Sustainable Plant Nutrition in a Changing World

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Sustainable Plant Nutrition in a Changing World

This book series aims to provide new insight and improve understanding of plant nutrition, a crucial component in plant production and food security. Plant nutrition encompasses the study of plant growth and metabolism, external supply of necessary chemical compounds and the biochemistry of various nutrients in plants. This field of study has grown in light of recent scientific advances and climate change and has expanded to include the impact of climate change, pollution, nanomaterials, biofortification and genomics on the nutrition of plants.

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Selenium and Nano-Selenium in Environmental Stress Management and Crop Quality Improvement

Springer

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Preface

Climate change provokes a plethora of environmental stresses in plants. These environmental stresses are the major limiting factors for constraining crop yield and quality of produce. In order to achieve sustainable development in agriculture and to increase agricultural production for feeding an increasing global population, it is necessary to use ecologically compatible and environmentally friendly strategies to decrease the adverse effects of stresses on the plant. Selenium is one of the critical elements from the biological contexts because it is essential for human health; however, it becomes toxic at high concentrations. It has been widely reported that selenium can promote plant growth and alleviate various stresses as well as increase the quantity and quality of the yield of many plant species. Nonetheless, at high concentrations, selenium causes phytotoxicity. In the last decade, nanotechnology has emerged as a prominent tool for enhancing agricultural productivity. The production and applications of nanoparticles (NPs) have greatly increased in many industries, such as energy production, healthcare, agriculture, and environmental protection. The application of NPs has attracted interest for their potential to alleviate abiotic and biotic stresses in a more rapid, cost-effective, and more sustainable way than conventional treatment technologies. Recently, research related to selenium-NPs-mediated abiotic stresses and nutritional improvements in plants has received considerable interest by the scientific community. While significant progress was made in selenium biochemistry in relation to stress tolerance, an in-depth understanding of the molecular mechanisms associated with the selenium- and nano-selenium-mediated stress tolerance and bio-fortification in plants is still lacking. Gaining a better knowledge of the regulatory and molecular mechanisms that control selenium uptake, assimilation, and environmental stress tolerance in plants is therefore essential to develop modern crop varieties that are more resilient to environmental stresses.

In this book, *Selenium and Nano-Selenium in Environmental Stress Management and Crop Quality Improvement*, we present a collection of 20 chapters written by leading experts engaged with selenium- and nano-selenium mediated environmental stress management and crop quality improvement. This book aims to provide a comprehensive overview of the latest understanding of the physiological, biochemical, and molecular basis of selenium- and nano-selenium-mediated environmental stress tolerance and crop quality improvements in plants. This endeavor would help researchers to develop strategies to enhance crop productivity under stressful conditions and to better utilize natural resources to ensure future food security and to reduce environmental pollution. We are extremely grateful to all the learned contributors and sincerely thank them for their contribution in compiling useful and updated information on different aspect of selenium- and nano-selenium-mediated stress tolerance and bio-fortification in plants. Finally, this book will serve as a unique key source of information and knowledge for graduate and postgraduate students, teachers, and frontline environmental stress researchers around the globe and would be a valuable resource for promoting future research in plant stress tolerance as well as crop quality improvement through bio-fortification and phytoremediation. We believe that the information presented in this book will make a sound contribution to this fascinating area of research.

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Contents

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Michela Schiavon is Associate Professor of Agriculture Chemistry (2017–) at the University of Turin (Italy). She obtained her MD in biology in 2002 and a PhD in crop productivity in 2006 from the University of Padova (Italy). She was research scientist at the Colorado State University (USA) from 2015 to 2017 and is still a faculty associate member of the same university. Her expertise is in plant nutrition and physiology, crop biofortification, phytoremediation, and plant-rhizosphere interactions. Her research activity was initially focused on studying the physiological and molecular mechanisms of heavy metal tolerance and acquisition by crops, and on metal-nutrient interactions during uptake processes. Then, she developed a major interest in the beneficial element selenium and biostimulants, with focus on their mode of action in crops to enhance NUE and resistance to abiotic stress. The main projects in which she has taken responsibilities or has been involved as an investigator are the following: US National Science Foundation grant IOS-1456361, US National Science Foundation grant MCB-9982432, PRID 2018 (Unipd), and Young Researchers (Unipd). She is a member of the Scientific and Economic Committee of the TEAM-NET (Foundation for Polish Science) Grant Program No. 1/4.4/2018. She has 53 publications in peer-reviewed journals and 14 book chapters. She is the topic editor of the *International Journal of Molecular Sciences* and associate editor of *Plants*.

Chapter 1
Sources of Selenium and Nano-Selenium in Soils and Plants

Hassan El-Ramady, Alaa El-Dein Omara, Tamer El-Sakhawy, József Prokisch, and Eric C. Brevik

1.1 Introduction

Many fascinating aspects of selenium (Se) have been documented since its discovery in 1817. Studies have discussed themes such as Se geochemistry and geopedology (do Nascimento et al. 2021; Favorito et al. 2021), Se biogeochemistry (Wang et al. 2022a), Se plant ecology (Pilon-Smits 2019), Se bioavailability in soil (Xiao et al. 2020a), Se essentiality and metabolism in plants (Lanza and Reis 2021; Trippe III and Pilon-Smits 2021), Se nano-biofortification (El-Ramady et al. 2021a, b), and Se in human health, especially its use against cancer (Li and Xu 2020a, b; Hou et al. 2021) and COVID-19 (Liu et al. 2021d; Majeed et al. 2021). The name

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selenium originated from the Greek name "*Selene*", which means "the goddess of the moon" (Bodnar et al. 2012). Selenium is a trace element that is only needed in very small amounts, and the difference between Se deficiency and its dietary toxicity is very narrow (40–400 μg d^{-1}; Fordyce 2013). This causes concerns in several areas worldwide regarding Se deficiency or Se toxicity (Xiao et al. 2021). The toxic cases of Se mainly depend on the Se content of the seleniferous soil (i.e., high soil content of Se); such soils are found in several locations worldwide including Punjab in India (Solovyev et al. 2018; Chawla et al. 2020), the Central Valley in California, Colorado in the United States (Ekumah et al. 2021; Favorito et al. 2021), and the Enshi region in China (Chang et al. 2019; Lyu et al. 2021). Areas with soil Se levels low enough that it causes health problems include the mountainous belt of northeast China to the Tibetan Plateau, parts of Africa, the Pacific Northwest, Great Lakes region, and east coast in the United States (Brevik 2009).

