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SELENIUM IN SOIL

ABSTRACT: Selenium (Se) is an essential microelement, necessary for normal functioning of human and animal organisms. Its deficiency in food and feed causes a number of diseases. In high concentrations, selenium is toxic for humans, animals and plants. Soil provision with selenium affects its level in food and feed via nutrition chain. However, selenium reactivity and bioavailability depends not only on its total content in soil but also on its chemical forms. Distribution of the different forms of selenium depends on soil properties such as reaction, aeration, contents of clay and organic matter and microbiological activity.

KEY WORDS: selenium, total Se, water-soluble Se, soil

INTRODUCTION

The biological importance of selenium is reflected in the fact that it is essential for humans and animals on one side (Rayman, 2000), and toxic when in high concentration on the other. This controversial element was discovered by Berzelius, a Swedish scientist, in 1817, although it was Marco Polo during his travel to Asia, as early as the 13th century, who observed toxic symptoms in animals feeding on plants that contained a high concentration of selenium. In the first half of the 20th century, selenium was considered exclusively from the standpoint of its toxicity, until it was identified as a component of a preparation which prevented the necrosis of liver in rats (Schwarz and Foltz, 1957). Soon afterwards, selenium was found to play a key role in glutathione peroxidase, an enzyme that catalyzes the decomposition of hydrogen peroxide thus protecting cells from oxidative damage. Selenium also plays an important anti-carcinogenic role and it neutralizes heavy metals toxicity.

Soil provision with selenium affects its level in food and feed via nutrition chain (Finley et al., 2000). However, selenium reactivity and bioavailability depends not only on its total content in soil but also on its chemical form. Depending on oxidation state, selenium is present in soil as selenide (Se^{2−}), elemental selenium (Se^{0}), selenite (SeO_{3}^{2−}), selenate (SeO_{4}^{2−}) and organic selenium. The water-soluble selenium fraction is considered to be most available to plants. Its content in normal tilled soil does not exceed 50 ppb
Although selenium is not essential for plants, they take up selenium and incorporate it in their amino acids and proteins (Shrift, 1973). The level of selenium accumulation in plants depends on the amount of available Se, pH value and redox potential, contents of sesquioxide, clay and organic matter and the microbiological activity of soil (Jump and Sabey, 1989).

GEOGRAPHIC DISTRIBUTION OF SELENIUM

Selenium is abundant in different parts of the world but its level in soil varies with native substrate, climatic conditions and vegetation cover (McNeal and Balistrieri, 1989). In central US, for example, there are regions in which plants contain Se levels 10 times higher than the toxic level, while Se levels in plants in eastern and western US are low (Kubota et al., 1967). In eastern Canada, Se concentrations in plant dry matter are much below 0.1 ppm (Winter and Gupta, 1979), while they are 10 times higher in western Canada. Selenium deficiency was observed in some parts of South America, selenium toxicity in others (Jaffe, 1973). Selenium deficiency was noted in western and southern parts of Australia and in New Zealand (Welsh et al., 1981).

Severe selenium deficiency registered in southeastern China has been associated with Keshan disease, a disease that occurs almost exclusively in children. In India, toxicity was observed in the region of Harayana and deficiency in the other parts of the country (Dhillon and Dhillon, 1991). Total Se content is slightly increased in Japanese soils as compared with the contents established in other countries (Kang, 1990). However, because these soils have an acid reaction and because of the humid climate of Japan, the concentration of water-soluble Se is low, making only 2.3—3.85% of the total Se content (Kang, 1990).

In Europe, toxic level was registered in several locations in Wales and Ireland (Fleming, 1962). Symptoms of Se deficiency were observed in cattle in England and Scotland (Rimmer et al., 1990). Suboptimal Se contents were reported for northern Europe. In Finland, before Se fertilization became a regular practice, wheat contained only 10—15 ppb Se (Koivistoinen and Varo, 1981). Low Se levels were registered in Poland (mean value 0.27 μg g⁻¹) (Borowska, 1998) and Hungary (Gondi et al., 1992; Horvath et al., 1996).

