

Chapter 15

Effects of Selenium on Plant Metabolism and Implications for Crops and Consumers

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Abstract Selenium (Se) is an essential trace element for many organisms including humans, while in plants it can trigger a variety of beneficial effects. Plants absorb Se mainly in the form of selenate using high affinity root sulfate transporters. Consequently, availability of sulfur (S) has a major impact on Se accumulation due to competition effects of the two oxyanions. In addition, Se has an impact on S uptake through interference with intrinsic regulatory mechanisms. Inside cells, selenate can access the sulfate assimilation pathway and influence the production of S-organic compounds that are of vital importance in plant responses to biotic and abiotic stress conditions. Selenium has been reported to mitigate stress in plants because of its capacity to induce the synthesis of S- and nitrogen (N) compounds, in addition to stimulating the activity of antioxidant enzymes and metabolites. Selenium can also alter the uptake of certain microelements like molybdenum, which functions as a cofactor for the enzyme nitrate reductase. Therefore, Se at high doses may interfere with N assimilation, causing a decrease in the level of N-compounds with structural and/or regulatory functions. Selenium interactions with multiple metabolic pathways in plants have relevant implications for plants and consumers that feed on them. Managing such interactions are useful to biofortify crops with organic forms of Se endowed with beneficial properties (selenomethionine and methylselenocysteine) and in other nutraceuticals like glucosinolates and antioxidants. Furthermore, Se at low doses may improve plant productivity or

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phytoremediation potential by enhancing photosynthesis and increasing the capacity of plants to tolerate stress.

Keywords Metals • Oxidative stress • Nutraceuticals • Biofortification

15.1 Selenium Metabolism and Its Close Relationship with Sulfur

Selenium (Se) is an important trace element for humans and many animals, as a component of selenoenzymes that display pivotal roles in cell metabolism by functioning as protectors from oxidative stress and controllers of cell redox status (Rayman 2012; Roman et al. 2014). Some organic forms of Se, like selenomethionine (SeMet), methylselenol and Se-methylselenocysteine (MetSeCys), have recognized anticarcinogenic properties (Combs 2005; Jackson and Comb 2008; Zeng and Combs 2008; Fernandes and Gandin 2015). MetSeCys for instance, has been reported to inhibit 7,12-dimethylbenz (a) anthracene (DMBA)-induced mammary tumors and act as a chemopreventative agent that blocks cell cycle progression and proliferation of premalignant mammary lesions (El-Bayoumy and Sinha 2004).

Despite the essentiality of Se for humans and animals, human Se intake in the diet is often lower than the recommended daily dose of 50–70 µg, which is required for full expression of protective selenoproteins (Brown and Arthur 2001). As a result, Se deficiency is a issue for concern in many countries worldwide (Combs 2001; Rayman 2002), being associated with a variety of diseases, such as reduced immune and thyroid function (Rayman 2012; Roman et al. 2014).

15.1.1 Uptake and Transport of Se

Plants represent one of the main dietary sources of Se for humans and animals. Depending on soil chemical properties, Se is available to plants mainly as either selenate or selenite. Selenate is usually the main soluble form of Se in soil. It is absorbed by plant cells via plasma membrane sulfate transporters and can be assimilated through the sulfur (S) assimilation pathway into Se-amino acids (Sors et al. 2005). This is because selenate and sulfate share high chemical similarity. In this respect, Se can interfere with S transport and assimilation in plants depending on Se/S ratio in the growth medium and/or in the plant (White et al. 2004; Schiavon et al. 2012). In Se non-hyperaccumulator plant species, selenate often induces a S deficiency response, which generally involves the up-regulation of genes coding for sulfate transporters and sulfate assimilation enzymes (Van et al. 2008; Harris et al. 2014; Schiavon et al. 2015). At low doses, Se can therefore cause an increase of sulfate uptake rates in these species, while at high concentration it will reduce S

entry into root cells via competition for transporters (White et al. 2004; Schiavon et al. 2012). The high levels of Se may lead to replacement of S-containing amino acids with Se-containing equivalents which then triggers the S-starvation responses directly through relief of feedback inhibition of gene expression, even in the presence of S.

Under S-deficiency and even in the presence of modest levels of Se, high levels of selenium will accumulate in plant tissues (Stroud et al. 2010b; Shinmachi et al. 2010). The S-deficiency results in an induction of sulfate transporters due to de-repression of gene expression (Smith et al. 1997); additionally S-deficient soils may aid in selenate uptake by reduced competition, resulting in substantially increased vegetative and grain tissue selenium (Stroud et al. 2010b; Shinmachi et al. 2010). Due to the positive health benefits of Se in human and animal diets considerable attention has been paid to enhancing content in food crops such as cereals (reviewed in Hawkesford and Zhao 2007). As already stated, S-fertilization as well as Se availability in soils (Fan et al. 2008; Stroud et al. 2010a) will strongly influence the total Se-accumulation, the chemical form of Se and its tissue cellular and subcellular localization. For example, Se usually accumulates in seed tissues in parallel with S (reflecting the replacement of S in S-containing amino acids) but localized hotspots are also apparent, perhaps indicating vacuolar sequestration (Moore et al. 2009).

