1} (Kotrebai *et al.*, 2000). However, certain vegetables, such as broccoli, onion, and garlic, when grown in Se-rich soil, can accumulate Se, resulting in Se enrichment from <0.5 up to $140\text{--}300 \text{ mg kg}^{-1}$. The main Se species in Se-enriched foods like onion is γ -glutamyl-Se-methyl-selenocysteine (63%), selenate (10%), selenomethionine (5%), and several other species (Hurst *et al.*, 2010). We may conclude that the Se species index in vegetables, such as garlic, broccoli, and onion, is different depending on the whole Se level of enrichment, the form of Se used for this enrichment, and the type of the vegetable. Se-methyl-selenocysteine or γ -glutamyl-Se-methyl-selenocysteine is the predominant species in Se-enriched vegetables. These forms of Se in plant foods have received attention due to purported protection against cancer in animal models when compared with other forms of this element (Fairweather-Tait *et al.*, 2011).

References

- [1] E. S. J. Arnr, History of selenium research. In: D. L Hatfield, M. J. Berry, V. N. Gladyshev (eds), *Selenium: its molecular biology and role in human health*. Springer, New York/Dordrecht/Heidelberg/London. (2012) 119.
- [2] P. D. Whanger, Selenocompounds in plants and animals and their biological significance. *The Journal of the American College of Nutrition*, 21 (3). (2002) 223–232.
- [3] D. F. Shriver, P. W. Atkins, *Inorganic chemistry*. 3rd ed. Oxford University Press, Oxford. (1999).

-
- [4] H. El-Ramady, É. Domokos-Szabolcsy, N. Abdalla, T. Alshaal, T. Shalaby, A. Sztrik, J. Prokisch, M. Fri, Selenium and nano-selenium in agroecosystems. *Environmental Chemistry Letter*, 12. (2014) 495–510.
- [5] C. Reilly, *Selenium in food and health*. 2nd ed. Springer, Berlin. (2006).
- [6] P. M. Chapman, W. J. Adams, M. L. Brooks, C. G. Delos, S. N. Luoma, W. A. Maher, H. M. Ohlendorf, T. S. Presser, D. P. Shaw, Ecological assessment of selenium in the aquatic environment. *Society of Environmental Toxicology and Chemistry (SETAC) Series*. CRC Press, Taylor & Francis, London. (2010).
- [7] D. V. Frost, Two faces of selenium – can selenophobia be cured? In: Hemphill D (ed.), *CRC critical reviews in toxicology*. CRC Press, Boca Raton. (1972) 467–514.
- [8] E. Kabata-Pendias, *Trace elements in soils and plants*. 4th ed. CRC Press, Taylor & Francis, Boca Raton. (2011).
- [9] N. Marmiroli, E. Maestri, Health implications of trace elements in the environment and the food chain. In: M. N. V. Prasad (ed.), *Trace elements as contaminants and nutrients: consequences in ecosystems and human health*. Wiley, Hoboken. (2008) 23–53.
- [10] S. Di Gregorio, Selenium: a versatile trace element in life and environment. In: A. S. Prasad (ed.), *Trace elements in human health and disease*, 2. Academic, New York. (2008) 593–622.
- [11] C. C. Johnson, F. M. Fordyce, M. P. Rayman, Symposium on Geographical and geological influences on nutrition: factors controlling the distribution of selenium in the environment and their impact on health and nutrition. *Proceedings of the Nutrition Society*, 69. (2010) 119–132.
- [12] U. S. Geological Survey (USGS). *Mineral commodity summaries*. <http://minerals.usgs.gov/minerals/pubs/mcs/2013/mcs2013.pdf>. 26, 1. (2013).
- [13] G. F. Combs, S. B. Combs, The role of selenium in nutrition. Academic Press, Orlando. (1986).
- [14] A. Kabata-Pendias, W. Sadurski, Trace elements and compounds in soil. In: E. J. Merian, M. Cramer Anke, M. Ihnat, M. Stoepppler (eds), *Elements and their compounds in the environment*. 2nd ed. Wiley-VCH, Weinheim. (2004) 79–99.