The global distribution of soils enriched in Se is generally in spots rather than sheets (Rosenfeld et al. 2018). Many factors create this heterogeneous Se distribution in soils, like microbial processes (Wells and Stolz 2020; Wang et al. 2022a), human activities, and geogenic conditions (Reynolds and Pilon-Smits 2018). Soil parent material is considered the major factor controlling soil Se. In general, the highest Se content occurs where the soil parent materials are siliceous and carbonaceous shales, whereas soils with parent materials originating from acidic rocks and Quaternary sediments have the lowest Se content (Liu et al. 2021b). Pedogenic process can also control Se release through the weathering of rocks and redistribution of minerals in soil (Imran et al. 2020; Xiao et al. 2020a). Human activities such as the application of Se fertilizers, smelting of metals, combustion of fossil fuels, and discharge of Se-containing wastewaters can affect Se distribution in soil (Lei et al. 2021). Furthermore, the soil microbial community can impact Se solubility and its release in soil by changing Se forms and valence in the soil (Wang et al. 2022a). Soil matter organic and pH are dominant factors influencing soil Se bioavailability (Liu et al. 2021b). Several studies have been published about global soil Se distribution (e.g., Ekumah et al. 2021), including countries like Brazil (do Nascimento et al. 2021), China (Lei et al. 2021; Liu et al. 2021a; Lyu et al. 2021; Zhong et al. 2021), Pakistan (Imran et al. 2020), the United States (Favorito et al. 2021), and France (Pisarek et al. 2021), whereas the global distribution of nano-Se in soils and plants need more investigation.

Therefore, the main objective of this chapter is to discuss different sources of both selenium and nano-selenium in soils and cultivated plants. Bioavailability of Se and nano-Se in soil, the factors that influence it, their microbial transformations, and their potential impacts on human health are also highlighted.

1.2 Sources of Selenium and Nano-Se in Soils and Plants

Selenium (Se) is widespread across all compartments of the Earth including the atmosphere, hydrosphere, lithosphere, and biosphere (Hossain et al. 2021). Selenium ranks as the 67th most abundant element, 145th among hazardous and toxic ingredients, and 125th as a priority pollutant (Hasanuzzaman et al. 2020). The main source of Se in soils are Se-containing minerals, which represent more than 50 types including berzelianite ($Cu_{2-x}Se$), clausthalite (PbSe), crookesite ($(Cu,Tl,Ag)_2Se$), klockmanite (CuSe), tiemannite (HgSe), and ferroselenite ($FeSe_2$). The mean Se content in the Earth's crust is estimated as 0.05 mg kg^{-1}, whereas the mean global Se content in soil is 0.44 mg kg^{-1} (Kabata-Pendias 2011). Selenium content in soil varies from place to place based on the parent material, with higher values in soils formed in argillaceous sediments (0.3–0.6 mg kg^{-1}) as compared to sandstones and limestones (0.01–0.1 mg kg^{-1}). Cretaceous rocks are often an enriched Se source (>100 mg kg^{-1}) because many of them were derived from volcanic dust and gases brought down by rain into the Cretaceous Sea (Kabata-Pendias and Mukherjee 2007). In general, there are two main sources of Se in the environment, natural sources and artificial or man-made sources (El-Ramady et al. 2015). Natural sources of Se include volcanic activity (Floor and Román-Ross 2012), weathering of rocks (Tian et al. 2020), sea spray, atmospheric flux (Roulier et al. 2021), volatilization, and recycling from biota and aerial deposition (Fordyce 2013; do Nascimento et al. 2021). Volatile Se compounds in the atmosphere include hydrogen selenide (H_2Se) and selenium oxide (SeO_2) as inorganic gaseous Se forms and dimethyl di-selenide (DMDSe), dimethyl seleno-sulfide (DMSeS), dimethyl selenone ($DMSeO_2$), and dimethyl selenide (DMSe) as organic Se gaseous forms (Hossain et al. 2021; Ye et al. 2021).

Selenium mining districts are widely distributed based on geogenic origin. There are many natural ores of Se, and mining depends on the composition of these ores, the tectonic setting, and the stratigraphic position of ore minerals (Funari et al. 2021). The main Se ore minerals are associated with igneous rocks like volcanogenic sulfides (i.e., volcanogenic massive sulfides and native sulfur) and sedimentary sources (e.g., polymetallic nodules, phosphorites, shales, and marine seafloor sediments) (Funari et al. 2021). The total content of soil Se can be divided into five levels based on Se abundance and its environmental risk: deficient, low, medium, high, and excessive ($<$ 0.125, 0.125–0.175, 0.175–0.40, 0.40–3.0, and $>$ 3.0 mg kg^{-1}), respectively (Lyu et al. 2021). Several spots of high Se content soils (seleniferous soils) have been observed in countries like China, the United States, Russia, Australia, Canada, and Ireland (Table 1.1), whereas more than 70% of countries have soils that are considered Se deficient including wide portions of Europe and New Zealand (Hossain et al. 2021). Selenium availability to cultivated plants depends on many soil chemical and biochemical characteristics, including sorption, soil pH, presence of other nutrients like S and P, and methylation process (Hossain et al. 2021). The total Se content in soils is not a reliable parameter for measuring plant-found Se or the amount of Se available to humans and animals through plants (Hossain et al. 2021). Humans may control the Se content in soil through many activities such as metal smelting, combustion of fossil fuels, and the over-use of mineral fertilizers (Hossain et al. 2021). In general, most cultivated plants have a low Se content (around 25 μg kg^{-1}), whereas high Se content (exceeding 100 μg kg^{-1}) is rare, but could be found in Se-accumulating plants. These plants may accumulate Se to extremely high levels of over 1000 mg kg^{-1}, which may cause toxicity to