In Se hyperaccumulators, Se tends to reduce S levels in tissues due to competition, but in these species there typically is no S deficiency response because the sulfate transporters and assimilatory enzymes are constitutively up-regulated (Schiavon et al. 2015).

15.1.2 Chemical Fate of Se Within the Plant

The two Se-amino acids produced in the S assimilation pathway are selenocysteine (SeCys) and selenomethionine (SeMet), which are analogues of the S-amino acids cysteine (Cys) and methionine (Met) (Fig. 15.1). In addition to being protein subunits, Cys and Met play several functions in cells. Cysteine is a component of glutathione (GSH), a pivotal molecule in plant responses to multiple types of stress, while Met is a precursor of aliphatic glucosinolates, which are compounds involved in plant-pathogen/herbivore interactions (Mithöfer and Boland 2012). Therefore, Se interactions with S metabolism at different levels may affect the capacity of plants to cope with stress. Also, a secondary effect of such interactions is the capacity of Se to interfere with N metabolism, given that the S and N pathways come together at the level of cys synthesis. Cys is at a key regulatory point and may influence flux through both the N-assimilatory pathway, particularly regulating the provision of the cysteine precursor, O-acetylserine, and in the synthesis of glutathione, both suggested regulatory molecules for S-assimilation (Leustek and Saito 1999).

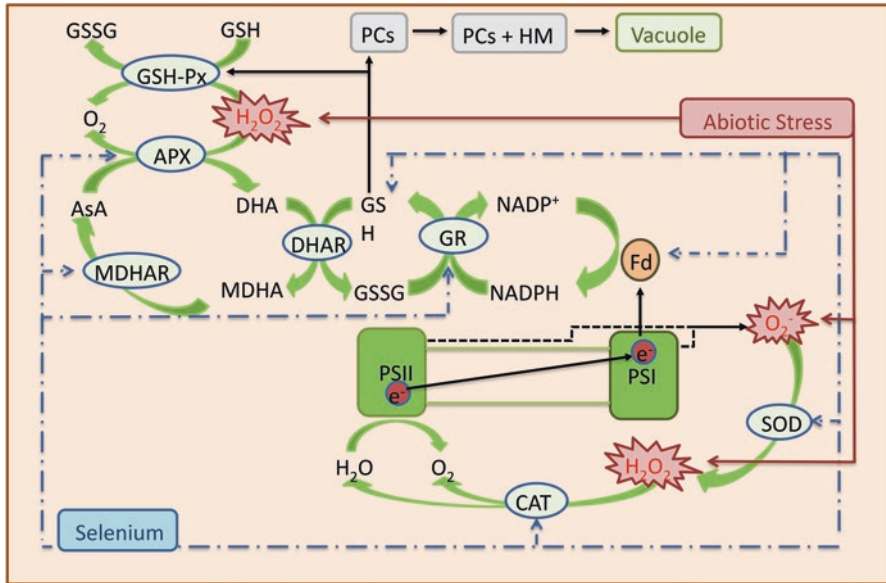


Fig. 15.1 Selenium induces enhanced antioxidant activity which stimulates plant productivity and resistance to oxidative stress. The image illustrates the pathway in photosynthetic tissues. *Enzymes*: Ascorbate peroxidase (APX), Catalase (CAT), Dehydroascorbate reductase (DHAR), Glutathione peroxidase (GSH-Px), Glutathione reductase (GR), Monodehydroascorbate reductase (MDHAR), SOD (Superoxide dismutase). *Metabolites*: AsA (Ascorbate), GSH (reduced glutathione), PCs (Phytochelatins). *Reactive Oxygen Species*: Superoxide radical ($O_2^{\bullet-}$); Hydrogen peroxide (H_2O_2)

15.2 Beneficial Effects of Se-induced Antioxidants (Enzymes and Metabolites) on Plant Productivity and Oxidative Stress Resistance

Plants can be faced with different environmental conditions that generate oxidative stress via production of Reactive Oxygen Species (ROS), and must activate different strategies to overcome it. ROS are the unstable and partially reduced forms of atmospheric oxygen (O_2), which show a great capacity to oxidize other cell compounds. These molecules are formed from the transfer of one, two or three electrons to the O_2 molecule, thus forming the superoxide radical ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2) and hydroxyl radical (OH^{\bullet}), respectively. This is particularly prone to happen in electron transfer processes in mitochondria, chloroplasts and peroxisomes (Shieber and Chandel 2014).

