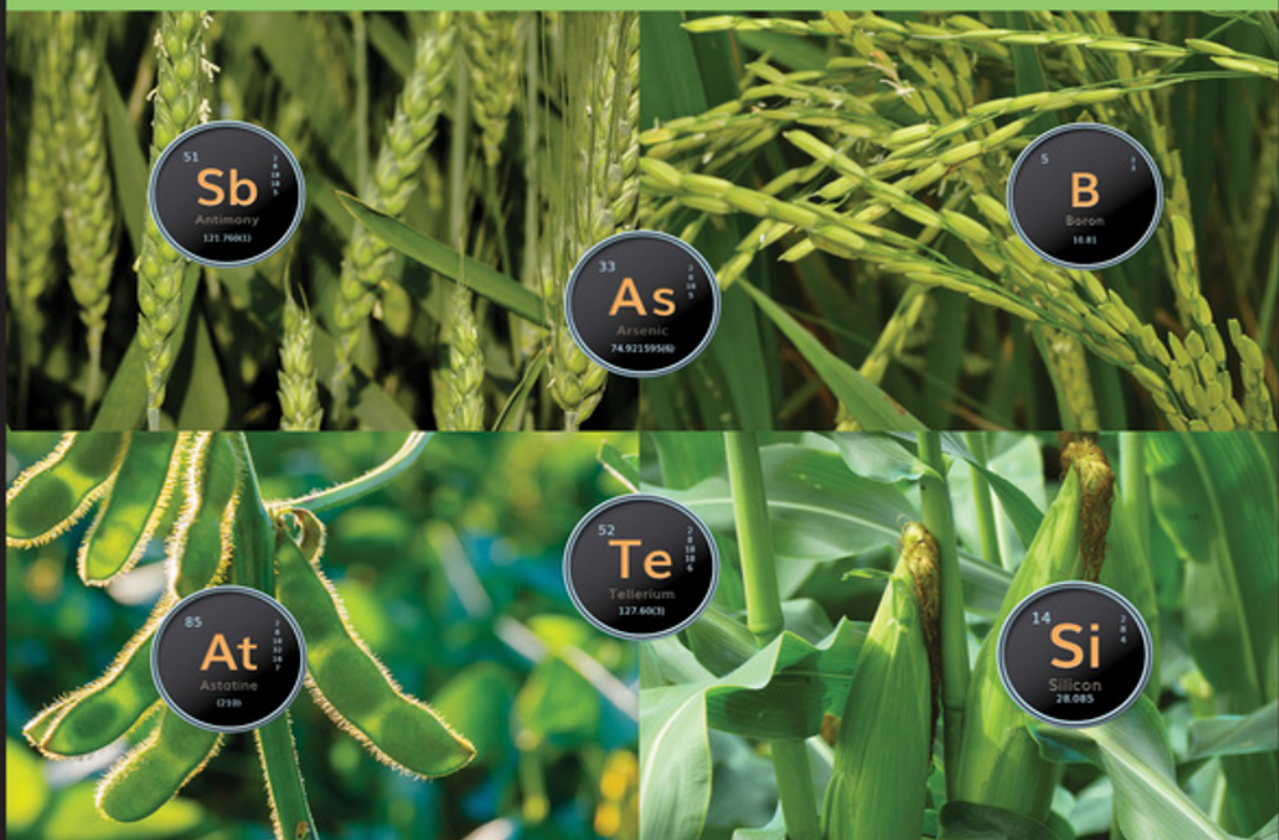


METALLOIDS IN PLANTS

ADVANCES AND FUTURE PROSPECTS



EDITED BY
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Metalloids in Plants

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Advances and Future Prospects

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Dedicated to one of the most eminent Agriculture Scientist of India who's work on rice helped to secure food for millions of poor people.

Prof. Tilak Raj Sharma



Executive Director
National Agri-Food Biotechnology Institute (NABI)
Mohali, Punjab, India.

Dr. Rupesh Deshmukh,
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Metalloids and Their Role in the Biological System

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Introduction

Metalloids encompass a group of chemical elements which are found widespread in nature (Bienert et al. 2008). Most of their physical and chemical characteristics are intermediate between metals and nonmetals, hence it is hard to classify them as either metals or nonmetals (Bhattacharjee et al. 2008). Physically, they are glittery, fragile with intermediate electric conductivity similar to metals, and chemically they behave as nonmetals. Metalloids possess intermediate amphoteric, electronegative values and ionization energies. They have an ability to form an alloy with metals. The number and identities of metalloids are determined based on the criteria used for their classification, which includes electronegativity, packing efficiency, the Goldhammer–Herzfeld ratio, atomic conductance, and bulk coordination number. Among them, electronegativity is the commonly used criterion to categorize metalloids. Most of the metalloids possess electronegative values ranging from 1.8 to 2.2, packing efficiencies between 34 and 41%, and the Goldhammer–Herzfeld ratio of 0.85–1.1 (Mann et al. 2000; Vernon 2013).