Table 1.1 Se abundance in many different soils around the globe

Studied location (the country)	Number of sampling sites	Total Se content (mg kg^{-1}) in soil	Soil type or Se category	Reference
Pine ridge Fort Collins, Colorado (USA)	–	8.20	Seleniferous soils	Yasin et al. (2015)
Punjab (India)	–	0.024–3.06 (0.449)	Seleniferous soils	Dhillon and Dhillon (2016)
Australia	1315	< 0.01–2.0 (0.06)	Australian soils	Reimann and de Caritat (2017)
The east bank of Dianchi Lake (China)	130	0.10–0.35 (0.20)	Greenhouse soils	Jia et al. (2019)
The USA	4857	< 0.2–8.3 (0.20)	U.S. soils	Smith et al. (2019)
Pothwar uplands (Pakistan)	45	0.27–7.05 (0.74)	Soils from different parent materials	Imran et al. (2020)
Hechi, Guangxi (China)	60	0.288–1.673 (0.705)	Cropland and woodland soils	Xiao et al. (2020a)
Karst area, Guangxi Zhuang, (Southwest China)	125	0.22–1.820 (0.676)	Soil of cropland, grassland, shrubland, and secondary forest	Xiao et al. (2020b)
Western phosphate resource area (the USA)	–	2.7–435	Seleniferous soils	Favorito et al. (2021)
Enshi, Hubei Province (China)	92	0.12–20.62 (2.01)	Seleniferous soils	Lyu et al. (2021)
Aksu, Xinjiang (China)	183	0.22–1.90 (0.56)	Oasis farmland soils	Lei et al. (2021)
Southwest China	3382	0.010–16.24 (0.171)	Mainland soils	Liu et al. (2021a)
Forest sites from the French RENECOFOR network (France)	51	25–1222	Forest soils	Pisarek et al. (2021)
Heilongjiang Province (China)	160	0.045–0.444 (0.228)	Black soil region	Zhong et al. (2021)
Rio Grande do Norte and Paraíba, northeastern (Brazil)	198	0.02–1.7 (0.30)	Se-deficient soils in the semi-arid regions	do Nascimento et al. (2021)
Southern Songnen plain (China)	20,929	0.01–1.14 (0.29)	Cropland soils	Yang eta l. (2021)
Naore Village, Ziyang County, Shaanxi Province (China)	14	1.99–8.54	Natural seleniferous soils	Zhou et al. (2021c)
Western Jinhua City, Zhejiang Province (China)	53	0.1789–0.5738 (0.40)	Farming pattern in Se-enriched soils	Wang et al. (2022a)

Values in parentheses show the mean value humans and animals (El-Ramady et al. 2015). The main source of Se to cultivated plants is applied through Se fertilizers; plants can uptake this nutrient in selenite ($SeO_3{}^{2-}$) and selenate ($SeO_4{}^{2-}$) forms (Trippe III and Pilon-Smits 2021). The uptake of Se and its bioavailability will be discussed in the next section. Elemental Se can be precipitated as Se homo-spheres during the biological preparing method of bio-nano-Se. Red elemental nano-Se spheres in water may produce H_2Se and H_2SeO_3 in small amounts as shown in Eq. 1.1:

$$3Se + 3H_2O \leftrightarrow 2H_2Se + H_2SeO_3 \tag{1.1}$$

H_2Se and H_2SeO_3 are formed in solution. When the solution dries, the H_2Se and H_2SeO_3 react with each other and elemental selenium is precipitated, forming crystals (El-Ramady et al. 2015).

1.3 Bioavailability of Se and Nano-Se in Soil and Controlling Factors

Selenium occurs in multiple valence states (i.e., −2, 0, +2, +4, and + 6), which include the metal selenide (Se^-, Se^{2-}), elemental Se or nano-Se (Se^0), thio-selenate ($SSeO_3{}^{2-}$), selenite ($SeO_3{}^{2-}$), and selenate ($SeO_4{}^{2}$). Several natural soil factors control the bioavailability of Se and nano-Se (i.e., Se that can be taken up by plants), including physical (e.g., sorption impacts of soils and sediments), chemical (soil pH, organic matter content, redox potential, Fe/Al oxides content [Jones et al. 2017; Fan et al. 2018; Xu et al. 2018; Deng et al. 2021; Wang et al. 2018a, b], and competitive ions [Lyu et al. 2021]) and biological (reduction and methylation) factors (Hasanuzzaman et al. 2020; Xu et al. 2020). Other factors that influence Se and nano-Se bioavailability include exogenous applied Se or Se fertilizer type (Li et al. 2021) and the kind of cultivated plants like wheat (El-Saadony et al. 2021; Liu et al. 2021b), rice (Lyu et al. 2021), soybean (Deng et al. 2021), and maize (Wang et al. 2019a). This is explored in more detail in Table 1.2.

1.3.1 Soil pH and Redox Potential (Eh)

The total Se content in soils is not an accurate indicator for Se bioavailability, whereas the fractionation of Se in the soil is the main factor controlling the transformation of Se, migration, and its bioavailability in soil (Fordyce 2013). The speciation of Se and its fractionation in soil can be regulated through processes such as dissolution/precipitation, adsorption/desorption, and oxidation/reduction. The classical method for Se sequential extraction is widely applied to determine soil Se fractions, and the results can be used to predict Se uptake by plants (Wang et al.

