Chapter

Uptake, Metabolism and Toxicity of Selenium in Tropical Plants

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Abstract

Selenium is a mineral element that is essential for both animal and humans and can also serve as an environmental toxicant. A narrow margin exists between an ideal and toxic intake of selenium. It is a useful microelement existing in minute amounts in animals, plants, microorganisms and humans. Although it is beneficial to both animals and humans as an antioxidant, it can be toxic at high concentrations as a result of it competing and replacing sulfur in amino acids leading to inappropriate folding of protein and eventually creating a nonfunctional protein and enzymes. Selenium exists in organic forms as SeMet and SeCys and inorganic forms as selenide, selenite and selenite in the environment. It is translocated in plants via the sulfate transporters in the plasma membrane of the plant root. Its translocation and distribution however depends on the plant species, their different developmental phases, forms, concentration and other physiological conditions like pH. Inorganic selenium is first converted to selenite via the action of two different enzymes (ATP sulfurylase and APS reductase), selenite is further converted to selenide by sulfite reductase. Selenide eventually couples with O-acetyl serine via the action of cysteine synthase to form SeCys. SeCys can either be methylated to methyl-SeCys through the action of selenocysteine methyltransferase or to elemental selenium via SeCys lyase or converted by a series of enzymes to selenomethionine. Selenium toxicity or Selenosis can occur when the optimal concentration of selenium is exceeded. Two major mechanism of selenium toxicity exists; either by induction of oxidative stress or malformation of selenoproteins. Selenium uptake, metabolism and toxicity in tropical plants are hereby discussed in this chapter.

Keywords: selenium, distribution, toxicity, tropical plants

1. Introduction

Selenium (Se) is a widely distributed trace metalloid found in the crust of the Earth. Jacob Berzelius, Chemist first isolated selenium in 1817 and it has been known for its toxic effect. However, in 1957, some importance of selenium was discovered. It is mostly linked to sulfur and an essential nutrient for human, animals and microorganisms. Many enzymes such as thioredoxin reductase and glutathione peroxidase are mostly composed of selenium which helps the enzymes to perform roles like reproduction, tumor prevention and antioxidation [1]. Selenium can also promote growth of lettuce seedlings by delaying senescence [2]. It can be toxic at large concentrations and can lead to pro-oxidative reactions. Also deficiency of selenium can occur in soils where selenium bioavailability is low leading to health risks for animals and humans. Supplementing fertilizers with sodium selenate has been shown to improve the food chain from soil to animals and then to humans [3]. The recommended daily intake of selenium should be adhered to for maximum utilization of its benefits. Within the plant and soil environment, selenium is converted to another chemical form [4]. The metabolism and mechanisms through which plants cope with high selenium concentrations are explained by the transformations of selenium form one form to another. The bioavailability, biotransformation, speciation, metabolism and functions all have great implications for both human and animal health. This chapter presents the physicochemical properties of selenium, its sources in the environment and locations, role of selenium in the body, metabolism, uptake and accumulation in plants.

2. Physicochemical properties of selenium

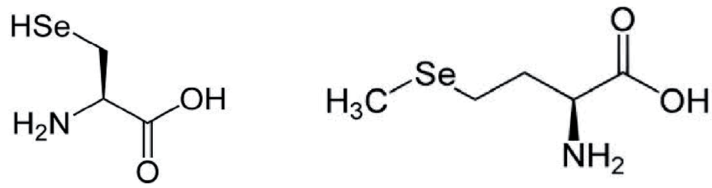
Selenium being a metalloid from the same family of sulfur and oxygen, has it name derived from the word "Selene" that is, moon goddess since it is mostly linked to tellurium [5]. It has six isotope coexisting in nature with mass numbers 74, 76, 77, 78, 80 and 82 [6]. It is similar to sulfur in terms of bond energies, oxidation state, atomic size and ionization potentials [7]. Selenium possesses properties of both non-metal and metal hence it is referred to as a semi metal. It is considered stable as it does not oxidize at room temperature. It produces selenium dioxide and blue flame when it burns which is followed by an unpleasant smell. Selenium can form compounds with elements (fluorine, bromine, hydrogen and phosphorus) having a close analogy to those of sulfur [8, 9]. It has a lower affinity for oxygen than sulfur with only two oxides known; SeO_3 and SeO_2. Combustion of selenium in air produces dioxide which dissolves in water to give selenious acid (H_2SeO_3); a solution that can oxidize most metals except platinum, palladium and gold [10–20].