Arsenic (As), antimony (Sb), boron (B), germanium (Ge), silicon (Si), and tellurium (Te) are usually recognized as metalloids (Vernon 2013; Bienert et al. 2008; Bhattacharjee et al. 2008). Primary sources of metalloids are the weathering of parent material, dissociation of minerals, mining, atmospheric deposition, burning of fossil fuels, use of fertilizer and pesticide, industrial emissions, anthropogenic sources, sewage, agrochemicals, and municipal and industrial wastes (Nagajyoti et al. 2010; Alloway 2013). They are important elements showing the effects ranging from the essential to highly toxic in nature. Metalloids play diverse roles ranging from nonessential elements like Ge and Te to essential elements like B, beneficial elements like Si, and highly toxic elements like As and Sb in the cellular processes (Bienert et al. 2008; Bhattacharjee et al.

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2008; Deshmukh et al. 2017). Generally, metalloids are not toxic; they only exhibit toxic effects when their internal concentration in the biological system exceeds a certain threshold. Few metalloids are essential in very small quantities for proper metabolism, growth, and development. In contrast, few metalloids show a toxic effect even at very low concentrations. The toxic effects of metalloids also depend on the various factors, including the type of metalloid, its concentration, organisms, plant species, and stage of growth (Appenroth 2010). Their higher accumulation in soils, drinking water, and food chain affects plant, animal, and human health. Bioavailability of metalloids also depends on pH, soil organic matter, soil structure, and chemical composition. The amount of metalloids in the earth's crust varies from Si being the second most common element to astatine (At) as the rarest element. The metalloid elements such as Ge, Te, Po and At are present in trace or ultra-trace levels and they are not found to affect environmental health (Adrees et al. 2015). Here, we briefly discuss the role of metalloids in a biological system, their transport, and detoxification mechanism.

Metalloids in Human and Animal Health

Metalloids are known to play both useful and harmful roles in human life. Boron is an essential trace element having an important role in humans and animals. Boron and its compounds have a role in bone development, cell membrane maintenance, regulation of numerous enzyme activities, embryonic development, a steroid hormone, carbohydrate, and mineral metabolisms in humans and animals (Nielsen 1998; Uluisik et al. 2017). The supplementation of boron through diet to chicken, pigs, and rats showed enhanced bone strength (Armstrong et al. 2000). Boron plays an important role in bone metabolism by interacting and regulating key players such as magnesium, calcium, vitamin D, and hormones which are crucial for bone growth and formation. Boron deficiency affects the reproduction and developmental processes in mice, frogs, rainbow trout, and zebrafish (Lanoue et al. 1998; Fort et al. 1998; Eckhert 1998). It has also been implicated in inflammatory response by repressing the 6-phosphogluconate activities and reduces the risk of inflammatory diseases. Boron also activates the antioxidant mechanisms that can destroy reactive oxygen species (ROS). Few studies have shown that daily intake of boron-containing diet reduces the risk of breast and lung cancers in women (Mahabir et al. 2008). Its deficiency causes abnormality in bone development, increased urinary calcium excretion, reduced blood steroid hormone levels, alteration in macromineral level, and impairment of growth in humans and animals (Murray 1995). In addition, its deprivation leads to the decrease in the brain's electrical activity, short-term memory, and reduced skills during performing tasks. However, high doses of boron consumption cause reproductive and developmental abnormalities. Prolonged exposure to boron causes diarrhea, kidney damage, anorexia, neurological effects, testicular atrophy, and weight loss (Nielsen 1997). Higher concentrations of boron impede the development of some organs in rat and chicken. A rare form of corneal dystrophy, called congenital endothelial dystrophy type 2, is linked to mutations in boron transporter, SLC4A11 which regulates the intracellular concentration of boron. The defect in SLC4A11 causes rare congenital endothelial dystrophy type 2 diseases (Kim et al. 2015).

Several boron-incorporated compounds have been discovered which have medicinal applications, for example boron neutrons for brain tumor therapy, Anacor, and

bortezomib used to treat many skin disease and multiple myeloma disease (Řezanka and Sigler 2008). Numerous natural products containing boron have shown antibiotic activity which includes boromycin, borophycin, tartrolon E, and aplasmomycin B and C (Uluşik et al. 2017). Boron and boron-containing molecules are also considered natural anticancer agents. Boron inhibits the enzyme activities by binding either to their cofactors (i.e. NAD) or some other mechanism, which is not understood clearly. Boronated compounds show potential in treating arthritis, while boron-10 has been used in boron neutron capture therapy (BNCT). Tavaborole-containing boron is an inhibitor of aminoacyl tRNA synthetase which is used to treat toenail fungus (Travers et al. 1990).

Arsenite plays an essential role in gene silencing and methionine metabolism in animals (Hunter 2008). Use of As-containing insecticides and herbicides in agricultural fields causes the contamination of soils and environment. This toxic metalloid enters through the plant roots and passes into the human and food-chain causing a potential threat to human and animal health. It causes severe diseases like lung and bladder cancer, skin lesions, and several other diseases in humans (Pearce 2003). Several As compounds, such as roxarsone, nitarson, and carbarson, are used as a veterinary feed to stimulate growth, weight gain, increase feed efficiency and treat various diseases in chickens, pigs, sheep, and cows. An example is roxarsone, which is used as a broiler starter by nearly 70% broiler growers in the US (Calvert and Smith 1980). Many As compounds including arspenamine and arsenic trioxide were used as medicines. Arsenic trioxide was commonly used for the treatment of promyelocytic leukemia, a cancer of the bone marrow and blood (Shen et al. 1997). The organoarsenic compound arspenamine (Salvarsan), used to treat syphilis, trypanosomiasis, cholera, and cancer cells (Williams 2009).