Table 1.2 Some recent published articles that explore Se fertilizers for different crops, the bioavailability of Se in soil, and controlling factors

Se fertilizer type (soil properties)	Applied dose of Se fertilizer (mg kg^{-1})	Target crop	Main aim of study	Reference
Pots filled with peatmoss and perlite at 2:1	Foliar applied nano-Se (50–150 nm) at 5, 10, 15, 20 mg l^{-1}	Korean ginseng (*Panax ginseng* C. A. Meyer)	Oxidative stress resulted from 20 mg l^{-1}, which accumulated high ginsenoside and increasing quality of ginseng roots.	Abid et al. (2021)
Field experiment: Soil pH 5.9; total Se 0.4 mg kg^{-1}; SOM 18.0 g kg^{-1}	Foliar se-doses (Na_2SeO_4) at 5, 10 and 20 g ha^{-1}	Wheat (*Triticum* spp.) var. IAC 385	Under lower Se doses (5 g ha^{-1}), highest absorption efficiency with supply up to 75% of the recommended daily intake	Delaqua et al. (2021)
Pot experiments (soil pH 5.68 & 7.87; SOM 15.32 & 16.28 g kg^{-1}; total Se 0.14 & 0.16 mg kg^{-1})	Soil applied Na_2SeO_4 at 2 mg kg^{-1}) with or without S-fertilizer (100 mg kg^{-1})	Soybean (*Glycine max* L.)	Se bioavailability in calcareous alluvial soil was higher compared to yellow–brown soil, whereas S application inhibited Se uptake in both soil types, without any impact on Se speciation in seeds.	Deng et al. (2021)
Bio- and chemical Se-NPs; pots filled with soil (50% sand and 50% clay)	Each Se-NP applied at 50, 75, 100, 125, and 150 µg ml^{-1}	Wheat (*Triticum asetivum* L.) cv. Masr1	Applied Bio-Se-NPs at 100 µg ml^{-1} reduced root rot disease incidence in wheat; enhanced plant tolerance to drought and heat stress by increasing the growth and productivity of wheat.	El-Saadony et al. (2021)
Mineral Se (soil pH 5.5; SOM 18 g kg^{-1})	Selenate/ selenite foliar applied at 0.075–0.15 kg ha^{-1}	Apple (*Malus domestica*)	Improved protein content in different varieties of apple by foliar Se fertilizer, which enhanced tolerant apple to stress.	Groth et al. (2021)
Field experiment: Soil pH 4.6; total and available Se 45 and 3.0 µg kg^{-1}	Foliar Se at 10, 25, 50, 100, and 150 g ha^{-1} as sodium selenate	Cowpea (*Vigna unguiculata* L.)	Optimal foliar Se was 50 g Se ha^{-1} to increase the yield and higher rates caused oxidative stress, which may be linked to stress attenuation caused by Se.	Lanza et al. (2021)

(continued)

Table 1.2 (continued)

Se fertilizer type (soil properties)	Applied dose of Se fertilizer (mg kg^{-1})	Target crop	Main aim of study	Reference
Organic Se fertilizer (soil pH 8.68; total Se 0.086 mg kg^{-1})	Se-IV at 36.4 mg kg^{-1}; NPK ≥ 5%; organic matter ≥45%	Naked oat (*Avena nuda* L.)	The grain yield and its quality were increased by combined foliar and soil Se fertilizer, as well as the total se, and organic Se content.	Li et al. (2021)
Hydroponics	Spray 20 ml of se, as Na_2SeO_3 at 2 mg L^{-1} every day for 5 consecutive days	Tea (*Camellia sinensis*) cv. Longjing 43	Under low temperature (4 °C), applied Se increased sugar accumulation, promoted the synthesis of amino acids and improved tea quality.	Liu et al. (2021c)
Field experiment (soil pH 6.8, SOM 23.3 g kg^{-1}, total Se 0.031 mg kg^{-1})	Foliar and root applied Na_2SeO_3 at 50, 75 and 100 g ha^{-1}	Peanut (*Arachis hypogaea* L.)	Se-fertilizer can enhance both inorganic and organic Se content in peanut kernels by foliar spraying as an effective bio-transformation of se.	Luo et al. (2021)
Greenhouse pots; pH 5.32; SOM 44.66 g kg^{-1}; total Se 0.66 mg kg^{-1}	–	Rice (*Oryza sativa* L.) cv. Minfengyou 3301	Se-bioavailability is controlled by SOM and pH; predominant Se fraction is OM-Se and has low mobility; exploring Se bioavailability in naturally seleniferous soils is crucial to the stable production of Se-enriched agricultural products.	Lyu et al. (2021)
Soilless system (nutrient solution, EC 3.6 mS cm^{-1} and the pH 5.6)	Fertigation was used for Se in the nutrient solution (1.0, 2.0, 4.0 µmol·L^{-1})	Cherry tomato (*Solanum lycopersicum* L)	Se applied at 2.0 µmol L^{-1} improved total fruit yield and N use efficiency by 31.4 and 31.5% in grafted plants, respt. With similar trend for 4.0 µmol L^{-1}.	Sabatino et al. (2021)
Biological nano-Se (soil EC 4.49 dS m^{-1}, pH 8.66)	Foliar application at 25 mg L^{-1}	Cucumber (*Cucumis sativus* L.)	Under combined salinity and heat stress, boi-nano-Se increased the growth and productivity of cucumber in net house.	Shalaby et al. (2021)

(continued)

Table 1.2 (continued)

