Chapter 17
Biological Activity of Selenium in Plants: Physiological and Biochemical Mechanisms of Phytotoxicity and Tolerance

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17.1 The Physicochemical Similarity of Selenium to Sulphur Determines the Biological Activity of Selenium in Plants

Selenium (Se) is an essential trace element for most organisms, including humans. However, it is toxic at concentrations exceeding the physiological tolerance threshold of a given organism. The chemical form of this element is also of great importance for its toxicity. Organisms for which Se is essential need this element for the biosynthesis of the 21st protein amino acid, i.e. selenocysteine (SeCys), which is a component of approximately 25 specific selenoproteins in the human organism (Van Hoewyk 2013). However, the essential Se metabolism in vascular plants is believed to have been lost during evolution, as deduced based on plant genome analysis demonstrating no evidence of a SECIS element in the coding regions of selenoprotein transcripts (Zhang and Gladyshev 2009). Selenium can be incorporated readily and non-specifically into various functional plant metabolites, some of which may be advantageous to plants (Schiavon and Pilon-Smits 2017). Therefore, in recent years, researchers have shown a growing interest in plant Se metabolism. The importance of this element for plants and the mechanisms of its phytotoxicity are still the object of genetic, molecular, physiological, and ecological studies.

The chemical properties of Se highly resemble those of sulphur (S). However, the radius of the Se atom is larger than that of S: the radii of Se^{2-} and S^{2-} are 0.191 nm and 0.174, respectively (White et al. 2004). These slight differences in the size and ionic properties of S and Se atoms may cause irreversible changes in the protein structure and disturb the catalytic functions of enzymes in Se-sensitive

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plants (Terry et al. 2000; Hasanuzzaman et al. 2020). The chemical and physical properties of Se are very similar to those of S, which is an essential macronutrient to all organisms. It is crucial for the uptake, translocation, and biological activity of Se. Like S, Se can exist in four main oxidation states: −2, +2, +4, and + 6. It commonly occurs as selenide (−2), elemental Se (0), selenite (+4), and selenate (+6). Each of these oxidation states exhibits different chemical properties. In nature, Se occurs in inorganic and organic forms, forming compounds with approximately 16 other elements (Kabata-Pendias 2010).

Due to the similarity to S, all plants can take up and metabolize Se relatively easily and fast via the S metabolic pathway. For example, in *Arabidopsis*, two high-affinity sulphate transporters (SULTR1;1 and SULTR1;2) are involved in the uptake and transport of selenate within plants. In Se hyperaccumulators, the constitutive expression of genes encoding SULTR1 and SULTR1;2 in roots results in high selenate absorption ability (Raina et al. 2021). Moreover, SeO_3^{2-} and SeO_4^{2-} ions, i.e. the chemical analogues of SO_3^{2-} and SO_4^{2-} ions, respectively, can be assimilated to organic Se forms, such as SeCys and selenomethionine (SeMet). The assimilation of Se is thought to compete with S assimilation. Selenium compounds also undergo biological methylation, and the volatile products of this reaction contribute to the geochemical cycle of the element in nature (Terry et al. 2000; White et al. 2004; Kabata-Pendias 2010; Schiavon and Pilon-Smits 2017).

Selenium in plants can be incorporated into other S compounds, e.g. glucosinolates and their associated aglycons or (seleno)glutathione (Schiavon and Pilon-Smits 2017). It can also be part of Fe-Se clusters, since the chloroplastic NifS-like enzyme releasing elemental S from cysteine (Cys) for the synthesis of Fe-S clusters may also use SeCys as a substrate (Van Hoewyk et al. 2005). Another Se-containing metabolite is Se-allyl-L-cysteine sulfoxide synthesized in *Allium* species from selenoglutathione or SeCys substrates (González-Morales et al. 2017). Moreover, different plant species can also produce other organic Se metabolites, e.g. selenoecholine, selenobetaine, and selenotaurine or volatile dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) (Chauhan et al. 2019).

As emphasized above, Se and S metabolism in plants is closely interrelated both at the stage of ion uptake, transport, subsequent compartmentalization, assimilation, and/or volatilization. This phenomenon critically determines the biological activity of Se in plant organisms.

17.2 Plants Vary in the Resistance and Ability to Accumulate Selenium

The current stage of knowledge does not classify Se as an element necessary for plants. However, recent experiments show that a low concentration (most often a few micromoles) Se exerts a positive influence on plant growth and resistance to some biotic and abiotic stress factors. It may therefore act as a beneficial element for plants altering several biochemical and physiological processes (Hawrylak-Nowak et al. 2018b; Hasanuzzaman et al. 2020). Selenium is very unevenly distributed in the Earth's crust, and its phytoavailability in soils is often low. In many areas of the world, the level of this element in soils is low/deficient in terms of dietary requirements. On the other hand, there are regions where the level of Se in soils is very high and its intake is higher than a certain threshold; then the element may be harmful to all living organisms (Oldfield 2002). While the Se concentrations in most natural soils are between 0.01 and 2.0 mg Se kg^{-1}, seleniferous soils are characterized by substantially higher levels of the element, i.e. from 2 to 1200 mg kg^{-1} (White 2018).

Although all plants have the ability to uptake and metabolize Se, they differ in their Se tolerance and capability to accumulate this element in aboveground organs. Therefore, three types of plants have been distinguished: Se hyperaccumulators, secondary Se accumulators, and non-accumulators (Fig. 17.1; Terry et al. 2000). The first group consists of a few species that are capable of active and specific accumulation of Se during their growth in soils with high Se levels. They are resistant to high Se concentrations. During growth on seleniferous soils, these species are capable of accumulation of over 1000 μg Se g^{-1} DW (0.1–1.5%) showing no symptoms of Se toxicity (White et al. 2007; Galeas et al. 2007; Lima et al. 2018).