Selenic acid (H_2SeO_4) is a hygroscopic diacid with a higher oxidizing potential than H_2SO_4. It is produced by the reaction of oxidizing agents such as chlorine, fluorine, bromine with Se, SeO_2, H_2SeO_3 in the presence of H_2O. Reaction of selenium with hydrogen and reaction of metal selenides with acids (or water) releases hydrogen selenide (H_2Se), a highly reactive compound. At about 160°C, it starts to decompose to Se and H_2, it also forms a deposit of red selenium in moist air [21].

3. The physical and chemical forms of selenium

Selenium exists in nature and in organisms in organic and/or inorganic forms. The organic form includes selenocysteine (Secys) and selenomethionine (Semet), while the inorganic forms includes selenate (SeO_4^{-2}), selenide (Se^{-2}), selenite (SeO_3^{-2}) and selenium (Se) (**Figure 1**) [22].

Selenium exists in a solid state at room temperature and can take up various physical forms [8, 23]. Precipitation from aqueous solution produces amorphous selenium (red brick powder) with a density of 4.26 with photoconductive properties. At very high temperature between 110 and 180°C, the color turns gray, this is a variety of selenium that is thermodynamically stable and it is obtained by cooling liquid selenium hence it is used for its semiconducting properties.



Selenocysteine Selenomethionine

Figure 1.
Selenocysteine and selenomethionine.

4. Sources of selenium in the environment and its location

4.1 In soils

Selenium occurs in soils via the erosion of rocks that contains selenides and selenites associated with sulfide minerals with mass fractions less than 1 mg/kg. Selenium is mostly found in soils either in its organic form or elemental selenium like selenite salts and ferric selenite. The common forms of selenium in soils are the anionic forms like Selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) and they are soluble and potentially toxic. Organic forms of selenium in soils are mostly from plants decomposition [24, 25].

The selenium content in soil varies depending on the organic matter, soil texture along with the level of rainfall. The rate of assimilation of selenium by plant is further influenced by the physicochemical factors of the soil, such as microbial activity, pH and redox status. The concentration of selenium in the soil varies from 0.1 to 0.7 mg kg^{-1}. Tropical soils have a concentration between 2 and 4.5 mg kg^{-1}, while clay soils are between 0.8 and 2 mg kg^{-1}. Granites and volcanic soils are usually low in selenium while the soils around mountains are rich in selenium. Normally, selenium is more concentrated in soils of the driest regions of the world. The toxic effect of selenium on animals occurs on these soils [26, 27]. The rate of soil acidity determines the amount of selenium in crops and plants; more selenium is released in alkaline soil than in acidic ones. In alkaline soils, selenite undergoes oxidation into a more soluble form that is easily assimilated by plants (selenite). However, in acidic soils, selenite combines with iron hydroxide making it to be permanently fixed by the soil [28].

4.2 Plant sources

The concentration of selenium in plants is dependent on the level of selenium levels in the soils. The physiological conditions and species of the plant also determine how the selenium are taken in and distributed by the plant root. The aerial silks normally contain about 80% selenite and 65% selenate [29]. Forages contain selenium from about 0.2 to 0.6 ppm and livestock are at risk of selenium poisoning [30]. In arid regions of the United States and China, some plants contain very high selenium content, as high as 10,000 ppm [4]. Some species of *Astragalus* usually accumulates very high level of selenium making them toxic to animals [31]. Wheat plants normally store selenium in their seeds in form of selenomethionine with varying levels depending on the environment [27, 32]. Plants assimilate selenite more than selenite. Selenate and selenite share similar chemical features with sulfur hence they both undergo metabolism via the same route (in the choloroplast). The first reaction is when selenite is activated by ATP sulfurylase-adenosine 5′-phosphoselenate which is followed by its reduction to selenite by adenosine

5′-phosphosulfate reductase and finally the selenite is further reduced by the action of glutathione into selenide. Depending on the rate of selenium accumulation by plants, two mechanism of metabolism exist.

4.3 Selenium in water

Selenium in water is initiated from ambience deposits or drainage in the soil, its concentration varies but does not exceed 9 mg L^{-1}. The World Health Organization recommends that the content of selenium in water for consumption should not exceed 10 μg L^{-1} [24]. When farm lands are supplemented with fertilizers, selenium content increases. Selenate sodium and selenide are mostly found in surface waters, while freshwater contains majorly selenite.

