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Biotechnological methods of selenium bioremediation from various compartments of environment: A review

Biotehnološke metode bioremedijacije selena iz raznih dijelova okoliša: pregled

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ABSTRACT

Selenium (Se) is an essential element for human health in trace amounts but is harmful in excess. Most plants contain a fairly low Se and crop Se supplements ensure adequate levels for human nutritional needs. Food is the primary source of Se for humans and due to differences in eating habits, its intake varies considerably. In the human body, selenium deficiency can lead to diseases of the endocrine, musculoskeletal, cardiovascular, reproductive, nervous and immune systems. Selenium is an important ingredient in glutathione peroxidase, the main cellular antioxidant enzyme, which can convert free radicals into peroxides, while vitamin E removes free radicals and neutralizes their potentially harmful effects. Excessive amounts of selenium in the human diet are considered toxic, causing liver and kidney damage, blood clotting, heart and liver necrosis, skin lesions, nausea, vomiting, and loss of hair and nails. Semiconducting properties of Se make it of special value for industry. Selenium is a rare element on the planet, and is a non-renewable resource due to its non-efficient and difficult recycling. Except of coal, which is commonly enriched in Se, there are no ores which could be mined for it. Herewith, the world's scarce Se resources need a careful management, monitoring, recycling, and stockpiling for future generations. The first part of this review outlines selenium concentrations in soil, water, and plants in terms of essential and toxicological effects on animals and humans, while the second part briefly overviews novel biotechnological methods of bioremediation of environmental selenium.

Keywords: metalloid, contamination, soil, health, biotechnology, plants

SAŽETAK

Niske koncentracije selenija (Se) bitne su za ljudsko zdravlje, ali one prekomjerne su štetne. Većina biljaka sadrži prilično nizak Se, a njegovi dodatci usjevima osiguravaju odgovarajuće razine Se za ljudske prehrambene potrebe. Hrana je primarni izvor Se za ljude, a zbog razlika u prehrambenim navikama, njegov unos znatno varira. U ljudskom tijelu nedostatak selenija može dovesti do bolesti endokrinog, mišićno-koštanog, kardiovaskularnog, reproduktivnog, živčanog i imunološkog sustava. Selenij je važan sastojak glutation peroksidaze, glavnog staničnog antioksidativnog enzima, koji može pretvoriti slobodne radikale u perokside, dok vitamin E uklanja slobodne radikale i neutralizira njihovo potencijalno štetno djelovanje. Pretjerane količine selenija u ljudskoj prehrani smatraju se toksičnima, uzrokujući oštećenje jetre i bubrega, zgrušavanje krvi, nekrozu srca i jetre, kožne lezije, mučninu, povraćanje te gubitak kose i noktiju. Poluvodička svojstva selenija čine ga posebno vrijednim u industriji. Selenij je rijedak element na planetu Zemlji te je neobnovljiv resurs zbog neučinkovitog i teškog recikliranja. Osim ugljena, koji je obično obogaćen selenijem, orudnjenja selenija ne postoje.

Stoga je oskudnim svjetskim resursima Se potrebno pažljivo upravljati, pratiti, oporabiti i skladištiti za buduće generacije. U prvom dijelu ovog preglednog članka prikazane su koncentracije selenija u tlu, vodi i biljkama u kontekstu esencijalnih i toksikoloških učinaka na životinje i ljude, dok su u drugom dijelu ukratko prikazane inovativne biotehnološke metode bioremedijacije selenija iz okoliša.

Ključne riječi: polumetal, onečišćenje, tlo, zdravlje, biotehnologija, biljke

PRACTICAL ASPECTS OF ENVIRONMENTAL SELENIUM

This chapter introduces the most important aspects of environmental selenium (Se). By comparing it with hazardous industrial chemicals, potentially toxic metals, pesticides, and air pollutants, selenium has been a largely unrecognized contaminant, especially in developing countries. However, as an important environmental contaminant, it has gained the attention of natural resource managers and water quality regulators worldwide. In the context of climate change, this issue is particularly important considering the affinity of Se for coal (Yudovich and Ketris, 2009). The authors note that selenium is a very coalphile element: it has strong affinity for coal matter – organic and (or) inorganic but is certainly authigenic. In coal geochemistry community, there is an agreement that more complete data are needed on the selenium content of fossil fuels and air, water, and sediment samples (Zhang et al., 2023). Unfortunately, this has been impeded by the lack of a convenient method for selenium assay. Additional information is needed on the natural and industrial cycling and industrial emissions of Se (Fig. 1). Scarce knowledge on the ecologic fate of Se has prevented researchers from making absolute statements regarding its cycling in the ecosphere. On the contrary to the broad qualitative pathways of the natural cycling of Se that are well outlined, the quantitative ones need more evidences, which will be facilitated by better analytical methodology (Schilling et al., 2015).

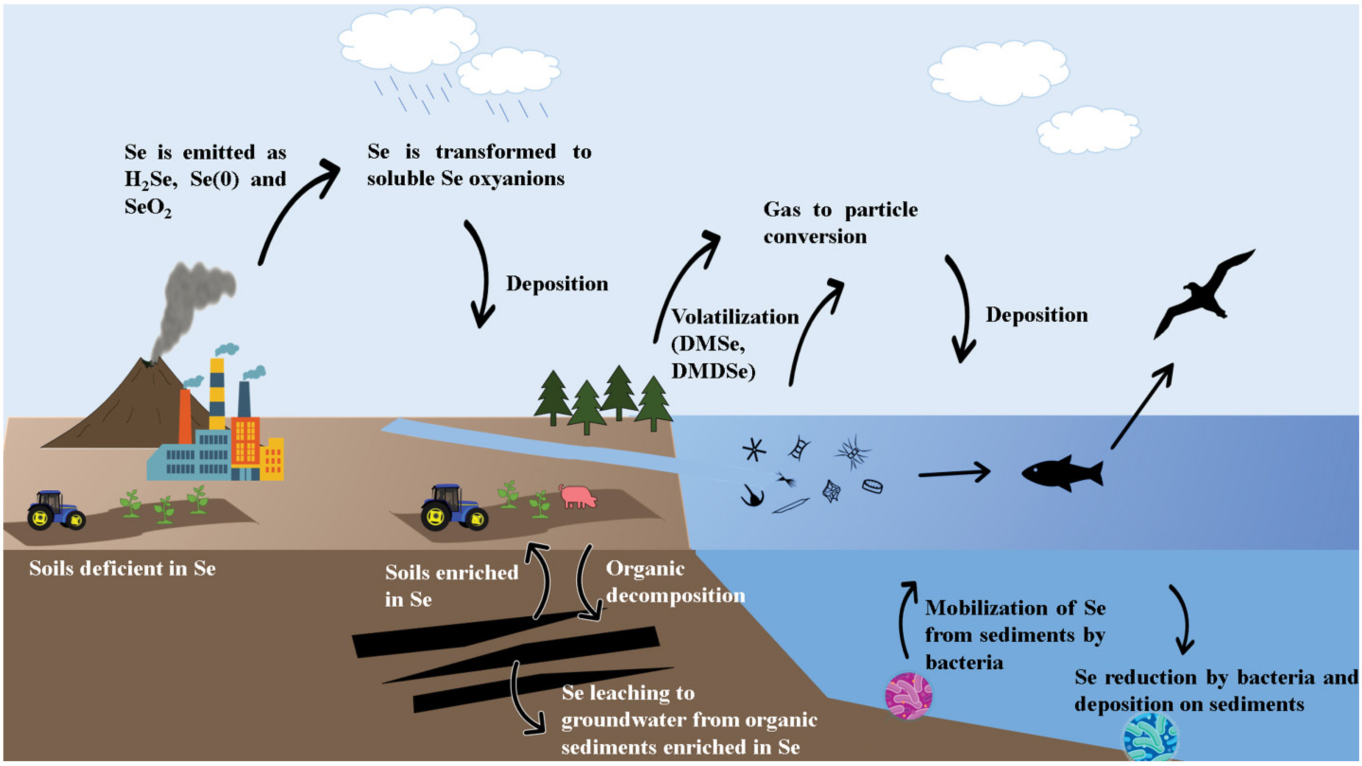

Figure 1. Simplified biogeochemical cycle of selenium. This scheme was taken from Petrović (2021). Comprehensive geochemistry and health pathways of Se can be found in Fordyce (2013).