Se fertilizer type (soil properties)	Applied dose of Se fertilizer (mg kg^{-1})	Target crop	Main aim of study	Reference
Field experiment (SOM 126 g kg^{-1}, available Se 0.21 mg kg^{-1})	Foliar applied sodium selenite at rate of 1.2 kg ha^{-1}	Alfalfa (*Medicago sativa* L.) cv. Kangsai	Proteomics level is an important tool to assist in a more detailed elucidation of Se enrichment in alfalfa for the future.	Wang et al. (2021a)
Pot experiment (soil pH 7.89; total Se 0.058 mg kg^{-1}, SOM 14.44 g kg^{-1})	Se fertilizers as selenate and selenite were applied at 1 and 10 mg Se kg^{-1}	Wheat (*Triticum aestivum* L.) eight cultivars	Applied Se at rate of 10 mg kg^{-1} decreased grain yield; Se selenite was almost accumulated in grain and roots, whereas in leaves and straw for Se selenate.	Wang et al. (2021b)
Field experiment (soil pH 4.71, total Se 0.38 mg kg^{-1}, SOM 41.26 g kg^{-1})	Foliar spray sodium selenite at rate of 12.5, 25, 50 and 100 mg L^{-1}	*Atractylodes macrocephala* Koidz	Optimal foliar Se fertilizer was at 25–50 mg L^{-1} Se on these medicinal plants to enhance plant growth, soil nutrients in the rhizosphere, and soil microbial community composition.	Zhou et al. (2021b)
Pot experiment (soil pH = 5.93; total Se 0.61 mg kg^{-1})	Se-fertilizer as Na_2SeO_4 or selenite applied to soil at 0.5 mg kg − 1	Rice (*Oryza sativa* L. cv. Xinliangyou 6)	Organic Se content of the rice grain enhanced by combined soil applied arbuscular mycorrhizal fungus and mineral Se fertilizer.	Chen et al. (2020)
Field experiment (soil pH 7.5, total Se 0.11 mg kg^{-1}, SOM 8.6 g kg^{-1}	Spraying Na_2SeO_4 at levels of 1.5 and 3 mg L^{-1}	Canola (*Brassica napus* L.)	High yield of canola could be achieved by Se spraying at 1.5 mg L^{-1} Se under sub-tropical dryland conditions.	Mohtashami et al. (2020)
Pot experiment (soil silty loam; pH 7.02)	Foliar applied 15 and 30 ppm Se as sodium selenate	Garlic (*Allium sativum* L.)	The simultaneous application of gypsum (20 and 40 mg S kg^{-1} soil) and Se foliar spraying improved the nutritional value of garlic plants.	Sohrabi et al. (2020)

SOM = soil organic matter

2019b). However, Se uptake by plants is a dynamic process, and the results of sequential extraction do not fully reflect Se fractionation and its dynamics in soil (Lyu et al. 2021).

Soil pH and redox potential (Eh) are considered important factors controlling Se bioavailability for plants (Natasha et al. 2018). The selenate form of Se is dominant in alkaline and oxidizing soils (with electron activity $pE + pH > 15$), whereas under acidic and neutral conditions, selenite will be present as $7.5 < pE + pH < 15$ (Elrashidi et al. 1987). Many studies confirm that Se bioavailability may vary across such distinct soil types with varying pH levels (e.g., Deng et al. 2021; Lyu et al. 2021). Xiao et al. (2020a) reported that Se bioavailability in soil generally declines with decreasing soil pH. Under low soil pH (acidic soil), total Se content tends to be low compared to alkaline or neutral soils (Table 1.3). In general, Se bioavailability decreases when the soil contains high levels of SOM, clay, and Fe-oxides. In acidic soils (low pH), SeO_3^{2-} is the dominant Se form, but in alkaline soils (high pH) the dominant form is SeO_4^{2-}.

Table 1.3 Impact of soil pH and organic matter content on total Se content in some Chinese soils

Sample no.	Chinese location	Soil pH	Soil organic matter (g kg^{-1})	Total Se in soil (mg kg^{-1})
3	Ertaihuang	5.21	36.33	0.50
1	Huangjintang	5.32	44.66	0.66
4	Longtan	5.72	25.56	1.76
10	Tongluo	5.78	15.82	0.55
9	Xiaomaotian	6.04	32.02	0.59
17	Hongyansi	6.15	32.35	0.27
20	Shenjiahuang	6.18	32.42	0.19
6	Menghualing	6.32	28.34	0.68
12	Guihuashu	6.52	26.63	0.75
7	Lanhongcao	6.53	54.51	3.32
21	Xinchang	6.54	26.79	0.12
13	Yujingba	6.65	27.19	0.47
2	Weijiaya	6.78	79.66	2.59
15	Juweihui	6.84	38.70	0.80
22	Heixiba	6.91	28.40	0.13
23	Yaoziping	6.96	64.15	20.37
64	Cheyun	7.01	27.54	1.53
36	Sunjiaba	7.16	36.73	0.44
53	Xiaqipeng	7.28	97.13	4.03
86	Fengchunba	7.35	19.59	1.31
38	Qiyangba	7.43	67.35	5.55
5	Chahouzi	7.46	21.43	0.19
42	Huangyan	7.65	53.53	0.99
44	Leijia	7.70	51.16	2.64
11	Huolong	7.72	34.33	1.49
30	Fenghuangguan	7.78	36.84	0.36
14	Yangjiaoshan	7.84	43.31	3.94

Source: extracted from Lyu et al. (2021)

1.3.2 Soil Organic Matter

Soil organic matter (SOM) is an important soil factor controlling Se bioavailability, which links to many human issues like Se risk environmental assessment and Se biofortification for human health (Li et al. 2017a). The interaction between SOM and soil Se content under soil–plant systems is a dual effect through two dimensions: enhancing or reducing Se bioavailability in soil (Wang et al. 2017). In other words, SOM can immobilize Se in soil through abiotic and biotic mechanisms and/or release of SOM-immobilized Se via the mineralization process (Li et al. 2017a). In general, selenite is less bioavailable in soil due to its easy adsorption and immobilization through Fe/Al-oxides or their hydroxides in soils (Francisco et al. 2018), whereas selenate is unlikely to be immobilized and/or adsorbed in soils leading to relatively high Se bioavailability (Deng et al. 2021). Soil organic acids may interact with Se in soil through many processes like adsorption, reduction, and complexation. These acids may lead to Se mobilization and immobilization in soil, which control Se bioavailability. Fulvic acid Se is considered a latent source of available Se in soil and humic acid Se is a sink of Se under some conditions (Dinh et al. 2017).