Silicon is another metalloid needed for the growth and development of animals. It is involved in hair, nail, bone, and skin development in humans (Jugdaohsingh 2007). Silicon is also required for the synthesis of elastin and collagen. Silicic acid is essential for bone structure, and it is present in almost all connective tissues to provide stability and elasticity. Some researchers have demonstrated that premenopausal women with higher dietary silicon intake have higher bone density, and it also increases bone density in patients with osteoporosis (Jugdaohsingh 2007). Silicone gel is applied to acutely burned patients to reduce scarring. A highly toxic rodenticide, silatran, also contains Si (Jugdaohsingh 2007). Inhalation of silica dust over a long period causes silicosis, which is a fatal disease of the lungs.

Selenium is another metalloid important for human health which provides protection against chronic neurological degenerative and neoplastic diseases. The methylated form of selenium is an effective anticarcinogenic agent against mammary gland cancer in rats. Selenium sulfide is found in shampoos used to treat skin infections such as tinea versicolor. The cyanobacterium *Spirulina platensis* had selenium-containing pharmaceuticals and it is used as dietary supplement in humans (Mosulishvili et al. 2002).

The metalloid antimony and its compounds are used as antiparasitic, antischistosomal drugs, and emetics in humans as well as animals. Lithium antimony thiomalate and anthiomaline have a conditioner effect on animal skin (Harder 2002). Germanium is another metalloid that has little or no impact on the environment and health. Some intermediate compounds of germanium are found to be reactive and poisonous. US Food and Drug Administration research has declared that inorganic germanium is a potential human health hazard. However, germanium compounds used to treat renal

dysfunction, hepatic steatosis, peripheral neuropathy, leukemia, and lung cancer (Tao and Bolger 1997). Tellurium is a rare trace element that does not have an important role in biological systems. However, tellurium and its compounds have demonstrated toxic effects on human and animal health. Organotellurium compounds oxidize sulfhydryl groups and deplete endogenous glutathione (GSH) cause cells damage. Tellurium dioxide is employed to treat seborrheic dermatitis, while other tellurium compounds were used as antimicrobial agents before the use of antibiotics. These compounds may substitute for antibiotics in the future, owing to their bacteria-resistant properties (Řezanka and Sigler 2008).

Role of Metalloids in Plants

Metalloids are implicated in diverse physiological processes in plants. Among them, Te and Ge have not demonstrated any essential functions, while others such as Si, B, and As are required in small amounts for proper plant growth and development. However, higher than the required concentration of these elements causes extreme toxicity to plants, which negatively affects plant growth, biomass, photosynthesis, and yield (Bienert et al. 2008). It has been demonstrated that accumulation of metalloids in all living organisms, including plants, causes numerous biochemical, physiological, and molecular changes (Hodson 2013; Bienert et al. 2008; Bhattacharjee et al. 2008). Among the metalloids, Si is the second most abundant element on the earth's crust. Although Si accounts for up to 10% of the shoot dry weight in higher plants, it is not considered an essential element for plants. Several researchers demonstrated that Si is beneficial for plant growth and development (Ouellette et al. 2017; Deshmukh and Bélanger 2016; Vivancos et al. 2015; Tripathi et al. 2017a,b). Tissue-cultured carnation plants supplemented with silicon improve stomatal development and enhanced root hydraulic conductance by regulating major intrinsic proteins (MIPs) (Sivanesan and Park 2014). It improves strength and structural integrity of the cell wall in rice plants (Asada and Tazaki 2001). It alleviates diverse abiotic stresses like heat stress, low-temperature stress, drought stress, and metal toxicity, and decreases lodging potential and salt stress (Řezanka and Sigler 2008; Tripathi et al. 2016). It decreases metal toxicity by reducing uptake and translocation of heavy metals in various plants species thereby enhancing plant growth and biomass. Hussain et al. (2015) show that Si reduces the uptake and translocation of cadmium (Cd) from shoot to grain in many plants. In cotton plants, it also enhances root length, plant height, leaf area, and a number of leaves per plant under Cd, zinc (Zn), and lead (Pb) stress (Anwaar et al. 2015; Keller et al. 2015). Application of Si significantly represses Zn deposition in many plant organs such as roots and leaves of cotton and maize. In addition, a negative correlation has been observed between external Si supply and uptake and concentration of As(III) in rice seedlings under hydroponic as well as soil culture conditions (Sanglard et al. 2014). Positive effects have been reported for Si application on chlorophyll content and photosynthesis under the heavy metal toxicity. Silicon application enhances chlorophyll content under aluminum (Al), chromium (Cr), and As toxicity in barley, wheat, mung bean, and rice (Tripathi et al. 2015). Silicon plays a critical role in the nutrient absorption by the plants under heavy metal stress and it also reduces oxidative stress by inhibiting the production of ROS. It has been shown that Si reduces the contents of electrolytic