Almost all primary Se is produced from copper refinery slimes, and the process is primarily designed for an effective recovery of precious metals, which is reflected in the low recovery achieved for Se. The apparent annual consumption of Se has increased recently, mostly in its use in electronic components. It is used in construction of the photoelectric cell, which utilizes the property of Se to convert light energy directly into electrical energy (Macaskie et al., 2010). The world's leading producers of Se include Canada, Belgium, Sweden, Japan, the USA and Mexico. The obtained compounds are used in devices with photovoltaic panels, as a light meter, photometer, counting device, controlled light switches, as well as in xerography. It is used as a burgundy and orange pigment, in combination with Cd sulphide, for plastics and ceramics. It increases the resistance of rubber to heat, oxidation and abrasion, and is used in the production of glass and as a lubricant to increase the machinability of stainless steel. Owing to its antioxidant properties, it is a useful component of mineral and vegetable oils, lubricants and inks (Adriano, 2001). A relatively high proportion of Se (about 20% of the total production) is used as a food supplement for humans and animals. Selenium is a relatively common component of numerous cosmetic products and medicines as a therapeutic agent, and recently it has been used in cardiology as the main antioxidant. In the agriculture, Se is used as an additive (mainly as sodium selenite) in insecticides, fertilizers and foliar sprays (Kabata-Pendias and Mukherjee, 2007).

Although selenium is an essential trace element needed for all living organisms, it is potentially toxic to natural ecosystems due to its bio-accumulative characteristics. It occurs naturally in the earth's crust, especially in carbonate rocks and volcanic and sedimentary soils (Reiman and de Caritat, 1998). Nearly 40% of the selenium emissions to atmosphere and aqueous environments derive from various industrial activities such as mining-related operations. In recent years, advances in water quality and pollution monitoring have shown that selenium is a contaminant of potential environmental concern. This has practical implications on industry to achieve the stringent selenium regulatory discharge limit of 5-10 µg/L for selenium containing wastewaters. According to research, possible harmful effects of long-term, low-level exposure to Se should be studied. Selenium deficiency, which is more common, is regarded as a major health problem for 0.5 to 1 billion people worldwide. Even more of them are consuming less Se than required for optimal protection against cancer, cardiovascular diseases, and severe viral infections. Over 20 structural selenoproteins and catalytic selenoenzymes have been identified in the human metabolism. They participate in antioxidant and anti-inflammatory processes and the production of thyroid hormones. Selenium and sulphur (S) are chemically similar elements that play vital roles in living systems. Yudovich and Ketris (2006) note that Se is far less mobile than S due to its easy reduction to elemental form with consequent sorption and immobilisation. Therefore, sulphates are commonly present in the environment, whereas selenates exist only in strongly oxidizing and alkaline environments. The most effective geochemical barriers for Se are Fe-hydroxides (e.g. goethite), which can strongly scavenge selenite-ion (SeO_3^-) from solution. Se-containing compounds were found to reduce carcinogenesis in animal models, and dietary supplemental Se might decrease cancer risk. Plant roots take up Se largely in the form of selenate (SeO_4^{2-}) via high-affinity sulphate (SO_4^{2-}) transporters. Thanks to the chemical similarity between Se and S, the availability of S plays a critical role in Se accumulation owing to competition effects in absorption, translocation, and assimilation. Moreover, naturally occurring S-containing substances have proven to exhibit anticancer potential, in addition to other bioactivities. Herewith, it is important to understand the interaction between Se and S, which depends on Se/S ratio in the plant or/and in the growing soil medium (Kabata-Pendias and Mukherjee, 2007).

Principally, a quantitative information concerning the natural cycling of selenium is still scarce. It is difficult to determine whether Se becomes more or less available to people through the food supply as a result of enrichment or depletion of Se in soils. Also, it is not feasible to assess the potential harm of airborne Se, since practically nothing is known concerning the toxicity or metabolism of Se compounds taken in via the lungs. Selenium has several profound metabolic interactions with other elements of ecologic concern, such as Hg, Cd, and As, and under some conditions, these interactions can be beneficial, but under other conditions they are harmful. Although reliable analytical methods for Se already exist, more convenient procedures should be developed prior to its routine screening. Undoubtedly, the difficulty of performing Se analyses partly reflects in the paucity of data on the Se content of various environmental samples (Fordyce, 2013).

According to the change of valence states of Se in the treatment processes, Li et al. (2022a) classified the treatment technologies into three categories as follows: 1) physicochemical separation including membrane technology, adsorption, coagulation, and precipitation; 2) redox decontamination employing the selenium separation from water by redox reactions, such as chemical reduction and catalysis; and 3) biological transformation, that uses plants, microbes, or wetland systems to bio-concentrate and/or convert inorganic selenium into organic species (e.g., selenoproteins, methyl selenium, etc.) to diminish the pollution and accelerate the flow and circulation of selenium in nature. Biological treatment has been regarded as the best treatment practice for Se-wastewaters due to low cost, scalability, lack of chemical sludge formation, and the ability to remove Se in a recoverable form. Biological treatment competently reduces the total effluent Se while allowing for lower operation costs and easier system operation. One major advantage of microbial reduction of Se is the production of biogenic selenium nanoparticles that have technical applications (Tan et al., 2016). Soil bioremediation implies that biological processes degrade, transform, break down, and/or essentially remove contaminants from soil, mainly using soil macrofauna and microorganisms. Reactions between Se and microorganisms can significantly influence the selenium oxidation state and therefore the transport through geological environment. Still, there are knowledge gaps concerning the dynamics, requirements and limitations on the functional organisms in soil. Also, bioremediation is mostly limited to biodegradable compounds, whereas biological processes and the conditions necessary for optimized growth and bioremediation effects of metabolically capable microbial populations are highly specific (Paul and Saha, 2019). There are some concerns that the products of biodegradation may be more persistent or toxic than the parent compound (McGuinness and Dowling, 2009), and regulatory uncertainty remains regarding acceptable performance criteria for bioremediation. A recent review by Werkneh et al. (2023) reports advantages of the biological techniques characterized by inoculation of several Se-respiring microorganisms in Se-laden wastewater. The treatment performance of the reviewed biological technologies (bioreactors systems) has shown higher removal efficiency, but the sustainability of continuous processes depends on the effects of operational parameters. Considering either small- or large-scale operations, the phytoremediation techniques utilizing microalgae and artificial wetlands performed a considerable Se elimination efficiency.

The aim of this review was to outline selenium concentrations in soil, water, and plants in terms of essential and toxicological effects on animals and humans, and to introduce briefly a few novel biotechnological microbe- and plant-assisted methods of bioremediation of environmental selenium.

SOIL SELENIUM

The chemical properties of selenium are similar to those of sulphur. It exists in nature in several oxidation states: -2, 0, +4, and +6. Selenium occurs in the +4 state as inorganic selenites that are highly toxic in soluble form. Selenite has an affinity for iron and Al sesquioxides, with which it forms stable adsorption complexes. This and the ease of selenite reduction to elemental selenium under acidic and reducing conditions make this form quite unavailable to plants and also reduce the probability of pollution of water with Se. Alkaline and oxidizing conditions favour the formation and stability of the +6 form, i.e. selenate, and most of them are quite soluble and highly toxic. This form of Se is not tightly complexed by sesquioxides, and in soils, selenates are easily leached away and are available to plants. Chemical, and possibly microbiological oxidation in alkaline soils solubilizes Se as selenate, thus available to plants. In acidic soils, Se exists in the more reduced forms that are not available to plants. Thus, two factors have been of major importance in the development of soils that produce crops containing too little or too much of Se, and these are the selenium content of the parent material, and the conditions of pH under which the soils are formed. To a large extent, the latter is related to rainfall, and the areas of excessive Se are the more arid ones (Kabata-Pendias and Mukherjee, 2007).

