Chapter 14
Arsenic-Induced Stress and Mitigation Strategies in Plants

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Abstract Arsenic (As) is a toxic metalloid and inorganic arsenic is carcinogenic to humans and animals. About 50 ppb (μg/L) has been the standard for arsenic in drinking water in the USA since 1942. In the 1960s, published data from Taiwan indicated that arsenic in drinking water could cause skin cancer. In 2001, USEPA reduced the limit from 50 to 10 μg/L. According to WHO, the newly recommended guideline value for drinking water is 10 μg/L (Australia 7 μg/L). Arsenic enters in the plant system via contaminated irrigation water or soil. The toxic effect of arsenic in plants causes many metabolic disorders and often leads to death of the plants. Plants are equipped with multilayer defense weapons to encounter arsenic toxicity inside the system. Arsenic is analogous to phosphate and competes with phosphate molecules at transporter site. Once it enters in the plant cell, phytochelatins are ready for sequestration and accumulation of arsenic in vacuoles. Plants have enzymatic and nonenzymatic defense systems for arsenic-mediated oxidative damage. The chapter presents the latest research and findings for interaction between plant cell and arsenic.

Keywords Arsenic · Plants · Transporter · Defense · Methylation · Antioxidants · Phytochelatins

Abbreviations

AR	Arsenate reductase
DMA	Dimethyl arsenic acid
GR	Glutathione reductase
Grx	Glutaredoxin-linked arsenate reductase
MMA	Monomethylarsonic acid
TMAsO	Trimethylarsine oxide
Trx	Thioredoxin-coupled arsenate reductase

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1 Introduction

Arsenic (As) contamination in soil, air, and water is a rising apprehension around the world. Arsenic is a crystalline toxic and carcinogenic metalloid from 5A group of a transition element. It exhibits various oxidation states such as As^{+3} and As^{+5} due to $4s^24p^3$ outer electronic configuration (Matera and Le Hecho 2001).

It is a major element of the earth's crust and exposed to the environment by mining activities and groundwater in rivers (Drewniak and Sklodowska 2013). Sulfide ores of gold, iron, and copper contain arsenic, for example, realgar (As4S4), arsenopyrite (FeAsS), and orpiment (As2S3) are common arsenic minerals (Hoang et al. 2010). The solubility of arsenic in water arises many health concerns especially in Southeast Asia (Abbas et al. 2018). The US Environmental Protection Agency (USEPA 2001) and WHO set 10 $\mu g\ L^{-1}$ as the permissible limit of arsenic in drinking water. Natural sources as volcanic discharge, weathering of rocks, and hot springs and anthropogenic sources such as the use of pesticide, herbicide, wood preservative, mining, combustion, and industrial effluents are also considered as major factors for increasing arsenic contamination in soil, irrigation water, and food chain. Freshwater resources have arsenic concentration ranging from 0.15 to 0.45 $\mu g\ L^{-1}$, where <2 $\mu g\ L^{-1}$ arsenic has been reported in marine water (Ng 2005). Generally, soil arsenic ranges from 0.2 to 41 mg Kg^{-1}, but the continuous use of pesticide and herbicide causes arsenic pollution 400–900 mg Kg^{-1} in field soil (Kabata-Pendias and Pendias 2001).

2 Interaction Between Arsenic and Plants

The plants are exposed to arsenic through contaminated soil and water. The inorganic forms such as arsenite and arsenate are more toxic than monomethyl arsine, dimethyl arsine, arsenobetaine, and arsenocholine. Microbes can methylate arsenic in the form of monomethylarsonic acid (MMA), dimethyl arsenic acid (DMA), and trimethylarsine oxide (TMAsO), and all these are bioavailable for plants (Ye et al. 2012). The MMA and DMA are basic components of herbicide and pesticide used in agricultural practices (Williams et al. 2007). Methylated arsenic forms are also observed in root and shoot of maize, *Holcus lanatus*, *Trifolium pretense*, and rice (Zavala et al. 2008; Roychowdhury et al. 2018, 2019). The uptake of DMA may be correlated with phosphate deficiency in the nearby area (Abbas and Meharg 2008). Another speculated report shows arsenate in epidermis and arsenite in ground tissue, endodermis, pericycle, xylem, and phloem in the root of wheat and rice exposed to arsenate (Kopittke et al. 2013).