The occurrence of Se hyperaccumulators in nature has been reported for at least 90 years. However, there has been increasing interest recently in using these amazing organisms in studies of Se metabolism in plants (Lima et al. 2018). No Se hyperaccumulators have been found in regions with low Se levels in the soil. Several *Stanleya*, *Astragalus*, *Neptunia*, *Morinda*, *Xylorhiza*, and *Oonopsis* species represent this group of plants. The greatest number of Se hyperaccumulator species represents the Fabaceae family (Terry et al. 2000; Gupta and Gupta 2017). Nevertheless, there is no close relationship between the Se accumulation ability and the plant family (Wrobel et al. 2020). The best-characterized Se hyperaccumulator is *Astragalus bisulcatus* (Fabaceae), which can accumulate up to 15,000 μg Se g^{-1} DW. This species grows in the south-western regions of the USA characterized by a naturally high concentration of Se in the soils (Galeas et al. 2007). It is assumed that

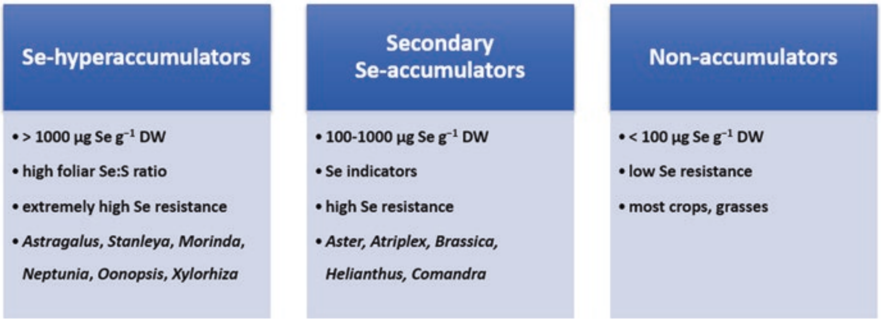

Fig. 17.1 Classification of plants in terms of their capability of selenium accumulation and tolerance

these species require Se for proper growth. Due to the high content of Se in their tissues, these species are highly toxic to humans and animals (Terry et al. 2000).

Not all species growing in seleniferous soils are able to accumulate Se. Even within one genus, there are large species differences, e.g. the genus *Astragalus* includes both Se-accumulators and species that do not accumulate this element. Some species can grow in the same habitat and yet accumulate very different amounts of Se (Terry et al. 2000; Lima et al. 2018). An extraordinarily high foliar Se:S ratio is believed to be one of the characteristic features of Se hyperaccumulators (White et al. 2007). However, Se is not disposed evenly in their tissues, and its levels may vary over the vegetative season. Generally, the highest foliar concentrations of Se are recorded in early spring. They are higher in younger leaves and reproductive tissues than in older leaves (Pilon-Smits and Quinn 2010). A study conducted by Galeas et al. (2007) suggests a specific flow of Se in hyperaccumulators during their vegetative season: from root to young leaves in spring, then Se remobilization from older leaves to generative parts in summer and retranslocation to roots in autumn. An ecological advantage of the capability of accumulation of abnormally high concentrations of Se in tissues is the protection of such plants against herbivore and pathogen attacks (Schiavon and Pilon-Smits 2017). Therefore, the ability to repel harmful organisms might have contributed to the evolution of Se hyperaccumulators (White 2018).

The second group of plants, known as secondary Se accumulators or Se indicators, is species that grow on soils with a low/medium level of this element and accumulate from several hundreds to 1000 μg Se g^{-1} DW. They do not require this element for proper growth. Secondary Se accumulators take up this element in direct proportion to the amount available in the soil. Some species of the genera *Atriplex*, *Comandra*, *Aster*, and *Brassica* are examples of this type of plants (Terry et al. 2000; Ellis and Salt 2003). Some researchers suggest that secondary Se accumulator species probably do not have any Se-specific metabolic pathways; they take up and metabolize Se and S ions indiscriminately, merely at increased rates in comparison to non-accumulator species (Pilon-Smits and Quinn 2010). A recent study carried out by Ogra et al. (2017) on two Se accumulator species, Indian mustard and garlic, have shown that both species supplemented with selenate and SeMet accumulate organic Se mainly as methylselenocysteine (MeSeCys) and γ-glutamyl-Se-methylselenocysteine (γ-GluMeSeCys). They suggest that Indian mustard may have a specific metabolic pathway for selenohomolanthionine (SeHLan) biosynthesis.

Most crops and grasses generally contain below 20 μg Se g^{-1} DW and are unable to accumulate Se in an amount exceeding 100 μg Se g^{-1} DW, even if they grow in Se-rich soils. They are Se-sensitive and cannot survive under excessive amounts of Se in the soil, showing stunted growth, chlorosis, and metabolism disorders. Such plants are regarded as non-accumulators (Terry et al. 2000; Gupta and Gupta 2017). They can tolerate low concentrations of Se in the rhizosphere through limitation of Se uptake and translocation to their aboveground organs (White et al. 2004) and rapid Se sequestration inside the vacuoles of mesophyll cells (Raina et al. 2021). However, S-rich plant species, like *Brassicaceae*, are characterized by two- to fivefold higher Se content than cereals grown in the same area (Terry et al. 2000; Gupta and Gupta 2017). Research conducted by Eurola et al. (1989) showed that, among non-hyperaccumulator species, onion and Brassicaceae vegetables had a higher Se level than other vegetables growing in soils supplemented with selenate in Finland.

17.3 Main Causes of Selenium Phytotoxicity: Malformed Selenoproteins and Oxidative/Nitro-Oxidative Stress

In higher plants, Se is toxic at concentrations exceeding the tolerance threshold, which is different for Se accumulators and for non-accumulators. Significant inhibition of root and shoot growth is a more characteristic consequence of excessive exposure to Se. In some cases, enhanced bioaccumulation of Se, especially in non-accumulators, can cause toxicity symptoms, e.g. leaf curl, reduction of the leaf blade surface, chlorosis, and necrosis (Fig. 17.2; Terry et al. 2000; Hawrylak-Nowak et al. 2015). In maize, the toxic effect of Se, mainly when it was supplied as organic SeMet, was manifested by a large increase in the concentration of anthocyanins in leaves (Hawrylak-Nowak 2008a, b, c). In turn, in cowpea grown in field conditions,