4.4 Food and feed sources of selenium

The content of selenium in vegetables and grains is largely dependent on selenium found in the soil. Vegetables like beans, peas and carrots can contain up to 6 mg g^{-1} of selenium, while onions contain more. However fruits generally contain a very low level of selenium, but nuts with high protein levels are also known for their high selenium concentration [33–35].

5. Role of selenium in the body

Selenium, an important component of selenoprotein, plays diverse biological roles ranging from antioxidant defense to synthesis of DNA to reproduction. Various metabolites formed from selenium could also play a role in the prevention of carcinogenesis. It could also improve tolerance and recuperation thus slowing down the aging process [36, 37].

5.1 Selenoprotein

5.1.1 Glutathione peroxidase (GPx)

An antioxidant, whose primary role is to counteract the effect of hydrogen peroxide and other hydroperoxides in the body. GPx exists in about eight different forms grouped according to their features. They differ by mode of action and site of action. They work alongside vitamin E to protect cells from accumulated H_2O_2 hence they ensure the integrity of the cell wall. The first four forms of GPx enzymatic activity are directly proportional to the intake of selenium. Hence there is a correlation between oxidative stress and lack of selenium in the body [38–40].

Glutathione peroxidase-1 (GPx-1) occurs mostly in the liver, erythrocytes, lungs and kidneys. Deficiency in selenium affects the activity of GPx-1. Glutathione peroxidase-2 (GPx-2) protects against oxidation and it occurs mostly in the gastrointestinal tissues and the liver [41]. GPx-3 is found in the plasma, heart, kidneys, liver and it covers over 20% of the plasma selenium. It reduces the level of hydroperoxides [42]. GPx-4 is located in the mitochondria, nucleus and cytosol with its highest activity in the testes [43]. In addition to its antioxidant role, it prevents occurrence of peroxidation on the membrane. It is involved in the conversion of cholesterol and its ester into non-toxic derivatives and also prevents oxidation that can lead to DNA damage. The role of GPx-5 is still unknown but it is found in the embryo, while the other GPx: 6, 7, 8 are less studied [44].

5.2 Roles of selenium in the immune response

The lymph nodes and the liver contain high amount of selenium which helps to brace up the formation of antibodies and increase the functioning of the helper T cells and cytotoxic NK cells. It also stimulates the migration of the phagocytic cells [8, 45]. Metabolites of selenium such as GPx-1 and thioredoxin reductase have also been implicated in the inflammatory and immune responses although the mode of action is not fully known [46, 47]. Deficiency of selenium in the endothelial cells reduced the production of prostaglandins. In addition, it was reported that dairy cows deficient in selenium had low production of blood neutrophils hence their ability to kill a pathogen was nullified [47]. A rapid production and differentiation of CD4+ and T cells were observed in subjects who ingested selenium leading to increased poliovirus clearance [48].

5.3 Cancer and cardiovascular disease

Davis et al. [49] illustrated the correlation between selenium and cancer. Their studies showed that one of the factors that promote cancer is selenium deficiency. The authors discovered and reported that high selenium levels reduced the risk of cancer by 4–6 times when compared with low intake levels of selenium (<50 μg/mL). Populations with a status of very low selenium signified more protection against lung cancer [49]. Liver cancer was reduced by 30% in a community whose diet was enriched with selenite supplements [49]. In a Nutritional Prevention of Cancer trial, a daily intake of selenium (200 μg) for a period of 7 years lowered the occurrence of prostate cancer among the participants [50]. In a similar fashion, selenium anticancer potential was observed in rodents where the enzyme that converts selenomethione to methylselenol was 700 times higher in the rodents [49].