leakage (EL), hydrogen peroxide (H₂O₂), and malondialdehyde (MDA) in the roots and shoots of cotton plants under Zn, Cd, and Pb stress (Anwaar et al. 2015). Silicon supply also enhances the activity of enzymatic antioxidant (catalase, peroxidases, superoxide dismutase, ascorbate) and non-enzymatic antioxidants (GSH, ascorbic acid, and non-protein thiols) under heavy metal stress (Li et al. 2015; Wang et al. 2015). Further, Ma et al. (2006) report that expression of *OsLsi1* was elevated in the presence of Si in the medium, while expression of *OsNramp5* gene implicated in the transport of Cd was significantly repressed in rice. *OsLsi1* mutant defective in Si uptake shows a reduction in grain yield and increased susceptibility to diseases and pests. Moreover, Si application enhances the expression of genes involved in photosynthesis under Zn stress in rice (Song et al. 2014). The underlying molecular mechanisms of Si-mediated alleviation of heavy metal toxicity is not understood completely (Deshmukh et al. 2017). It would be interesting to investigate relationships between Si and heavy metal stress and study the regulation of genes implicated in the uptake, deposition, and translocation of metals and metalloids in plant species. Silicon also plays a crucial role in controlling numerous plant pests and diseases caused by bacteria and fungi, including stem borer, planthopper, blast, and powdery mildew (Fauteux et al. 2005; Tripathi et al. 2014; Deshmukh et al. 2017; Ouellette et al. 2017). Si-derived resistance of the plant to abiotic and biotic stresses is mainly attributed to the mechanical barrier made by the deposition of Si along the cell wall thus impeding their progress. For instance, silicon accumulation in the exodermis and endodermis in the roots of rice plants decreases the transport of sodium which is strongly correlated with salt tolerance (Gong et al. 2006). Silicon regulates the genes involved in water transport and stress-related pathways including the jasmonic acid pathway, ABA-dependent or independent pathway, and phenylpropanoid pathway (Vivancos et al. 2015). Si also interferes with host-pathogen recognition, probably by inhibiting effectors and signaling molecules from recognizing their specific targets. It also induces the plant's defense by changing the composition of plant volatiles induced by herbivores (Vivancos et al. 2015).

Boron is another metalloid regularly used in agriculture, owing to its role in plant growth and development. Boron plays a critical role in plant cell wall synthesis, strengthening cell wall structure and membrane integrity. It cross-links complex polysaccharides in plant cell wall, which is critical for cell wall strength, stability, membrane integrity and expanding organs (O'Neill et al. 2004). Boron deprivation leads to altered cytoskeletal polymerization. Impaired cell wall formation affects the plasma membrane permeability and induces oxidative damage, causing cell death. In addition, root elongation, leaf expansion, and flower and fruit development are also impeded (Dell and Huang 1997). Boron deficiency also affects numerous cellular processes including carbohydrate, protein, and nucleic acid metabolism (Miwa et al. 2007). Higher concentrations of boron lead to marginal and tip necrosis in leaves, disturbances to metabolic reactions, poor growth of roots and shoots, and reduced chlorophyll and lignin content in plants. Boron has been also used as an insecticide, antifungal, and antimicrobial agent (Nable et al. 1997).

Increased concentration of arsenite in soil and water affects plant growth and yield and poses threats to global food security and human health. The excess presence of As in soil and water affects plant growth, inhibits photosynthesis and respiration, and increases the secondary metabolism resulting in yield losses (Cozzolino et al. 2010). Arsenite is toxic to bacteria, fungi, and insects and hence it is used as a wood

preservative as well as an insecticide in agriculture to control many pests. For example, lead hydrogen arsenate is a common insecticide on fruit trees. Arsenite(III) interferes with redox signaling, induces oxidative stress and affects the general function of proteins (Islam et al. 2015).

The Metalloid Requirement in Microorganisms

Metalloids have beneficial as well as toxic effects on soil microflora. Most of the agricultural soils are rich in beneficial metalloids like silicon and boron. However, significant acreage has been contaminated with toxic metalloids like As, mainly because of anthropological activities (Singh et al. 2015). Many microorganisms can grow in soils contaminated with toxic metalloid and heavy metals. Microbes can reduce the variety of such toxic metalloids to insoluble forms like methylates along with the generation of volatile derivatives. For instance, the fungus *Acremonium falciforme* reduces tellurite through volatilization (Chasteen and Bentley 2003; Kumar et al. 2015).

Boron plays a crucial role in physiological and metabolic activities of microorganisms. It is essential for the growth and biological nitrogen fixation in bacteria, cyanobacteria, and actinomycetes (Mateo et al. 1986). It is found in autoinducer-2 (AI-2), produced by marine bacteria which is involved in quorum sensing (Wolkenstein et al. 2010). Other than bacteria, boron is also required for lower eukaryotes such as brown algae, algal flagellates, and diatoms. Bennett et al. (1999) report that yeast cells grow and divide when supplemented with boron. However, increased supplementation shows inhibition of yeast growth. Boron is also required for interacting and stabilizing the glycolipids of the heterocysts (Hunt 2003). Boric acid has antiseptic, antifungal, and antiviral properties, and several antibiotics are known to contain boron, including boromycin (*Streptomyces antibioticus*), tartrolons (*Sorangium cellulosum*), borophisin, and aplasmomycin (*Streptomyces griseus*) (Kohno et al. 1996). Boromycin hampers the growth of gram-positive bacteria and the replication of HIV-1; however, no effect has been found on the growth of some gram-negative bacteria and fungi.