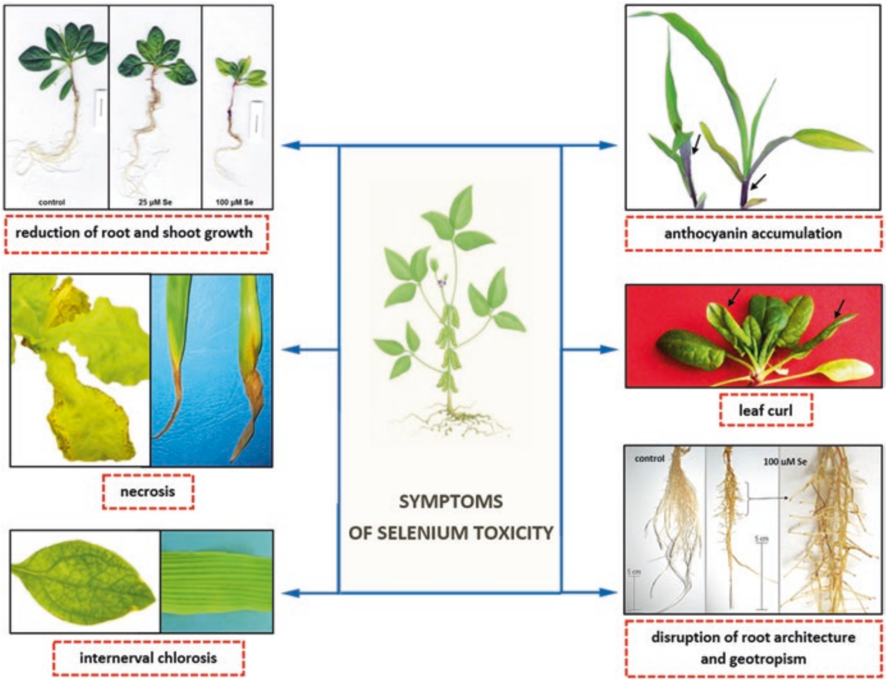

Fig. 17.2 Common visible symptoms of selenium toxicity in plants

foliar application of selenite exceeding 50 g ha^{-1} caused necrotic brown spots on leaves and deposition of pink salt in the interior. The leaf lesions were located mainly close to the trichomes (Silva et al. 2018). Microprobe X-ray fluorescence (μ-XRF) spectroscopy revealed a simultaneously elevated accumulation of Se and calcium (Ca) within necrotic lesions on the leaves of cowpea treated with foliar application of high selenate levels. Disarrangement of the upper epidermis was observed as well (Lanza et al. 2021).

The accumulation of huge quantities of Se in the root system of selenite-treated plants may induce significant alterations in the root architecture (Lehotai et al. 2012) and disturbances in the geotropic reaction of these organs (unpublished data; Fig. 17.2). This phenomenon may be influenced by damaged root ultrastructure (Ulhassan et al. 2019), highly disturbed metabolism of the root cells (Hawrylak-Nowak et al. 2015), loss of cell viability in the root apex, and/or hormonal imbalance (Lehotai et al. 2012).

The bioavailable chemical form of Se has considerable importance not only for its uptake and translocation but also for phytotoxicity. Selenite exhibits higher toxicity to most species than selenate (Hawrylak-Nowak 2013; Hawrylak-Nowak et al. 2015; Łukaszewicz et al. 2019). The translocation of selenate from the root system to shoots is easier and faster than that of either organic Se or selenite, since selenite is largely retained in root cells where it is quickly transformed into organic phytotoxic Se forms (Zayed et al. 1998). When both selenite and selenate are available in the growth media, the prevalent pattern is that of selenite. Selenite can probably inhibit the translocation of selenate to aboveground organs and is more hazardous at high concentrations than selenate (Guerrero et al. 2014). Organic Se forms, e.g. SeCys and SeMet, can be taken up by plants as well (Terry et al. 2000). Their toxicity is higher than that of the inorganic forms of this element, especially selenate. SeCys and SeMet can be directly misincorporated into proteins, and SeCys can additionally induce protein-thiol oxidation, which leads to disturbances in many physiological and molecular processes (Lazard et al. 2017). Moreover, it has recently been found that SeMet contributes to oxidative stress through an effect on hormone homeostasis (enhanced ethylene biosynthesis and reduced auxin production) and on plant primary metabolism (Malheiros et al. 2020).

In contrast to Se accumulators, non-Se-accumulating plant species (e.g. crops) are unable to discriminate efficiently the absorption of Se as selenate and S as sulphate during transport and assimilation of these elements (Bañuelos et al. 2017). Therefore, non-specific incorporation of Se-amino acids, i.e. SeCys and SeMet, into proteins is regarded as the major cause of Se phytotoxicity (Brown and Shrift 1981). The malformed selenoprotein hypothesis emphasizes that Se toxicity appears when tRNA^{cys} accidentally binds to SeCys instead of Cys during the translation process, thereby producing malformed and thus toxic selenoproteins. This hypothesis is supported by studies on transgenic plants, which suggest that diversion of SeCys away from non-specific protein misincorporation is related to enhanced Se resistance (Van Hoewyk 2013). In comparison to Cys, SeCys is larger, more easily deprotonated, and has greater nucleophilicity; thus, it is more reactive in redox reactions

(Hondal et al. 2012; Lazard et al. 2017). SeMet can be generated from SeCys during a three-step enzymatic process (Schiavon and Pilon-Smits 2017). It has been found that SeMet is the principal Se-amino acid in non-accumulator species (Brown and Shrift 1982).

The replacement of Cys with SeCys may interfere with the formation of disulphide bridges in proteins, which may weaken their stability, possibly leading to their inactivation or aggregation (White et al. 2004; Lazard et al. 2017). It has been reported that the bond between the Se atoms of SeCys is longer, weaker, and thus more labile than the disulphide bond, which may cause slight fluctuations in the protein tertiary structure (Terry et al. 2000). Proteins having selenosulphide or diselenide bonds are expected to have lower redox potentials than proteins with disulphide bridges, which can disturb the catalytic activity of enzymes (Hondal et al. 2012). Moreover, Se reduces the rate of protein synthesis, since SeMet substituted for Met probably interferes with the formation of the peptide bond (Terry et al. 2000).