5.4 Role of selenium in reproduction

Studies have reported the association of selenium in animal and human reproduction. Selenium plays unique roles in fertility, placenta retention, synthesis of sperm and testosterone. Consumption of selenium deficient diet has been linked to poor growth and reduced fertility [51]. Changes in the luteinizing hormone receptors of Leydig cells observed selenium deficiency as it affects secretion of testosterone (Thomson and Robinson; [52]). Several studies have reported the protective effect of selenium in cadmium-induced toxicity. Selenium plays a role in inhibiting the growth of cancer cells in prostate cancer subjects by inhibiting RNA, DNA and protein synthesis [53]. Selenium has been reported to impact the entire morphology of the testis [54]. Selenium has been shown to increase fertility in dairy sheep [55]. Pastures with very low selenium levels were found to have increased fertility when administered selenium supplements [40]. Such an increase was not observed when the supplement was replaced with vitamin E. Administering selenium supplements to pregnant Ewes increased the rate of lamb's survival during the first 10 days [37]. Injection of selenium decreased the formation of ovarian cyst in cows with deficient diet [56]. Prolapse of the cervix was attributed to selenium deficiency, while red blood cells with low selenium concentrations were reported in women undergoing uncontrolled abortions [57]. Fertility and sperm was improved after consumption of selenium in a study conducted in Scotland [57].

6. Metabolism of selenium

6.1 Transformation, absorption and transport

Glutathione plays a major role in the metabolism of selenium; it is involved in reduction reactions where selenite is converted to hydrogen selenite (H_2Se) which further releases the selenium for selenoprotein synthesis. The hydrogen selenide undergoes several methylations to finally arrive at formation of trimethylselenonium ion [$(CH_3)_3Se^+$] [57]. The rate of absorption of selenite in sheep much lower (29%) when compared with pork (80%) while selenate and selenomethionine have greater absorption rate in poultry animals. This is a result of reduction of selenite that is not available in ruminants [40]. Absorption occurs mostly inside the caecum and duodenum by active transport via a sodium pump. The mode of action differs depending on the specific form of selenium. Adsorption could be by simple diffusion e.g. selenite or by cotransport while the selenomethionine are absorbed via the amino acid uptake method [52, 58]. Elements like lead, sulfur and arsenic slows down the rate of absorption of selenium either through competing with selenium or by formation of complexes that are not capable of being assimilated [59]. Selenium level in the hepatocytes determines the level of absorption in the intestine. Erythrocytes take up selenium rapidly and it undergoes reduction by glutathione reductase and finally