3 Bioavailability of Arsenic to Plants

Arsenic forms complex molecules with ferrous and aluminum in the soil. Arsenate is present in immobilized complex form than arsenite within the aerobic environment. The anaerobic conditions support the reduction of arsenate to arsenite; therefore, higher influx rate of arsenite is reported by iron plaques formed in roots of rice crop grown in water-logging fields (Yamaguchi et al. 2014). The solubility and bioavailability areas are affected by soil pH, speciation, and leaching; therefore, a limited amount of arsenic is available to plants. The arsenite (As^{+3}) is a more toxic and soluble form than arsenate (As^{+5}). According to a study, arsenite adsorbed on soil particle at pH 7.0 and arsenate at pH 4.0 (Pierce and Moore 1982). The reduction reactions in rhizospheric microorganism play a significant role in the bioavailability of arsenic to plant roots (Nearing et al. 2014). It has been reported by various researchers that root and shoot extract has 95% arsenite in plants grown in arsenate-rich medium (Carey et al. 2010). The genes involved in arsenic uptake are identified by researchers in different plant species.

4 Arsenic Uptake Mechanism in Plants

The uptake mechanism for arsenate and arsenite is different as arsenate enters via phosphate transporter system whereas arsenite through nodulin 26-like intrinsic protein (NIP) aquaglyceroporin or natural channels (Zhao et al. 2009). The arsenite is analogous to silicon due to the same tetrahedral and Pka value; therefore, silicon transporter Lsi1 (*NIP2;1*) also supports AsIII influx in rice roots (Ma et al. 2008). Figure 14.1 summarizes the newly identified arsenite (As^{+3}) transporters and their functions in plant cells. The similar structure of arsenate and phosphate activates phosphate transports to facilitate the transport of arsenate (Sharma and Travlos 2012). Recently traced phosphate transporters are AtPHT1;4, AtPHT1;7, OsPHT1, and PvPht1;3 reported in *Arabidopsis*, *Oryza sativa*, and *Pteris vittata* (LeBlanc et al. 2013; Kamiya et al. 2013; DiTusa et al. 2016; Roychowdhury et al. 2018, 2019). Monomethylarsonic acid (MMA), Dimethyl arsenic acid (DMA) and trimethylarsine oxide (TMAsO) are taken up by aquaglyceroporins and aquaporin *Lsi1* and *NIP2;1* in rice roots. The translocation rate of DMA is faster than inorganic arsenic in roots and shoots of rice (Carey et al. 2011).

5 Phytochemistry of Arsenic Toxicity

Arsenic is considered as an important toxic and stress factor in plants which leads to metabolic disorders during the transition of oxidation states. The toxicity appears in a symptom such as wilting of leaves, slow root growth and shoot growth, leaf