Through their pro-oxidative action, toxic concentrations of Se induce oxidative stress in plants (Hartikainen et al. 2000). Reduced concentrations of non-enzymatic antioxidants, e.g. reduced glutathione (GSH) and L-ascorbic acid (L-AsA), found in Se-exposed plants are believed to be involved in an increase in the accumulation of reactive oxygen species (ROS) (Freeman et al. 2010; Ulhassan et al. 2019). GSH biosynthesis can probably be reduced due to the Se/S competition for uptake and assimilation (Schiavon et al. 2020). Also, decreased activities and levels of the expression of antioxidant enzymes, such as catalase (CAT), glutathione reductase (GSH-Px), and dehydro-ascorbate reductase (DHAR), may be responsible for a reduced level of cell protection against ROS (Ulhassan et al. 2019). The presence of selenoproteins in mitochondria and chloroplasts may weaken electron transport, thereby increasing the accumulation of superoxide (Van Hoewyk 2013). Furthermore, the transformation of selenocompounds into H_2Se or selenols (SeCys, MeSe, RSeH: GSeH, etc.), which are easily oxidized with simultaneous production of ROS, contributes to induction of oxidative stress (Lazard et al. 2017). Consequently, plants treated with toxic Se concentrations exhibit increased accumulation of harmful lipid peroxidation products (Hartikainen et al. 2000; Łabanowska et al. 2012; Hawrylak-Nowak et al. 2015). Oxidative stress induced by Se can be linked not only to ROS overproduction but also to an impaired methylglyoxal (MG) detoxification system. MG is a very reactive cytotoxic compound formed in cells both through non-enzymatic and enzymatic reactions. Se triggers MG toxicity by decreasing the activities of glyoxalases I and II, by which MG is largely neutralized (Mostofa et al. 2017). The pro-oxidative activity of Se seems to explain its toxicity when the intracellular concentration of this element exceeds the antioxidant defences and methylation capacity; it may also be responsible for programmed cell death (Spallholz 1997).

Besides ROS, Se phytotoxicity induces changes in the concentrations of reactive nitrogen species (RNS), i.e. peroxynitrite and nitric oxide (NO). Thus, researchers suggest consideration of nitro-oxidative stress, in addition to oxidative stress, as an underlying cause of Se toxicity (Kolbert et al. 2016). As shown by Chen et al. (2014), the selenite-induced oxidative injury is a consequence of generation of

NADPH oxidase-dependent ROS in the roots of wild-type field mustard. The authors assumed that NO increased the production of ROS through enhancement of the expression of several *Br_Rbohs* genes encoding NADPH oxidase. They claimed that endogenous NO performed a toxic function in mustard under selenite-induced stress by initiating ROS burst. Furthermore, the reduction of selenite to SeCys may generate additional inorganic Se intermediate metabolites that can also provoke oxidative stress (Van Hoewyk 2013. Accordingly, an augmented level of H_2O_2 in *Arabidopsis* primary roots was found. It exhibited a positive correlation with both cell mortality and bioaccumulation of Se applied as selenite (Lehotai et al. 2012). Furthermore, glutathione-mediated non-enzymatic reduction of selenite can produce selenodiglutathione (GS-Se-SG), which has higher toxicity than selenite and can induce mitochondrial superoxide over-accumulation and cytotoxicity (Wallenberg et al. 2010). As suggested by Łabanowska et al. (2012), under Se exposure, carbohydrate molecules serving as electron traps can participate in the production of long-lived radicals.

Recent results reported by Kolbert et al. (2019) demonstrate that Se phytotoxicity targets the plant proteome, i.e. the whole set of proteins expressed by the genome, cell tissue, or organism at a certain time and in specified conditions. It has been demonstrated that not only seleno- and oxy-proteins but also nitro-proteins are produced as a result of Se stress. Certain plants are able to limit Se-induced proteomic damage via redirection of SeCys away from protein synthesis, thus preventing the formation of Se proteins. Furthermore, proteasomes, i.e. protein complexes that degrade unneeded or damaged proteins by proteolysis, can eliminate malformed selenoproteins, oxyproteins, and nitroproteins.

One of the factors by which trace elements influence the metabolic and physiological processes of plants is their interaction with essential nutrients. Many research reports have shown that Se ions can disturb the mineral balance in plants (Hawrylak-Nowak 2008a, b, c; Ríos et al. 2008a, b; Łukaszewicz et al. 2019; Ríos et al. 2013). Due to the SeO_4^{2-} and SO_4^{2-} antagonism, the ratio between these ions in the medium influences their uptake and accumulation. However, synergism can also occur between them when the concentrations of S and Se in the growth medium are relatively low, causing increased accumulation of S and Se and the end products of assimilation of these elements in plants (Lyons et al. 2005; Ríos et al. 2008a, b). In field conditions, the interactions between S and Se are very complicated, as S fertilization can improve the availability of Se in soil but inhibit selenate uptake by plants (Stroud et al. 2010).

It has been found that selenite rather than selenate exerts a stronger impact on the nutritional mineral status in plants, especially in the case of N, P, Mg, S, and Zn (Ríos et al. 2008a, b). In a study conducted by Hawrylak-Nowak (2008a, b, c), selenite treatment increased maize shoot P and Ca contents, while K declined with an increasing Se concentration. Since phosphate transporters are involved in selenite transport (Gupta and Gupta 2017), the plant P level can be particularly affected by selenite treatments. In cucumber treated with selenite or selenate, the shoot K, P, and S bioconcentrations were especially highly disturbed by toxic concentrations of Se. In turn, the N level was generally maintained unchanged (Hawrylak-Nowak et al. 2015). Feng et al. (2009) suggest antagonistic and synergic effects of Se on the uptake of Ca, Mg, and K at low and high Se concentrations, respectively, in Chinese brake fern, which is a Se accumulator. It has also been suggested that damage and changes in the permeability of root cell membranes induced by increased lipid peroxidation may contribute to mineral homeostasis disorders (Hawrylak-Nowak et al. 2015).

17.4 Mechanisms of Selenium Resistance and Tolerance

As mentioned above, the non-specific incorporation of SeCys and SeMet into proteins causes disturbances in their structure and functions. However, Se-hyperaccumulating species can tolerate high Se levels in their tissues and colonize seleniferous soils due to the effective metabolic detoxification of Se by sequestration of the element in vacuoles, production of non-toxic Se metabolites, e.g. non-protein amino acids, and/or efficient volatilization of Se compounds (White 2018).