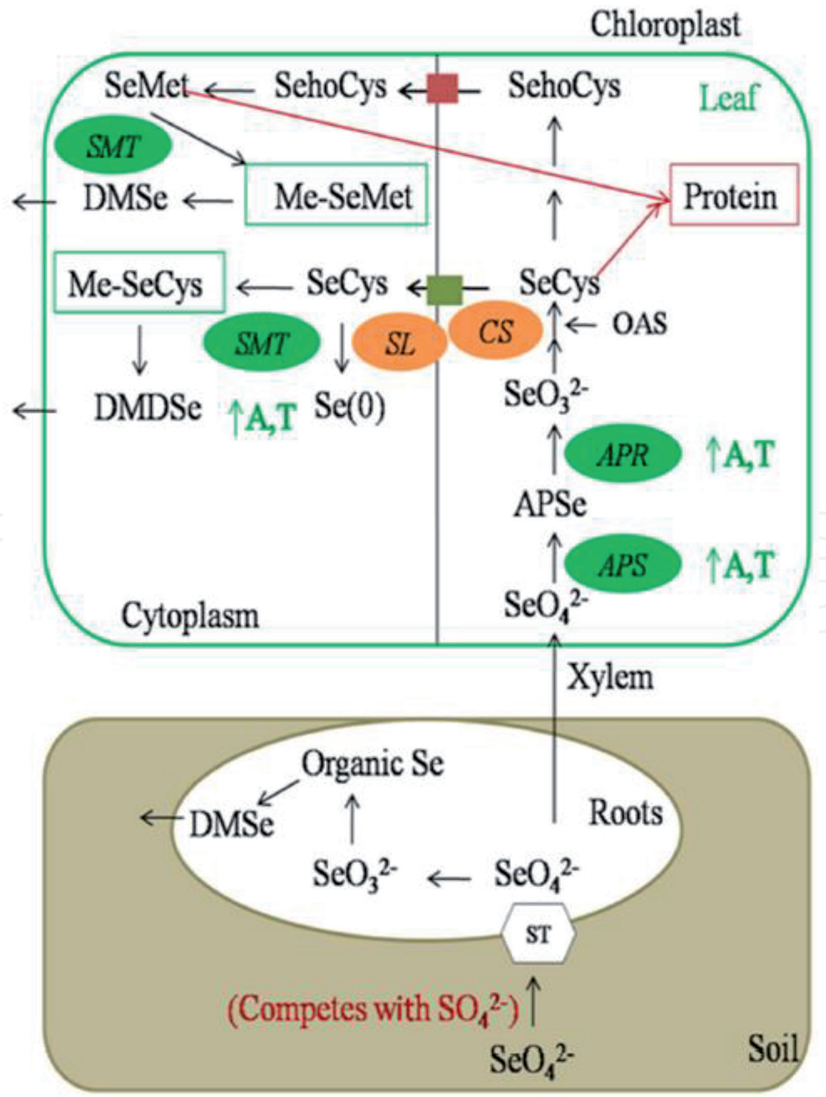


Figure 2.
Selenium metabolism in plants.

transported in the form of selenide in the plasma to the liver [60]. Selenium can also bind to either α and β globulins and can be transported in the form of selenoprotein by the blood [40].

6.2 Selenium metabolism in plants

Selenium is transported in plants via the sulfate transporters in the plasma membrane of the root due to its chemical similarity to sulfur [13, 14]. It is further transported to the leaves and undergoes metabolism through the sulfur assimilation pathway either to a selenium methionine (SeMet) or a selenium cysteine (SeCys).

Inorganic selenium is first converted to selenite via the action of ATP sulfurylase (APS) and APS reductase (APR). The hydrolysis of adenosine triphosphate to adenosine phosphoselenate which is then reduced to selenite is catalyzed by APS and APR, respectively [13]. Sulfite reductase then converts selenite to selenide although glutaredoxins or glutathione can also reduce this step in plants [17]. The selenide couples with O-acetyl serine (OAS) to form selenium cysteine (SeCys) by cysteine synthase. The selenium cysteine can either undergo methylation to methyl-SeCys by selenocysteine methyltransferase or converted to selenium or selenomethionine by SeCys lyase or other enzymes, respectively. Sulfur analog of selenium can then be methylated and undergo vaporization to a non-toxic form in the atmosphere (**Figure 2**) [15].

7. Selenium uptake and accumulation in plants

7.1 Selenium uptake

Selenium exists as both as organic (seleniumcysteine (SeCys) and selenium-methionine (SeMet)) and inorganic (selenate (SeO_4^{2-}), selenide (Se^{2-}), selenite (SeO_3^{2-}) and selenium (Se)) [61, 62]. The various species of plants, their developmental phases, type and concentration of selenium, the soil pH and its salinity determines the uptake and distribution of selenium in plants [14, 16]. Selenate is the most bioavailable form of selenium in agriculture and it is also more soluble in water than selenite [63]. Selenite is found in acidic soils, whereas selenate is found in alkaline soils [14]. According to Kikkert and Berkelaar [64], the rate of translocation of selenate is higher than that of selenium methionine while that of selenium methionine is greater than that of selenite or selenium cysteine by studying the translocation factors. Uptake of selenium is mostly carried out by transporters in the cell membrane of the root; selenate is transported by sulfate transporters while selenite is transported by phosphate transporters [14, 65]. The plants nutritional state determines the choice of the transporters [66]. Transporters for selenium decrease under extreme sulfate concentrations while the inducible transporters show greater affinity for sulfate than selenate than the constitutive ones [66]. Lack of sulfur and phosphorus in *Triticum aestivum* enhanced the uptake of selenium [14].

7.2 Se accumulation in plants

Selenium are usually concentrated in younger leaves during the period of seedling and tend to accumulate in the vacuoles of plant cells and are discharged via sulfate transporters in the tonoplast [67–69]. Different categories of selenium accumulation exist in plants: non-accumulators, secondary accumulators and hyperaccumulators (**Figure 3**; [61]). The non-accumulators are plants that