Various cellular defense responses are important for maintaining low concentrations of ROS, and involve both enzymatic and non-enzymatic antioxidant mechanisms (Fig. 15.2). Superoxide dismutases (SOD) constitute the first enzymatic barrier against oxidative stress by the dismutation reaction of $O_2^{\bullet-}$ in order to form O_2 and H_2O_2 (Shieber and Chandel 2014). Subsequently, H_2O_2 can be quickly con-

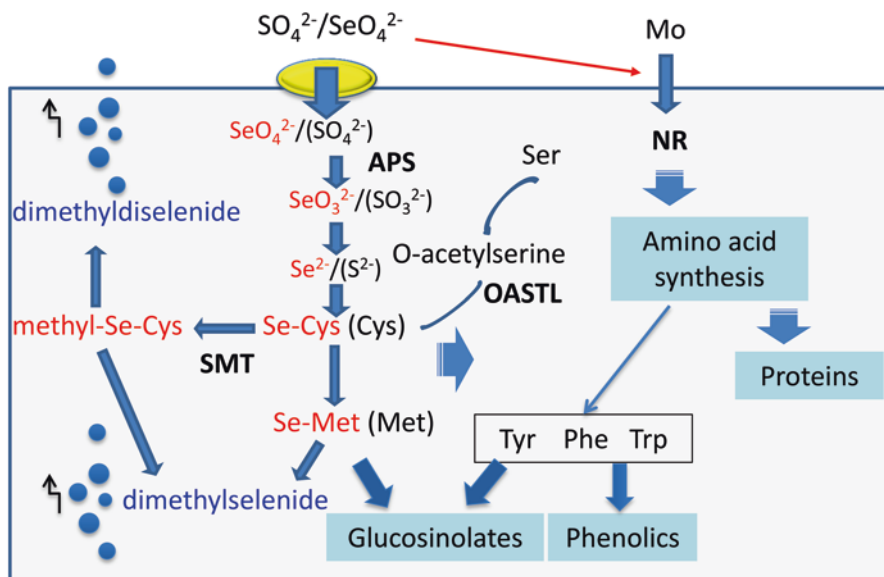


Fig. 15.2 Interaction of Se assimilation with other metabolic pathways. Selenium can influence the synthesis of glucosinolates by altering the content of precursor amino acids. Selenium can also alter the uptake of molybdenum (Mo), which is a cofactor of the enzyme nitrate reductase (NR), thus exerting an effect on nitrogen (N) assimilation into amino acids, proteins and phenolics

verted into H_2O and O_2 by specific peroxidases (POX), enzymes such as catalase (CAT) and glutathione peroxidase (GSH-Px) (Roychoudhury et al. 2012). High concentration of H_2O_2 in the cellular environment as a response to a stressful condition or SOD activity can cause oxidative damage. Non-enzymatic molecules implied in ROS detoxification are also important to preserve the cellular redox state, and mainly include the reduced form of glutathione (GSH), ascorbate, phytochelatins (PCs), proline, flavonoids, alkaloids and carotenoids (Foyer and Noctor 2012).

Selenium has been reported to help plants cope with stress by stimulating the plant cell antioxidant capacity through the enhancement of the activity of antioxidant enzymes (SOD, CAT and GSH-Px) and the synthesis of GSH, PCs, ascorbate, proline, flavonoids, alkaloids and carotenoids. Furthermore, Se may induce the spontaneous dismutation of the superoxide radical ($O_2^{\cdot-}$) into H_2O_2 (Feng et al. 2013). As a result of Se-increased antioxidant defense systems, lower levels of lipid peroxidation were observed under metal-induced oxidative stress conditions, because of reduced ROS accumulation (Feng and Wei 2012) (Fig. 15.2).

In addition to its function in mitigating heavy metal stress in plants, Se at low dosage has been shown to protect plants from a variety of other abiotic stresses including drought, cold, heat, salinity, and UV-B radiation, which also cause oxidative stress (Feng et al. 2013; Kaur et al. 2016).

