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REVIEW PAPER

SELENIUM IN THE ENVIRONMENT

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Abstract

Selenium is an element that is of interest to many researchers. As a trace element, it occurs in all compartments of the natural environment. It can be found both in an organic and inorganic form in water, rocks and air. For a long time, this element had been identified as a hazardous substance due to its toxicity. It was only in recent years that the physiological need to use it as a micronutrient fundamental to the health of humans and animals was noticed. However, it is not necessary for the growth of plants. In appropriate doses, selenium significantly affects the health of humans and animals because it is a component of many enzymes and it has antioxidative and anticancerogenic activity, but in excessive amounts it exhibits a toxic effect and causes a disease called selenosis. Its deficiency, however, is a much greater problem. It may occur in people living in most areas of the world. Selenium is an exogenous element, which is supplied to the human organism with food. Because plants are the main source of this element, it is important to increase its plant level. This can be achieved in different ways. One of the most promising approaches in addressing the problem of a low level of Se transfer from soil to the food chain is the agronomic biofortification of Se. Other interesting solutions are genetic engineering and the use of naturally selenium-rich materials. A new approach to fertilization of plants with Se is the use of nanomaterials. However, an excess of this element can induce toxic effects, such as the growth inhibition, wilting and drying of leaves, reduced protein synthesis and death of immature plants.

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INTRODUCTION

In 1817, a Swedish scientist Jöns Berzelius discovered a new substance when developing a novel method of the extraction of sulfuric acid from sulfur-containing rocks. The element was later called selenium, Se (Lenz, Lens 2009). For a long time, this element had been identified as a hazardous substance due to its toxicity. It was only in recent years that the physiological need to use it as a micronutrient fundamental to the health of humans and animals was noticed (Fernández-Martínez, Charlet 2009). This element is a component of many proteins described as selenoproteins, which play a key role in metabolic transformations. It also participates in scavenging, decomposition and inhibiting of the formation of free radicals (Rayman 2012).

It has one of the narrowest ranges between deficiency in a diet (>40 μg day^{-1}) and a harmful effect (<400 μg day^{-1}) (Fernández-Martínez, Charlet 2009). The level of Se intake in a diet depends on its total concentration and bioavailability in food sources (crop plants, fish and products of animal origin), which are affected by various factors such as soil Se content, irrigation, and type of animal feed. Significant differences in the selenium content has been found depending on the source and geographical origin of food, and selenium deficiency is more common than its excess, both under natural conditions and in crops. The content of this element in food products is proportional to its concentration in the soils in a given area (Winkel 2015).

Selenium in the environment

Selenium exhibits a complex chemical behavior that allows it to be combined with various elements in nature. Owing to this characteristic, it is widespread in all comparrtments of the Earth such as air, water, rocks and soil (Fernández-Martínez, Charlet 2009).

The Se content in the air varies and depends on a region. According to Niedzielski et al. (2000), this element occurs at a level of 0.004 ng m^{-3} over the North Pole, but in industralized areas this value rises even up to several dozen ng m^{3}. The natural sources of Se in the air include the eruption of volcanoes, the processes of oxidation from the surface of seas, oceans, and soils as well as the plant growth (Čuvardić 2003). Because of the significant chemical similarity between sulfur and selenium, almost 5% of sulfur dioxide (SO_2) emitted is converted to a gas stream of SeO_2 (Fernández-Martínez, Charlet 2009). Apart from its natural sources, selenium enters the atmosphere due to human activity, which includes hard coal and crude oil combustions as well as the processing of elements such as copper, zinc, uranium, phosphorus and lead (Yudovich, Ketris 2006).

The amount of Se in water is affected by many factors which include the leaching of this element from rocks, contaminants, the geochemical environment and pH. The largest amount of this micronutrient can orginate from underground and groundwater that flows through rocks rich in Se-containing minerals. Groundwater also contains selenium leached from waste disposal sites; such waste primarily includes ash produced by coal combustion. The average content of this element in fresh water is 0.02 μg l^{-1}, while in sea and ocean water it is less than 0.08 μg l^{-1} (Santos et al. 2015).

Selenium is recognized as a trace element and its average content in the Earth's crust varies and ranges from 0.05 to 0.09 μg g^{-1} (Lakin 1972). Volcanic activity and materials produced as a result of this activity, such as black shales, carbonate sandstones and sulfide ores, are considered to be the primary sources of Se. The total content of Se in rocks accounts for 40% of the total amount of this element found in the Earth's crust (Fernández-Martínez, Charlet 2009). This element occurs in almost 50 minerals; it can most frequently be found in sulfides of heavy metals (Ag, Cu, Pb, Hg, Ni, etc.), in the form of selenides, and also when it replaces the sulfide ion (Čuvardić 2003).

