Chapter 8

The Use of Iodine, Selenium, and Silicon in Plant Nutrition for the Increase of Antioxidants in Fruits and Vegetables

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Additional information is available at the end of the chapter

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Abstract

Iodine, silicon, and selenium are considered elements not essential for the metabolism of plants. However, these elements are vital for humans, and their presence as traces in food is beneficial. The use of I, Si, and Se in the fertilization programs of the plants allows, on the one hand, the mineral biofortification of the crops and, on the other hand, through mechanisms not yet fully understood, the production and accumulation of more antioxidants in the edible organs. This chapter provides an overview about the use of I, Si, and Se both for mineral biofortification and for the increase in the concentration of antioxidants in plants, with an emphasis on redox metabolism adjustments and antioxidant chemical species studied. The scope of the chapter is on horticultural species in the open field and under greenhouse or tunnels.

Keywords: food and human health, functional foods, nutraceuticals, plant stress, trace elements

1. Introduction

Elements I, Se, and Si are not considered essential for plants but are essential elements for humans and domestic animals. These three elements have been the objective of biofortification programs and projects, to increase their intake by improving their concentration and bioavailability in food. On the other hand, it has been found that by using I, Se, and Si in crop plants, applied in seeds, plants, or fruits, favorable responses are obtained such as increased growth and tolerance to stress. Tolerance to stress is associated with a higher concentration of antioxidants. Thus the use of these elements is a useful technique for the nutritional improvement of crop plants, both in antioxidant level and biofortification. This chapter presents the advances in the last 10 years about the use of I, Si, and Se both for mineral biofortification and for the increase in the concentration of antioxidants in plants, with an emphasis on redox metabolism adjustments and antioxidant chemical species studied. The scope of the chapter is on horticultural species in the open field and under greenhouse or tunnels.

2. Iodine, selenium, and silicon in agricultural systems

The contents of iodine, selenium, and silicon in the Earth's crust range from <0.1 to 150 mg kg^{-1} and 0.05 to 1.5 mg kg^{-1} and 540,000 mg kg^{-1} (54%) [1, 2]. This data establishes iodine and selenium as trace elements and silicon as the second most abundant element. Although silicon reaches 23–46.5% of the mass of the parent rocks in the soil, most of this element is present in mineralized form as crystalline or amorphous SiO_2 [3]. It has been found that the concentration of Si in the soil solution can be as low as 0.09 mg L^{-1}, reaching a maximum of 23.4 mg L^{-1}. The amount of bioavailable silicon depends mainly on the composition of the parent rock of the soil, as well as on factors such as the content of organic matter, the pH, and the oxidation-reduction potential (Eh) [4].

Regarding iodine and selenium, uniformly low concentrations have been found in most of the minerals in the parental rocks. However, there is a positive correlation between the amount of organic matter and the availability of I and Se in soils derived from sedimentary rocks [5].

The availability of iodine and selenium in the soil seems to be based on factors other than the geology itself. In iodine, the most significant influence is exerted by the distance to the ocean, because the ocean is the primary reservoir of iodine on the planet [6]. However, in the soil, the amount of organic matter is the most studied factor regarding the dynamics of the I and Se. In general, it has been established that in the presence of a high content of organic matter, low volatility of I and Se is found, and that the presence of metal oxides and hydroxides such as aluminum, iron, and manganese plays an essential role in retention, and this process is directly related to pH and Eh [7].

In the soil, the predominant chemical species with reducing conditions and low pH (<7) are the iodides (I^-) and selenite (Se^4), species with a great affinity for organic matter; additionally under these conditions, the Se^4 can be reduced to Se^0 by precipitating and thus becoming less available [8, 9]. On the contrary, under basicity conditions (pH > 7) and soils with oxidizing conditions, the predominant forms will be IO_3^- and Se^6, which have been shown to have binding affinity with the metal oxides and hydroxides present in the organic matter, through weak electrostatic attractions, thus allowing availability for mobilization and absorption by plants [10]. On the other hand, the Si available in the soil depends on the type of parent rock,

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since this comes from the weathering of the original material. Greater solubilization has been found from granite rocks than from basalt rocks [11]. The bioavailable form of Si is monosilicylic acid (H_4SiO_4) which is found in the liquid phase of the soil [12]; it has been established that it remains in a non-charged and bioavailable form in a pH range of 4.5 to <8, and it is de-protonated to $H^+ + H_3SiO_4$ at pH > 9, forming polymers of different molecular weights [13, 14]. A high degree of polymerization of H_4SiO_4 has been found under conditions of high concentration of aluminum in the mineral fraction of the soil, as well as during the processes of evaporation of soil water and freezing [15]. The application of acidic solutions in the soil favors solubilization, whereas liming reduces it [16].