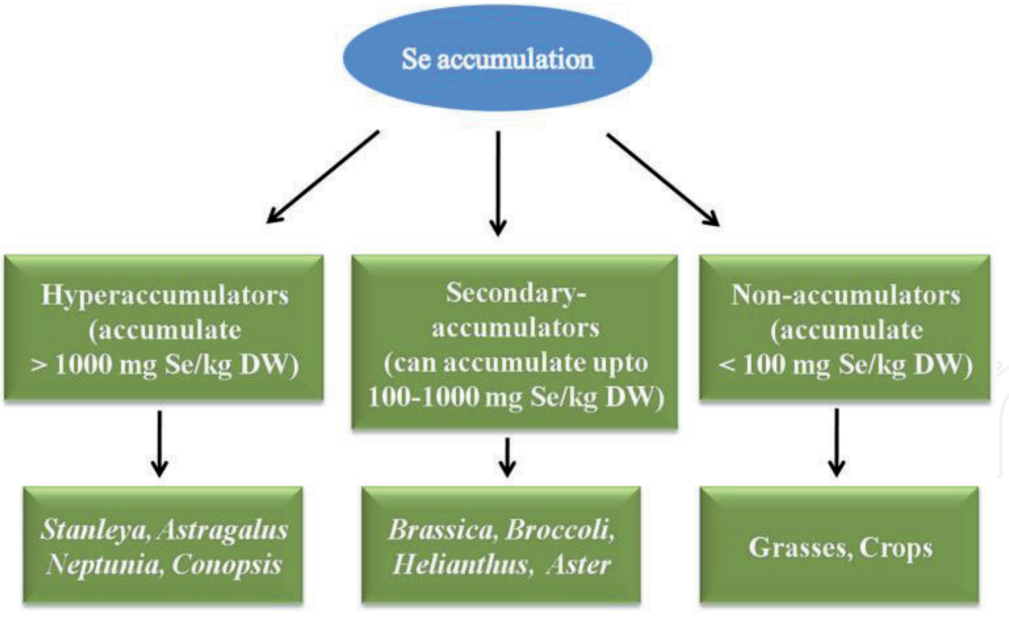


Figure 3.
Classification of plants based on selenium accumulation.

accumulate lesser than 100 mgSe/Kg of their DW, cannot survive on selenium-rich soils and volatilize selenium in form of dimethylselenide (DMSe), for example, grasses [61]. The secondary accumulators show no sign of toxicity at 1000 mgSe/Kg DW, for example, *Camelina, Brassica napus.* Finally, the hyperaccumulators by their name accumulates greater amount of selenium (>1000 mgSe/Kg DW), flourish in selenium-rich areas of the world and they release selenium as dimethyldiselenide, such plants includes *Xylohiza* and *Conopis.*

8. Beneficial effects of selenium in plants

8.1 Metabolic importance of selenium for plants

Selenium is a non-metal that is toxic at high concentration in plants but plays an important role at lower concentrations in them. Selenium increases plant growth when triggered by ultra-violet irradiation. The selenium and UV light share a synergistic relationship in the absence of selenium the UV light is capable of damaging the plant but in the presence of Se, plant growth is increased [70]. Selenium also functions as an antioxidant in plants. This antioxidant activity is also responsible for the improved growth in the plant. Selenium exerts its antioxidant activity by alleviating lipid peroxidation through GSH-Px activity. Se induced two selenoproteins, which are the thioredoxin reductase and GSH-Px these enzymes protect the plant from oxidative stress (Djanaguiraman et al., 2010). Se protects some plants from abiotic stress at low concentrations [71].

8.2 The functions of selenium in plants

Selenium functions differently in various plants;

i. It induces starch accumulation in chloroplast [72]

ii. Promotes germination [73]

iii. Increases respiratory potential [74]

iv. Improves nitrogen assimilation [75]

v. Increases the shoot and dry matter production (Djanaguiraman et al., 2010)

9. Selenium toxicity in plants

Selenium toxicity in plants arises from an increased concentration of selenium beyond the optimum threshold [70, 76]. High concentrations of Se in plant root can cause them to exhibit symptoms of injury, stunting of growth, chlorosis, withering and drying of leaves, decreased protein synthesis and premature death of the plant [77, 78]. Selenium toxicity is caused by two mechanisms: the first by inducing oxidative stress and second by malformed selenoproteins [70] plant from oxidative stress (Djanaguiraman et al., 2010). Se protects some plants from abiotic stress at low concentrations [71].