The amount of Se in soils depends on many environmental variables, such as the type of bedrock, intensity of the processes of leaching and transfer of the element from rocks to water bodies, but also topographic features and soil age. Moreover, it is also affected by the processes of sorbtion by iron oxides (Martinez et al. 2006), the oxidation-reduction potential of soil (Čuvardić 2003) and the content of clay materials (Borowska, Koper 2011). The selenium concentration in the soil at a level from 0.01 to 2 mg kg^{-1} is considered to be non-toxic (Rodriguez et al. 2005, Chen et al. 2006). On the other hand, the soil selenium content is generally at a level of mg kg^{-1} (Yamada et al. 1999). The highest concentration of selenium is found in soils that are rich in iron compounds and organic matter, while its lower amount can be found in magma-origin rocks and acidic soils. The form in which selenium occurs in soil depends on pH, redox potential, free oxygen concentration and moisture content (Wang, Gao 2001).

Distribution of Se in soils in Poland

In her study, Piotrowska (1984) showed that the average Se content in Polish soils is 0.27 mg kg^{-1}.This value is lower than the world's average, which is 0.33 mg kg^{-1} (Butterman, Brown 2004). However, there are significant differences in the content of this micronutrient depending on the type of soil. The largest amount of Se occurs in soils developed from loams, whereas the lowest amount is in soils originating from sands (Patorczyk-Pytlik, Kulczycki 2009). Dudka (1992) reported the average Se content in Polish soils as from 0.070 to 0.410 mg kg^{-1}. This difference may be due to the fact that his research focused on sandy soils and to a lesser extent on loamy and clayey soils. Studies on the soil Se content have also been conducted by Trafikowska (2000), who reports the average content of 0.024 mg kg^{-1}, as well as by Biernacka and Małuszyński (2006), who determined this content in the range of 0.108 - 1.570 mg kg^{-1}.

Selenium in crops

Diseases caused by selenium deficiency can occur in organisms that use only a plant-based diet. This is a result of the diverse distribution of this element in the soil and its insufficient uptake by plants. Therefore, management strategies designed to minimize Se deficiency and related disorders should focus on the combination of agricultural food products with the soil content and availability of Se (WINKEL et al. 2015).

Biofortification

One of the most promising approaches in addressing the problem of a low level of the Se transfer from soil to the food chain is agronomic biofortification of Se, which is defined as increasing the concentration of bioavailable essential elements in the edible parts of crop plants (BROADLEY et al. 2006). Increased consumption of this micronutrient as well as its bioavailability and accumulation by edible plants can be achieved by adapting cultivation systems, selecting Se-accumulating cultivars and using modern genetic engineering technologies (WINKEL et al. 2015).

Speciation of Se in crops – Se uptake by plants

Plants can take up Se from the soil as selenate(VI) (SeO_4^{2-}), selenate(IV) (SeO_3^{2-}) as well as in the form of organic compounds (ABRAMS et al. 1990). The former ones present in the soil are taken up by the roots, whereas the leaves take up organic forms present in the air (ZIEVE AND PETERSON 1981). Plants do not take up elementary Se and metal selenides. Water soluble forms are easily taken up, but this process is dependent on the plant species and cultivar (NIEDZIELSKI et al. 2000, GALEAS et al. 2007).

Selenium-accumulating plants favour this element during the transport process and can take it up even up to several mg kg^{-1} of dry matter, whereas those that are not classified as selenium accumulators (fodder plants and most of crop plants) rarely contain 0.1 mg kg^{-1} of dry matter (TERRY et al. 2000). Currently, the view prevails that selenium is not an element necessary for plants (PILON-SMITS et al. 2009) and hence plants have not developed selenium-specific uptake pathways. Nevertheless, because Se is a chemical analogue of sulfur, the uptake of selenates(VI) occurs along the same pathway as that of sulfates(VI). For membrane transport, plants use sulfur transporters which show high affinity for Se (TERRY et al. 2000, SORS et al. 2005). Under the conditions of sulfur deficiency, the expression of the genes responsible for encoding sulfate permeases and of the enzymes responsible for Se/S metabolism increases, and thereby there is an increased uptake of selenates(VI) (TERRY et al. 2000). After absorption, selenium gains access to the assimilation pathway and is then reduced to selenate(IV) through the selenide form. Selenide can be incorporated into selenocysteine, which can be subsequently transformed to selenomethionine in three enzymatic steps.