In Se hyperaccumulators, the enzyme SeCys methyltransferase (SMT) found in plastids transforms SeCys to non-protein amino acid methyl-SeCys, thereby preventing its misincorporation into proteins and toxic action (Schiavon and Pilon-Smits 2017). The additional possible Se tolerance mechanisms in Se-hyperaccumulating species are based on sequestration of methyl-SeCys in epidermis cells (Freeman et al. 2010) and transformations of organic Se to alkylated volatile Se species, e.g. dimethyldiselenide (DMDSe) (Ellis and Salt 2003; Wrobel et al. 2020). It has been found that Se hyperaccumulators treated with SeO_4^{2-} store Se predominantly as methyl-SeCys, while non-accumulators such as *Arabidopsis* and secondary accumulators such as *Brassica juncea* accumulate primarily SeO_4^{2-}, indicating differences in Se metabolism. Moreover, interesting Se sequestration patterns, which are not observed in non-hyperaccumulating taxa, have been detected in Se hyperaccumulators: approximately 90% of Se was accumulated as methyl-SeCys in leaf epidermis or leaf hairs (Freeman et al. 2006). In turn, oilseed rape metabolized SO_3^{2-}/SO_4^{2-} into various organic Se forms, mainly SeMet, whereas SeCys, i.e. a precursor of non-protein Se-amino acid, was not detected in the seeds and leaves of this species (Seppänen et al. 2018). Furthermore, hyperaccumulator species translocate Se more effectively in the xylem (from root to shoot) and phloem (from leaves to generative organs) than non-accumulators and differ in their tissue Se accumulation patterns (Pilon-Smits 2019).

The levels of L-ascorbic acid, GSH, non-protein thiols, and total S were higher in the Se-hyperaccumulator *Stanleya pinnata* than in the secondary Se-accumulator *Stanleya albescens*. This suggests that the tolerance to Se may be related to improved antioxidant capacity and increased S accumulation (Freeman et al. 2010). The multiomics research on Se tolerance in the Se-hyperaccumulating species *Cardamine enshiensis* revealed that GSH, flavonoid, and lignin biosynthetic pathways can be of great importance in protecting plants from Se-induced stress (Huang et al. 2021).

Although the Se tolerance mechanisms have similar features, there is genetic variation between populations of individual species with regards to the degree of Se accumulation, as demonstrated in the case of *Stanleya pinnata* (Parker et al. 2003). Tamaoki et al. (2008) reported that both ethylene and jasmonic acid (JA) are important compounds for enhancement of Se resistance in Arabidopsis. It was found that augmented accumulation of ROS was connected with increased ethylene and JA biosynthesis in a Se-tolerant *Arabidopsis* ecotype. Similarly, auxin and ethylene may increase Se tolerance, since their reduced levels caused greater sensitivity to Se in *Arabidopsis*; simultaneously, high concentrations of cytokinin contributed to considerable enhancement of plant resistance to selenite (Lehotai et al. 2012). Recently, a novel Se tolerance mechanism has been proposed, in which endoplasmic reticulum-assisted degradation (ERAD) is involved in the elimination of misfolded selenoproteins (Van Hoewyk 2018).

Non-accumulators can avoid incorporation of SeCys into proteins either by breaking down this amino acid to alanine and elemental Se (Van Hoewyk et al. 2005) or by transforming SeCys to volatile DMSe (Schiavon and Pilon-Smits 2017). The transformation of SeMet and SeCys to volatile Se compounds is an effective strategy increasing plant tolerance to Se. Generally, Se is volatilized as DMSe in non-accumulators and as DMDSe in Se-hyperaccumulators (White 2018). The resistance to Se in Se-sensitive non-accumulator plants can be increased via genetic engineering. Overexpression of key enzymes responsible for Se detoxification in hyperaccumulators, such as SMT, may lead to increased Se tolerance in non-accumulators. Such transgenic plants may be useful in Se phytoremediation. They are also of great interest to medical practitioners and nutritionists due to the presence of organic Se forms with potentially high anticancer activity (Ellis et al. 2004). Recent comparative transcriptomics experiments reported by Zhou et al. (2018) indicated that the storage function, transamination, oxidation, and selenation play vital roles in Se tolerance in *Cardamine hupingshanensis* (Brassicaceae) – a novel species included in the group of Se hyperaccumulators. Additionally, a dissimilar degradation pathway for malformed Se proteins improved Se tolerance in this species.

17.5 Beneficial Role of Selenium in Plants: Growth-Promoting Effects and Enhanced Stress Tolerance

Recent research has demonstrated that Se can be regarded as a beneficial element to plants (Baker and Pilbeam 2015). This was mainly indicated by research proving the growth-stimulating effect of low Se concentrations and its positive influence on plant resistance to various abiotic and biotic stresses (Seppänen et al. 2003; Hawrylak-Nowak et al. 2018b). Selenium plays its beneficial role as a growth-promoting agent and stress modulator mainly by inhibition of ROS production and over-accumulation via the following pathways: (i) modulation of the levels and activity of non-enzymatic and enzymatic antioxidants, (ii) stimulation of the spontaneous dismutation of $O_2^{\bullet-}$ to H_2O_2, and (iii) direct ROS quenching (Feng et al. 2013; Chauhan et al. 2019). Other mechanisms can be associated with the influence of Se on the integrity and stability of photosystems and photosynthesis machinery, which in consequence leads to limited ROS formation (Chauhan et al. 2019). In *Brassica napus*, exogenously applied Se markedly improved plant growth by increasing the uptake of essential mineral elements, photosynthetic efficiency, and gas exchange parameters. It also elevated the concentrations of water-soluble proteins and sugars (Ulhassan et al. 2019). Selenium can also act as an anti-senescent agent and support plants in the maintenance of cellular function and structure, thereby contributing to the improvement of plant growth and development (Kaur et al. 2014).

Appropriate Se concentrations are highly effective in mitigation of cell oxidative damage induced by various environmental stressors. Selenium ions may regulate or improve the function of the injured photosynthetic machinery and/or repair the chloroplast ultrastructure to rebalance the electron transfer chain (Feng et al. 2013). Some results suggest that Se may activate protective mechanisms mitigating the effects of photooxidative stress in potato chloroplasts (Seppänen et al. 2003). In these experiments, the synergistic effect of Se on the transcription level of chloroplast antioxidant enzymes, such as Cu/Zn superoxide dismutase (Cu/ZnSOD) and GSH-Px, was demonstrated. Moreover, decreased lipoperoxidation in thylakoid membranes has been suggested to protect and stabilize enzymes involved in the biosynthesis of photosynthetic pigments (García Márquez et al. 2020).