In our country, preliminary studies of soil, cereal and animal feed samples (Krajinović, 1983) indicated the presence of low Se levels. Later studies of Se content in geological materials (Jovic et al., 1995; Dangic et al., 1989), soil (Jakovljević et al., 1995; Maksimović et al., 1992; Ćuvardić et al., 1997) and biological materials (Maksimović et al., 1992) confirmed a pronounced Se deficiency on this territory. Perilously low Se contents were found in blood serum and hair of two groups of male examinees, miners in the Majdanpek coal strip mine and inhabitants of a region in the vicinity of Belgrade (serum — 31 ppb and 25 ppb, respectively; hair — 76 ppb and 73 ppb, respectively). According to these results, the ana-
lyzed populations were comparable to the inhabitants of the countries suffering a severe Se deficiency, such as China, New Zealand and Finland (Maksi-mović et al., 1992).

SELENIUM IN LITOSPHERE

The primary sources of Se in nature are volcanic rocks and metal sulfides formed by volcanic activity (NAS, 1974). Although some 50 minerals contain Se, it occurs most frequently in sulfides of heavy metals (Ag, Cu, Pb, Hg, Ni, etc.), either in the form of selenide or substituting the sulfur ion (S) in the minerals’ crystal grid (Adriano, 1986). Average Se content in the Earth’s crust is considered to vary from 0.05 to 0.09 μg g⁻¹ (Lakin, 1972). Total Se content varies from 0.1 to 2 μg g⁻¹ in most soils (Swaine, 1955). Increased amounts of Se are found in the soils formed by the decomposition of shale, mostly in arid and semiarid regions (Rosenfeld and Beath, 1964).

Selenium content in magmatic rocks seldom exceeds 0.05 μg g⁻¹ (Kabata-Pendias, 1993). An extremely low Se content was found in magmatic rocks from Serbia (mean value 46 ppb Se) (Maksi-mović et al., 1986). In these rocks, Se is part of sulfides in which it substitutes sulphur. So, Se content depends on the size of sulfide phase. In magmatic rocks, Se concentration decreases from basic and ultra basic to acid and neutral rocks (Dansić et al., 1989).

In sedimentary rocks, Se is bound to the organic and clay fractions. Lowest Se concentrations are recorded in sandstones and limestones (Table 1). Selenium is most frequently found in phosphates, uranium ore, fossil coal and oil and in shale with a high content of organic matter. Soils formed on such substrates typically have high or toxic Se concentrations, unlike the soils formed on magmatic rocks which have a low Se content (Fleming, 1980).

The metamorphic rocks of Serbia have a lower Se content than the magmatic and sedimentary rocks. An analysis of 89 samples of metamorphic rocks from Serbia showed a low Se content of 28 ppb (Jović et al., 1995), leading to a conclusion that the high temperature and pressure present during metamorphic processes tend to extrude Se from these rocks.

Tab. 1 — Selenium in main rock types — μg Se g⁻¹ (Kabata-Pendias, 1993)

<table>
<thead>
<tr>
<th>Igneous rocks</th>
<th>μg Se g⁻¹</th>
</tr>
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<tbody>
<tr>
<td>Ultra basic (dunit, peridotite, pyroxenite)</td>
<td>0.02—0.05</td>
</tr>
<tr>
<td>Basic (basalt, gabbro)</td>
<td>0.01—0.05</td>
</tr>
<tr>
<td>Intermediate (syenite)</td>
<td>0.02—0.05</td>
</tr>
<tr>
<td>Intermediate to acidic (rhyolite, trachyte, dacite)</td>
<td>0.02—0.05</td>
</tr>
<tr>
<td>Acidic (granite, gneiss)</td>
<td>0.01—0.05</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Sedimentary rocks</th>
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<tbody>
<tr>
<td>Shale</td>
<td>0.40—0.60</td>
</tr>
<tr>
<td>Sandstone</td>
<td>0.05—0.08</td>
</tr>
<tr>
<td>Limestone, dolomite</td>
<td>0.03—0.10</td>
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</table>
SELENIUM IN WATER AND AIR