Selenates(IV) are probably taken up by passive diffusion and the phosphorus pathways participate in their transport. Despite that the uptake of Se(IV) is not dependent on metabolism, its uptake can be inhibited by the metabolic inhibitor CCCP (carbonyl cyanide m-chlorophenylhydrazone), but also by phosphates present in the soil solution. To sum up, it can be said that in the transport of elements sulfates compete with selenate(VI), while phosphates with selenate(IV) (Rosen, Liu 2009).

The main factor determining the bioavailability of Se in sources of food fortified with this element is its speciation. Selenium can occur in the inorganic form, but the prevalent form of selenium extracted by enzymatic hydrolysis from plants is the organic form – selenomethionine (SeMet), methylselenocysteine (MeSeCys) and γ-glutamyl-methylselenocysteine (γ-Glu-MeSeCys). It is still necessary to carry out more research that would determine how the soil-applied dose, Se form and foliar fertilization affect the speciation and proportion of organic forms produced in the edible parts of the plant. Organic forms of Se produced during its metabolism are the preferred choice of long-term supplementation strategies for the entire population because they can have an additional health value apart from the correction of Se deficiency.

Toxicity of selenium in plants

Cultivation of crops in selenium-rich soils can cause its substantial accumulation in the plant tissues. An excess of this element can induce toxic effects such as: growth inhibition, wilting and drying of leaves, reduced protein synthesis and death of immature plants (Wierzbicka et al. 2007). The threshold of selenium toxicity is dependent on the plant species and age, and the presence of phosphate and sulfate ions in the soil solution can increase this threshold (Terry et al. 2000).

Some plants can accumulate non-protein organic compounds of Se such as methylselenocysteine, γ–glutamyl-methylselenocysteine and/or selenocystathionine, sometimes to very high contents in the tissues, but without the disease symptoms (Terry et al. 2000, Malagoli et al. 2015). On the other hand, erroneous incorporation of seleno-amino acids into proteins instead of cysteine and methionine may cause metabolic dysfunctions and the deactivation of enzymes (Sabbagh, Van Hoewyk 2012).

Soil application of Se

In countries where selenium occurs in soils at a very low level, it is important to supply selenium not only by growing selenium-loving plants, but also by supplying selenium in the form of inorganic fertilizer (Alfthan et al. 2014). An application of inorganic or organic forms of Se in the form of fertilizers is used in countries such as Finland, the UK, New Zealand (inorganic form), and in the USA (organic form). Management of selenium-fortified crops must take into account the fact that we should not unnecessarily supply sulfur which reduces the uptake of Se. Owing to such practices, many countries, e.g. Finland, have been successful in increasing the level of selenium in blood in most of the population (ALFTHAN et al. 2014). All of major food groups except vegans do not have to supplement their diet with Se because intake exceeds the dietary recommendations. Supplementation of fertilizers with Se has a positive influence on animal health. Furthermore, fertilization with Se has shown no discernable effect on the water environment. Addition of Se to fertilizers increases the amount of total Se in Finnish agricultural soil. The value can be estimated to have risen by an average of about 20% in 20 years. This method has been proven to be effective and harmless (ALFTHAN et al. 2014).

Another effective method of biofortification is foliar application. It has been shown that inorganic forms are more readily available to plants if applied directly onto the leaf surface, as opposed to soil application (KÁPOLNA et al. 2009). What is important, direct foliar fertilization ensures high Se availability to plants, since it does not depend on the transport of this element from the roots. The degree of Se biotransformation from the inorganic form to the organic one depends on the plant species and specific biochemical transformation pathways (FREEMAN et al. 2010).

Genetic engineering

The strategies for genetic biofortification of plants use transgenic technologies and genetic variability to increase the ability of plants to take up selected micronutrients and accumulate them in the edible parts. A theory exists that there are substances called promotors (such as β-carotene, ascorbate, and cysteine polypeptides) which can accelerate the absorption of micronutrients by plants. One of the methods to increase the level of a particular micronutrient in the plant is to add an appropriate promoter and increase its level in the plant by genetic engineering methods. Substances that have an opposite effect, such as oxalates, polyphenols and phytates, are also known (NESTEL et al. 2006, ZHAO, MCGRATH 2009).