Regarding geological formations, the most common sources of Se are slates (e.g. Joaquin). High evaporation rates have also contributed to the formation of seleniferous soils in such areas. Soils containing low concentrations of Se can produce forage having Se content insufficient for the nutritional needs of livestock, and such soils or plants can be artificially enriched in Se-compounds. There are three common ways of increasing the concentration of Se in plants, e.g. the application of Se fertilizers to the soil, foliar spraying, and seed treatment. In Eastern Croatia for example, food, plants study showed that daily intake of Se was just 60% of required dose (Klapec et al., 1998, 2004), in comparison with animal diet, and that vegetation foliar spraying and/or seed treatment and/or fertilization was recommended management practice (Manojlović et al., 2019). When applying Se fertilizer to the soil, the amounts applied can vary from ten grams only to several kilograms per hectare, depending on the type of soil, type of crops and other factors (Adriano, 2001). In New Zealand, grazing pasture with about 70 g Se per ha as Na_2SeO_3 or Na_2SeO_4 caused elevated Se concentrations that were toxic to livestock for more than a year following the application (Grant, 1965). The high levels of Se found in plant tissue were attributed to foliar absorption and resulted in uptake that was higher compared with Se applied directly to the soil (Adriano, 2001). Foliar application of Se is a potentially effective and safe method for increasing Se concentration in forage for livestock feeding (Gupta and Gupta, 2000). Also, one of the main advantages of foliar application of Se compared to application directly to the soil is that it avoids the influence that soil conditions could have on plant uptake. Furthermore, seed treatment with Se has been shown to be effective in increasing Se concentration in plants. Fertilizers containing macronutrients are another source of Se in agriculture, especially phosphate fertilizers. It is reasonable to expect that phosphate fertilization can provide the necessary amount of Se for livestock if that fertilizer contains a sufficient amount of Se (Adriano, 2001).

The amount of Se present in the soil is a predictor of the amount of Se in plants and animal nutrition. The content of soil Se depends on its parent substrate. The average content of soil Se is approximately 0.33 mg/kg, but the range of its concentrations varies widely, from 0.005 mg/kg to 3.5 mg/kg (Adriano, 2001). The increase in soil Se concentrations in some regions of the world, either due to geochemical or anthropogenic factors, has resulted in substantial concerns. The soil of the US Great Plains is mostly alkaline and contains Se in the range of 6 to 28 mg/kg, which caused selenium poisoning of livestock (James and Shupe, 1984). Sandy soils developed in humid climates have the lowest Se concentrations, especially in podzols. The average concentration of Se recorded in the sandy soils of some countries was: 0.14 mg/kg in Poland, 0.14 mg/kg in Lithuania, 0.18 mg/kg in Russia, 0.21 mg/kg in Finland, and 0.27 mg/kg in Canada (Antapaitis et al. 2004; Eurola et al. 2003; Kabata-Pendias 2000). Cultivable soils in Sweden contain Se in the range of 0.11 – 0.53 mg/kg, with the mean value of 0.23 mg/kg (Eriksson, 2001). The usual range of Se in the soil of New Zealand is 0.3 - 0.9 mg/kg, with ranges in the surface layers 0.1 – 4.0 mg/kg. Higher Se contents were observed in the surface layers of forest soil, organic soils rich in limestone and volcanic soils (Kabata-Pendias and Mukherjee, 2007). In Croatian agricultural soils, low concentration (0.15-0.33 mg Se/kg, NE Region-Koprivnica) to high (4.17-5.38 mg Se/kg, NW Region-Istria) were noted (Popijač and Prpić-Majić, 2019; Medunić et al., 2021). The main factors controlling the form of Se and its behaviour in soil are redox potential (Eh) and pH, but several other parameters such as ligands, clays and hydroxides also play a very significant role (Kabata-Pendias and Mukherjee, 2007). Nakamaru et al. (2005) reported that the main factors in Se adsorption in Japanese agricultural soils were active Al and Fe. Nearly 80 – 100% of absorbed Se was associated with Al (28 – 78%) and Fe (14 – 53%) bound fractions. The concentration and form of Se in the soil solution is determined by various physico-chemical and biological factors. High mobility of Se can be expected in soils with high pH and Eh, and low mobility in soils with high contents of hydroxides, organic matter and clay fractions. In acidic soils, Se will appear as Se^{4+}, strongly absorbed by Fe oxides to give iron selenite ($Fe_2(OH)_4SeO_3$) and iron selenide (FeSe). The maximum adsorption of Se occurs at pH 3 – 5 and decreases as the pH increases. In alkaline soils, the Se^{6+} form predominates, which is very weakly adsorbed. Therefore, selenates (Se^{6+}) occur in soluble form in soils of arid and semiarid regions (Kabata-Pendias and Mukherjee, 2007).

SELENIUM IN WATER

Natural spring waters usually contain <1 µg/L Se. It has been estimated that 2.6 kt of Se is introduced into the rivers annually (Gaillardet et al., 2003), while 7.7 – 8.0 kt of Se is introduced into the sea annually (Schrauzer, 2004). The concentration of Se in seawater varies between 0.1 and 0.35 µg/L (Reiman and de Caritat, 1998), while average level of Se in the oceans is 0.09 µg/L (Kabata-Pendias and Mukherjee, 2007). The organic selenide (dimethyl selenide, $(CH_3)_2Se$) accounts for about 80% of the total dissolved Se in surface ocean water (Steinnes, 2003). The average global concentration of Se in river waters is 0.07 µg/L with a range of 0.02 – 0.5 µg/L (Gaillardet et al., 2003). However, some rivers such as the Colorado River contain much higher Se in the range of 1 – 4 µg/L (Kabata-Pendias and Mukherjee, 2007). Research was conducted on wastewater discharged from oil refineries in San Francisco Bay, and an average selenium concentration of 67 µg/L was determined in the range of 6.6 – 156 µg/L (Barceloux, 1999). Groundwater usually contains higher concentrations of Se than surface water. Extremely high levels of Se, up to 1000 µg/L were found in seleniferous groundwater areas of some arid regions in China. Also, some countries (USA, China, Pakistan, Venezuela) had water containing Se > 2000 µg/L (Plant et al., 2004). Usually, labile Se in soil and atmospherically deposited Se on the soil surface are rapidly leached into groundwater (Haygarth, 1994; Fig. 1).

Wang et al. (1994) determined that Se levels in streams and river waters of Finland increased up to 180 µg/L, and in the sediment up to 4 mg/kg shortly following the Se fertilization program. The permissible amount of Se in water intended for drinking has been established by the World Health Organization as 10 µg/L. The maximum permissible level of Se pollution in the US states is 50 µg/L, while the limit value of Se in irrigation water is 20 µg/L (Kabata-Pendias and Mukherjee, 2007). In NW Croatia (the Raša coal mining area, Istria), total water Se concentrations ranged from 0.60 µg/L (Raša town tap water) to 10.9 µg/L in Raša coal mine water (Medunić et al., 2020a).

According to Lemly (2004), selenium pollution should be perceived as a worldwide phenomenon, resulting from excessive Se released in the waste materials from certain mining, agricultural, petrochemical, and industrial manufacturing operations. The author notes that Se in the aquatic environment can rapidly attain toxic levels regarding fish and wildlife due to bioaccumulation in food chains and resultant dietary exposure. Such a rapid bioaccumulation could cause the very steep response curve for selenium poisoning (Fig. 2), and the author emphasizes that a transition from no effect to complete reproductive failure in fish can occur within a range of only a few mg/L waterborne selenium. Lemly (2004) concludes that if adequate foresight and planning are lacking, selenium contamination can result in a cascade of events that can quickly lead to irreversible ecosystem disruption.