There are differences with respect to the hydrological mobilization of these elements. For the Se and Si occur by the dragging of sediments or dissolved chemical species through continental aquatic flows, with an estimated 14,000 t per year toward the ocean in the case of Se [17]. Iodine mobilization presumably occurs in reverse to that of Se and Si, that is, from the ocean to continental waters, mainly through rainfall. The rainfall has an iodine concentration of 0.5–5 μg L^{-1}, and probably such concentration is a reflection of the gaseous dynamics of iodine in the atmosphere [18]. In surface water, iodine has been reported in ranges of <20 μg L^{-1}, while in groundwater the reported concentrations have been higher (from 430 to 4100 μg L^{-1}), probably due to the desorption of organic matter rich in iodine, sediment leaching, or concentration by evaporation in arid zones [19]. Silicon solubilized from the parent rock and converted to its bioavailable forms, both by the physicochemical processes and by the metabolism of different organisms such as plants, has been estimated to be 240 ± 40 μg L^{-1} [20].

The natural uptake of these elements by the plants will be conditioned to the different growth conditions. The low biodisponibility is the typical situation; thus, the resulting level of I, Se, and Si in the plants will be similarly low (**Table 1**). In the case of soilless crops grown under protected conditions, both the availability of these elements and the resulting concentration in the plants will be very low, since in this case, the primary source would be irrigation water, which contains a small amount of I, Se, and Si.

Concentration in soils (mg kg^{-1})	Concentration in plants (mg kg^{-1})	Reference
Iodine concentration in soils and agricultural plants		
3.35 (Forest zone in Russian plane)	0.128 Gramineae, 0.121 leguminoseae	[21]
11.8 (Andosol upland in Japan)	20 in wheat and 7.7 in barley	[22]
0.66 (Agricultural soils in Pakistan)	0.01 in wheat grain	[23]
0.92 (Samples from the last 105 years in an experimental field in Rothamsted, UK)	4.8×10^{-5} in weeds	[24]
Selenium concentration in soils and agricultural plants		
0.06 (Se plant available in South Dakota)	0.63 in wheat grain	[25]
1.6 (samples from the last 105 years in an experimental field in Rothamsted, UK)	5.5×10^{-6} in weeds	[24]
58.7–304 (agricultural soil in Songpan, Tibetan Plateau)	0.009 in barley grains	[26]

Concentration in soils (mg kg^{-1})	Concentration in plants (mg kg^{-1})	Reference
Silicon concentration in soils and agricultural plants		
500 (rice fields in Chiba, Japan)	15.6 mg g^{-1} leaves of rice plants	[27]
7.3 mg kg^{-1} amorphous Si, 0.092 mg kg^{-1} dissolved Si (Serengeti, North of Tanzania, and South of Kenia)	*Themeda triandra* 36.9 mg g^{-1}	[28]

Table 1. Concentration of I, Se, and Si in soils, irrigation waters, and crop plants.

In regard to the concentration of I, Se, and Si, the use of soilless crops results in plants with a lower level of these elements than in soil crops. Hydroponic production of crops for human consumption has increased substantially in recent years, mainly due to the efficient use of water and nutrients from the crop. However, as far as commercial production is concerned, nutrition only considers the application of the elements deemed essential for plants [29], leaving aside those that are beneficial as I, Se and Si. These beneficial elements raise the antioxidant content in plants, giving an advantage against oxidative stress, in addition to its use allows obtaining biofortified crops with high nutritional value for human consumption.