Some species of microorganisms also partially metabolize tellurium to form dimethyl telluride. Tellurium compounds are also used as pigments for ceramics. Tellurite agar is used to identify members of the corynebacterium genus such as *Corynebacterium diphtheria* which causes diphtheria. Tellurium incorporated into amino acids in place of sulfur and selenium such as tellurocysteine and telluromethionine in fungi (Kwantes 1984; Ramadan et al. 1989). Microorganisms have shown a highly variable tolerance to tellurium compounds, for example *Pseudomonas aeruginosa* takes up tellurite and reduces it to elemental tellurium, which deposits and results in a dramatic darkening of cells (Chua et al. 2015). The biogenic silica is used as structural material for skeletons in siliceous, Radiolaria, and diatoms.

Interestingly, As compounds, particularly organic ones, play an important role in many organisms, for instance arsenic-containing natural products are found in various terrestrial as well as aquatic species (Řezanka and Sigler 2008). Arsenobetaine is predominately found in the arsenic accumulating mushrooms *Agaricus placomyces*, *Agaricus haemorrhoidaius*, and *Sarcosphaera coronaria*. A major arsenic compound, dimethylarsinic acid, is found in another mushroom, *Laccaria amethystina* (Byrne et al. 1991). In the bacteria from hot spring biofilms, As(III) is used as an electron donor for

anoxygenic photosynthesis (Kulp et al. 2008). Similarly, selenium-accumulating microorganisms including cyanobacterium spirulina have shown promise as food supplements and as a source of nutrition, especially in developing countries.

Metalloid Uptake and Transport Mechanism

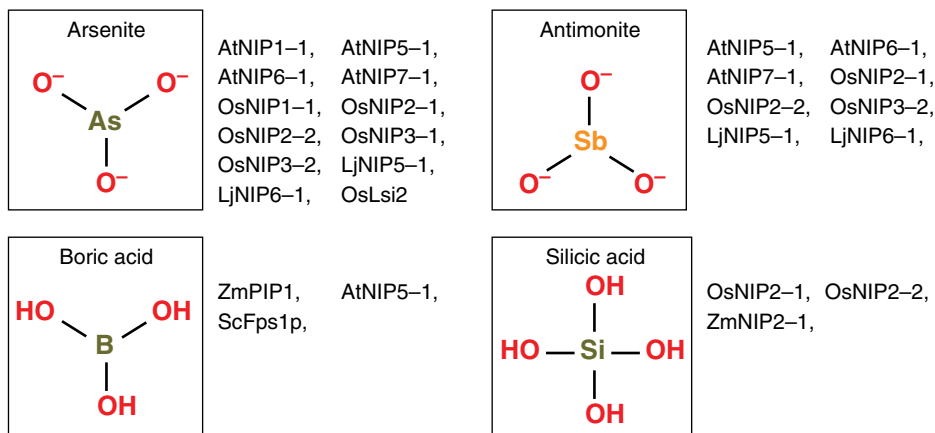
All living organisms exhibit substantial variations in metalloids, which are essential for active metabolism. To maintain the metalloid homeostasis nodulin 26-like intrinsic proteins (NIPs) a particular class of aquaporins (AQPs) play a vital role (Deshmukh and Bélanger 2016; Mitani-Ueno et al. 2011). The AQPs transport water and many other small uncharged molecules across membranes at the cellular level in bacteria, yeast, amphibians, plants, and mammals (Figure 1.1a). AQPs are found in almost all living organisms. Several AQP encoding genes including NIPs and glycerol uptake facilitator (GlpF) implicated in metalloids transport have been identified and characterized. Sanders et al. (1997) identified a mutant of GlpF in *Escherichia coli*, which is resistant to antimonite, Sb(III). GlpF mutant also exhibits a 90% decrease in arsenite uptake in *E. coli* (Figure 1.2a). Fps1p is the homolog of GlpF also involved in osmoregulation in yeast (Lin et al. 2006). Fps1p mutant is resistant to As(OH)₃ and Sb(OH)₃, while the cells overexpressing Fps1p are hypersensitive to As(OH)₃ and Sb(OH)₃ compared to wild-type cells (Wysocki et al. 2001).

Five genes (arsRDABC) have been implicated in As detoxification in *E. coli* and three genes in *Sinorhizobium meliloti* (Figure 1.2a). Arsenite, As(V), induces the arsR expression which then activates the expression of arsC, which encodes arsenate reductase. The arsD encodes arsenate As(III)-binding metallochaperone which facilitates As(III) to the As(III) extrusion pump, encoded by arsA and arsB. Collectively these genes exhibited increased resistance to As(V) and Sb(V) in *E. coli* (Figure 1.2a) (Carlin et al. 1995). Similar to the Ars cluster in *E. coli*, the yeast harbors three genes implicated in As(V) detoxification. ACR1 codes for an As-responsive transcription factor, which activates the expression of the ACR2 and ACR3 genes. ACR2 codes for cytosolic arsenate reductase (Acr2p) and produce As(III), while ACR3 codes for an H[±] antiporter (Acr3p) that facilitates the extrusion of As(III) (Figure 1.2a) (Wysocki et al. 2001).