In plants exposed to heat stress, Se fertilization may improve yields by alleviation of ROS-induced injuries through activation/modulation of the cellular antioxidant machinery (Hasanuzzaman et al. 2014; Iqbal et al. 2015; Balal et al. 2016; Hawrylak-Nowak et al. 2018a). Under heat stress, disruption of AsA-GSH cycle components resulting in overproduction of ROS was detected. Nevertheless, supplementation with Se enhanced enzyme activities and the plants accumulated higher concentrations of GSH and L-AsA (Hasanuzzaman et al. 2014). Exogenous Se was also found to modify physiological responses of cucumber exposed to short-term cold. The Se-supplemented plants showed increased foliar content of proline and reduced lipid peroxidation in root tissues both directly after chilling and after re-warming (Hawrylak-Nowak et al. 2010).

The effect of exogenous Se on plants grown under salt stress is well documented, as many salt-exposed species reacted very positively to Se supplementation (Hawrylak-Nowak 2009; Diao et al. 2014; Jiang et al. 2017; Atarodi et al. 2018). As recently shown by Elkelish et al. (2019), Se supplementation protected wheat plants against salt-induced oxidative stress and strengthened stress tolerance by up-regulating antioxidant systems, enhancing osmolyte biosynthesis, and preventing excessive bioaccumulation of Na^+. Moreover, Jiang et al. (2017) demonstrated that the shoot K^+ accumulation increased and the root Na^+ level decreased at a low Se concentration. The authors found that Se can up-regulate the *ZmNHX1* gene in root cells, which may be involved in the compartmentalization of Na^+ in conditions of excessive salinity. Similarly, in rice treated with Se prior to salinity stress, Subramanyam et al. (2019) showed increased transcript levels for OsNHX1, an important Na^+/H^+ antiporter responsible for Na^+ sequestration in the vacuole. The role of free proline in the Se-induced enhancement of plant resistance to salinity is ambiguous. Its level fluctuates in plants supplemented with Se and exposed to salt stress. In some salt-stressed species, the level of this amino acid can increase under the influence of exogenous Se, which is associated with simultaneous growth stimulation (Hawrylak-Nowak 2009). In turn, the Se growth-promoting effect on other species was not connected with a significant increase in foliar accumulation of proline (Hawrylak-Nowak 2015). Se-induced stabilization of the proline level in leaves and limited loss of this amino acid from roots were demonstrated in other plants (Regni et al. 2021).

Selenium ions can also be effective in counteracting the stress associated with toxic trace elements. Exogenous Se has been found to prevent their uptake and negative impact on plants. Under Cd- and As-induced phytotoxicity, the supplementation of potato with Se reduced the accumulation of Cd and/or As in plants and modulated the metabolism of N and carbohydrates. The enhanced C-metabolism and decreased N losses associated with the Se supplementation improved plant growth (Shahid et al. 2019). In experiments with Cd-exposed cucumber (Hawrylak-Nowak et al. 2014), the enrichment of the growth medium with Se caused decreased lipid peroxidation and reduced Cd and phytochelatin (PC) accumulation in root tissues. The leaf cell membranes exhibited improved stability, but the growth-promoting effect of Se was not pronounced. A positive impact of low Se concentrations on the maintenance of the structure and fluidity of chloroplast biomembranes was demonstrated by Filek et al. (2010) in Cd-exposed rape. The enhanced Fe uptake and bioaccumulation under Se supplementation can be regarded as one of the mechanisms of reducing both metal toxicity (Feng et al. 2009) and the negative impact of salt stress (Atarodi et al. 2018) on plants, since Fe is a key component of chloroplasts and the photosynthetic electron transport chain. In turn, in a summary of the considerations on the mechanisms underlying the Se-mediated restriction of the uptake of some toxic metals, Feng et al. (2021) pointed to the co-precipitation of Se and metals in soil as a key factor limiting the uptake of metal ions by plants. The downregulation of genes encoding proteins involved in Cd uptake may also be important (Feng et al. 2021). As in many other cases, the chemical form of Se may also play a significant role in the amelioration of some negative effects caused by toxic metals. In Ni-exposed lettuce treated with a low dose of selenate, the root growth was stimulated, while selenite in general intensified the phytotoxicity of Ni. Although a decreased concentration of this metal was detected in the roots, the Ni level in the shoot increased, regardless of the Se form (Hawrylak-Nowak and Matraszek-Gawron 2020). In turn, in Cd-exposed pak choi, both chemical forms of Se mitigated Cd-induced oxidative stress, but selenite caused a decrease in shoot Cd accumulation, whereas selenate increased it (Yu et al. 2019).

The protective effect of Se is related not only to its antioxidant activity. This element has been found to exert a multidirectional effect on various physiological processes, especially on water balance. The protective influence of exogenous Se in water-deficit conditions may result from its direct impact on more effective water uptake from the soil (through stimulation of water uptake by roots) and/or its inhibitory effect on the intensity of transpiration and thus water loss from plant tissues (Kuznetsov et al. 2003). Recently, Han et al. (2022), who compared the effectiveness of selenite and selenate in mitigation of drought stress in tobacco, demonstrated that both chemical forms were useful, but the beneficial effects of selenate exceeded those associated with the application of selenite.

The accumulation of toxic Se compounds can effectively protect plants against fungal and other pathogen and herbivore attacks. The accumulation of Se in tissues has been found to protect plants against fungal infections and invertebrate herbivores, which become poisoned after feeding on Se-rich leaves (Hanson et al. 2003). Similarly, aphids evidently distinguished and avoided Se-containing leaf tissues (Hanson et al. 2004). It was later found that differences in the Se assimilation pathway allow achievement of maximum Se bioconcentrations, which are indispensable for introduction of sufficiently high doses of toxic Se compounds into the organisms of herbivores resulting in poisoning of the pests. This led to the evolution of plant species with an ability to colonize seleniferous soils (Schiavon et al. 2017; White 2018). Selenium hyperaccumulation not only can protect plants against Se-sensitive pathogens and herbivores but can simultaneously reduce neighbouring vegetation by deposition of plant biomass with extremely high Se content (elemental allelopathy) (Pilon-Smits 2019).

17.6 Selenium Biofortification Improves the Quality of Yield

Selenium uptake and assimilation by plants affects the S and nitrogen (N) metabolic pathways; therefore, current investigations are focused on the influence of Se exposure on the biosynthesis and accumulation of S and N secondary metabolites to enhance the nutraceutical profile of food (D'Amato et al. 2020). Selenium can be incorporated into several secondary Se metabolites of SeMet and SeCys (Malagoli et al. 2015; White 2018). The effect of Se enrichment on the content of these phytochemicals has been evaluated in several studies. The impact of Se on the products of plant specialized metabolism in Se-enriched plants is presented in Table 17.1.