Therefore, the composition of SOM can play a crucial role in Se bioavailability or its binding speciation with Se (Li et al. 2017a). Moreover, based on the strong adsorption capacity of SOM and its large specific surface area, soil Fe/Al oxides and minerals may play decisive roles in Se adsorption and fixation in soil, which directly affect Se bioavailability (Liu et al. 2021b). Thus, the main dominant influential factors for soil Se bioavailability should be clarified as well as establishing a proper prediction model for Se bioavailability, and Se bioavailability can be regulated by different agronomic parameters for the proper utilization of the soil Se resource to produce natural Se biofortified foods (Dinh et al. 2018, 2019; Liu et al. 2021b). Many studies have investigated the bioavailability of Se in soil and the role of SOM in this context, such as Li et al. (2017a), Cheng et al. (2020), Lyu et al. (2021), and Liu et al. (2021b). There are few published materials on SOM and nano-Se, but Wang et al. (2019c, d) reported that particulate organic matter (at a level of 60 mg L^{-1}) can impact the fate of Se-NPs in the environment by inhibiting their homo-aggregation and hetero-aggregation as well as enhancing the stability of Se-NPs. More investigations are needed to focus on the bioavailability of nano-Se in soils and its transformation under cultivated plant conditions.

1.3.3 Parent Materials

Parent materials play a crucial role in Se bioavailability because the soils are mainly derived from these materials, and the chemical composition of soils is largely determined by their parent materials. Selenium content in soils also depends on pedogenic processes (i.e., additions like OM, losses by processes, such as erosion and leaching, transformations by weathering, and translocations within the profile

[Simonson 1959]). Thus, soil Se level could be determined based on the parent materials as main sources (Reynolds and Pilon-Smits 2018, Jia et al. 2019). Parent materials also can exert a strong control on many soil physicochemical properties, further impacting the behavior of Se in soils (Carvalho et al. 2019). The total Se in soil could be used in general to assess potential Se uptake and its utilization by plants, however, based on the selectivity of plants and the bioavailability of Se, the Se content of plants grown in seleniferous soils may not achieve Se-enriched standards (Li et al. 2017a; Wang et al. 2019a, b). Therefore, identifying the bioavailable Se or soil Se supply capacity is important for predicting the Se content in plants (Liu et al. 2021b). Many studies have investigated the role of parent materials in determining Se bioavailability in soil such as Jia et al. (2019), Xiao et al. (2020a), and Liu et al. (2021b).

1.3.4 Land Use

Changes in land use or land cover are an important aspect of global change, which is accompanied by changes in the communities of plants which strongly influences the properties of soil, particularly SOM. This change can be linked to the biogeochemical cycles of many essential nutrients like N, P, K, S, Ca, Mg, Cu, Mn, Mo, etc. (Li et al. 2018). Recently, several studies confirmed that land use influences many soil properties and processes (Wang et al. 2018b). Local geology may greatly influence the effects of land use on different biogeochemical cycles of nutrients, including selenium (Xiao et al. 2020b). Land use change has a direct relationship with many soil attributes like pH, soil organic carbon, and metal oxides contents (Lizaga et al. 2019), which are closely related to the behavior of Se in the environment (Li et al. 2017b). Thus, it could logically be assumed that the cycling of soil Se might be substantially changed by land use conversions. Therefore, there is an urgent need for precise understanding of the fate and behavior of soil Se as well as factors controlling the magnitude and direction of land use effects to manage soil Se resources and improve Se status in human populations under future land use change scenarios (Xiao et al. 2020a).

In addition, the climate and its changes are also important factors controlling Se biogeochemistry in soil, which can impact soil Se abundance directly through atmospheric Se deposition (Sun et al. 2016) or indirectly by influencing the uptake of Se by plants, which climatic elements including temperature and moisture control this uptake. Depending on climatic conditions and soil type, the previous factors (climate and soil factors) may act alone, or in combination with each other, to mediate soil Se abundance and its bioavailability (Xiao et al. 2020b). There are limited studies on Se variations in soil under various land use or land cover types (Plak and Bartminski 2017), and there is no general consensus yet on the magnitude and direction of land use change effects on Se abundance and its bioavailability in soil. Some authors, such as Xing et al. (2015), reported that Se is more enriched in forest soils compared to agricultural soils, but Shang et al. (2015) reported the opposite.

Therefore, there is a need for more information on Se dynamics in soil under different scenarios of global change, particularly changes in global land use/land cover (Xiao et al. 2020b).

1.3.5 Soil Amendments

Any material added to improve soil properties (e.g., permeability, aeration, drainage, water retention, infiltration, nutrient status, biome changes) is called a soil amendment. This amending action could be achieved by applying organic (e.g., mulching, green manure, compost, peat, biochar) and/or inorganic or mineral amendments (e.g., gypsum, fly ash, lime, vermiculite, fertilizers). Organic or mineral amendments could improve Se bioavailability in soil (Table 1.4). Several studies have been published that investigate Se bioavailability under different soil amendments such as zinc sulfate (Xue et al. 2020), chicken manure (Dinh et al. 2021), vermicompost (Liu et al. 2020), biochar (Wang et al. 2019d; Mandal et al. 2020; Wei et al. 2021), and nanomaterials like nano-biochar (Mandal et al. 2020).