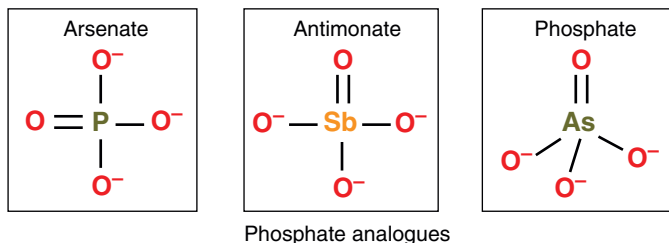
In plants, As(III) is transported by phosphate transporters, which quickly reduce it to As(V). As(III) is also transported through OsNIP2;1/Lsi1 in rice roots which is a member of the NIP subfamily of AQPs (Figure 1.2b) (Mitani-Ueno et al. 2011). The size and structure of As(V) is similar to silicic acid. Hence the transport of As in the root to shoot of rice is mediated mainly by the silicon transporter (Ma et al. 2007). OsNIP2 mutants exhibited germanium resistance which suggests that OsNIP2 also transports germanium. Several researchers have demonstrated that NIPs subfamily facilitates transport of As(OH)₃, Sb(OH)₃, boron, silicon, antimonite, tellurium and germanium (Figure 1.1a,b; Figure 1.2b). OsNIP2;1 and OsNIP2;2 permeable to both silicic acid and As(V), while OsNIP1;1 and OsNIP3;1 transport As(V) but not to silicic acid. Hence, MIPs show selectivity among various metalloids (Figure 1.2b) (Bhattacharjee et al. 2008). The mammalian aquaporins AQP3, AQP7, and AQP9 have also been known to conduct As(OH)₃ (Figure 1.2a) (Liu et al. 2002).

Plants absorb the boron from the soil in the form of boric acid. AtBOR1 is an efflux transporter of boron responsible for boron transport and loading into xylem of

(a) Solutes transported by MIP channels



(b) Solutes transported by phosphate transporters



(c) Solutes transported by bicarbonate transporter homologs

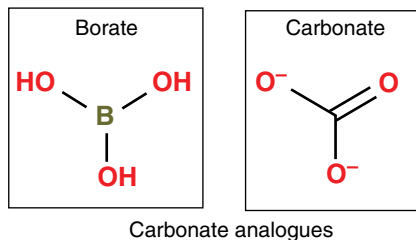


Figure 1.1 Metalloids transported with different transporters. (a) The MIPs facilitate the transportation of Arsenite, Antimonite, Boric acid, and Silicic acid (metalloids) across the cell membrane in bacteria, yeast, and plants. Abbreviations: At, *A. thaliana*; Lj, *L. japonica*; Os, *O. sativa*; Sc, *S. cerevisiae*; Zm, *Z. mays*; Fps, fdp1 suppressor; NIP, nodulin26-like intrinsic protein; PIP, plasma membrane intrinsic protein. (b) The structure of oxyanions of metalloids which are transported by phosphate and bicarbonate transporter homologs. Arsenite, $\text{As}(\text{OH})_3$, and antimonite, $\text{Sb}(\text{OH})_3$, can be oxidized to oxyanions arsenate, H_2AsO_4 , and antimonate, H_2SbO_4 . (c) Boric acid, $\text{B}(\text{OH})_3$, a carbonate analogue, is a weak acidic form at low pH but converted into borate, $\text{B}(\text{OH})_4^-$, at increasing pH, which is transported by bicarbonate transporter homologs, like BOR1. The figure was based on the information provided by Bienert et al. (2008).

Arabidopsis roots for transport into shoots. *A. thaliana* bor1-1 mutant is not able to transport boron from roots to shoots. The growth of shoots is also inhibited in the bor1-1 mutant (Figure 1.2b; (Takano et al. 2006; Miwa et al. 2007). *A. thaliana* genome contains six homologs of AtBOR1. AtBOR1 homologs also found in organisms such as