Besides litosphere, atmospheric precipitation is another source of selenium in soil. Selenium is released into the atmosphere from natural deposits or due to anthropogenic influences (burning of coal and other fuels, releases for mines, oil refineries and other industries). Soils, plants, microorganisms, animals and volcanoes release up to 0.04 ng m\(^{-3}\) Se (EHC, 1987). The total annual anthropogenic emission of selenium in the USA was estimated at 4670 t (Herring, 1991). The atmospheric precipitation in Norway and Sweden brings annually 0.5—1.0 g Se ha\(^{-1}\). Under natural conditions, Se contents in air and water are quite low — less than 10 ng m\(^{-3}\) in air and a few μg l\(^{-1}\) of water (EHC, 1987). Se contents in rain and snow samples gathered in different parts of the world ranged from 0.03 to 0.3 μg l\(^{-1}\) (Cutter, 1989). Se concentration in atmospheric precipitation in Sweden was below 0.1 μg l\(^{-1}\) (Johnsson, 1991).

SELENIUM IN SOIL

Selenium content in soil is highly variable. It varies from 0.1 to 2 μg Se g\(^{-1}\) in most soils, but it is most frequently between 0.2 and 0.4 μg g\(^{-1}\) (McNeal and Balistrieri, 1989). Some soils are low in selenium, from 0.03 to 0.08 μg g\(^{-1}\) (NAS, 1976). Toxic concentrations occur in arid and semiarid parts of China, in Hawaii, Mexico, Columbia and western parts of the USA and Canada (McNeal and Balistrieri, 1989). Soils containing less than 0.5 μg g\(^{-1}\) of total Se are considered as deficient in this element (Mayland et al., 1989).

Selenium concentration in soil is determined by selenium content in soil native substrate, climate, relief and age (Mayland et al., 1989). These factors may contribute either to selenium accumulation during soil forming or its removal during or after soil forming. The soils formed on sedimentary rocks that contain high amounts of organic matter typically have high to toxic selenium concentrations. The soils formed on magmatic rocks, which are poor in Se, usually have a low Se content (Fleming, 1980).

Besides native substrate, amount of rainfall plays an important role in determining selenium content in soil (Fleming, 1980). In regions with less than 500 mm of rain, the soil formed from rocks with a high Se content contains potentially toxic Se concentrations. The same kind of soil formed in humid regions typically contains high amounts of Se, but it is bound to iron in a poorly soluble complex. When the substrate is low in selenium, the soil forming on it will have a low Se concentration regardless of climate.

Since the total Se content in soil is predominantly determined by its content in the native substrate, it is understandable why the soils in certain regions of our country have very low Se concentrations. For example, the soils in northern Pomoravlje have the Se contents from 0.12 to 0.44 ppm, with the mean value of 0.24 ppm (Jakovljević et al., 1995), in western Serbia 119.5±70.5 ppb Se (Maksimović et al., 1992), in the valley of the Zeta
River from 0.2 to 0.41 ppm Se, with the mean value of 0.28 ppm Se (Jakovljević et al., 1995)

Low Se concentrations have also been registered in the Vojvodina Province. In 46 soil samples from the regions of Srem and Banat, taken from plots used for vegetable production, the contents of Se ranged from 0.11 to 0.45 ppm, with the mean value of 0.25 ppm Se (Čuvardić et al., 1997). In samples of chernozem, distric cambisol, humogley, humofluvisol, arenosol, solonetz and solonchak taken in the Vojvodina Province, Se contents in the surface soil layer ranged from 0.024 to 0.194 μg Se g⁻¹ (Čuvardić, 2000).