-
- [15] A. Kabata-Pendias, A. B. Mukherjee, *Trace elements from soil to human*. Springer, Berlin. (2007).
- [16] D. A. Martens, D. L. Suarez, Sequential extraction of selenium oxidation states. In: W. T. Frankenberger, R. A. Engberg (eds), *Environmental chemistry of selenium*. Marcel Dekker, New York. (1998) 61–79.
- [17] M. Germ, V. Stibilj, I. Kreft, Metabolic importance of selenium for plants. *European Journal of Plant Science and Biotechnology*, 1, 1. (2007) 91–97.
- [18] M. P. Rayman, H. G. Infante, M. Sargent, Food-chain selenium and human health: spotlight on speciation. *British Journal of Nutrition*, 100. (2008) 238–253.
- [19] A. K. Shanker, Countering UV-B stress in plants: does selenium have a role? *Plant and Soil*, 282. (2006) 21–26.
- [20] K. Pyrzyńska, Solid phase extraction for preconcentration and separation of selenium. *Solvent Extraction Ion Exchange*, 13. (1995) 369–389.
- [21] N. Terry, A. M. Zayed, M. P. de Souza, A. S. Tarun, Selenium in higher plants. *Annual Review of Plant Physiology and Plant Molecular Biology*, 51. (2000) 401–432.
- [22] A. M. Zayed, C. M. Lytle, N. Terry, Accumulation and volatilization of different chemical species of selenium by plants. *Planta*, 206. (1998) 284–289.
- [23] M. Turakainen, *Selenium and its effects on growth, yield and tuber quality in potato*. University of Helsinki, Helsinki. (2007).
- [24] N. Rani, K. S. Dhillon, S. K. Dhillon, Critical levels of selenium in different crops grown in an alkaline silty loam soil treated with selenite-Se. *Plant and Soil*, 277. (2005) 367–374.
- [25] E. A. H. Pilon-Smits, C. F. Quinn, Selenium metabolism in plants. In: R. Hell, R. R. Mendel (eds), *Cell biology of metals and nutrients. Plant cell monographs 17*, Springer, Berlin. (2010) 225–241.
- [26] M. Hasanuzzaman, M. A. Hossain, F. Masayuki, Selenium in higher plants: physiological role, antioxidant metabolism and abiotic stress tolerance. *Journal of Plant Science*, 5. (2010) 354–375.

- [27] R. Hajiboland, Effect of micronutrient deficiencies on plants stress responses. In: P. Ahmad, M. N. V. Prasad (eds), *Abiotic stress responses in plants: metabolism, productivity and sustainability*. Springer, Berlin. (2012) 283–329.
- [28] H. El-Ramady, T. Alshaal, É. Domokos-Szabolcsy, T. Shalaby, Y. Bayoumi, N. Elhawat, A. Sztrik, J. Prokisch, M. Fri, Selenium and its role in higher plants. In: E. Lichtfouse (ed.), *Environmental chemistry for a sustainable world*, 6. Springer, Berlin. (2014b).
- [29] F. M. Fordyce, Selenium deficiency and toxicity in the environment. In: O. Selinus, B. Alloway, J. A. Centeno, R. B. Finkelman, R. Fuge, U. Lindh, P. Smedley (eds), *Essentials of medical geology*. Elsevier, London. (2005) 373–415.
- [30] U. C. Gupta, S. C. Gupta, Selenium in soils and crops, its deficiencies in livestock and humans: implications for management. *Communications in Soil Science and Plant Analysis*, 31. (2000) 1791–1807.
- [31] L. Duscay, O. Ložek, L. Varga, T. Lošák, Wheat supplementation with selenium. *Chem. Listy*, 100. (2006) 519–521. (in Slovakian and cited from Kabata-Pendias, 2011).
- [32] K. Ge, G. Q. Yang, The epidemiology of selenium deficiency of endemic disease in China. *The American Journal of Clinical Nutrition Supplement*, 57. (1993) 259–263.
- [33] G. S. Baniñuelos, Z. Q. Lin, I. Arroyo, N. Terry, Selenium volatilization in vegetated agricultural drainage sediment from the San Luis Drain, Central California. *Chemosphere*, 60. (2005) 1203–1213.
- [34] J. J. Acuña, M. A. Jorquera, P. J. Barra, D. E. Crowley, M. Mora, Selenobacteria selected from the rhizosphere as a potential tool for Se biofortification of wheat crops. *Biology and Fertility of Soils*, 49. (2013) 175–185.
- [35] G. F. Combs, Global importance of selenium and its relation to human health. In: R. M. Welch, I. Åakmak (eds), *Impacts of agriculture on human health and nutrition. Encyclopedia of life support systems (EOLSS)*. Developed under the auspices of the UNESCO. EOLSS Publishers, Oxford. (2005). <http://www.eolss.net>.