1.4 Microbial Transformation of Se and Nano-Se in Soils

Selenium and nano-Se have distinct chemical reactions and transformations in soil. These include oxidation, reduction, methylation, and demethylation (Nancharaiah and Lens 2015). Microbial Se oxidation did not receive a significant amount of attention during the last decades due to the low oxidation rate of Se, which increased the difficulty of researching this element (Wells and Stolz 2020). Due to its essentiality for microorganisms, Se microbial transformations in soils have received increasing attention recently including Se dissimilatory reduction under aerobic and anaerobic conditions and its bioremediation applications (Wang et al. 2022b). Many studies on the transformations and applications of Se have been published recently focusing on topics such as Se bioremediation (Paul and Saha 2019; Huang et al. 2021a), Se biogeochemistry and its ecophysiology (Wells and Stolz 2020; Wang et al. 2022a), assimilatory genomes (Davy and Castellano 2018), Se biosynthesized nanoparticles (Mulla et al. 2020; Borah et al. 2021; El-Saadony et al. 2021; Sun et al. 2021), Se applications (Ojeda et al. 2020; Huang et al. 2021b), reducing plant uptake of heavy metals from soil by Se (Handa et al. 2019; Niu et al. 2020; Feng et al. 2021a, b), effects of Se nanoparticles on plant biology (Zsiros et al. 2019; Zhou et al. 2021d) and their tolerance against stress (Joshi et al. 2021; Qi et al. 2021; Shalaby et al. 2021), Se volatilization from soils (Ye et al. 2021; Zhou et al. 2021a), and Se microbial reduction and its resistance (Lusa et al. 2019; Zhou et al. 2021a; Wang et al. 2022b).

Selenium is characterized by its ability to volatilize some Se forms into the atmosphere such as H_2Se, DMSe, DMDSe, DMSeS, and $DMSeO_2$, where "DMSe" is the

Table 1.4 Impact of some soil amendments on the bioavailability of Se in soil

Experimentation and soil properties	Applied Se dose (mg kg^{-1})	Applied soil amendment	Main effects of applied soil amendments on Se availability.	References
Pot experiment (soil pH 7.75, 55.0 g kg^{-1} $CaCO_3$; total Se 0.1 mg kg^{-1}; SOM 16.3 g kg^{-1})	Applied selenite at 1.0 and 2.5 mg se·kg^{-1} soil	Applied cow or chicken manure at 2, 4 and 6%	Simultaneously applied chicken or cow manure with Se as selenite could lead to decreased Se availability to Chinese mustard.	Dinh et al. (2021)
Pot experiment (soil pH 5.42; available cd 2.96 mg kg^{-1})	Total Se content in soil was 0.31 mg kg^{-1}	Lime at 0.03–0.12%, bentonite at 6 and 12 g kg^{-1}; biochar at 0.3, 0.9, 1.8 g kg^{-1}	Applied agricultural lime, ca − bentonite, and rape straw biochar or lime and biochar increased soil pH values and SOC to remediate high Se soil polluted by cd.	Xu et al. (2021)
Batch experiments (pH 6.3)	Applied Se (VI) at 2 mg L^{-1}	Biochar added at 3 g L^{-1} soil	Biochar supporting iron-based nano-particles had high removal rate of SeO_4^{2-} by highly reversible adsorption.	Wei et al. (2021)
Batch experiments (pH 6.36, total Se 0.093 mg kg^{-1})	Applied Se (VI) at 150 mg kg^{-1}	Biochar added at 10 g kg^{-1} soil	Biochar-supported nanoscale zero-valent iron and polysulfide decreased Se availability by 77.3% after 30 days.	Mandal et al. (2020)
Rhizobox experiment (pH 5.0, SOM 41.1 g kg^{-1}; total Se 0.34 mg kg^{-1})	Applied Se at 0.5 and 5.0 mg kg^{-1} soil as Na_2SeO_3	Root secretion of organic acids (indigenous)	High Se rice cultivar could activate Se by increasing soil pH and regulate rice root secretion of organic acids compared to the low-Se rice cultivar.	Zhang et al. (2019)
Pot experiment (soil pH 7.75; SOM 16.3 g kg^{-1}; total Se 0.1 mg kg^{-1})	Selenate as fertilizer applied at 1.0 mg kg^{-1}	Wheat straw & pak choi-Se enriched at 21.35 & 47.48 mg kg^{-1}, respectively	Exchangeable Se and fulvic acid-bound Se-fraction could better reflect availability of Se in organic materials amended soils, where Se-enriched pak choi was better in Se-utilization efficiency than wheat straw.	Wang et al. (2018a)

main dominant volatile Se species (Ye et al. 2021). Se volatilization due to biological methylation into the atmosphere is considered an important process of Se biogeochemical cycling in agroecosystems. About 50–70% of total global emission is the gaseous emission of Se from natural sources into the atmosphere (Ye et al.

2021). The volatile Se fractions can be produced in natural environments through the biological methylation of organic and inorganic Se species by microorganisms, plants, and animals. There are many precursors or intermediates in the Se methylation process including inorganic (i.e., selenate and selenite) and organic Se fractions such as methyl-seleninic acid (CH_3SeO_3H), seleno-methionine (SeMet), selenocystine, and dimethyl-selenoniopropionate (Moreno-Martin et al. 2021). There are limited studies on Se volatilization, particularly as regards Se-enriched plants/soils and Se-polluted environments (Ye et al. 2021). The great role of microorganisms in the Se cycle is to biosynthesize nano-Se. Bacteria can biosynthesize spherical Se-nanoparticles (11–700 nm in diameter), whereas fungi can biosynthesize smaller Se-NPs that range from 17 to 150 nm (Wang et al. 2022b).