SELENIUM DISTRIBUTION ALONG SOIL PROFILE

Selenium content in soil typically decreases with depth because it binds with proteins, fulvic acids and other organic compounds that contain nitrogen. As organic matter decreases along soil profile, so does total selenium (Abrams et al., 1990; Alemi et al., 1991; Gustafsson and Johnsson, 1992). Selenium fixation may also be due to microbiological incorporation into amino acids and other Se-containing organic compounds (Mao, 1999). In addition to humus distribution, Se distribution along soil profile resembles those of Fe, Al and clay (Levesque, 1974; Gondi et al., 1992; Čuvardić, 2000). Selenium binds with clay and arranges itself along the profile. Total Se increases with the increase of small fractions in the soil (Čuvardić, 2000). The most important characteristics of the fine soil fraction are the large total area of its particles and specific mineralogical composition which distinguishes it from the coarse fractions. Secondary minerals predominate in the finest fraction, clay, while the coarsest fraction is composed mainly of quartz (Jakovljević and Pantović, 1991). For that reason, the fractions of coarse and fine sand have a low adsorption capacity. Ions of Al octahedral layer, whose sides are bare, may be considered as positively charged sites on the surface of clay minerals. Ions of the Al octahedral layer of caolinite, which, in contrast to the minerals from the montmorillonite group, are not covered with the tetrahedral sheet, may be positively charged not only at the sites of crystal fractures but also their planes may be charged, attracting HSeO₃⁻ as a substitute for OH⁻ (Bar-Yosef and Meek, 1987).

FACTORS AFFECTING SELENIUM SOLUBILITY AND AVAILABILITY TO PLANTS

Organic and mineral forms of selenium are present in the soil (Cary and Allaway, 1969). The organic forms of Se result from partial decomposition of selenium-loving vegetation. Mineral Se occurs as a selenide of metals (Se²⁻), elementary Se (Se⁰), selenite (HSeO₃⁻) and selenate (SeO₄²⁻). Se partitioning is affected by soil pH and redox potential, content of sesquioxides, clay, organic matter and microbiological activity (Elrashidi et al., 1987; Jayaweera and Biggar, 1996).
Se solubility and availability to plants is predominantly affected by pH-value and redox potential (Geering et al., 1968). According to pe+pH diagram (Figure 1) (Elrashidi et al., 1987), selenide and elementary Se are favored in a reducing environment (pe+pH < 7.5), selenite in a slightly oxidizing environment (pe+pH 7.5—15.0), and selenate in an oxidizing environment (pe+pH > 15.0). In humid regions and acid soils, the prevailing form is selenite, which is firmly adsorbed on sesquioxides and clay minerals and thus not readily available to plants. High annual precipitation and low temperature tend to reduce Se content in plants. This is due to reducing conditions in the soil and reduction of selenate \( (\text{SeO}_4^{2-}) \) into less available forms: selenite \( (\text{SeO}_3^{2-}) \); elementary selenium or selenids \( (\text{Se}^2-) \) (Geering et al., 1968). Increased leaching of available Se forms also leads to reduction in uptake (Johnsson, 1991). Under well-aerated conditions in the alkaline soils of semiarid regions, selenium is present in the form of selenate which is not adsorbed, does not form insoluble salts and is readily available to plants (Cary et al., 1967).

Although soil reaction plays a major role in determining Se solubility and availability, its influence lessens as the contents of clay and organic matter in the soil increase (Johnsson, 1991). Because of Se affinity for clay minerals, the soils having increased clay content are typically better provided with Se than sandy soils (Gissel-Nielsen, 1975). As described in the previous chapter, Se binds with the positively charged ions of AL-octahedral sheets, which occur on the edges of clay minerals, primarily caolinite (Bar-Yosef, 1987). Gissel-Nielsen (1971) studied the effect of pH value and texture on Se uptake from loamy and sandy soils. In the first two cuttings of Lo-
lium multiflorum grown on a slightly acid soil, Se uptake dropped with increase in clay content. In subsequent cuttings, however, the effect of soil acidity evidently weakened because Se became more and more available. When the soil pH exceeded 7, the effect of clay disappeared altogether. Se adsorption occurs also on iron (Fe), aluminium (Al) and manganese (Mn) oxides and hydroxides in acid environments, when these particles become positively charged (Balistreri and Chao, 1990). Namely, a specific characteristic of these oxides is that they change their electric charge with a change of ambient reaction. The charge is negative under alkaline conditions and positive under acid conditions.