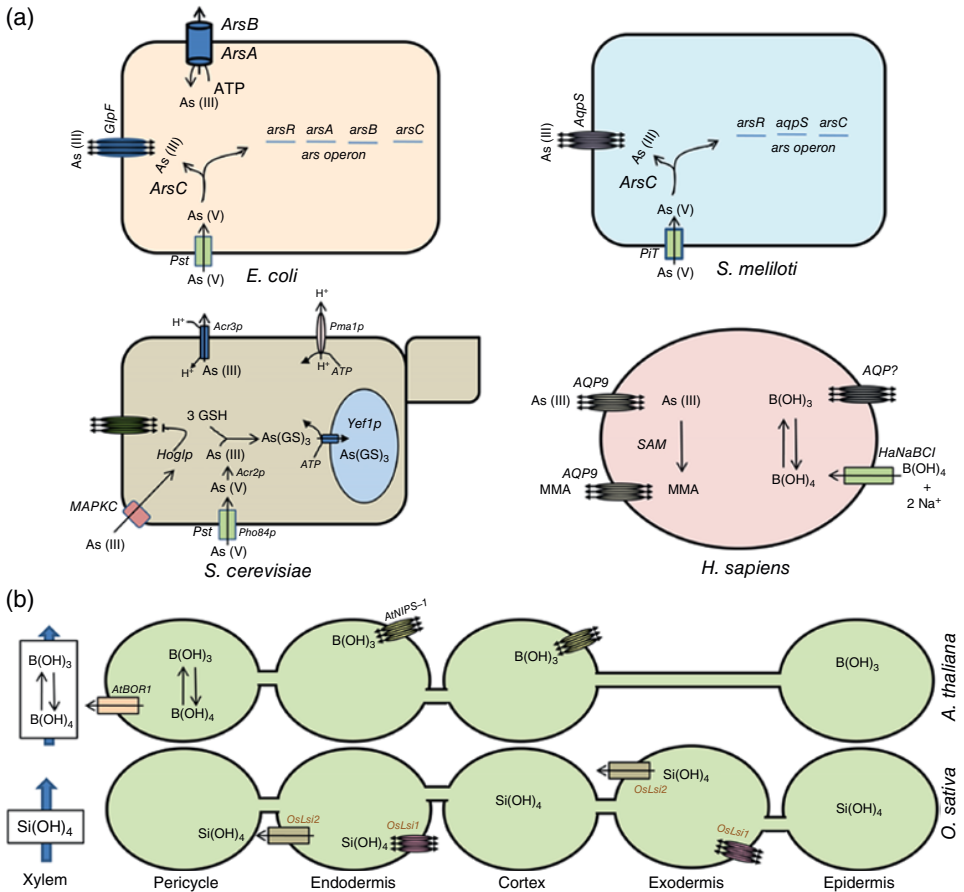


Figure 1.2 Metalloid uptake and transport system. (a) MIPs implicated in uptake, transportation, and extrusion of toxic metalloids outside of cells in *E. coli*, *S. meliloti*, *S. cerevisiae*, and *H. sapiens*. *E. coli*, *S. meliloti*, and *S. cerevisiae* have an As resistance (*ars*) operon or gene clusters. While borate, $B(OH)_4^-$, uptake catalyzed by Na^+ by HsNaBC1 and aquaglyceroporin protein channel the boric acid, $B(OH)_3^-$. (b) The uptake and transportation of essential (boron) and beneficial (silicon) metalloids in *A. thaliana* (At) and *O. sativa* (Os) from the soil to epidermis, then epidermis to xylem and finally through xylem transport to the shoot. The figure was based on the information provided by Bienert et al. (2008).

mammals (NaBC1), yeast (YNL275w), lotus (LjNIP5;1, LjNIP6;1), maize (ZmPIP1, ZmNIP2;1), and rice (OsBOR1, bicarbonate transporters) (Figure 1.1a–c, and Figure 1.2b) (Park et al. 2004; Nakagawa et al. 2007; Takano et al. 2007). Boron transporters also identified and characterized from *Vitis vinifera* and *Citrus macrophylla* (Pérez-Castro et al. 2012; Cañon et al. 2013). In addition to ScBOR1, ScDUR3, and ScFPS1 are implicated in boron transport and tolerance in yeast. HsNaBC1, which is the homolog of BOR1, improves cell proliferation in mammals when boron concentrations are low. HsNaBC1 catalyzes the uptake of borate across the plasma membrane into the cell (Figure 1.2a) (Park et al. 2004; Henderson et al. 2009). Several AQPs are involved in boron transport in plants. AtNIP5;1 belongs to the aquaporin family, which facilitates boric acid transport in *Arabidopsis*. Under boron-deficient conditions,

AtNIP5;1 shows an increased expression in *Arabidopsis* roots. The lack of AtNIP5;1 causes boron deficiency, resulting in reduced growth and small rosette leaves (Takano et al. 2002; Takano et al. 2006). Another aquaporin, AtTIP5;1, has also been reported in the vacuolar compartmentation of boron in *A. thaliana* and *Citrus macrophylla* (Figure 1.2b) (Martínez-Ballesta and Carvajal 2016).

The molecular mechanism of metalloid transport is poorly understood. These transporters play an essential role in metalloid homeostasis in plants; however, it is unclear whether other MIPs also participate in metalloid transport in animals and plants. The above-mentioned studies demonstrate that metalloid transport proteins are conserved in all kingdoms of life. Mutants had defective AQP proteins, which is exhibited by an impaired uptake or extrusion of metalloids. Overlapping substrate specificities of AQP proteins to many metalloids might provide the key to the identification of potential molecular networks involved in metalloids homeostasis. The elucidations of physiological roles of other AQP proteins advance our understanding of metalloid homeostasis in bacteria, yeast, animals, and plants.