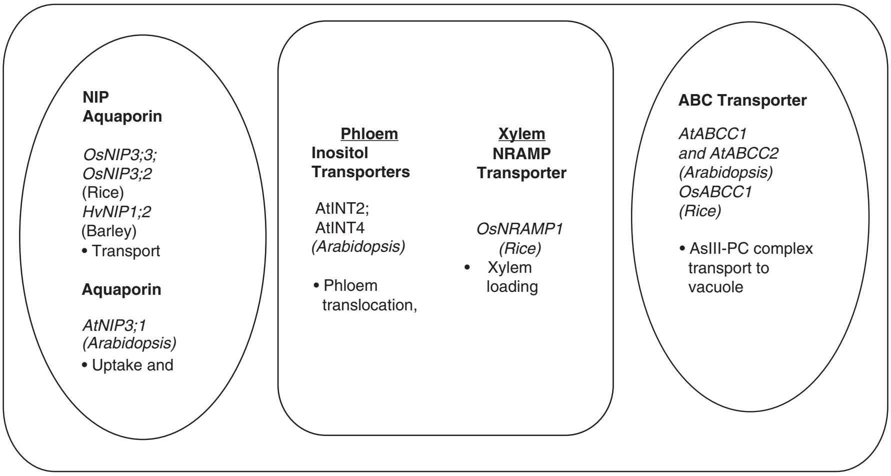

Fig. 14.1 Arsenite (As^{+3}) transporters and their functions in plant cells

necrosis, violet leaf color, and ultimately plant loss (Adriano 1986). Most of the arsenite is chelated with phytochelatins, but some amount of arsenic can affect the activity of enzymes and proteins due to affinity toward sulfhydryl groups (Oremland and Stolz 2003). Arsenate remains neutral, but methylated arsenic (DMA) can form dimethylarsinothioyl glutathione (DMAS-GS) with thiol groups residing in sulfur-rich plant cells of *Brassica oleracea*. Arsenate is analogous to phosphate; therefore, it can disrupt oxidative phosphorylation and production of ATP (Oremland and Stolz 2003). The replacement of phosphate with arsenate in ATP is known as aminolysis (Meharg and MacNair 1994). Fowler (1977) also reported that arsenate can replace phosphate in DNA molecule and consequently damage the nucleic acid of the organism.

6 Defense Against Arsenic in Plants

The plant copes with potential stress factors by developing stress resistance. This implies all morphological and physiological measures required to inhibit the stress (Sharma and Anita 2016). The following strategies can be differentiated according to the requirement:

1. Tolerance toward the stress factor without suffering great damage
2. Defense against the stress factor by suitable protective mechanisms
3. Reversion of the stress effect by repairing the damage which has occurred

Plants have genetically tolerant traits against high levels of arsenic. Potatoes, cabbage tomatoes, carrots, tobacco, rye, Sudan grass, and grapes are highly tolerant, whereas strawberries, corn, beet, and squash are moderately tolerant. Similarly, onion, cucumbers, and legumes show low tolerance against arsenic (Su et al. 2010). According to various studies, the conversion mechanism is less efficient in higher plants; therefore, numerous species of plants have inorganic soluble forms of arsenic accumulated in plant cells. Some specific plant species are reported as hyperaccumulator which can accumulate more than 1000 mg Kg^{-1} arsenic in their cells. *Agrostis tenuis*, *Agrostis stolonifera*, *Agrostis canina*, *Jasione montana*, *Calluna vulgaris*, *Holcus lanatus*, *Ceratophyllum demersum*, *Cheilanthes sinuata*, *Adiantum raddianum*, *Polystichum acrostichoides*, *Actiniopteris radiata*, *Pellaea rotundifolia*, *Nephrolepis cordifolia* (Eisler 1994; Srivastava et al. 2010), *Pteris vittata* (Ma et al. 2001), and *Pityrogramma calomelanos* are well-known hyperaccumulators of arsenic. *Pseudotsuga menziesii* is hyperaccumulator gymnosperm (Haug et al. 2004), whereas rice is considered as hyperaccumulator monocot angiosperm as 722 μg g^{-1} arsenic is accumulated in edible grains cultivated near mining areas (Okkenhaug et al. 2012). *Hordeum vulgare and Triticum aestivum* also store a small amount of arsenic within plant cell (Su et al. 2010).

6.1 First Line of Defense

6.1.1 Methylation

Once arsenic enters in the lower plant cell, the activated defense system leads to methylation and biotransformation for the conversion of inorganic arsenic into nontoxic organic forms such as monomethyl arsenic, dimethyl arsenic, arsenobetaine, and arsenocholine. The arsenic is methylated by Challenger's pathway, in fungi and microbes, but the pathway is still not clear in higher plant.

Algal cells have the gene for S-adenosylmethionine methyltransferase (ArsM) and ArsM proteins for methylation of arsenic (Qin et al. 2006). However, researchers identified AS3MT enzyme which is able to transfer thiol group from GSH to arsenite and leads to the formation of MMA and DMA (Hayakawa et al. 2005). The ArsM enzyme is also identified in *Cyanidioschyzon merolae* and *Prochlorococcus* for methylation of arsenic in higher plants (Ajees et al. 2012; Saunders and Rocap 2016).

6.1.2 Phytochelatins

The higher plants have distinct defense mechanism for detoxification and accumulation of arsenic at first checkpoint. The higher plants have thiol-rich, heavy-metal-binding polypeptide called phytochelatins for holding and accumulation of inorganic arsenic molecules immediately after the entry in to the cells (Zenk 1996; Roychowdhury et al. 2018, 2019). The arsenic binding with phytochelatins is also reported in *Rauvolfia serpentina*, *Arabidopsis* sp., and *Silene vulgaris* (Kamiya and Fujirawa 2011).