3. The impact of iodine, selenium, and silicon on the antioxidant system of plants

The energy metabolism of aerobic organisms inevitably produces reactive oxygen species (ROS), which are free radicals that react with the different biomolecules in the cell causing damage. Additionally, when there is some stress, both biotic and abiotic, a substantial increase in ROS content is induced. As an adaptive response to neutralize these species, the synthesis of enzymatic and nonenzymatic antioxidants is used, granting tolerance to stress [30]. A partial explanation of the beneficial effect provided by I, Se, and Si is the stimulation of the increase in antioxidants. **Table 2** shows results obtained with the application of different chemical species and concentrations of I, Se, and Si on the antioxidant content in soilless crops.

Plant species	Chemical species and concentration	Effect	Reference
Iodine application in soilless crops			
Lettuce	KI ≤40 μM	Increase of 6, 2, 1.5, 1.2, and 1.2 times, respectively, in the total phenols, flavonoids, anthocyanins, ascorbate, and antioxidant potential	[31]
Lettuce	IO_3 80 μM	Increase of ascorbic acid by 1.2 times in the leaves of plants	[32]
Lettuce	IO_3 < 40 μM	Increases the antioxidant potential by double in the leaves of plants	[33]
Tomato	KI 1 μM daily foliar application	Increase of ascorbic acid by 22% and glutathione by 85% in the leaves of seedlings	[34]
Tomato	KIO_3 7.88 μM	Increase of 8% in the concentration of ascorbic acid and 6% in total phenols in tomato fruits	[35]

Plant species	Chemical species and concentration	Effect	Reference
Strawberry	I– ≤0.25 mgL^{-1} or IO_3– ≤0.50 mg L^{-1}	Increase in vitamin C content of 80 and 30%, respectively, in fruits	[36]
Pepper	KI 1 mg L^{-1}	Increase in ascorbic acid by 35% in fruits and 50% reduction in total acidity	[37]
Lettuce	KIO_3 40 μM and salicylic acid 40 μM	Increase in vitamin C and phenylpropanoids by 50 and 14%, respectively, in the leaves	[38]
Selenium application in soilless crops			
Plant species	**Chemical species and concentration**	**Effect**	**Reference**
Lettuce	Na_2SeO_4 40 μM	Increase in glutathione and ascorbic acid by 38% and three times, respectively, in the leaves of the plants	[39]
Tomato	Na_2SeO_3 5 mg L^{-1}	Increase in total antioxidant capacity by 38% in fruits	[40]
Tomato	Na_2SeO_4 1 mg L^{-1}	Increase of seven times the quercetin content in fruits	[41]
Tomato	Na_2SeO_4 25 μM	Increase of three times the glutathione in leaves during 5 days of exposure to the treatment	[42]
Silicon application in soilless crops			
Plant species	**Chemical species and concentration**	**Effect**	**Reference**
Wheat	Na_2SiO_3 1 mM	Increase of 28% in the concentration of glutathione in leaves sensitive and resistant to salinity	[43]
Rice	H_4SiO_4 1 mM	Increase cysteine content by 78% in plants subjected to arsenic stress	[44]
Cucumber	Na_2SiO_3 1 μM	Increase in the activity of APX and GPX of four and two times in leaves relieving the stress by salinity in *super dominus* cultivar	[45]
Tomato	K_2SiO_3 2.5 mM	Increase in the concentration of ascorbate and glutathione to double, at 7 and 3 days of treatment, respectively, in the roots of tomato plants subjected to water stress	[46]

Table 2. Impact of I, Si, and Se on the antioxidants of various crop species grown in soilless cultivation systems.

4. Proposed mechanisms of action of iodine, selenium, and silicon as inducers of the accumulation of antioxidants

Iodine is considered the first inorganic antioxidant used by ancestral organisms when the concentration of atmospheric O_2 increased as a result of oxygenic photosynthesis [6]. This mechanism is widely elucidated in algae, where the direct neutralization of species such as superoxide (O_2^-), hydroxyl (OH^-), singlet oxygen ($^1O_2$), and hydrogen peroxide (H_2O_2) [47] has been proven, mainly due to iodine oxidation–reduction power. **Figure 1** illustrates the possible mechanisms of reaction proposed by Luther et al. [48].

