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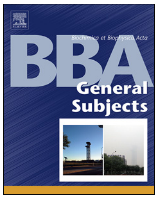

Review

Mechanisms of selenium hyperaccumulation in plants: A survey of molecular, biochemical and ecological cues[☆]

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ABSTRACT

Background: Selenium (Se) is a micronutrient required for many life forms, but toxic at higher concentration. Plants do not have a Se requirement, but can benefit from Se via enhanced antioxidant activity. Some plant species can accumulate Se to concentrations above 0.1% of dry weight and seem to possess mechanisms that distinguish Se from its analog sulfur (S). Research on these so-called Se hyperaccumulators aims to identify key genes for this remarkable trait and to understand ecological implications.
Scope of review: This review gives a broad overview of the current knowledge about Se uptake and metabolism in plants, with a special emphasis on hypothesized mechanisms of Se hyperaccumulation. The role of Se in plant defense responses and the associated ecological implications are discussed.
Major conclusions: Hyperaccumulators have enhanced expression of S transport and assimilation genes, and may possess transporters with higher specificity for selenate over sulfate. Genes involved in antioxidant reactions and biotic stress resistance are also upregulated. Key regulators in these processes appear to be the growth regulators jasmonic acid, salicylic acid and ethylene. Hyperaccumulation may have evolved owing to associated ecological benefits, particularly protection against pathogens and herbivores, and as a form of elemental allelopathy.
General significance: Understanding plant Se uptake and metabolism in hyperaccumulators has broad relevance for the environment, agriculture and human and animal nutrition and may help generate crops with selenate-specific uptake and high capacity to convert selenate to less toxic, anticarcinogenic, organic Se compounds.

1. Background

The element selenium (Se) is characterized by several intriguing properties. It is required in trace amounts for the healthy metabolism of many life forms like microalgae, many Prokaryotes and animals, including mammals [1–3]. However, Se intake higher than a certain threshold may be harmful to these organisms. Inorganic Se anions can be pro-oxidants in cells, causing oxidative stress through depletion of intracellular glutathione; protein misfolding may also occur due to replacement of sulfur by seleno-aminoacids [4,5].

In humans, the window between deficiency and toxicity for Se is extremely narrow as compared to other micronutrients [6]. Selenium deficiency has been estimated to affect at least one billion people [7], especially in parts of China, North-West Europe, Australia, New Zealand, sub-Saharan Africa, Southern Brazil and parts of the USA [8,9,11]. This number may be growing, according to a moderate climate-change model scenario. Jones et al. [12] analyzed several environmental variables that may influence Se distribution worldwide and predicted that climate and soil organic matter changes will be responsible for a significant reduction of soil Se concentration in 2080–2099 as compared to a more recent situation (1980–1999), especially in agricultural regions.

Selenium concentration in soil, which mostly ranges between 0.01 and 2.0 mg Se ppm, primarily correlates with Se availability in the human diet [7]. Because plants represent the main portal for Se in the food web, Se biofortification programs are carried out to enrich staple crops with Se in order to overcome the Se-deficiency issue [13,14]. The success of these programs largely depends on understanding the mechanisms of Se uptake, assimilation, and tolerance by plants [3,13,14]. On the other side of the spectrum, in parts of the USA, Canada, China and India, soils occur that are rich in Se and named seleniferous soils; these contain 4–1200 ppm Se, which may be harmful to humans and livestock [8,15–17].

Se deficiency and toxicity concerns are not only related to Se concentration in soil, but also to its chemical form [3,9,11]. Selenium in soil and organisms can exist in different oxidation states and in various

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inorganic and organic forms, which can interconvert via chemical or biochemical processes [3,6]. Owing to its chemical similarity to S, conversion of inorganic Se into organic compounds can be realized via a non-specific route that involves the sulfur (S) assimilation pathway, as described for plants [18,19]. In addition, in organisms that have an essential requirement for Se, its conversion can be mediated by Se-specific enzymes, particularly its Se-specific incorporation into selenoproteins [6,20–23].

Evolutionary analyses support the assumption that essential Se metabolism in animals and certain algae (e.g. *Chlamydomonas reinhardtii*) evolved early and the environment played a crucial role in its further evolution, loss or persistence in different clades [3,24]. The loss of selenoproteomes in plants, fungi and some animals arguably happened via independent events and because of one or more undetermined environmental factors [1,24]. It has been hypothesized that aquatic life preserved Se metabolism in photosynthetic organisms, while terrestrial habitats dramatically reduced the metabolic dependence on Se because of its restricted availability [5,24].

Although lacking essential Se metabolism, plants can experience an array of beneficial properties from Se [25–27]. At low tissue concentrations, Se promotes plant growth and productivity and enhances resistance against certain types of abiotic stresses. With increasing tissue Se concentrations, Se also increasingly protects plants from herbivores and pathogens. Plants readily take up Se even though they do not require it, owing to the similarity of Se and S. The capacity of plants to accumulate Se is important for the food web, because plants represent the main entry of Se in the food chain.

The natural occurrence and distribution of Se in soil is a result of early geological soil formation and deposition, mainly as a response to volcanic activity in the Cretaceous period in the Mesozoic era (145 million years ago), in which ashes and gases containing Se were deposited in the ocean due to rain, largely ending up in the clay section of sedimentary rocks in the earth's crust from this geological period [28]. Reportedly, the average Se concentration worldwide is 0.44 mg kg^{-1} [28]. Soil Se concentration, composition and availability varies dramatically in relation to the physicochemical characteristics of soils. The accumulation of Se by plants is, to a large extent, influenced by Se concentration and phytoavailability in soils. In addition, differences between plant species exist with respect to their capacity to accumulate Se under the same environmental conditions [19,29,30]. Plant species thriving on seleniferous soils hold a special position in this respect, because they have evolved strategies to prevent Se toxicity while often accumulating high tissue Se concentrations [21,31–33].