Metalloid Toxicity and Tolerance Mechanisms

Plants acquire several protective mechanisms pertaining to physical, biochemical, and molecular adaptations in order to sustain themselves while under diverse biotic and abiotic stresses. The perception of external and internal stimuli and the transfer of information through signaling networks is the key step that turns on the appropriate response. This activates the expression of specific genes, resulting in changes concerning physiological and cellular processes surviving harsh environments (Sarwat et al. 2013). The signaling pathway such as mitogen-activated protein kinase (MAPK), ROS, phosphorylation cascade, calcium ions, nitric oxide and hormones signaling play an important role during heavy metal and metalloids stress. Tyrosine kinase-like (TKL), CT10 regulator of the kinase (CRK), wall-associated kinases (WAK), and receptor-like cytoplasmic kinases (RLCKs) are the main kinases which are up-regulated in As stress. These signaling pathways change the metabolic pathways leading to changes in cell response to survive metalloids toxicity. In general, metalloid toxicity affects various physiological processes in biological systems (Islam et al. 2015). Metalloid toxicity leads to DNA damage, impairment of DNA repair mechanisms, increases in the oxidative system, and inhibition of protein folding and function. Adaptive responses include significant changes in the expression of membrane transporters involved in the uptake, translocation, and sequestration of metalloids (Bhattacharjee et al. 2008; Bienert et al. 2008). Other typical adaptive responses include altered export of the metalloid out of the cell, storage of the metalloids in intracellular organelles, and reduced import of metalloid-binding proteins and peptides. Similarly, increased expression of genes related to superoxides, peroxides, dismutases, and heat-shock proteins have also been observed to be associated with metalloid stress tolerance. Transcriptomic studies demonstrated that genes involved in the oxidative stress, protein chaperones (heat shock protein and small heat shock protein), sulfur, and GSH metabolism highly induced in the metalloid toxicity which oxidizes proteins alter the cell wall composition and lignin. Also, several metal-binding proteins include metalloenzymes, metallothioneins (MTs), metal-activated enzymes, and many metal transporters, and storage; proteins are also

elevated in metalloid toxicity (Chen et al. 2003). MTs are a class of small cysteine-rich metal-binding proteins which primarily exist in the cytosolic compartment. They exist in all living organisms, ranging from prokaryotes to eukaryotes. MTs have been implicated in the development, senescence, and abiotic stress particular to the detoxification of heavy metals and metalloids (Islam et al. 2015). MTs are primarily associated with metal and metalloid homeostasis. A clear role of MTs has been demonstrated in animals; however, their exact roles in plants are poorly understood. The characterization of MTs in model organisms will advance our understanding of the biological response of metalloids and also biomonitoring of metalloid contamination in the environment (Morris et al. 1999).

Phytochelatin (PCs) are the small family of peptides that consists of a repeat of γ -Glu-Cys dipeptide and a terminal Gly (γ -Glu-Cys) $_n$ -Gly ([PC] $_n$), where “n” represents the range of two to five. Several other structural variants of PCs have been identified in plants, including (γ -Glu-Cys) $_n$ -Ser, (γ -Glu-Cys) $_n$ -Glu, and (γ -Glu-Cys) $_n$ - β -Ala (Wysocki et al. 2001). PCs are induced in response to many heavy metals and metalloids and synthesized from GSH by phytochelatin synthase (PC synthase). GSH is a precursor of phytochelatin synthesis, which is involved in metal detoxification, and also helps to cope with other abiotic and biotic stresses. The primary metalloid detoxification mechanisms in plants are subcellular compartmentalization, chelation, or extrusion from the plant body (Verbruggen et al. 2009; Adrees et al. 2015). Arsenic taken up as As(V) or As(III) leads to oxidative stress and also depletion of GSH, an essential antioxidant through the formation of As(III)-GSH complexes or As(III)-GS₃ and As(III)-induced PC synthesis. A significant strategy adopted to detoxify excess metalloids involves the synthesis of specific chelators to avoid binding to physiologically active proteins and to facilitate their transport into the vacuoles. GSH has the ability to bind with several metals and metalloids. GSH is synthesized by glutathione synthetase (GS) and gamma-glutamylcysteine synthetase (g-ECS). Excess GSH production is considered to enhance metalloid-binding capacity and enhance cellular defense against oxidative stress. Since GSH is the precursor molecule of PC, constitutive expression of GS and g-ECS leads to increased accumulation of PC under metal and metalloid stresses (Li et al. 2005). The methylation of As is another detoxification mechanism in plants because methylated As is less toxic compared to inorganic ones. Exposure to an As species, As(V), has shown upregulation of several methyltransferases. As is less methylated in plants compared to the animals indicating that methylation may not be the main mechanism for As detoxification in plants (Norton et al. 2008). Transcriptome analysis of arsenic stressed plants revealed up-regulation of abscisic acid, ET, and jasmonic acid signaling genes, which suggests a significant role of hormones under metalloid toxicity. Moreover, hormonal signaling also participates in GSH biosynthesis (Hirschi et al. 2000). There is a strong need to identify key target genes to completely understand these signaling pathways to produce plants which can perform well in metalloid-contaminated soil and water.

Conclusion

In recent years tremendous progress has been made to understand the molecular mechanisms of the uptake, transport, distribution, and detoxification of metal and metalloids. Furthermore, the identification and characterization of responsible genes will

be necessary for future work in medical, agriculture, and industrial fields. This knowledge can be exploited to develop better medicine, insecticide, antibiotics, and plant varieties which are resistant to metalloids. These can also reduce the uptake of metalloids and minimize the risk of toxicity through the food chain and enhance crop production in metalloid-contaminated soils and water. Recently, NIP subfamily proteins have been shown to facilitate the transportation of metalloids such as silicon, boron, arsenic, and antimony and play a crucial role in metalloid homeostasis. Thus, engineering of NIP encoding genes to reduce metalloids permeability is a convenient approach for preventing entry of metalloids into the food chain. A detailed understanding of the underlying molecular mechanisms of metalloid action may further improve tolerance against biotic and abiotic stresses and crop yield.

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