-
- [36] H. Hartikainen, Biogeochemistry of selenium and its impact on food chain quality and human health. *Journal of Trace Elements in Medicine and Biology*, 18. (2005) 309–318.
- [37] S. J. Fairweather-Tait, R. Collings, R. Hurst, Selenium bioavailability: current knowledge and future research requirements. *The American Journal of Clinical Nutrition*, 91. (2010) 1484S–1491S.
- [38] S. J. Fairweather-Tait, Y. Bao, M. R. Broadley, R. Collings, D. Ford, J. E. Hesketh, R. Hurst, Selenium in human health and disease. *Antioxid Redox Signal*, 14, 7. (2011) 1337–1383.
- [39] World Health Organization (WHO), *Selenium in drinking water – background document for development of WHO guidelines for drinking-water quality*. WHO/HSE/WSH/10.01/14. (2011).
- [40] G. S. Bañuelos, Z. Q. Lin, X. Yin, *Selenium in the environment and human health*. Taylor & Francis, London. (2014).
- [41] FAO/WHO, *Preparation and use of food-based dietary guidelines*. Report of a joint FAO/WHO consultation. World Health Organization, Geneva (WHO technical report series, no 880). (1998).
- [42] M. P. Rayman, Selenium and human health. *The Lancet*, 379 (9822). (2012) 1256–1268.
- [43] M. P. Rayman, The use of high-selenium yeast to raise selenium status: how does it measure up? *British Journal of Nutrition*, 92. (2004) 557–573.
- [44] M. P. Rayman, H. G. Infante, M. Sargent, Food-chain selenium and human health: spotlight on speciation. *British Journal of Nutrition*, 100. (2008) 238–253.
- [45] D. T. Juniper, R. H. Phipps, E. Ramos-Morales, G. Bertin, Effect of dietary supplementation with selenium-enriched yeast or sodium selenite on selenium tissue distribution and meat quality in beef cattle. *Journal of Animal Science*, 86. (2008) 3100–3109.
- [46] L. H. Reyes, J. L. Mar, G. M. Rahman, B. Seybert, T. Fahrenholz, H. M. Kingston, Simultaneous determination of arsenic and selenium species in fish tissues using microwave-assisted enzymatic extraction and ion chromatography inductively coupled plasma mass spectrometry. *Talanta*, 78. (2009) 983–990.

- [47] E. Lipiec, G. Siara, K. Bierla, L. Ouerdane, J. Szpunar, Determination of selenomethionine, selenocysteine, and inorganic selenium in eggs by HPLC-inductively coupled plasma mass spectrometry. *Analytical and Bioanalytical Chemistry*, 397. (2010) 731–741
- [48] V. I. Fisinin, T. T. Papazyan, P. F. Surai, Producing selenium-enriched eggs and meat to improve the selenium status of the general population. *Critical Reviews in Biotechnology*, 29. (2009) 18–28.
- [49] O. Muniz-Naveiro, R. Dominguez-Gonzalez, A. Bermejo-Barrera, P. Bermejo-Barrera, J. A. Cocho, J. M. Fraga, Selenium speciation in cow milk obtained after supplementation with different selenium forms to the cow feed using liquid chromatography coupled with hydride generation atomic fluorescence spectrometry. *Talanta*, 71. (2007) 1587–1593.
- [50] M. Kotrebai, M. Birringer, J. F. Tyson, E. Block, P. C. Uden, Selenium speciation in enriched and natural samples by HPLC-ICP-MS and HPLC-ESI-MS with perfluorinated carboxylic acid ion-pairing agents. *Analyst*, 125. (2000) 71–78.
- [51] R. Hurst, C. N. Armah, J. R. Dainty, D. J. Hart , B. Teucher, A. J. Goldson, M. R. Broadley, A. K. Motley, S. J. Fairweather-Tait, Establishing optimal selenium status: results of a randomized, double-blind, placebo-controlled trial. *The American Journal of Clinical Nutrition*, 91. (2010) 923–931.