15.2.1 *Effects of Se on Plant Productivity*

Even when growing under optimal conditions, plant cells accumulate ROS to some extent, particularly in mitochondria and chloroplasts at the sites of electron transport. Therefore, the ROS scavenging machinery described in the previous section is constitutively important (Fig. 15.2). This may explain the reported beneficial effects of Se on plants via promotion of growth, (Terry et al. 2000; Pilon-Smits and LeDuc 2009; White and Broadley 2009) and productivity (Xue et al. 2001; Djanaguiraman et al. 2010; Zhang et al. 2014; Jiang et al. 2015; Kaur and Nayyar 2015) under both stress and no stress environments. There is evidence that Se may improve plant productivity via amelioration of photosynthesis, as this process is stimulated in plants by optimal supplementation with Se during the vegetative period. For instance, the application of Se in rice has been reported to positively influence photosynthesis, which resulted in increased rice grain yield and Se grain concentration (Zhang et al. 2014). Similar results were reported in other plant species treated with Se, like ryegrass (Hartikainen et al. 2000), potato (Turakainen et al. 2004), *B. rapa* (Lyons et al. 2009), and lentil (Ekanayake et al. 2015).

The positive effects of low Se concentrations on the photosynthetic process may be explained via the enhancement of the antioxidant activity in cells at different levels (Fig. 15.2). Selenium can up-regulate the amount and activity of antioxidant enzymes (GSH-Px, GR, SOD, APX and CAT) and metabolites (GSH, ascorbate) resulting in higher ROS scavenging capacity of plants, as well-documented under stress conditions (Germ et al. 2007; Tadina et al. 2007; Djanaguiraman et al. 2010; Feng et al. 2013). In addition to this effect on the antioxidant machinery, appropriate Se concentrations could significantly improve photosynthesis by increasing the production of chlorophyll (Hawrylak-Nowak 2009; Yao et al. 2011; Liu et al. 2011; Zhang et al. 2014), stomatal conductance, intercellular CO₂ concentration, and transpiration efficiency (Germ et al. 2007; Djanaguiraman et al. 2010; Zhang et al. 2014).

In other photosynthetic organisms such as algae, no significant effect of Se on photosynthesis or modification of chloroplast ultrastructure were observed, with the exception of the increase in content of carotenoids, which are known to act as important intracellular antioxidants (Schiavon et al. 2012).

15.2.2 *Heavy Metals*

As mentioned in the previous sections, Se can stimulate the cell antioxidant capacity in plants that grow in the presence of heavy metals through the enhanced activity of antioxidant enzymes and the synthesis of non-enzymatic metabolites such as GSH and PCs, and may induce the spontaneous dismutation of the superoxide radical (O₂⁻) into H₂O₂ (Feng et al. 2013). The lower concentration of ROS would result in reduced lipid peroxidation generally caused by metal-induced oxidative

stress (Feng and Wei 2012). The interactions of Se with a number of toxic elements are highlighted below.

15.2.2.1 Cadmium (Cd)

Cadmium (Cd) is one of the most toxic among heavy metals. This metal can be complexed with the organic fraction of soil, and be released as Cd^{2+} , which is easily assimilated by plants through membrane transporters involved in the uptake of chemically similar nutrients, like Ca^{2+} , Fe^{2+} , Mg^{2+} , Cu^{2+} and Zn^{2+} (Qin et al. 2013). The presence of high concentrations of Cd in soil can cause a decrease of plant capacity to accumulate these and other nutrients and affect the synthesis of molecules such as chlorophylls, carotenoids and a broad spectrum of proteins, including antioxidant enzymes, which contain one or more of these nutrient metals in their active sites to function as catalysts (Cuypers et al. 2010; Hasanuzzaman et al. 2012). For instance, Cd can replace Zn, Cu or Fe in the active sites of antioxidant metalloenzymes, e.g. SOD and CAT, thus causing their inactivation (Cuypers et al. 2010).

Recent studies reported the positive effect of Se on the activity of antioxidant enzymes in response to Cd stress. Lin et al. (2012) showed that the application of 3 μM Se to rice (*Oryza sativa*) plants can increase the activity of SOD, peroxidase or guaiacol peroxidase (POD/GSH-Px) enzymes in roots and leaves. Treatment with 50 μM Se was shown to enhance the activity of CAT, GSH-Px, glutathione reductase (GR), ascorbate peroxidase (APX) and enzymes related to the ascorbate-glutathione cycle, like monodehydroascorbate reductase (MDHAR) and dehydroascorbate reductase (DHAR), as well as non-enzymatic compounds of this cycle like GSH, especially in the oxidized form (GSSG), in oilseed rape (*Brassica napus*) (Hasanuzzaman et al. 2012). Similarly, 5 and 10 μM of Se increased the activity of CAT, APX and GR in leaves of sunflower (*Helianthus annuus*) (Saidi et al. 2014a), and concomitantly decreased ROS production, lipid peroxidation, oxidative stress, and recovered the membrane physicochemical characteristics.