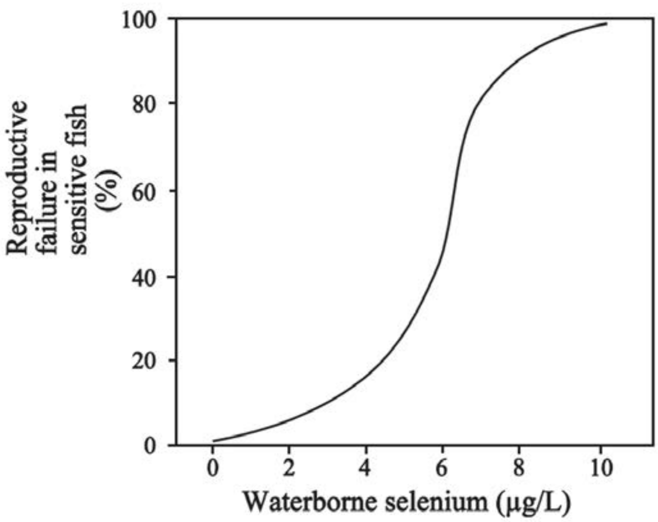

Figure 2. Relationship between the concentration of selenium in habitats favorable for bioaccumulation (e.g., wetlands, lakes and impoundments, off-channel bays along rivers), and degree of reproductive failure in sensitive fish species (e.g., bluegill, *Lepomis macrochirus*). This graph was taken from Lemly (2004).

SELENIUM IN PLANTS

Plants take up and incorporate Se into their proteins and amino acids. They can accumulate large amounts of Se that can be toxic to humans and animals (Ellis and Salt, 2003; Sasmaz, 2009). Most plants contain a fairly low concentration of Se, around 25 µg/kg, rarely exceeding 100 µg/kg, while some plants showed the ability to accumulate over 1000 mg/kg. Plants primarily take selenium from the soil as selenate or selenite. Selenate is found in alkaline soil, while selenite is found in soil with a neutral pH. If the soil is acidic or poorly aerated, selenium can form insoluble complexes with $Fe(OH)_2$ and become difficult to obtain. According to tests, plants growing in soil with a pH of 6 absorbed 47% of Se into rye leaves, and by increasing the pH to 7, the absorption increased to 70% (Haygarth et al., 1995). Selenate is more easily transported from the roots to the aerial parts of the plant than the organic form of selenium or selenite (Terry et al., 2000). The distribution of Se in the plant following the absorption depends on the species, the physiological state of the plant and the stage of development. Crop Se content has recently received much attention due to its importance in the food industry. Therefore, most of the available data refer to food crops and fodder plants. Cereals, as the biggest source of Se in the diet, are analysed the most. In general, average grain Se concentrations are higher in countries with an arid climate than in countries with a humid climate (Kabata-Pendias and Mukherjee, 2007). An exception is Finland, which implemented a program of adding Se to fertilizers. The average content of Se in some food crops in Finland, after the Se supplementation program, varied in the period from 1989 to 2001, e.g. potatoes 31 – 110 µg/kg, carrots 20 – 40 µg/kg, cabbage 160 – 580 µg/kg, and strawberries 10 – 11 µg/kg (Eurola et al., 2003). All food plants cultivated in seleniferous or Se-contaminated soils contain much more Se than plants grown in low-Se soils. Plants use selenomethionine to synthesize amino acids that make up over 50% of the total Se in cereals, but also in most fodder. The highest concentrations of selenomethionine are stored in roots and seeds, while lower concentrations of this amino acid are stored in stems and leaves (Schrauzer, 2003). The richest source of Se for humans is Brazil nuts, in which selenomethionine occurs as the most abundant amino acid (Vonderheide et al., 2002). The amount of Se present in cereals at the world level is estimated to be around 100 – 800 µg/kg (Fordyce, 2005). The average value of Se ranges from 142 to 970 µg/kg for countries with high levels of Se in grains, and from 14 to 90 µg/kg for countries with low levels of Se in grains. However, adding Se to the soil (about 10 g/ha) affected its content in barley and oat grains, ranging from 19 to 260 µg/kg or from 32 to 440 µg/kg (Gupta and Gupta, 2000). Food crops in the USA contain 100 µg/kg. Its average concentration is higher in roots and tubers (13 µg/kg in potatoes and 17 µg/kg in carrots) than in fruits (from 1 µg/kg in oranges to 4 µg/kg in apples) (Kabata-Pendias and Mukherjee, 2007). Legumes (clover and alfalfa) usually contain more Se than grasses. Average values of Se in grasses vary from 13 µg/kg (in Canada) to 352 µg/kg (in India) (Oldfield, 2002); the author notes that grass (*Agrostis tenuis*) could sometimes accumulate 2 to 7 times more Se than white clover (*Trifolium repens*). Selenium is easily absorbed by direct deposition from the atmosphere, which is clearly shown by its high accumulation in mosses and fungi. Also grasses, monocots and dicots absorb volatile Se from the atmosphere via the leaf surface. Haygarth (1994) determined that the absorption of Se in plants by direct atmospheric deposition contributed 33 – 82% of the total amount of Se in plants. Mosses from Scandinavian countries contain Se on average from 390 µg/kg to 2900 µg/kg (Berg and Steinnes, 1997). Mosses sampled in Germany from 1995 to 1996 contained Se ranging from <140 µg/kg to >560 µg/kg, and increased Se concentrations were observed in industrialized regions (Oldfield, 2002).

Plants heavily contaminated with Se are divided into three categories: (i) obligate accumulator plants that contain large amounts of Se and probably need this element, (ii) facultative accumulator plants that absorb about 100 µg/kg of Se, and (iii) non-accumulator plants (Kabata-Pendias and Mukherjee, 2007). Plants that are considered obligatory accumulators and contain large amounts of Se stored in leaves and stems are *Astragalus*, *Oonopsis*, *Stanleya*, *Xylorhiza* and *Machaeranthera* (Terry et al., 2000). These plants can accumulate significantly more than 100 µg/kg when grown on Se-rich soils, but even when grown on soils with low and medium Se content, it can accumulate up to 100 µg/kg Se. In certain species of *Astragalus*, Se content > 5000 µg/kg was recorded (Streit and Stumm, 1993), and they represent one of the primary sources of possible poisoning. Plants that fall under facultative accumulators also accumulate significant amounts of Se even in soils that are not rich in selenium. The most important genera are *Astragalus*, *Aster*, *Atriplex*, *Comandra*, *Castilleja*, *Brassica*, *Grazyia*, *Gutierrezia*, *Grindelia*, and *Machaerantheran* (Terry et al., 2000). Plants that are not accumulators and usually contain less than 30 µg/kg in field conditions are considered non-accumulator plants (Kabata-Pendias and Mukherjee, 2007).