However, increasing the level of Se in plants by genetic engineering methods is primarily focused on sulfur enzymes. Overexpression of ATP sulfurylase, a key enzyme in the transformation of selenate(VI) to selenate(IV), was carried out in *Brassica juncea* (Indian mustard), which led to an increased accumulation of organic Se (e.g. methylselenocysteine) in the plants. Transgenic APS plants accumulated more selenium and also tolerated it better (PILON-SMITS et al. 1999). In another study, SeCys methyltransferase (SMT) was overexpressed in *Arabidopsis thaliana* (thale cress) and *B. juncea,* and transgenic SMT plants showed increased accumulation of Se in the organic form of methyl-SeCys (ELLIS et al. 2004). In both cases, greater accumulation of selenium occurs and its speciation is more appropriate for biofortification. Genetic engineering methods can be based not only on the modification of sulfur enzymes, but selenate transporters from selenium hyperaccumulators will be a good choice as well (MALAGOLI et al. 2015).

Nano-selenium in fertilization

Nanomaterials exhibit new properties, which include their high surface activity, a large area of the surface on which many active sites are located, and high catalytic efficiency. Owing to their high surface reactivity and a small size of particles, they are used in many areas of life. Nano-selenium is used to produce safer food supplements and additives, anticancer drugs, but also in electronics as photosensors or chemical sensors (EL RAMADY et al. 2014). Therefore, an attempt to use nano-selenium in plant fertilization is not surprising. Several studies comparing the action of fertilizers in the form of nano-Se and inorganic Se have been published to date (EL RAMADY et al. 2016). DOMOKOS-SZABOLSCY (2011) discovered that nano-Se does not have a significant effect on the growth of tobacco shoots, but inorganic Se applied at a dose of more than 50 mg l^{-1} inhibited it completely. At higher doses (50-100 mg l^{-1}), nano-Se stimulated the regeneration of the root, which was wider and denser, and the fresh weight of plants increased, too. The stimulating effect of nano-Se can be noticed already at the rooting stage. It has been found that the range of nano-Se concentration of 50-100 mg kg^{-1} stimulates organogenesis and root system growth by about 40%, whereas selenate does not exhibit such properties and, additionally, inhibits the callus growth and root regeneration. Further research is necessary to obtain more information on various biological effects of nano-Se (DOMOKOS-SZABOLSCY et al. 2012).

Selenium in animals

Selenium is an important element for animals, as it determines their good growth. The selenium content in animal tissues is a good source of this element for humans (MARKIEWICZ et al. 2006). Deficiency of selenium in cows may lead to degeneration of muscles, diarrhoea in young cattle, death of fetuses and inferior reproductive potential. Deficiency of selenium during lactation may cause muscular dystrophy, also known as white muscle disease, in calves, foals, kids and poultry from birth to 3 months of age (ŻARCZYŃSKA et al. 2013). Diseases which may be caused by an insufficient level of this element are exudative diathesis in poultry, dietary necrotic liver degeneration and mulberry heart disease in pigs. There are studies suggesting that a diet enriched with Se, Zn and vitamin E improved the lipid profile of lamb meat and ovine milk (GABRYSZUK et al. 2005, GABRYSZUK et al. 2007*a*, *b*). Many metabolic pathways occurring in an animal organism require the presence of selenium, and its action is complemented by sulfur amino acids and vitamin E. The most important selenium-containing enzyme is glutathione peroxidase. Its role is to protect haemoglobin and polyunsaturated fatty acids against oxidation and to scavenge free radicals. Other important selenium-containing enzymes include thioredoxin reductase and selenoprotein P.

The reductase activates the growth factors, apoptosis inhibitors and hydroperoxidase reductases, and participates in DNA transcription, while selenoprotein P protects against endothelial oxidants (Burk et al. 2003, Włodarczyk, Birkle 2010, Żarczyńska et al. 2013).

Selenium takes part in stimulating the immune system, while its compounds affect humoral immunity and increase the level of M-type immunoglobulins. Selenium supplementation increases the level of antibodies and enhances the phagocytic activity of neutrophil granulocytes (Żarczyńska et al. 2013). It is also necessary in the production of interleukin-2, that is the factor inhibiting the migration of lymphocytes (Wintergers et al. 2007). Furthermore, it is responsible for the proper regulation of thyroid hormones, it protects the liver andd the pancreas against damage, and it also has insulin-like activity (Zwolak, Zaporowska 2005).