Selenium also binds well with organic matter in acid soils (Christensen et al., 1989; Gustafsson and Johnsson, 1992). Because of a high content of organic matter in topsoil, higher selenium content may be expected there than in deeper soil layers (Levesque, 1974). When in the organic fraction, selenium either forms complexes with organic compounds or is built in amino acids and proteins by microorganisms and plants (Cary et al., 1967; Hamdy and Gissel-Nielsen, 1976). Se fractionation from three profiles of Swedish podzols showed that considerable amounts of Se were present in the soil organic matter, especially in the Bs horizon which has a high capacity for adsorption of anions (Gustafsson and Johnsson, 1992).

Microorganisms play an important role in Se transformations in the soil. They are capable of transforming the absorbed selenite into organic compounds or inot selenate (Doran, 1982). It was also found that microorganisms take part in the transformation of selenate into less mobile forms, especially in soils rich in carbon (Alemi et al., 1991). Products of microbiological activity are also volatile Se organic compounds, primarily dimethyl selenide. This is a way for selenium depletion from the soil (Frankenberger and Karlson, 1989). Hamdy and Gissel-Nielsen (1976) measured the volatilization of added selenite under laboratory conditions. The volatilization was higher from a sandy soil (about 8% of the added Se) than from a humic soil (about 5% of added Se).

Se availability to plants depends also on competing ions, especially phosphates and sulfates. Interaction between selenium and phosphorus (P) in the soil has been observed by several researchers, but its mechanisms have not been fully revealed. In a greenhouse test, Singh (1979) examined the effect of added Se and P on dry matter mass and chemical composition of Brassica juncea Cos. In the variant without P and with 10 ppm Se, the selenium content in the plant was 100 times higher than in the control. The increases were 258- and 336-fold with 50 and 100 ppm P. Similar results were obtained by Singh and Malhotra (1976) who found that the application of 50 and 100 ppm P positively affected Se uptake by Trifolium alexandrinum in all variants of Se level, as well as in the experiment with residual Se. Effect of P on Se availability depends on the auxiliary ion in the phosphorus fertilizer, Se form and the presence of other ions (Khattak et al., 1991). Fleming (1962) studied the effect of P from superphosphate, Ca(H₂PO₄)₂, on Se uptake in an experiment in pots. All three doses of superphosphate reduced Se uptake, probably due to the influence of sulfate that was a component of the superp-
hosphate. Unlike superphosphate, dicalcium phosphate and monocalcium phosphate increased Se content in grasses (Fleming, 1965). A possible explanation is that P, if incorporated into the soil together with Se, substitutes Se in some sorption points, thus increasing Se mobility and uptake (Carter et al., 1972). Another possible explanation of this interaction is that P increases Se uptake by stimulation cell division in plant root. High cell division increases the contact between the root and soil, which increases the active root surface and Se uptake (Carter et al., 1972).

Because of a large chemical similarity between sulfur (S) and selenium and because of the fact that most S compounds have Se analogues, it seems reasonable to expect antagonistic interaction during uptake of these two elements. Several authors found that Se concentration in the plant decreases after adding sulfate to the nutritive medium (Wan et al., 1988; Mikkelsen and Wan, 1990). In an experiment in pots filled with peaty soil, Williams and Thornton (1972) examined the effects of different S compounds on Se uptake. All S compounds tested (elementary S, sulfate S, sulfite S, sulfide S and methionine) tended to reduce Se uptake. The situation was opposite in the case of alkaline soils, where the application of sulfate increased Se uptake (Carter et al., 1972).

**WATER-SOLUBLE SELENIUM IN SOIL**

Total Se content in the soil is not always in correlation with its content in plants because Se solubility is affected by several factors: soil reaction, the contents of sesquioxides, clay and organic matter (Elrashidi et al., 1987; Jayaweera and Biggar, 1996; Pezzarossa, 1999). Because of that, when assessing soil provision with selenium, concentration of available Se and factors that affect the dynamics of Se in the soil have to be taken into account in addition to the total Se content. The water-soluble Se fraction is considered

![Fig. 2 — Contents of total and water-soluble Se in the profiles of the examined soils in the Vojvodina Province (Čuvardić, 2000)](image-url)
to be most available to plants (Jump and Sabey, 1989). Non-adsorbed Se and water-soluble organic Se are released from the soil by extraction with boiling water (Wang and Sipola, 1990; Seby et al., 1997; Kang et al., 1993).