Phenolic compounds, i.e. N-containing secondary metabolites, are formed in the shikimate and phenylpropanoid pathways (Tohge and Fernie 2017). As shown by Hawrylak-Nowak et al. (2018a), Se biofortification of lamb's lettuce not only enhanced the thermo-tolerance of the plant but also improved its nutritional value. The foliar concentrations of total phenolics, chlorogenic acid, and flavonoids in Se-supplemented plants growing at an optimal temperature were significantly elevated, and the plant biomass was simultaneously enriched with Se. The authors suppose that low concentrations of Se are able to stimulate the phenylpropanoid pathway, but only in optimal thermal conditions. Similarly, in experiments on hydroponically grown Se-biofortified strawberry reported by Mimmo et al. (2017), enhanced accumulation of flavonoid and polyphenol compounds was found in

Table 17.1 Effects of exogenous selenium on the level of secondary metabolites in selected crop plants

Plant species	Experimental conditions	Form, dose, and method of Se application	Effects of Se on secondary metabolites	References
Basil (*Ocimum basilicum*)	Natural conditions; soil	Selenate; foliar application of 30, 60, or 120 mg Se L^{-1}	Increased the content of soluble phenols in leaves	Oraghi Ardebili et al. (2015)
Basil (*O. basilicum*)	Heated glasshouse; hydroponic cultivation	Selenate; 4, 8, or 12 mg Se L^{-1} applied to the nutrient solution	Elevated level of total phenolics and rosmarinic acid in leaves	Puccinelli et al. (2020)
Basil (*O. basilicum*)	Climate chamber; soil substrate	Selenate; foliar application of 1–50 mg Se L^{-1}	Increased the concentration of total phenolic compounds in leaves	Hawrylak-Nowak (2008a, b, c)
Broccoli (*Brassica oleracea* var. *italica*)	Greenhouse; hydroponic cultivation or soil substrate	Selenate; 25 μM Se applied to the nutrient solution or soil substrate	Reduced accumulation of total glucosinolates, mainly glucoraphanin, in leaves and florets	Tian et al. (2018)
Celery (*Apium graveolens*)	Field conditions; soil	Se nanoparticles; foliar application of 5 mg Se-NPs L^{-1}	Increased accumulation of total phenols and flavonoids (rutin, apigenin, ferulic acid, p-coumaric acid, luteolin, kaempferol) in leaves, enhanced antioxidant activity of leaves	Li et al. (2020)
Coriander (*Coriandrum sativum*)	Greenhouse; soil substrate	Se nanoparticles; foliar application of 25 or 50 Se-NPs L^{-1}	Increased essential oil yield and enhanced accumulation of essential oil constituents: Camphor, linalool, geranyl acetate, α-pinene, δ-terpinene in fruits	El-Kinany et al. (2019)
Endive (*Cichorium endivia*)	Greenhouse; open hydroponic floating system	Selenate; 1, 2, 4, or 8.0 μmol L^{-1} applied via fertigation or foliar spray	Increased the concentration of total phenolic compounds in leaves	Sabatino et al. (2019)
Lamb's lettuce (*Valerianella locusta*)	Climate chamber; soil substrate	Selenate; foliar or soil application of 50 mg Se L^{-1}	Elevated level of total phenolics, chlorogenic acid, flavonoids in leaves	Hawrylak-Nowak et al. (2018a)
Lemon balm (*Melissa officinalis*)	Greenhouse; hydroponic cultivation	Selenite; 0.2 or 5 μM applied to the nutrient solution	Elevated caryophyllene, caryophyllene oxide, z-citral, citral, and geranyl acetate contents in leaves	Tavakoli et al. (2020)

(continued)

Table 17.1 (continued)

Plant species	Experimental conditions	Form, dose, and method of Se application	Effects of Se on secondary metabolites	References
Rocket (*Eruca sativa*)	Growth chamber; hydroponic cultivation	Selenate; 5, 10, 20, or 40 μM Se applied to the nutrient solution	Reduced accumulation of total glucosinolates and individual glucosinolates, decreased concentration of some phenolic compounds in leaves	Dall'Acqua et al. (2019)
Strawberry (*Fragaria* × *ananassa*)	Climate chamber; hydroponic cultivation	Selenate; 10 μM Se or 100 μM Se applied to the nutrient solution	Increased flavonoid and phenolic compounds in fruits	Mimmo et al. (2017)
Tomato (*Solanum lycopersicon*)	Greenhouse; unknown method of cultivation	Selenate; foliar application of 1 mg Se L^{-1}	Increased concentrations of flavonoids and tocopherols in fruits	Zhu et al. (2018)
Tomato (*S. lycopersicon*)	Climate chamber; hydroponic cultivation	Selenate; 5–100 μmol L^{-1} applied to the nutrient solution or via foliar spray at 2 or 20 mg Se per plant	Increased level of quercetin, quercetin-hexose-deoxyhexose pentose, naringenin chalcone, and kaempferol, and a decrease in cinnamic acid derivatives in fruit peels; stimulated biosynthesis of phenolics in leaves	Schiavon et al. (2013)

addition to an increased fruit Se concentration. These substances were found to contribute to the organoleptic traits and antioxidant capacity of strawberry fruits. Moreover, the content of total soluble solids (TSS) and the sweetness index of the Se-biofortified strawberries were elevated, which can exert a positive effect on the fruit taste. Another example demonstrating that the quality of plant products can be favourably modified to some extent by Se supplementation is Se-biofortified sweet basil (Hawrylak-Nowak 2009). In this species, foliar spraying with a Se solution (3–20 mg L^{-1} as selenate) increased the total content of phenolic compounds (up to 44% vs. the control). A similar impact of Se on the accumulation of selected phenolics in basil was also confirmed later in natural conditions (Oraghi Ardebili et al. 2015). Biofortification with Se modifies the phenylpropanoid pathway mainly by enhancing the enzymatic activity of phenylalanine ammonia-lyase (PAL), i.e. a crucial enzyme in phenylpropanoid metabolism and biosynthesis of secondary metabolites from the group of phenolic compounds (Oraghi Ardebili et al. 2015; García Márquez et al. 2020). Proteomic analysis demonstrated that proteins involved in phenylpropanoid biosynthesis were up-regulated in Se-biofortified tomato fruit causing increased flavonoid accumulation (Zhu et al. 2018). The phenomenon of the improved accumulation of phenolics may be also attributed to the Se-affected hormonal homeostasis, especially that of salicylic acid (SA), JA, and ethylene, leading to defence-related responses (Tamaoki et al. 2008; Oraghi Ardebili et al. 2015). In turn, Dall'Acqua et al. (2019) reported reduced levels of some phenolic compounds, i.e. kaempferol-3,4′-diglucoside, kaempferol-3-glucoside, and kaempferol-3-(2-sinapoil-glucoside)-4′-glucoside in salad rocket and quercetin-3,3,4′-triglucoside, quercetin-3,4′-diglucoside, and kaempferol-3.4′-diglucoside in wild rocket under selenate exposure. The authors suggest that Se may affect the shikimate pathway, i.e. the entry to the biosynthesis of phenylpropanoids, in various ways, i.e. by redirecting one of the final products of this pathway – phenylalanine from production of phenolics to serve as a substrate for glucosinolate biosynthesis or by direct inhibition of enzymes involved in the shikimate pathway.