Subsequently, these organisms incorporated iodine as a cofactor in the reaction between the vanadium-dependent iodoperoxidase enzyme (IPO-V) and H_2O_2, thus becoming an essential element against oxidative stress, but not only directly but through a specialized enzymatic mechanism. In terrestrial plants neither of these two processes is fully established, but it has been shown that it exerts a direct function as an electron donor (inorganic antioxidant) at least on the superoxide radical [34], and it has been further verified that iodine can act as a moderate prooxidant, promoting the synthesis of nonenzymatic and enzymatic antioxidants, potentiating tolerance to stress [33, 49].

Selenium participates in antioxidant metabolism with different mechanisms, both directly and indirectly. An example of the direct effect is observed with the application of Se at low concentrations (≤ 2 μM) in plants subjected to different stresses such as heavy metal toxicity [50, 51], low temperature [52], high temperature [53], or UV radiation [54], where a direct neutralization of the radicals $O_2^{\cdot -}$ and H_2O_2 occurs. Also among the direct mechanisms is the function of Se as a cofactor in the activity of the enzyme glutathione peroxidase [55]. The indirect relationship occurs with the overproduction of reactive oxygen species due to an excess of selenium (≥ 6 μM). This process is attributed to the assimilation of Se and is dependent on the chemical species. An example of this was demonstrated by Paciolla et al. [56], in cinerary leaves, where the application of Na_2SeO_3 showed an increase in the concentration of H_2O_2, while Na_2SeO_4 did not show the same effect. The difference was probably due to the reduction to which Se^4 must to be subjected to L-selenomethionine for its subsequent transport through the plant; instead, Se^6 is transported directly to the shoot of the plants, as has been shown in rice and broccoli [57]. The use of the reducing potential to assimilate Se^4 causes an increase in the formation of ROS, which triggers a higher synthesis of antioxidants such as ascorbate, tocopherol, and glutathione as well as enzymatic antioxidants such as superoxide dismutase (SOD), catalase (CAT), and ascorbate peroxidase (APX) [58].

The mechanisms through which Si reduces oxidative stress can be divided into three modalities: structural, reducing the absorption of heavy metals, and physiological mechanisms.

The structural mechanism is of a mechanical nature, attributed to deposition of stable Si in the form of biosilica (SiO_2) in the cell walls, giving it rigidity and resistance [59].

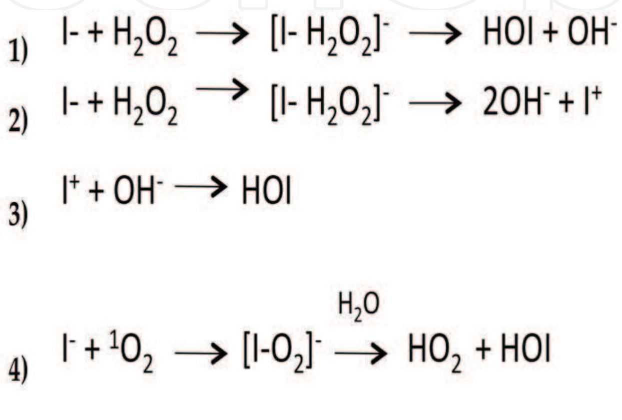

Figure 1. Mechanism of reaction between iodide (I^-) and reactive oxygen species such as hydrogen peroxide (1 and 2), hydroxyl (3), and singlet oxygen (4). Figure designed from data obtained from Medrano-Macías et al. [34].

The ability of silicon to reduce the uptake of elements that cause toxicity in plants is well studied in the case of salinity stress, where there is a reduction in uptake and transportation from the root to shoot of Na^+ and Cl^- [60]. A reduction in the absorption of heavy metals such as aluminum [61], cadmium [62], and chromium [63] has also been found. This beneficial effect has been attributed mainly to the reduction, by Si, of the impact that different stress factors have on the permeability of the plasma membrane, allowing it to retain selectivity in the ion flow [59].

The physiological mechanism is related to the induction of antioxidant metabolism. It has been proposed that this occurs due to a possible dual effect: decrease in ROS synthesis and increase in the activity of antioxidant enzymes [64]. Debona et al. [65], showed in wheat plants subjected to biotic stress (*Pyricularia oryzae*) a reduction in the activity of SOD, CAT, peroxidase (POD), APX, and glutathione-S transferase, explaining this phenomenon through a possible inhibition of Si on the fungus ability to colonize plant tissues.