HEALTH PERSPECTIVES OF LOW AND HIGH LEVELS OF ENVIRONMENTAL SELENIUM

The most striking feature of Se is the fact that it is a nutrient metalloid trace element, essential in small quantities, but too much of it is toxic for life forms. People, animals, and plants commonly face hardships both from too much of it and from too little, depending on the levels of Se in the soil where they live. Marco Polo was the first to report on the toxicity of Se, which he observed in the 13th century during his travels through western China. At first, selenium was considered toxic to humans, until the 1950s when Schwarz and Foltz (1957) described an association between dietary Se intake and prevention of liver necrosis in rats. The significance of Se intake for humans was noticed in the 1970s, when cardiomyopathy was found in certain areas of China, which was associated with Se deficiency in the diet. This disorder is called Keshan disease and is endemic at areas of China that have some of the Se-poorest soils in the world (Ge et al., 1983). These studies have established that selenium deficiency in the environment can cause numerous diseases in humans and animals (Kieliszek and Blazejak, 2013). In nature, Se occurs in organic and inorganic forms. The inorganic form can be found in various minerals such as selenide, selenite and selenate. In cereals, selenium is an integral part of the organic component that contains SeMet (amino acid selenomethionine), while SeCys (selenocysteine) can be found in foodstuffs of animal origin. Therefore, selenium is taken in food in the form of selenomethionine and it is considered the most effective form for human and animal nutrition (Adriano, 2001). Food is the primary source of selenium for humans and due to differences in dietary habits, its intake varies considerably. Because of its significant role in numerous organ systems, its excessive presence or absence can result in various disorders.

Currently, the lack of Se in the daily human diet is a significant problem involving about 0.5–1 billion people worldwide (Holben and Smith, 1999). Although according to the data of the World Health Organization, the recommended daily intake is about 70 µg Se per day, residents of many European countries consume an average of 30 µg Se per day (Klapec et al., 1998, 2004; Kieliszek and Blazejak, 2013). An intake of a daily Se dose of 400 µg or more will have a negative effect and is considered toxic. In the human body, a lack of selenium can lead to diseases of the endocrine, musculoskeletal, cardiovascular, immune, reproductive and nervous systems. Therefore, Se is considered a key element for the normal functioning of the immune system, metabolism, growth and development. Excessive concentrations of Se in the human diet cause gastrointestinal disorders. New research conducted around the world indicates that sufficient amounts of Se in the body can minimize the risk of certain types of cancerous diseases, possible male infertility, viral infections, changes in mood and cardiovascular diseases. In the human body, Se is primarily required for the synthesis of selenoproteins, a group of proteins whose role is to regulate the immune system and defense against antioxidants, and the detoxification of heavy metals (Martens et al., 2015).

Selenium deficiency in the human diet is a problem that is prevalent in areas of North America, China and Europe, especially in Scandinavia, where the soil contains too little Se (Adriano, 2001). Although no significant disorders in the population caused by Se deficiency have been observed in Finland, its low intake was considered as one of the causes of increased risks of death from cardiovascular disorders and certain types of cancer (Salonen et al., 1982). Estimated Se intakes across the world were found to be as follows (µg Se per day): the USA 70 – 150, Canada 110 – 220, the Netherlands 110, Italy 140, France 170, New Zealand 25, Japan 210, the United Kingdom 200, and Germany 60 (ATSDR, 2002; Combs, 2001).

Selenium deficiency in humans was first identified as an endemic cardiomyopathy, i.e. Keshan disease in China and in some parts of Russian Federation, what was later defined as Kashin-Beck's disease. More than 20 structural selenoproteins and catalytic selenoenzymes have been identified in human metabolism, which participate in antioxidant and anti-inflammatory processes, and in the production of thyroid hormones. Recently, its role in chemoprevention against HIV and AIDS has been recognized (Baum et al., 2000). The correlation of Se deficiency with cardiovascular diseases, cirrhosis and diabetes has also been recorded (Navarro-Alarcón and Lopez-Martinez, 2000). Symptoms of Se deficiency in humans include muscle weakness and pain, muscle inflammation, fragile red blood cells, pancreatic degeneration, abnormal skin coloration, cardiac muscle dysfunction, prolonged illness, susceptibility to cancer, Keshan's disease (cardiomyopathy), and Kashin Beck's disease.

Symptoms of Se toxicosis in humans are characterized by liver and kidney damage, blood clotting, heart and liver necrosis, skin lesions, hair and nail loss, and nausea and vomiting (KabataPendias and Mukherjee, 2007). Selenium is considered essential for the functioning of certain enzymes and proteins, especially glutathione peroxidase, an enzyme that prevents oxidative damage to cells by various peroxides. Rotruck et al. (1973) were the first who showed that Se was an obligatory component of this key antioxidant enzyme. Over 100 Se-proteins, enzymes and other compounds have been identified in biological samples. The most common organic compounds are selenomethionine (SeMet), selenocysteine (SeCy), dimethylselenide (DMSe), dimethyldiselenide (DMDSe), selenomethyltransferase (SMT), semethylmethionine (SeMM), and glutathione peroxidase (GSH-Px) (Kabata-Pendias and Mukherjee, 2007). According to Spallholz (1994), selenium and its compounds have been considered the most effective antioxidants in the prevention and treatment of cancer. Selenomethionine (SeMet) is involved in oxidation processes as a promoter and inhibitor, and in cooperation with glutathione, SeMet acts catalytically as a cellular antioxidant (Schrauzer, 2003), and also enhances the antioxidant effect of vitamin E. Selenium is considered to have a protective role in many diseases, such as cardiac arrhythmia, atherosclerosis, cirrhosis of the liver, cancer (especially of the colon and prostate). It also serves as an effective detoxifier of some metals, due to its ability to bind Cd, Pb, Hg, and Ta, thus reducing their toxicity. Its immunological functions increase the antibacterial and antiviral defence of the organism (Kabata-Pendias and Mukherjee, 2007).

Increasingly, the available amounts of Se in food are being measured, due to its important role in human and animal nutrition. Selenates are the most available forms (SeO_4). The availability of Se is increased in a diet rich in methionine and vitamins E, A, and C, while a diet enriched in metals and sulphur inhibits the availability of Se (Kabata-Pendias and Mukherjee, 2007). Excessive intakes of As accelerate the excretion of Se out of the body. According to Spallholz et al. (2004), the addition of As to animal feeding items suppressed Se toxicity, while Wuyi et al. (2003) described the possibility of mitigating endemic arsenicosis by adding Se. The tolerable upper intake level for adults is 400 µg per day, while the no-observed-adverse-effect level is 800 µg per day (Schrauzer, 2004). The recommended intake of Se depends to a large extent on the life stage of a person.

In China, Se toxicity (selenosis), resulting in hair and nail loss and nervous system disorders in the human population, has been recorded in Enshi District, Hubei Province and in Ziyang County, Shanxi Province. There, some villages underlain by carbonaceous strata had several cases of Se toxicosis whereas other villages sited in apparently similar geological and geochemical environments had no recorded cases of human or animal toxicosis. Therefore, Fordyce et al. (2000) examined soil, grain, drinking water and human hair samples to determine the controls on Se availability in three Se environments in Enshi District. The results showed that the majority of samples in low-Se villages were deficient or marginal in Se, and that Se availability to plants was inhibited by adsorption onto organic matter and Fe oxyhydroxides in soil. In high-Se villages, localised lithological variations resulted in considerable ranges in Se concentrations in all sample types. Notably, deficient and excessive levels of Se were recorded in samples from the same village. Selenium bioavailability in the high-Se toxicity villages was found to be controlled by the total soil Se concentration and pH. The study found that a greater proportion of the Se was plant available in villages where the carbonaceous strata were interbedded with limestone. Herewith, Fordyce et al. (2000) advised the local villagers against the planting crops in the studied areas.

Along local inhabitants, domestic animals (e.g. chickens and pigs) also suffer from Se poisoning, and only a few animals survive once they develop the disease. Fordyce (2013) reported that chronic selenium intoxication led to two conditions known as alkali disease and blind staggers in grazing animals. Alkali disease was characterized by dullness, lack of vitality, emaciation, rough coat, sloughing of the hooves, erosion of the joints and bones, anemia, lameness, liver cirrhosis, and reduced reproductive performance. Regarding blind staggers, pathological changes included liver apoptosis, cirrhosis, kidney inflammation, and impaction of the digestive tract. Additionally, Fordyce (2013) noted that high selenium intakes in pigs, sheep, and cattle had been shown to interfere with normal fetal development.