9.1 Toxicity due to malformed selenoproteins

Malformed selenoproteins result from the substitution of seCys/seMet into the protein chain in place of Cys/Met, these se amino acids are unstably unfavorable to protein functioning. Cysteine plays a primary role in the structure and function of a protein chain, disulfide bond formation, chemical catalysis and also functions a metal-binding site. Substitution of Cys with seCys produces result in alteration to the protein structure and capacity due to the seCys being bigger, responsive and more effectively deprotonated than cysteine [79], as in the case of methionine sulfoxide reductase enzyme which lost its function as a result of the substitution of SeCys [19]. SeCys substitution mutilates the tertiary structure of protein because of its large diselenide bridge formation and modified redox potential affect enzyme kinetics [79]. Fe-S group proteins of chloroplast and mitochondrial electron transport chain [80] are inclined to SeCys substitution for instance as in the event of chloroplast NifS-like protein [81]. Fe-Se bunch are bigger in size and do not fit appropriately in apoproteins.

9.2 Selenium toxicity due to oxidative stress

A high dosage of selenium acts as a pro-oxidant and creates receptive oxygen species which cause oxidative stress in plants. Under selenium-induced stress, glutathione is diminished [82], except for Se-tolerant plants where raised level of glutathione is increased [83]. Previously studied plants such as *Arabidopsis* and *Viciafaba* have shown that reactive oxygen species accumulation under Se stress increased lipid peroxidation, cell mortality [20].

10. Selenium phytoremediation

Phytoremediation is a plant-based technology, which is eco-friendly, cheap and used in the treatment of contaminated soil and water resource [70, 84]. It does not reduce the fertility of the soil and this method of decontamination of the soil has been enhanced by the use of genetic engineering. Certain plants are suitable for phytoremediation, these plants are selected based of certain factors such as:

i. The plants must possess large biomass production capacity, volatilization and high accumulation of selenium

ii. It should be easily cultivated and harvested under different growing conditions

iii. The plants must have deep roots [70]

iv. They should be cheap to cultivate [85].

10.1 Methods of phytoremediation

There are various methods of phytoremediation, but phytovolatilization, rhizofiltration and phytoextraction are the most stable of selenium decontamination of soil and water bodies [70].

10.1.1 Photoextraction

Phytoextraction is the use of higher plants which are se-hyperaccumulators in the removal of se-contaminates from the soil [70, 86]. These se-hyperaccumulator plants grow on seleniferous soil and they are able to accumulate up to 15,000 mg/kg selenium. These plants are cultivated on the contaminated soil then after they have successfully removed the se in the soil they are disposed of. The main drawback of the method is that these se-hyperaccumulator plants grow slowly; this makes this strategy time consuming. They also have limited biomass production this leads to insufficient selenium decontamination for the soil [87].

10.1.2 Phytovolatilization

Phytovolatilization is the process of plants absorbing contaminants from the soil and releasing it to the atmosphere. Green plants are able to convert inorganic forms of selenium which are toxic to a less toxic organic selenocompounds [70]. This method is advantageous over phytoextraction, because it does not require the disposal of contaminated plant. The particular volatile selenium released by se-hyperaccumulator plants is dimethyldiselenide, while nonaccumulator plants release dimethylselenide from its leaves [88]. A more efficient method of phytoremediation is the combination of phytovolatilization and phytoextraction. This method increases the se-decontamination of soil by 2–3 times more than when carried out individually. Phytovolatilization method depends on certain factors such as the specie of plant, the microorganism in the rhizosphere, the selenium specie, temperature and so on [89].

10.1.3 Rhizofiltration

This strategy uses plant roots to decontaminate flowing water. It uses plant biomass to remove the contaminants as in the case of phytoextraction. Although they share same principle, rhizofiltration is used to decontaminant strictly water bodies and it involves the disposal of the root and shoot of the contaminated plant unlike phytoextraction which is only used to decontaminate the soil and involves the disposal of only the shoot of the contaminated plant.

10.1.4 Selenium biofortification

Selenium biofortification is a method used in the disposal of waste plants by decomposition [90, 91]. The selenium present in the plant is used to enrich the soil which aids in improvement of food quality [92]. Biofortification is an agricultural practice used in enriching food productions with different nutrients such as selenium in this case, with the purpose of increasing dietary intake by various biotechnological methods such as genetic engineering, plant breeding and manipulation of agronomic practices practices (Kieliszek and Blazejak, 2012) [93, 94]. Genetic engineering is a useful method of obtaining Se-biofortified food products, this is carried out by manipulation of selenium-related enzymes for uptake, evaporation and assimilation of selenium. Biofortification is cheap, safe and it also helps in carving out various nutrient deficiencies in diets [95–97]. Selenium biofortification is used to increases selenium contents of farm produces, this helps reduce selenium malnutrition among a population.

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