1.5 Selenium and Nano-Se for Human Health

Humans need Se as an essential element (Brevik 2009). Therefore, Se supplementations can be important to improve human immunity and fertility, as well resistance to problems like tumors and pathogens (Fig. 1.1). However, excessive Se supplementation can cause toxic impacts due to Se duality, and may in severe cases lead to death (Lv et al. 2021). Several years ago, Se was thought to be poisonous, but in 1957, its essentiality and importance in small amounts were established. Now, Se is

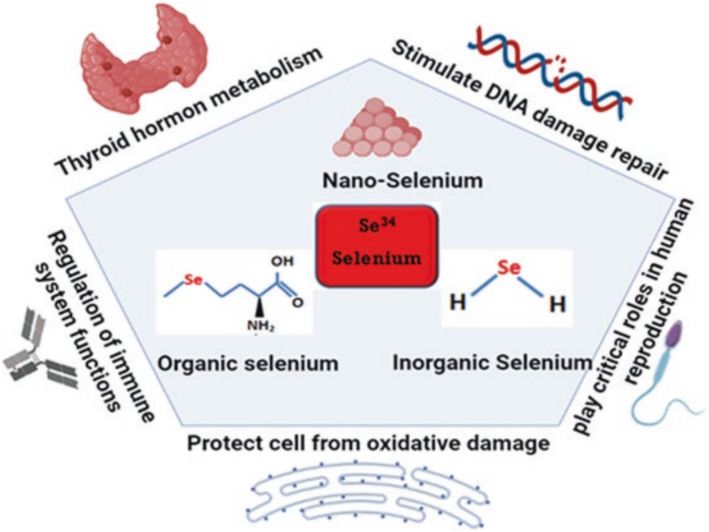

Fig. 1.1 Forms of selenium in the human diet and its physiological effects on body functions, which include the role of Se in protecting human cells from oxidative damage, its crucial role in human reproduction, repairing DNA damage, importance for metabolism of thyroid hormone, and regulation of immune system functions. (This figure was created at BioRender.com)

recognized as an essential micronutrient for the proper functioning of several physiological processes, such as its antioxidative properties, synthesis of thyroid hormone, and its support for metabolic functions (Pappas et al. 2019; Ryant et al. 2020). The antioxidative properties of Se are linked to its significance as a component of certain proteins, which are referred to as selenoenzymes and selenoproteins (Santesmasses et al. 2020; Ekumah et al. 2021). Selenium deficiency in humans can result in "Kashin–Beck disease" and "Keshan disease", whereas Se toxicity leads to nail and hair loss, nervous system disorders, and other symptoms in humans (Liu et al. 2021a).

Biofortification can be used to increase available Se content in soil and, through that, in crops raised for human consumption. Several studies have investigated the production of crops biofortified with Se (e.g., Shalaby et al. 2017; Schiavon et al. 2020; Sarwar et al. 2020; Zagrodzki et al. 2020; Kleine-Kalmer et al. 2021; Izydorczyk et al. 2021; and Tiozon et al. 2021). Biofortification with nano-Se still needs more investigation (El-Ramady et al. 2020, 2021a, b; Ranjitha and Rai 2021). Considering the health benefits of nano-Se and its applications, Kumar and Prasad (2021) reported that these applications may include (1) using nano-Se as antioxidant agents to prevent cellular damages caused by free radicals (Qamar et al. 2021), (2) Se-NPs as anticancer agents (Li and Xu 2020b), (3) nano-Se to control the growth of various pathogenic microbes (Rajagopal et al. 2021), (4) nano-Se to control diabetes (Abdulmalek and Balbaa 2019), (5) nano-Se for bioremediation and wastewater treatment (Chauhan et al. 2021), and (6) Se-NPs for the fabrication of nano-biosensors that could be used to diagnose diseases, test drugs, and monitor and detection environmental pollutants (Huang et al. 2021b).

1.6 Conclusions

Selenium is an essential nutrient for human health but still needs to be confirmed as essential for higher plants. A great amount of recent attention has been paid to the use of nano-Se to enhance human health, particularly against diseases like COVID-19. The main sources of Se in soils include parent materials, which depends on their mineralogic composition. Several recent studies confirmed that Se applied at a low concentration shows positive impacts on the growth of cultivated plants, including their development and yield. Therefore, Se is a vital nutrient through the way it changes many physiological and biochemical processes in plants (e.g., antioxidant defense, tolerance against many abiotic stresses like drought, salinity, extreme temperature, and toxic element stress). Many factors control the bioavailability of Se such as soil pH, redox potential (Eh), soil organic matter, clay content (soil texture), parent materials, land use or cover, and soil amendments.

The main forms of Se include selenite, selenate, and selenide, as well as nano-selenium. Soil microorganisms have roles in several reactions that influence the species of Se found in soils. Selenium bioavailability in soil depends heavily on Se speciation and how that affects binding to different soil fractions. Available soil Se fractions (i.e., exchangeable Se and its water-soluble fraction) are a more critical indicator of Se deficiency or Se excess than total content. Cultivated plants have the ability to uptake Se from soil and alter Se bioavailability and mobility via many processes such as excreting organic acids (e.g., citrate, oxalate, and malate), which lead to complexation, adsorption, and reduction of soil Se. The fate and behavior of Se in soil is important for crops and of consequence to human health. Selenium may be either detrimental or beneficial to human health, and the range between deficient and toxic is small. Therefore, understanding soil Se and the processes that influence its bioavailability as well as its association with human health are of great concern for both policy makers and the scientific community. There are still many open questions about Se in soils.

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