Jaczuszuk-Kubiak et al. (2015) state that selenium is not only an effective antioxidant but is also a regulator of gene expression. They assure that a dietary level of selenium is affected on mRNA expressions patterns of several selenoproteins like GPX1, SEPN1, SEP15, SEPM and SEPHS2. Moreover, the results of their study suggest that changes in the Se intake lead to different levels of gene expression related with lipid metabolism.

Selenium – its effect on humans

Selenium is an exogenous element, supplied to the human organism with food; its main sources include maize, nuts, and also products of animal origin such as kidneys, liver, fish, seafood, and egg yolks (Krzysik et al. 2007). Selenium is available better from protein than from plant products and a diet rich in small molecule proteins as well as vitamins A and E also increases Se bioavailability. If, on the other hand, a diet includes many simple carbohydrates, compounds of heavy metals such as cadmium, lead or arsenic as well as sulfur derivatives, the availability of Se decreases (Kuczyńska, Biziuk 2007). The chemical form of Se and its intracellular distribution in the organism affect its availability. The encountered forms of Se supplied with food or diet supplementation are organic forms, selenomethionine and selenocysteine, and also inorganic forms such as selenates(IV) and selenates(VI) (Rayman 2012)

The main function of Se in the organism is its antioxidant activity (Sobiech, Kuleta 1999). It is present in the active site of the enzyme glutathione peroxidase (GPX) which participates among others in the reduction of toxic hydrogen peroxide and lipid peroxides (Frączek, Pasternak 2013). Selenium also exhibits immunostimulating activity – it causes the stimulation of proliferation of T lymphocytes, enhances the response to antigens, and also increases the activity of NK cells and cytotoxic lymphocytes. It shows the ability to regulate the expression of the receptor for IL–2 on the surface of activated lymphocytes and NK cells. This interaction is necessary for clonal expansion and cell differentiation. Se deficiency can lead to disorders in the functioning of type B lymphocytes and in cell response, which results in the development or exacerbation of diseases whose occurrence is related to immune deficiency (Krzysik et al. 2007). Furthermore, it is suspected that the production of selenocysteine by leukocytes requires the presence of this micronutrient. Selenocysteine is one of selenoproteins participating in enhancing the immunity of the organism (Rayman 2000, Hardy, Hardy 2004)

Research is also carried out on the effect of Se on lowering the risk of the development of lung, large bowel and prostate cancer. The results suggest that this element may improve the action of chemotherapeutic agents by removing oxidation reaction products formed during the application of drugs. Moreover, Se affects the expression of the tumor suppressor gene p53 and the apoptosis suppressor gene Bcl-2 and thereby it suppresses the growth of neoplastic cells (Zachara1992, Bojarowicz, Dźwigulska 2012). There are studies showing potential protective (for humans) effects of plasma/serum selenium levels between 120-160 ng mL^{-1} and a reduced risk of some types of cancer compared to the low plasma selenium levels, namely <120 ng mL^{-1}. Above 160 ng mL^{-1} the protective effect against cancer is likely to diminish and even cause an opposite effect, probably an increased risk of some types of cancer will be noticed (Fairweather-Tait et al. 2011).

Selenium also plays a significant role in the functioning of the thyroid. The amount of selenium consumed affects the activity of thyroid selenoenzymes, also including iodothyronine deiodinases, while supplementation of a diet with this element stimulates the functions of the thyroid (Corvilainet al. 1993, Zagrodzki, Kryczyk 2014). The research has shown a much lower selenium concentration in the blood serum in patients with Hashimoto's disease than in healthy people and therefore selenium supplementation may be helpful in treating this disease (Socha et al. 2012, Nacamulli et al. 2010).

Se deficiency may lead to the development of many diseases, such as Keshan's disease and Kashin-Beck's disease. Moreover, it may induce the development of depressions, anxiety and also some diseases of affluence such as a stroke or cardiovascular diseases. Furthermore, deficiencies of selenium and vitamin C may cause nutritional muscular dystrophy (Żarczyńska et al. 2012).

An excess of Se is harmful. Prolonged intake of this element at a dose higher than 1000 µg per day may induce toxic symptoms such as nausea, dizziness, fatigue, hair loss, metallic aftertaste in the mouth, and irritation of the airways. These symptoms are part of a disease called selonosis. The safe dose of Se supplementation for adults is 50-70 µg per day (Kise 2004).

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