Plants absorb Se using different types of transporters depending on the form of Se available for uptake [29,34–38]. The expression of these transporters and their kinetic properties and substrate specificity vary in the plant kingdom and contribute to plant adaptation to high-Se environments. Selenium is mostly present in soil in inorganic forms, primarily as selenate (SeO_4^{2-}) or selenite (SeO_3^{2-}), which are both soluble and thus readily available for plant uptake. However, plants can also take up organic Se compounds, especially in the form of selenoamino acids. They do not show substantial uptake capacity for the less bioavailable forms: elemental Se, metal selenide compounds or colloidal elemental Se [19,39]. Once inside plant cells, selenate can be assimilated into selenocysteine (Se-Cys) and selenomethionine (SeMet) through the biochemical pathway that is normally involved in sulfate reduction and assimilation [11,18,19,22,40]. The non-specific incorporation of these two Se-amino acids in proteins in the place of the analogs cysteine (Cys) and methionine (Met) causes the disruption of protein folding, which is considered the main cause of Se toxicity to plants [41]. In this respect, plants have evolved a range of strategies to mitigate Se toxicity, which include conversion of SeCys to elemental Se and alanine, methylation of SeCys and SeMet, and conversion of these compounds to volatile dimethyl(di)selenide (DMDSe) [18,42]. Accumulation of Se in plant tissues and production of methylated volatile Se species are both critical for Se cycling in the environment [43]. Selenium volatilization into the atmosphere by plants and microalgae may be responsible for a significant portion of Se fluxes and may contribute to the formation of seleniferous regions [43,44].

Plant species differ in their capacity to accumulate Se in their natural environment and to produce Se volatile compounds, as well as in their preferential strategy to avoid Se toxicity [3,30,45]. According to their capacity to accumulate Se, plants can be divided in three main categories: non-accumulators, which include species that accumulate less than 100 μg Se g^{-1} dry weight; secondary accumulators like *Brassica juncea* and *Brassica napus*, which can contain up to 1000 μg Se kg^{-1} dry weight, can thrive on both non-seleniferous and seleniferous soils, and their tissue Se concentration is directly indicative of the Se phytoavailability in the soil (Se-indicators); hyperaccumulators, such as certain species of the genera *Stanleya* (Brassicaceae) and *Astragalus* (Fabaceae), able to accumulate over 1000 μg Se g^{-1} dry weight in all organs (0.1–1.5%) when growing on seleniferous soils [3,19,30,46–49]. Within these three ecological groups, variation in Se concentration may also be observed between genera, species and even ecotypes within species [19,29,30,50–53].

The observed differences in physiology and biochemistry between these taxa in response to Se might have ecological significance and raises the question which benefits and potential constraints are associated with high concentrations of Se in plants, both physiologically and with respect to interactions with ecologic partners [3]. Selenium may enhance plant fitness via enhanced growth and abiotic stress resistance, protection from pathogens and herbivores, or via elemental allelopathy, i.e. competition towards other plant species that are sensitive to Se [3,19,32]. Plants that exhibit the fascinating trait of Se hyperaccumulation are of great interest in the field of Se research not only for intrinsic interest but because their study may benefit applications in Se phytotechnologies, i.e. biofortification and phytoremediation [3]. A particularly interesting trait in this respect is the capacity to accumulate Se specifically in the presence of high S concentration.

2. Selenium uptake in plants

2.1. Selenate transport and evidence for specific mechanisms of Se uptake in hyperaccumulators: model species Stanleya pinnata

Generally, selenate is more common and bioavailable than selenite in well-drained/oxidized and alkaline soils, while selenite is the prevalent water-soluble species in wetlands and anaerobic soils with a neutral to acidic pH [30,54,55]. Selenate is a chemical analog of sulfate (S), and thus it can enter the root cells and move throughout the plant via sulfate transporters [29,56]. Solid evidence for a role of the sulfate transport system in selenate movement across cell membranes derives from a study conducted in *Arabidopsis thaliana* selenate-resistant mutants by Shibagaki et al. [57] and El Kassis et al. [56]. SULTR1;2 in particular, i.e. the main group 1 root high affinity sulfate transporter involved in the active uptake of sulfate from the soil solution, was identified as the major portal for selenate entry into the plants, as *A. thaliana sultr1;2* mutants were more tolerant to selenate than wild-type plants and *sultr1;1* mutants [58]. In addition to SULTR1;2, under low external S concentration or in the absence of selenate/sulfate competition, another member of the group 1 root high affinity sulfate transporters, SULTR1;1, seems to mediate selenate transport as well [33,56,59,60]. Expression of these sulfate/selenate transporters is regulated by several factors, including the S status of the plant, the Se:S ratio in the plant organs and growth medium, and also the plant species [19,29,33,36,38].

Non-hyperaccumulators and hyperaccumulators often exhibit different expression levels of sulfate transporters in response to external Se and S availability, which in turn influences Se accumulation in their organs [29,33,36,38]. Hyperaccumulators typically show more abundant expression of sulfate transporters than non-hyperaccumulators (Fig. 1); while this explains their high Se concentrations, it does not