Furthermore, selenosis had been known to cause congenital malformation in sheep and horses and reproductive problems in rats, mice, dogs, pigs, and cattle whereby females with high selenium intakes had fewer smaller young that were often infertile.

On the other hand, Se deficiency in cattle is associated with white muscle disease that causes mortality of newborn calves and reduced productivity of growing and adult cattle (Hefnawy and Tórtora-Pérez, 2010). Similarly, Enjalbert et al. (2006) reported delayed conception, muscular degenerative disease in calves, myocardial necrosis and heart failure, immune dysfunction, increased risk of mastitis, abortion and perinatal mortality, and growth retardation in young animals, all caused by Se deficiency. A study by Hailu et al. (2022) shows that cattle Se deficiency is likely to be highly prevalent in Ethiopia (characterized by widespread Se deficiency), which will negatively affect the health and productivity of livestock. The authors predict it to be geographically dependent, and recommend more extensive surveys to map Se concentration in soil-feed-livestock-human cycle in Ethiopia and elsewhere.

BIOREMEDIATION OF ENVIRONMENTAL SELENIUM

Microbial detoxification of the environment is becoming a powerful remediation technique with many advantages, including not only the low cost and the absence of by-products but also the ubiquity and wide selection of available microorganisms, their rapid characterization, reuse, as well as the possibility of in situ and ex situ application (Fiket et al., 2020a). Since the water, our most precious resource, is particularly vulnerable to the contamination by hazardous trace elements, much efforts have been put into its treatment with microorganisms. It has proved highly efficient and cost-effective. Zhao et al. (2023) successfully isolated As-tolerant bacteria (*Acinetobacter gandensis* and *Delftiatsuruhatensis*) from polluted water and studied biotransformation and bioaccumulation mechanisms of As under the symbiotic immobilization of bacteria and algae systems (*Chlorella*), which was constructed to provide technical support for the cleaner production of such a wastewater. Considering the sustainable energy production, biotransformation technological studies convert low rank coal reserves to alternative fuels and non-fuel organic chemicals by isolating fungi from coal environments, that are optimized for coal degradation processes (Sabar et al., 2019).

Regarding the biological selenium reduction, it has emerged as the leading technology for Se removal from wastewaters since it offers a cheaper alternative compared to physicochemical treatments, and is suitable for treating dilute and variable selenium-laden wastewaters. One way is to transform toxic soluble Se species into insoluble Se species like nanoparticles, which get separated by sedimentation, coagulation and filtration processes. Elemental selenium nanospheres exhibit unique optical and spectral properties for various industrial applications, i.e. medical, electrical, and manufacturing processes. Despite the advances in biotechnology based on selenium reduction, there are still several challenges, particularly in achieving stringent discharge limits, the long-term stability of biogenic selenium and predicting the fate of bio-reduced selenium in the environment. Tan et al. (2016) recommend further improvements of the treatment efficiency regarding Se removal and recovery, and the simultaneous reduction of SeO_4^{2-} and other oxyanions (NO_3^-/SO_4^{2-}). Furthermore, operation conditions should account for the real wastewater properties such as pH, temperature and volume. According to Jain and Tembhurkar (2022), research on the plantation of bio-energy crops over the fly ash dumpsites serves remediation along with distinct energy outcomes. The issue of the slow growth of plants, due to lack of nutrients and microbial activities is being resolved through advances in bioremediation research done in conjunction with organic matter, microbial inoculants, and inclusion of wastewater. New sustainable solutions are sought by employing various plants and microbes in the matrix combination, and by using wastewater to supplement required nutrients.

Since toxic Se oxyanions and S species are often jointly present in contaminated waters and soils, Song et al. (2022) investigated the effect on kinetics and resulting products for bio-reduction of selenium oxyanions in the presence of biologically produced sulfur resulting from bio-oxidation of sulfide in (bio)gas-desulfurization (bio-SO) and of sulfate. It was found that S as bio-SO enhances selenite removal for two different microbial consortia, 'Emmtec' and 'Eerbeek'. The bacterial generation of sulfide from sulfur chemically reacted with selenite to form SeS_2, that was further bio-reduced to black crystalline elemental Se and sulfide. Thus, biological sulfur cycling could reduce toxic selenite mobility in the environment by producing hydrophobic and thermodynamically stable crystalline selenium.

Environmental Se usually coexists with other hazardous elements, such as chromium, arsenic, mercury, etc., and the latest research explores the antagonism among them in various aspects. For example, due to structural similarities between sulfate and chromate, the latter has been reported to cross the cell membrane via the sulfate transport system (Cervantes et al., 2001), which is also the case with selenate (Terry et al., 2000). It leads to potential competition among Se, S and Cr for an uptake or assimilation by plants and other organisms. Therefore, Zou et al. (2020) used microalgae *Chlorella vulgaris* for Se/Cr bioremediation and evaluated their mutual effects on the removal efficiency. The results showed high removal for selenate (50%), selenite (93%), chromic nitrate (89%), and dichromate (88%) over the 72-h period. According to the findings, Cr(VI) significantly impeded Se removal (selenite in particular), due to competition between the both for the algal uptake, whereas Cr(III) enhanced Se removal. Similarly, Se significantly increased Cr removal rates (up to 95%) for the algal uptake under co-exposure to Se(IV) and Cr(III). The study showed the promising potential for Se/Cr removal using *C. vulgaris*, which could contribute to the development of an algal treatment system for the remediation of Se/Cr contaminated waters. Furthermore, Paul and Saha (2019) reviewed an issue stemming from the bioaccumulation of Se and As, resulting from specific geogenic circumstances aggravated by anthropogenic activities. Hereby, the bioremediation techniques may involve the use of plants (phytoremediation) (Salt et al., 1998), plant-microbe interactions (rhizoremediation) (Kuiper et al., 2004), bioaccumulation assisted by live cells and use of dead microbial biomass (biosorption) (Hlihor et al., 2017) to clean up the contaminated sites. Also, the use of genetically engineered plants for uptake, transport, and sequestering of hazardous metals opens up new avenues for enhancing the efficiency of phytoremediation. Mal et al. (2021) demonstrated the simultaneous removal of lead (Pb) and Se as PbSe biominerals using anaerobic granular sludge, which is eco-friendly, sustainable, and cost-effective method.

Borah et al. (2021) isolated a native strain of *Bacillus paramycoides* from the leachate of coal mine overburden rocks for the purpose of producing selenium nanoparticles (SeNPs) by biogenic reduction of selenite, one of the most toxic forms of Se. The authors note that the high resistance to selenite toxicity coupled with the facile and eco-friendly biosynthesis process of SeNPs indicates a potential use of *B. paramycoides* SP3 for SeNPs biosynthesis and biological removal of selenite from highly contaminated environments. Additionally, the biogenic SeNPs could be potentially applied in the biomedical and industrial sectors, and that would require further studies to substantiate their use as alternatives to the chemical counterparts. Zhang et al. (2019) isolated two bacterial strains (*Lysinibacillus xylanilyticus* and *Lysinibacillus macrolides*) from a naturally occurred Se-rich soil at a tea orchard in southern Anhui Province in China. The both strains aerobically reduced selenite with an initial concentration of 1.0 mmol/L to elemental Se nanoparticles completely within 36 hr. The study implies that the microbes from Se-rich environments are more tolerant to Se and generally quicker and more efficient than those from Se-free habitats in the reduction of Se oxyanions, and biologically synthesized SeNPs could be applied in agriculture, food, environment, and medicine. Vogel et al. (2018) explored the interaction between the toxic oxyanions selenite and selenate and the plant growth promoting bacterium *Azospirillum brasilense*, supported by a comprehensive characterization of the formed selenium-sulfur nanoparticles. The study showed its ability to biotransform selenite to selenium particles containing a certain amount of sulfur, even if environmental waters supplemented with selenite were used, they may significantly contribute to the biogeochemical cycling of both elements in soil as well as to their soil-plant transfer.