In comparison to control plants, Se-biofortified tomatoes had higher concentrations of some flavonoids (naringenin chalcone and quercetin) in their fruits after foliar Se application and a higher level of phenolic compounds in their leaves after administration of Se through the roots (Schiavon et al. 2013). In turn, increased accumulation of phenolic acids and anthocyanins was detected in two differently pigmented lettuce genotypes supplemented with Se (Pannico et al. 2019). Biofortification with Se also increased the rosmarinic acid content in basil (Puccinelli et al. 2020). Furthermore, the presence of selenosugars, possibly originating from the cell wall, has been described in Se-supplemented plants (Aureli et al. 2012). The results reported by Bañuelos et al. (2012) revealed the presence of non-protein methylselenocysteine (MeSeCys) in Se-enriched fruits of Opuntia cactus pear. This compound is nutraceutically very interesting, since it is one of the least toxic and thus the safest chemical forms of Se, simultaneously characterized by high anti-carcinogenic activity (Yang and Jia 2012). As an element that enhances the accumulation of many compounds with strong antioxidant properties, Se was found to increase the antioxidant capacity in Se-enriched leafy vegetables (Ríos et al. 2008a, b), herbs (Oraghi Ardebili et al. 2015; Tavakoli et al. 2020), and edible sprouts (Woch and Hawrylak-Nowak 2019).

Recently, Se nanoparticles (Se-NPs), i.e. bioavailable and low-toxic Se forms with high efficiency, were used for enhancement of the yield and quality of various crops (El-Ramady et al. 2020). Li et al. (2020) revealed that foliar application of Se-NPs in celery increased the concentration of total phenols, flavonoids, L-ascorbic acid, β-carotene, arginine, and tryptophan and enhanced the antioxidant capacity of plants, probably by regulating the α-linolenic acid pathway. The foliar application of Se-NPs also increased the nutraceutical potential of fruits of coriander grown under salinity by increasing the essential oil yield and the concentration of the major constituents of essential oil (El-Kinany et al. 2019).

Selenium treatment can also exert direct or indirect positive effects on the post-harvest storage of some crops. For example, Se application can delay the decline in firmness, titratable acidity, and weight loss during the storage of tomato (Zhu et al. 2016) and guava (Choudhary and Jain 2018) fruits. The reduced production of ethylene detected in Se-treated basil stored for 5 days may indicate that Se enrichment can prolong the shelf-life of basil leaves (Puccinelli et al. 2020). In turn, foliar spraying with selenate improved the respiratory potential in young chicory, but not in plants at harvest time (Germ et al. 2007). An indirect influence was associated with the reduction of the germination rate and mycelial growth of some detrimental fungi (Puccinelli et al. 2017).

17.7 Conclusions

Selenium accumulated in plants from the soil is then ingested by animals and humans with food, and in this way, Se is easily incorporated into the food chain. Although plants do not require Se for proper growth and development, the process of phytoaccumulation and further volatilization of Se can be applied in both crop biofortification in Se-deficient regions and phytoremediation of areas contaminated with this element. The biological activity of Se and plant resistance to this element are strictly dependent on the species, age, and developmental stage of plants, the phytoavailable chemical form of Se, and environmental factors influencing its uptake and accumulation. Therefore, plants can react to the presence of Se both positively and negatively (Fig. 17.3). Despite the increasing knowledge of plant responses to the presence of Se, a number of issues regarding the specific mechanisms of its toxicity and resistance in Se accumulators and non-accumulators still need elucidation. In particular, the molecular and physiological processes determining the beneficial effects of this element in crops in the changing climate conditions may be of key importance. In this aspect, the use of low-toxic Se nanoparticles with high bioavailability and efficiency may prove very promising in the future. Moreover, the knowledge of the factors controlling the uptake, translocation, and assimilation of different chemical forms of Se will help to prevent their negative impact on the primary and secondary metabolism in Se-enriched plants.

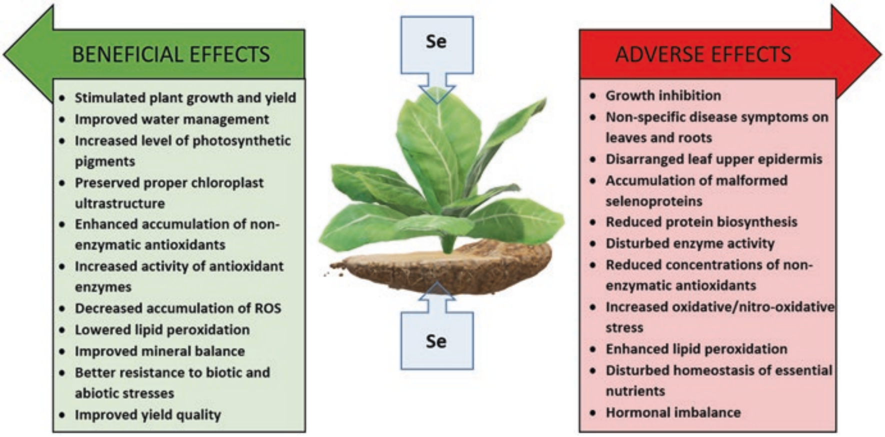

Fig. 17.3 Beneficial and adverse effects of selenium on plant growth and metabolism

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