The non-enzymatic mechanism for cellular detoxification against Cd works in parallel to the enzymatic system to maintain proper cellular redox state. Phytochelatin represents one of the most important strategies used by plants to counteract Cd stress by complexing this element and storing it in the vacuole, as is the case for other heavy metals (Foyer and Noctor 2012). In this context, S as a component of the amino acid Cys plays an essential role in GSH and PCs synthesis (Roychoudhury et al. 2012). Plants absorb more S when they grow in the presence of Cd in order to synthesize more GSH and PCs that chelate Cd (Feng et al. 2013).

15.2.2.2 Arsenic (As)

Arsenic (As) is a metalloid that is mainly found in the forms of arsenate (AsO_4^{3-}) or arsenite (AsO_3^{3-}) in soils and waters. Arsenic contamination in soils is mainly due to anthropogenic activities like the application of pesticides and sewage sludge on

crop fields, as well as to other activities not directly related to agriculture, such as mining and metal melting. The detrimental effect triggered by this metal in plants is related to a reduction of growth and development caused by photosynthesis inhibition, inefficient nutrition and oxidative stress (Malik et al. 2012; Han et al. 2015).

Similar to Cd^{2+} , As binds to the S presented in the thiol (SH) group of GSH. When Se is provided to plants, it may compete with As for the binding to thiol groups, thus actively reducing As absorption (Han et al. 2015). Likewise, 5 μM Se was reported to reduce As uptake in mung bean (*Phaseolus aureus* Roxb.), and alleviate oxidative stress by enhancing the activity of SOD, POD, APX enzymes and the synthesis of GSH and ascorbic acid (ASC) (Malik et al. 2012). Similar results were found in tobacco (*Nicotiana tabacum*) plants treated with 0.1 mg/L selenite (Han et al. 2015). Srivastava et al. (2009) found that 5 μM and 10 μM selenate decreased the lipid peroxidation process in *Pteris vittata* L., likely because of higher production of the non-protein thiol GSH.

15.2.2.3 Lead (Pb)

Lead is one of the most dangerous pollutants worldwide, with as main sources fertilizers, pesticides, mining, metal smelting, automobile fumes and industrial waste or discharge. This heavy metal is considered carcinogenic to humans, as it causes DNA damage and inhibition of DNA synthesis. In plants, Pb can disrupt membrane structure and permeability, causing dehydration and decreased electron transport in photosynthesis. Lead also binds to the thiol groups of amino acids, enzymes and proteins and, as a result, induces the overproduction of ROS and oxidative stress (Mroczek-Zdyrska and Wojcik 2012).

The beneficial effects of Se against Pb stress in plants have been described by several authors recently and are directly related to ROS scavenging in cells (Mroczek-Zdyrska and Wojcik 2012; Yuan et al. 2013; Hu et al. 2014). For instance, 1.5 μM selenite supply lowered the superoxide radical ($\text{O}_2^{\cdot-}$) production and concentration in the apical part of the root in *Vicia faba* L. *minor*, and increased the activity of POD/GSH-Px enzymes and non-protein thiol content (Mroczek-Zdyrska and Wojcik 2012). In addition, 1 μM selenite improved the leaf biomass of coleus (*Coleus blumei* Benth.) and decreased the rate of lipid peroxidation, likely because of the higher GSH level in roots (Yuan et al. 2013). Furthermore, Hu et al. (2014) demonstrated that 0.5 mg/kg selenite could reduce Pb accumulation in rice (*Oryza sativa*) shoot and husk tissues.

15.2.2.4 Other Heavy Metals

Excess of some metal micronutrients in plants can increase the production of ROS and cause decreased activities of antioxidant enzymes, via denaturation and inactivation. Manganese (Mn) is an important microelement for plants, but at high concentration it can be toxic. The toxicity is related to photosynthesis suppression,

membrane integrity disruption, lower protein metabolism and oxidative stress. As shown by Saidi et al. (2014b), 5 μM of selenate can effectively counteract the detrimental effects of Mn in sunflower (*Helianthus annuus*) by improving CAT, APX and GSH-Px activities.

Chromium (Cr) has no biological function in plants and can be toxic at any concentration in soil, especially near areas with industrial activities. Selenium supply at 3 μM enhanced SOD activity in rice roots, alleviating the toxic effects of Cr on growth, and increased H^+ ATPase activity, thus protecting the plants from Cr-induced oxidative stress (Cao et al. 2013).

Mercury (Hg) is also a harmful environmental pollutant, and soil contamination by this metal comes from mining, metal smelting, and industrial activities. Its presence in plants causes growth inhibition, oxidative stress, lipid peroxidation, and reduced chlorophyll production and photosynthesis (Zhao et al. 2013). Selenite and selenate treatment improve growth of garlic (*Allium sativum*) under Hg stress and reduced Hg absorption, translocation and accumulation in roots and leaves, when applied at levels higher than 1 mg/L (Zhao et al. 2013).