Herewith, microbial biotransformation of selenite under certain circumstances could be used for various bioremediation and biotechnological applications. Gan et al. (2021) evaluated the use of earthworm *Eisenia fetida* and organic materials for Se remediation. Earthworms are key representatives of soil macrofauna, and are able to assimilate various pollutants through direct dermal contact and/or soil ingestion. The study demonstrated that earthworms removed Se, particularly selenite, from contaminated soil, especially when supplied with manure. Selenium in soil greatly increased the bacterial diversity of earthworm casts, with more Se-reducing bacteria found in the casts of selenite-exposed earthworms as part of defense mechanism against Se toxicity.

PHYTOREMEDIATION OF ENVIRONMENTAL SELENIUM

Phytoremediation is a green technique by which soil plants, including grasses, energy crops, and trees, and associated soil microbes are used to mitigate contaminant trace elements. Essentially, plant roots stabilize the soil and inhibits the mobilization of toxic trace elements. Its efficiency depends on the selection of plant species and sites as well as the bioavailability of contaminants. This strategy certainly requires time and the development of a site-specific plan with plant species appropriate for the particular remediation site. For example, Srivastava et al. (2021) reviewed phytoremediation method as an aesthetically appreciable and successful approach that can be used for arsenic (As) decontamination with use of the best approach(es) and the most promising plant(s). However, the authors note that phytoremediation lacks the required speed and sometimes the stress caused by As could diminish plants' potential for remediation. They recommend the augmenting plants' potential with appropriate technological methods including microbial and nanoparticles applications and genetic modification of plants to alleviate the As stress and enhance As accumulation in phytoremediator plants. On the other hand, the accumulation of essential and non-essential trace metal(loid)s in medicinal plants beyond the permissible limits can pose a human health hazard. Similarly, if plants growing on contaminated sites are used as raw materials, lack of knowledge on presence of such toxic substances and no regulatory guidelines can lead to serious health risks (Tripathi et al., 2012).

The long-term ecological risks of contaminated sites are commonly investigated by assessing adverse effects in plants due to chronic exposure to multiple stressors. That approach was used by Skoko et al. (2023) who found that blackberry from a coal ash disposal site showed the best adaptation to coal ash stressors, whereas the plant species itself was the most significant factor that influenced the magnitude and direction of differences in biochemistry of plants that grew on coal ash compared to the control ones. The biochemical/physiological variations in plant responses to heavy metals stress govern plant's ability to phytoremediate/tolerate contaminant trace metals. Natasha et al. (2019) found out, by comparing the physiological modifications, photosynthetic performance and detoxification potential of *Brassica oleracea* under different levels of Cr, Ni, and Se that Ni was more phytotoxic than Cr and Se. The phytoremediation/tolerance potential of *B. oleracea* to Ni, Cr and Se stress varied with the type of metal, their applied levels, response variables and plant organ type (root/shoot). Similarly, Reynolds and Pilon-Smits (2018) emphasize that the ecological studies have shown negative effects in Se-sensitive ecological partners of Se hyperaccumulators, while offering a niche and having positive effects on Se-resistant partners. Negative effects were found for many generalist herbivores, sensitive plant species, and sensitive fungal pathogens. Resistance was found for several leaf and seed herbivores, neighboring vegetation, endophytic fungi and likely certain pollinators. Bacteria do not seem to suffer toxicity from the Se levels commonly found associated with Se hyperaccumulators, but plant Se does appear to affect microbial competition, since it can affect the plant microbiome. Considering algae, they mostly absorb Se in the form of selenate or selenite using mechanisms similar to those reported in plants. By exhibiting the capacity of efficiently converting Se to less harmful volatile compounds, as a strategy to cope with Se toxicity, some microalgae play a crucial role in Se-cycling through the ecosystem. On the plus side, if enriched in Se, they may be used in Se biofortification programs aimed to improve Se content in human diet via supplementation of valuable food. Depending on several factors, Se may act as pro-oxidant or antioxidant in algae (Schiavon et al., 2017).

Concerning fauna, Yue et al. (2021) employed the earthworm *Eisenia fetida* as a bio-indicator of environmental pollutants to investigate Se acute toxicity, enrichment, and distribution through exposure tests using filter paper, artificial soil and cow manure. They note that Se is a beneficial element in humans and animals, but its excessive levels may have fatal effects on earthworms in soil and compost. Therefore, they point out that more attention should be paid to the potential pollution of Se in the environment, especially the agricultural environment which is subject to significant human interference, and where earthworms reside. Hladun et al. (2013) conducted a two-year semi-field study by which the weedy plant *Raphanus sativus* (radish) was exposed to three selenate treatments and two pollination treatments to evaluate the effects on pollinator-plant interactions. Honey bee (*Apis mellifera* L.) pollinators were observed to readily forage on *R. sativus* for both pollen and nectar despite high floral Se concentrations. Se treatment increased both seed abortion (14%) and decreased plant biomass (8-9%). Moreover, herbivory by birds and aphids was decreased on Se-treated plants, implicating a potential reproductive advantage for the plant. The study confirmed that Se could accumulate in the flowers of *R. sativus*, and foraging pollinators thus might receive significant doses of Se.

Selenium uptake and translocation in plants are largely accomplished via sulfur transport proteins, and plant Se metabolism also largely follows the S metabolic pathway (Trippe and Pilon-Smits, 2021). Hyperaccumulators, which can accumulate Se at up to 1000 times higher concentrations than normal plants, present interesting specialized systems of Se transport and metabolism. There are around fifty known Se hyperaccumulator taxa that span seven families, but most belong to three families, i.e. *Fabaceae*, *Asteraceae* and *Brassicaceae* (Reynolds and Pilon-Smits, 2018). According to Wu et al. (2020), *Cardamine violifolia* (*Brassicaceae*) is a novel Se hyperaccumulator special vegetable rich in nutrients (a seleniferous area of the Enshi county, China). Their results showed that biofortification with different exogenous Se forms and concentrations had different effects on the growth, Se accumulation, nutrition quality, element uptake, and antioxidant response in *C. violifolia*. Regardless of inorganic or organic Se treatments, high Se (400–800 mg/L) significantly inhibited the growth, impacted the absorption of some nutrients, and caused oxidative stress in the plant. The phytotoxic effects of Se can be overcome by employing transgenic plants involving expression of specific bacterial genes. In this regard, Usmani et al. (2019) reviewed the mechanism and enzymatic pathways behind Se accumulation including upregulation of genes concerned with S or Se assimilation and volatilization, selenocysteine methylation, and selenocysteine conversion to elemental Se. Li et al. (2022b) report that the Se-treated transgenic plants showed higher levels of alanine and methylselenocysteine than wild-type plants, which indicated that this approach might have successfully redirected Se flow in the plant. The transgenic plants showed, following the treatment with selenate and selenite, enhanced tolerance to them, and their substantial removal, i.e. 40% and 130%, respectively, compared to wild-type plants. Hereby, their study offers a glimpse of hope that genetically modified plants could play a role in the restoration of Se-contaminated environments. Considering semi-arid lands (e.g. the Southwestern U.S.), with poor quality waters (high salinity and B) that are unsuitable for typical agronomic crops, Bañuelos et al. (2022) recommend the growing of an industrial crop called guayule (*Parthenium argentatum A. Gray*), that could be useful for the purpose of phytoremediation of environmental Se.