Regarding the synthesis of antioxidants, Kim and collaborators in 2017 [66] made an extensive compendium of the effects of Si on antioxidant metabolism, evidencing that there is more information related to the increase of enzymatic antioxidants such as SOD, CAT, and APX in plants subjected to a variety of abiotic stresses such as heavy metal toxicity [44, 67], salinity [68, 69], and UV radiation [70], among others.

On the contrary, Ma et al. [71] conducted an experiment on soil with stressed wheat plants with water deficit, finding an increase in the concentration of nonenzymatic antioxidants (ascorbate, glutathione, total phenolic compounds, and total flavonoid content) as well as a decrease in the lipid peroxidation. Gong et al. [72] in a similar experiment found an increase in SOD activity, but not CAT or POD.

Figure 2 shows the proposed mechanisms in which I, Se, and Si intervene in the antioxidant metabolism.

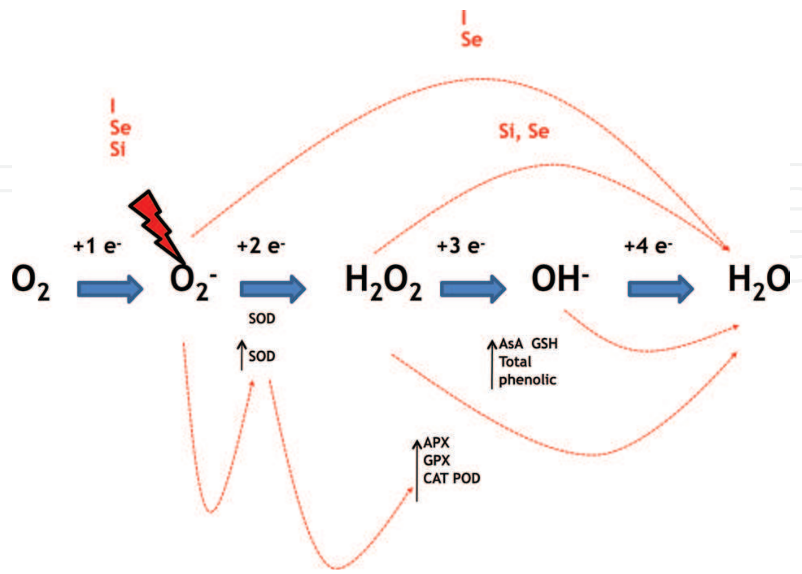

Figure 2. Mechanisms of action proposed for I, Se, and Si in the antioxidant metabolism of plants. In the three elements, there are two forms of action: (1) the direct form which is exemplified by the upper red arrows, where the I and Se can reduce the superoxide radical directly to water and Se and Si directly reduce the peroxide (H_2O_2) to water. (2) The indirect form, which occurs by the influence of Se, I, and Si on ROS overproduction (big red ray) and consequently an increase in enzymatic and nonenzymatic antioxidants, represented by lower red arrows [34, 39, 43, 45, 47, 48, 53, 66, 71].

5. Perspectives and recommendations

Expanding the list of elements used in the fertilization of plants cultivated in soil and in soilless systems will allow obtaining advantages for both agricultural producers and consumers. In particular, the use of the beneficial elements I, Se, and Si in crops for human consumption is expected to increase the functional quality of food, due to the increase in antioxidants that occur in response to the presence of these elements. On the other hand, the exogenous application of quantities as low as 50 μM of KIO_3, 5 μM of Na_2SeO_4, and 2 mM Na_2SiO_3 in soilless crops provides enough to trigger an increase in antioxidants such as ascorbate, glutathione, and phenolic compounds, which give more reducing power useful to deal with various types of stress.

6. Conclusion

In the present chapter, the use of I, Si, and Se, as alternatives in plant nutrition, was described to increase the content of antioxidants, the tolerance to stress, as well as a mechanism of biofortification of crops. However, the information so far published presents the impact on the crop plants of only one element at a time, lacking information that describes the results of the use of two or the three elements simultaneously.

Conflict of interest

The authors have no conflict of interest to declare.

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