The maintenance of cellular homeostasis under heavy metal contamination depends on several interlinked and complex mechanisms that together constitute the antioxidant defenses. The contributions of the various components may differ depending on various factors such as plant species, concentration, exposure time, nutrient concentration in soil, plant developmental stage, organs, and tissues analyzed. Thus, plant defense against heavy metals and other abiotic stresses is a dynamic and adaptive system. There is extensive evidence that different forms of Se can improve both enzymatic and non-enzymatic antioxidant responses, and thus counteract heavy metal induced stress.

15.2.3 Drought and Salt Stress

Water stress, particularly drought stress, causes the production of ROS in plants. The protective role of Se against this type of stress has been reported in various plant species and it occurs by quenching the accumulation of ROS via regulation of the level of enzymatic and non-enzymatic antioxidants (Pukacka et al. 2011; Yao et al. 2012; Durán et al. 2015). Yao et al. (2011) showed that optimum Se concentrations could help wheat seedlings maintain high growth performance under drought stress by significantly increasing the peroxidase and CAT activities that lower the level of ROS. In particular, Yao et al. (2012) observed that Se improved the recovery of wheat seedlings from drought stress after re-watering because Se turned the rate of $\text{O}_2^{\cdot-}$ production, MDA content, and CAT activity back to the control values. The reduction of ROS levels by Se in plants subjected to drought stress has also been observed in other plant species like rapeseed seedlings (Hasanuzzaman et al. 2010; Hasanuzzaman and Fujita 2011), *Trifolium repens* L. (Wang 2011) and wheat (Nawaz et al. 2013, 2015).

The effects of drought stress in plants widely overlap with those caused by salt stress, as they are both able to generate osmotic stress. The activity of the enzymes SOD and POD was increased by 10 μM Se in cowpea plants grown in the presence of 50 mM NaCl (Manaf 2016). In tomato (*Solanum lycopersicon*), Se was found to alleviate salt-induced oxidative stress by up-regulation of the antioxidant defense systems (Diao et al. 2014). In a previous study, Hawrylak-Nowak (2009) suggested that Se could enhance salt tolerance in plants by protecting the cell membranes against lipid peroxidation due to the antioxidative activity of Se at low concentration. Furthermore, the growth-promoting effect of Se under salt stress conditions could be due to the increased accumulation of proline accumulation and/or a decrease in the content of chloride ions (reduced salt uptake) in shoot tissues.

15.2.4 *Extreme Temperatures*

Similar to drought stress, high temperature and cold can increase the production of ROS in plants, particularly in species that possess low antioxidant capacity to detoxify ROS (Wang et al. 2009; Djanaguiraman et al. 2010). Also under these types of stress, Se has been observed to protect plants from oxidative damage. In wheat, for instance, Se application was reported to ameliorate the symptoms related to cold stress by reducing MDA content and via enhanced production of antioxidant metabolites, such as anthocyanins, flavonoids, and phenolic compounds (Chu et al. 2010). Similar results were observed in potato (Seppänen et al. 2003), cucumber (Hawrylak-Nowak 2009), and sorghum plants (Abbas 2012, 2013) grown under low temperature and treated with Se.

With respect to heat stress, in a recent study Iqbal et al. (2015) found that exogenous application of Se reduced oxidative stress and induced heat tolerance in spring wheat, thus avoiding loss of grain yield. In these plants, Se-mediated the up-regulation of antioxidative systems, both enzymatic and non-enzymatic.

15.2.5 *UV-B Stress*

Increasing level of ultraviolet-B (UV-B) light because of thinning of the stratospheric ozone layer is one of the abiotic stress factors that can affect almost every aspect of plant productivity (Yao et al. 2013). Selenium can display a protective effect in plants against the harmful effects of UV-B radiation. Yao et al. (2010) showed that adequate Se supplementation (1.0 mg/kg) to wheat had a protective role in plants subjected to UV-B, via the decrease of oxidative stress-related damage to cellular components produced by high level of this type of radiation. Similar findings have been reported for lettuce and ryegrass (Xue and Hartikainen 2000).

In another study on wheat, Yao et al. (2010) reported that Se fertilization induced an evident increase in chlorophyll content, spike length, weight per spike, grain

yield, protein content, N, Fe, Cu, and Se concentration under UV-B stress, leading to improved yield and quality of winter wheat to some extent. Other possible mechanisms by which Se may protect plants against UV-B stress are through increased levels of compounds that either absorb UV light (in the epidermis) or can reflect UV light (Golob et al. 2017).