Their general makeup is two or more γ-glutamylcysteine units that repeat and have glycine as the terminal residue. The glutathione is a nonprotein thiol donor or precursor for phytochelatins. The glutathione produces phytochelatins in the presence of transpeptidase phytochelatin synthetase enzyme (Pawlik-Skwronska 2001). The synthesized phytochelatins are able to bind some metals in the cytosol, and the phytochelatin–metal complex is transported to the plant vacuole (Rauser 1990). It has been proven in X-ray absorption spectroscopy reports that both root and shoot cells of *Brassica juncea* and *Arabidopsis thaliana* have arsenite-tris-thiol complex, which is similar to As(III)-tris-glutathione (Castillo-Michel et al. 2011). The researchers suggest that the thiol group is contributed by glutathione and phytochelatins (Pickering et al. 2006). Zhao et al. (2003) reported that only 4.5% of total arsenic concentration is complexed as glutathione–arsenite–phytochelatin complex with phytochelatins in *Pteris vittata*. Similarly, only 1% arsenic is present as phytochelatin complex in arsenic hyperaccumulator, *P. cretica* (Raab et al. 2004). Kamiya and Fujirawa (2011) reported that the PC-deficient mutant (cad1-3) of *Arabidopsis* is highly susceptible to arsenate than control plants. Sequestration of As–PC complex in plant vacuoles and efflux depends on the phytochelatin synthetase and specific transporter located on the tonoplast such as PvACR3, AtABCC1, AtABCC2, OsABCC1, and ABCC transporters (Song et al. 2010). Arsenic accumulation and simultaneously high efflux rate of arsenite to surrounding medium also balanced the arsenic stress in the plant cell (Chen et al. 2016).

The latest report suggests that increased sulfur supply has a correlation with decreased arsenic concentration in rice plants (Dixit et al. 2015; Zhang et al. 2016; Nishida et al. 2016). Similarly, Zhang et al. (2016) also notified that sulfur-mediated downregulation of phosphate transporters and aquaporin gene and upregulation of ABC transporter and phytochelatin synthetase gene are important strategies for mitigation of arsenic in the plant cell (He et al. 2016; Yang et al. 2016). It has been reported that phytochelatins are able to complex and capture arsenic only in a limited range of concentration. Therefore, phytochelatins may not be the main source of detoxification of arsenite in arsenic hyperaccumulator.

6.1.3 Arsenate Reductase (AR)

Arsenate is analogous to phosphate and subsequently leads to replacement reaction and metabolic disorders. The enzyme arsenate reductase (Arsc) is able to reduce arsenate into arsenite using glutathione as an electron donor. The resulting arsenite is available for detoxification through phytochelatins. The arsenate reductase shows some variation in the active site of catalytic cysteine residue and reduction mechanism. Therefore, researchers have isolated and characterized various classes of arsenate reductase, such as thioredoxin-coupled arsenate reductase (Trx) and glutaredoxin-linked arsenate reductase (Grx). The arsenate reductase is evident in both prokaryotic and eukaryotic organisms (Mukhopadhyay et al. 2000). Table 14.1 shows the genes cloned and characterized by AR in different plant species. In plants

Table 14.1 The genes cloned and characterized for AR in different plant species

Genes	Plant	References
ATQ1 (AR)	Mouse-ear cress (*Arabidopsis thaliana*)	Chao et al. (2014) and Sanchez-Bermejo et al. (2014)
ACR3	Mouse-ear cress (*Arabidopsis thaliana*)	Ali et al. (2012)
ScACR3	Rice (*Oryza sativa*)	Duan et al. (2011)
AtACR2	Mouse-ear cress (*Arabidopsis thaliana*)	Duan et al. (2007)
OsACR2	Rice (*Oryza sativa*)	Duan et al. (2007)
HlAsr	Velvet grass (*Holcus lanatus*)	Dhankher et al. (2006)
PvACR2	Chinese brake (*Pteris vittata*)	Ellis et al. (2006)

also arsenate reductase is isolated from the root extract of hyperaccumulator *Pteris vittata*.