DISCUSSION AND CONCLUSION

The intensive anthropogenic activities worldwide are discharging toxic pollution into rivers, soils, and sediments, and in some instances, violating national standards for waste discharges, whereas local environmental authorities fail to stop or prevent the violations. Due to the large amount of mentioned activities, huge areas are at risk of being affected by associated pollution. Usually, it takes several years to complete an individual remediation scheme, from beginning a scoping study to installing a full-scale treatment system, and it can be very costly. Various reports estimate staggering costs over the next decades to deal with such pollution issues. A clear understanding of the sources of pollution, provided by assessments and reports, is a valuable resource for long-term planning of effective remediation (clean-up) programmes of such sites. Commonly, waste treatment methods include physico-chemical processes (e.g. chemical oxidation, membrane processes, adsorption, etc.), biological methods (e.g. in situ bioremediation), stabilization and solidification, thermal methods, and land disposal (e.g. LaGrega et al., 1994; Oreščanin et al., 2007, 2009; Rađenović and Medunić, 2015). Relatively recently, biological processes are used to degrade hazardous wastes, and it has been coupled with many obstacles and uncertainties.

For instance, LaGrega et al. (1994) emphasize that a key complexity is that the isolation of microbes must be specific, but the problem is that countless different enzymes, acting in a sequential manner and not necessarily coming from a single species, are needed to degrade a persistent compound. The authors note that the potential of genetic engineering to go beyond naturally occurring microorganisms provides numerous possibilities for degrading persistent compounds. Furthermore, the necessity of innovative integration of biological treatment with physical-chemical processes is emphasized.

Previously, coal mining industry and coal combustion have represented massive sources of unregulated pollution as power plants had no limitations on the levels of toxics they were allowed to put into waterways. Nowadays, communities bear the costs of required expensive treatments. Coal and ash waste commonly degrade soil and water resources due to improperly disposed mineral residues at unprotected landfills (Voltaggio et al., 2015; Fiket et al., 2020b, 2021; Petrović et al., 2022). Also, abandoned mines are still causing pollution, decades following their closure, since the waters draining from the mines often contain high concentrations of toxic trace metal(loid)s (Pavlović et al., 2004; Sasmaz et al., 2015; Medunić et al., 2020a, b). One of them is selenium that has been related to many health issues, which are attributed to natural geochemical processes and/or anthropologic activities, that fall in the scope of medical geology (Li et al., 2012; Petrović, 2021). According to Loomba et al. (2020), many studies have shown that overexposure to environmental selenium may exert a wide pattern of adverse effects on human health, but much uncertainty still surrounds some of them as well as the exact amounts of exposure involved. The authors studied a population chronically-exposed to high selenium levels (Punjab, India), and observed abnormalities in blood chemistry, particularly adverse lipid profiles and altered thyroid hormone levels, as well as increased hepatic and pancreatic enzymes. They conclude that the wide spectrum of blood chemistry alterations observed highlights the potential for adverse health effects of intermediate to severe selenium overexposure, and identifies sensitive endpoints for the detection and monitoring chronic selenium intoxication.

Considering China, Croatia, and India, the three countries are somewhat similar in terms of coal environmental legacy and selenium environmental distributions. Papers have reported low as well as high levels of environmental Se in different parts of the three countries, and some of them (high ones) are directly related to either (highly sulphurous) coal (Yang et al., 1983; Zheng et al., 1999; Zhu et al., 2001, 2004, 2008; Qin et al., 2012; Medunić et al., 2021; Kang et al., 2022; Prevendar Crnić et al., 2022) or agricultural practices (Gao et al., 2007; Dhillon and Dhillon, 2014, 2016; Eiche et al., 2015, 2019). Undoubtedly, the environmental implications of excessive Se and the associated threats to ecosystems and human health have been documented by a number of papers.

For instance, Lemly (1997) discussed how rain-driven leachate and overflow rich in Se from coal piles and ash ponds could make its way into rivers and streams. Afterwards, selenium gets bioaccumulated in aquatic food chains, contaminating the diet of fish, wildlife, and sometimes humans. Based on collected blood, hair and nail samples from 680 adult volunteers (267 men and 413 women) living in seven villages located in the seleniferous area of Punjab (India), Chawla et al. (2020) measured Se levels in the specimens. Association of a number of adverse health endpoints with serum and hair selenium was stronger than for nail selenium contents. The endpoints were as follows: higher prevalence of nausea and vomiting, bad breath, worm infestation, breathlessness exert and bad breath, chest pain, hair and nail abnormalities and loss, garlic odour, edema, spontaneous abortion, and overall selenosis. That study confirmed the occurrence of adverse health effects in subjects exposed to high levels of environmental selenium. In addition to positive as well as negative health aspects of environmental Se, it is by all means a valuable element the market price of which is increasing. From the circular point of view, the paper by He et al. (2018) essentially emphasizes necessity of shifting attention from Se remediation to Se recovery as Se resources have become critical in recent years due to an increased market demand. However, removal of Se from various wastes has been challenging (Lenz and Lens, 2009; Medunić et al., 2019). On the plus side, a number of studies have showed promising trends in this regard recently. Bañuelos and Dhillon (2011) conducted multi-year field and greenhouse studies with different plant species in California, USA and Punjab, India under high Se growing conditions. The plant species were as follows: canola (*Brassica napus*), mustard (*B. juncea*), broccoli (*B. oleracea*), spearmint (*Mentha viridis*), sugarcane (*Saccharum officcinarum*), guar (*Cyamopsis tetragonoloba*), wheat (*Triticum aestivum*), and poplar (*Populus deltoides*). They found out that the remediation efficacy was strongly influenced by sulphate content in the soil. On California soils, the presence of sulphate salts reduced the efficacy of phytomanagement of Se in contrast to the low sulphate soils in Punjab, India. Herewith, in northwestern India the *Brassica* and poplar based cropping systems were highly suitable for managing Se-contaminated soils under low sulphate growing conditions, and remediation of Se-contaminated soils might be possible within a period of 20–35 years (depending on uptake efficiency over time). At the same study locality in India, Dhillon and Dhillon (2000) had investigated the direct and residual influence of sulphur application as gypsum on Se accumulation, yield and tissue composition of wheat and rice crops grown in a sequence on a naturally-occurring seleniferous soil. Their findings point at reduced Se in grain and straw of rice and wheat crops owing to the application of gypsum on the soil. According to Lusa et al. (2019), Se(IV) tolerant, Se0 producing soil bacteria isolated from boreal, harsh bog environment, can influence Se accumulation in a common crop plant *B. oleracea* (kale). The authors suggest that this feature could be highly beneficial for the further development of phytoremediation and biofortification applications, especially as these bacteria seem not to distinguish between their habitat or plant partner. Wadgaonkar et al. (2019) reported for the first time on the potential of *Delftia lacustris* as a selenate and selenite reducing bacterium, capable of tolerating and growing in the presence of ≥ 100 mM selenate and 25 mM selenite. It proved to be able to reduce both selenate and selenite under aerobic conditions, and showed a unique metabolism of selenium oxyanions to form elemental selenium and possibly also selenium ester compounds; hereby, it could be a potential candidate for the remediation of selenium-contaminated wastewaters in aerobic environments. The authors emphasize how their novel finding would advance the field of bioremediation of selenium-contaminated sites and selenium bio-recovery and the production of potentially beneficial organic and inorganic reactive selenium species.

Overall, future environmental contamination with selenium is imminent if the increasing energy demand is covered by fossil fuels (coal in particular). On the other hand, selenium has beneficial roles in human and animal health. Research has demonstrated how selenoproteins are essential components of living organisms as they regulate many biochemical processes, governing growth and development and preventing many disorders and diseases (Bodnar et al., 2012). Ongoing investigations should expand knowledge on their other functions in the body and protective roles against diseases, principally cancer. In this regard, the use of plants capable of taking up and accumulating large amounts of Se as genetic material might help understand the exact mechanisms by which Se gets accumulated, and hence render the phytoremediation of seleniferous soils more efficient. Recycling of selenium for the purpose of increasing industrial uses is one more reason for such a research. Therefore, this review should lead to a better understanding of how various activities affect ecological risks posed by increased as well as low levels of environmental Se. It also outlines latest studies on bioremediation and phytoremediation of Se in order to protect the animal and human health.

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