15.3 Effects of Se on Plant Nutraceuticals

Given the importance of Se in human nutrition and Se deficiency-related issues existing in many areas worldwide, in recent years many efforts have been made to increase the concentration of Se in crops, especially when they are cultivated in soils that are low in this element. To date, the results achieved are promising, as several plant species have been successfully biofortified with organic forms of Se (Thavarajah et al. 2008; Brummell et al. 2011; Schiavon et al. 2013; Avila et al. 2014; Poblaciones et al. 2014; Rodrigo et al. 2014; Bañuelos et al. 2015; Bachiega et al. 2016). These plants represent high-nutrition value food that can be used to counteract the problem of Se deficiency where it occurs.

Biofortification is generally defined as the agricultural process aimed to improve the uptake and accumulation of specific phytochemicals in food derived-products by plant breeding, genetic engineering, and manipulation of agronomic practices (Rouached 2013; Wu et al. 2015). Despite the advantage they offer, biofortification technologies must be carefully performed in the case of Se because the concentration of this element in plant tissues should not exceed the threshold that is toxic for the plant and for the organisms that feed on it (Finley 2006). Selenium at high dosage may exert detrimental effects on human and animal metabolism due to Se replacement of S in proteins (Wilber 1980; Vinceti et al. 2001; Misra et al. 2015). Furthermore, Se biofortification may positively or negatively influence the synthesis of other health promoting compounds in plants (Robbins et al. 2005; Schiavon et al. 2013; Bachiega et al. 2016).

On this account, the challenge of Se biofortification is to produce plants enriched in organic Se forms without adversely impacting the synthesis of other nutraceuticals. Encouragingly, Se at low doses has been reported to enhance the levels of other beneficial health compounds in some studies (Schiavon et al. 2013, 2016; Avila et al. 2014; Tian et al. 2016). It is clear that Se biofortification programs, to be successful, should take into account the interactions of Se with the plant pathways that produce nutraceuticals, in addition to the concentration and the form of Se used to enrich plants in this element and/or the method employed for achieving Se enrichment. In the next section, the interactions of Se with plant metabolic processes involved in the synthesis of a number of (other) nutraceutical compounds are highlighted.

15.3.1 *Glucosinolates*

As already mentioned, Se can replace S in many S-containing compounds, including the Se-amino acids SeCys and SeMet. Selenomethionine and the methylated form of SeCys (SeMetCys) provide important beneficial properties to humans as their supplementation can alleviate thyroid disorders, prevent different types of cancer, treat male infertility, and enhance the immune system (Rayman 2012; Roman et al. 2014). These organic forms of Se can be produced by different plant species, either growing on Se-containing soil, or after Se fertilization (Sepúlveda et al. 2013).

In *Brassicaceae* spp. the S-amino acid methionine (Met), in addition to being an essential constituent of proteins, is a precursor of the anticarcinogenic aliphatic glucosinolates (GLSs). Therefore, as a consequence of Se interference with S assimilation in plants, Se fertilization may affect the levels of Met-derived GLSs in these plants. Contrasting results are reported in this respect. A weak decrease in aliphatic GLSs, especially glucoraphanin, was observed by Robbins et al. (2005) and Barickman et al. (2013) after supply of broccoli (*Brassica oleracea*) plants with high Se concentrations. The level of sulforaphane, a sulfur-containing aglycon produced during the GLS hydrolysis mediated by myrosinase, significantly decreased in response to Se application. In contrast, Sepúlveda et al. (2013) did not measure any variation in the content of GLSs and sulforaphane, nor in myrosinase activity in the same plant species treated with 100 μM selenate. However, when Se dosage applied to plants was lower than 0.8 mg/L (10 μM) or S concentration in the medium was increased, plants could maintain high levels of GLSs in their tissues (Barickman et al. 2013). This was likely because low Se concentration can stimulate S uptake in plants (Harris et al. 2014), thus promoting the synthesis of S-organic compounds.

In addition to this Se concentration-related effect on S assimilation, the chemical form of Se used in biofortification approaches and the method of supplementation must be considered. For instance, when Se in the form of selenium dioxide (SeO_2) was supplemented via root irrigation to *Brassica rapa* plants, an increase of several GLSs was observed, including the aliphatic GLSs glucobrassicinapin and glucoalylsin (Thiruvengadam and Chung 2015).

A differential effect of Se on the levels of GLSs in broccoli plants was observed between plant organs (Avila et al. 2014). GLSs in the florets of broccoli treated with selenate were reduced, while GLS levels in the sprouts were not affected. Rather, sprouts were enhanced in the content of the potent anticarcinogenics glucoraphanin and SeMetCys, and therefore exhibited improved potential anticancer activity. Tian et al. (2016) also observed an increase of myrosinase activity and sulforaphane in broccoli sprouts treated with 100 μM selenite or selenate; meanwhile the amount of GLSs was unchanged. The same authors reported up-regulation of genes related to GLSs biosynthesis.