In normal tilled soils, the concentration of the water-soluble Se fraction typically does not exceed 0.050 μg g⁻¹ Se (Workman and Soltanpour, 1980). Exceptionally low concentrations of water-soluble Se, ranging from traces to 0.013 μg g⁻¹, were registered in the soils of Srem and Banat used for vegetable production (Čuvardić et al., 1997). Low concentrations of water-soluble Se were found for seven different soil types in the Vojvodina Province (Čuvardić, 2000). These concentrations ranged from traces to 0.014 μg Se g⁻¹ of soil, or from 0.59% to 16.35% of the total Se (Figure 2). In Hungary, Gondi et al. (1992) found that the mobile Se fraction did not exceed 10% of the total Se in most of the tested soils, with the exception of several profiles of alkaline soils in which this fraction ranged between 20% and 35% of the total Se.

SELENIUM UPTAKE

Plants take up Se in the form of selenate or selenite, or as organic Se (Hamilton and Beath, 1963, 1964). Probably they may also take up atmospheric Se (Asher et al., 1967). Capacity for Se uptake varies among plant species (Hurd-Karren, 1935). Still, differences among plant species were smaller regarding Se uptake from low Se soils than regarding Se uptake from high Se soils (Ehlig et al., 1968). Furthermore, the rate of uptake depends on the form of Se prevailing in the soil or a nutritive medium (Zhang et al., 1988). Generally, plants exhibit preference for selenate over selenite (Banuelos and Meek, 1990). This seems to be due to high adsorption of selenite by hydrated oxides, or selenite reduction to elementary Se or selenide (Cary et al., 1967; Gissel-Nielsen et al., 1984). In an experiment in vegetation pots, Gissel-Nielsen (1973) found that the Se uptake by barley was 40 times higher from selenate than from selenite.

CONCLUSION

Selenium is an essential microelement, necessary for normal functioning of human and animal organisms, whose deficiency in food and feed causes a number of diseases. In high concentrations, selenium is toxic for humans, animals and plants. Soil provision with selenium affects its level in food and feed via nutrition chain. Selenium bioavailability depends not only on its total content in soil but also on its chemical forms.

Organic and mineral forms of Se are present in the soil. The organic forms of Se result from partial decomposition of seleniferous vegetation. Mineral Se occurs as a selenide of metals (Se²⁻), elementary Se (Se⁰), selenite (HSeO₃⁻) and selenate (SeO₄²⁻). Se partitioning is affected by soil pH and re-
dox potential, content of sesquioxides, clay, organic matter and microbiological activity.

In humid regions and in acid soils, selenite is the predominant form. It is firmly adsorbed on sesquioxides and clay minerals and thus not readily available to plants. In well-aerated alkaline soil in semiarid regions, Se is found in the form of selenate, which is not adsorbed, does not form insoluble salts and is readily available to plants.

Since Se solubility and availability to plants are governed by several factors, concentration of available Se and factors that affect Se dynamics in the soil should be considered in addition to the total Se content in the soil when estimating soil provision with selenium.

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СЕЛЕН У ЗЕМЉИШТУ

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Резиме

Селен је есенцијални микролеменат, неопходан за нормално функционисање организма људи и животиња, чији недостатак у храни доводи до низа обилјења. У исто време, у високим концентрацијама, селен (Se) је токсичан, како за
људе и животиње, тако и за биљке. Обезбеђеност земљишта се преко ланца исхрane одражава на ниво селена у храни људи и животиња, али реактивност и биоприступачност селена не зависи само од његовог укупног садржаја, него и од хемијских форми у којима се селен налази у земљишту. На дистрибуцију између појединих облика селена утичу својства земљишта, као што су: реакција земљишта, аерација, садржај глине и органске материје и микробиолошка активност.