In recent years, Se-glucosinolates have also been identified in plants. Matich et al. (2012, 2015) in particular, showed that *Brassicaceae* spp. fertilized with Se contained (methylseleno) glucosinolates and their Se-containing aglycons. The

major aliphatic Se-GLSs identified were glucoselenoraphanin and glucoselenoerucin in broccoli. In these species, Se-GLSs concentrations exceeded that reported for their S analogs. Results obtained in these studies have important implications for human health, because it seems the Se-containing isothiocyanates derived from Se-GLSs are more potent anticarcinogenic compounds than their S counterparts (Emmert et al. 2010).

15.3.2 Health Beneficial Nitrogen Containing-Compounds

The S and N metabolic pathways are strictly associated (Bielecka et al. 2015; Zhang et al. 2015) and a number of metabolites in plants contain both of these elements in their structure (e.g. cysteine, methionine, GSH, coenzyme A, GLSs). As a result of Se interaction with S assimilation, the N metabolic pathway may undergo changes in the synthesis of N compounds. Selenium can influence N metabolism also by interfering with the uptake of molybdenum (Mo) (Harris et al. 2014), which is a cofactor of nitrate reductase (NR), the enzyme that mediates the conversion of nitrate to nitrite in N assimilation. As a result of decreased nitrate reduction, the synthesis of all amino acids could be affected.

Some amino acids like methionine, tryptophan, phenylalanine and tyrosine, function as precursors for the synthesis of glucosinolates (Agerbirk and Olsen 2012). The same amino acids, with the exception of methionine, also function as precursors of other important metabolic compounds, including auxins, phenylpropanoids, tannins and alkaloids, synthesized through the shikimate pathway. Phenylpropanoids in particular, are reactive metabolites present in a wide range of plant-derived foods and display an important role in welfare and human health due to their antioxidant and antimicrobial properties (Ozcan et al. 2014). Among phenylpropanoids, phenolic acids and flavonoids have additional anti-carcinogenic and anti-mutagenic effects since they act as protective agents of DNA against free radicals, by inactivating carcinogens, inhibiting enzymes involved in pro-carcinogen activation and by activating xenobiotics detoxification enzymes (Ramos 2008).

In *Brassica rapa*, the application of SeO₂ caused the enhancement of phenolics and flavonoid accumulation, as well as the up-regulation of genes related to their biosynthesis (Thiruvengadam and Chung 2015). Similar results were obtained by Bachiega et al. (2016) in broccoli, especially at the stage of seedlings, as application of selenate increased their phenolic compounds content and antioxidant activity, and in tomato (*Solanum lycopersicum*), where the stimulation of flavonoids and phenolic acids was also observed after selenate supplementation, and fruits enriched in naringenin, chalcone and kaempferol were generated (Schiavon et al. 2013). However, Robbins et al. (2005) reported contrasting findings in broccoli, as Se fertilization in this case decreased the level of phenolics, without altering the profile distribution of specific compounds.

Given the role of phenolics as antioxidants in plants, it cannot be excluded that the capacity of Se to alleviate some types of stress in plants may be in part related

to the stimulation of the shikimate pathway, in addition to its potential to elicit other antioxidant enzymatic and non-enzymatic systems.

15.4 General Conclusions and Further Prospects

Despite not being essential for plants, Se has been shown to exert beneficial effects on them depending on the chemical form supplied and the plant species. For instance, Se can improve plant defense systems by detoxifying intracellular free radicals directly, acting as antioxidant, and/or indirectly by increasing the activity of enzymatic (SOD, CAT, POX, GR) and non-enzymatic (GSH, proline, flavonoids, alkaloids carotenoids and PCs) antioxidants, which may help plants scavenge ROS and prevent oxidative stress. ROS may be produced by plant electron transport processes, even under optimal conditions, explaining the beneficial effect of Se on photosynthetic performance. ROS accumulation is particularly high during biotic and abiotic stress, which is when Se supplementation can be particularly beneficial for plants. In the case of heavy metals, Se may also reduce metal translocation from the root to the shoot by stimulating sulfate uptake and assimilation and the associated production of metal chelators GSH and PCs. All these processes result in better management of ROS production and concentrations in cells and, as a result, reduced oxidative stress-induced damage to cell membranes, proteins, DNA and other structures.

Low Se concentrations also have a beneficial effect on plants in terms of productivity and nutritional value. The enrichment of plants in organic forms of Se with recognized health properties, as well as in other precious nutraceuticals, through Se biofortification practices has significant implications in human and animal nutrition, especially in areas poor in Se where the local populations suffer of Se deficiency related-health issues.

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