6.2 Second Line of Defense

Another form of arsenic toxicity is oxidative stress due to the production of reactive oxygen species (ROS) during the conversion of oxidation state. Some ROS such as superoxide anions, hydrogen peroxide (H_2O_2), and hydroxyl radicals cause damage to cell components (Gill and Tuteja 2010). These ROS are also developed during the methylation of arsenite within plant cells (Zaman and Pardini 1996). Plants which are exposed to severe stress show increased susceptibility to photo-inhibition with subsequent development of chlorosis (Cenkci et al. 2010). Although generation of ROS is a common phenomenon of electron transport system in plant cells, addition of liberated free electron during conversion of As^{+5} to As^{+3} (Sharma 2012), electron leakage, or inhibition of enzymes related to electron transport system are other ways of ROS generation in plant cells exposed to arsenic (Talukdar 2013). Sometimes hydrogen peroxide and superoxide anions react with each other during Haber–Weiss and Fenton reaction and consequently form highly damaging ROS called hydroxyl radical. The hydroxyl radical immediately attacks DNA and protein and initiates lipid peroxidation of membranes (Fenton 1899).

These reactive oxygen species are highly reactive and destructive for many biological reactions. Plants have specified enzymatic and nonenzymatic components to detoxify arsenic-induced reactive oxygen species. In response to the creation of ROS, plants synthesize enzymatic and nonenzymatic antioxidants. The nonenzymatic antioxidant molecules are L-ascorbic acid, reduced glutathione (GSH), α-tocopherols, and carotenoids, whereas antioxidant enzymes are superoxide dismutase (EC 1.15.1.1), ascorbate peroxidase (EC 1.11.1.11), peroxidase (EC 1.11.1.7), catalase (EC 1.11.1.6), glutathione reductase (EC 1.6.4.2), and arsenate reductase (give the EC1.20.2.1) (Sharma 2013).

6.2.1 Enzymatic Antioxidants

The singlet oxygen is the first excited state of oxygen produced in photosystem II (PSII) electron transfer reaction of the chloroplast. It is highly reactive and destructive to nearby biomolecules (Garg and Singla 2011). The superoxide anion (O_2^-) is produced during Mehler reaction and photooxidation reaction in chloroplast, mitochondria, glyoxysome, and peroxisome (Alscher et al. 2002). The enzyme superoxide dismutase (SOD)-mediated reduction of molecular oxygen produced superoxide radical. The consumption of oxygen takes place in cytochrome oxidase of mitochondria or reduction of singlet oxygen in flavoprotein region of NADH dehydrogenase during respiration. The superoxide may also develop through transfer of electron between ubiquinone to cytochrome C_1 region of the respiratory chain (Mubarak et al. 2016). Superoxide dismutase is associated with various metal cofactors: CuSOD and ZnSOD are located in cytosol, peroxisome, plastid, and root nodules; MnSOD is located in the mitochondria; and FeSOD is located in the plastids. Because SOD can degrade superoxide anions, it can play a very important role in the defense of cells upon stress (Fridovich 1995).

The dismutation of superoxide radical by superoxide dismutase (SOD) enzyme results in the generation of comparatively less toxic hydrogen peroxide. The catalase is a tetrameric heme-containing enzyme found in the peroxisomes, glyoxysome, cytosol, mitochondria, and root nodules to convert hydrogen peroxide into water and molecular oxygen in peroxisome (Sharma and Ahmad 2014).

$$O_2 + H_2O_2 \rightarrow H_2O + 1/2O_2$$

High catalase activity is reported in arsenic-tolerant and hyperaccumulator plants such as *Zea mays* L. and *P. vittata* (Mylona et al. 1998). There are several forms, or isozymes, of CAT like CAT-1 and CAT-2. These isozymes may respond differently under the same conditions (Horváth et al. 2002). The reaction occurs in the presence of ascorbate peroxidases (APX), and ascorbate acts as an electron donor for peroxidation reaction. Hydrogen peroxide converts in water and mono-dehydro-ascorbic acid within the chloroplast. A vast literature is available on arsenic-mediated oxidative damage and role of enzymatic antioxidant battery for defense against stress factor (Mylona et al. 1998; Hartley-Whitaker et al. 2001; Singh et al. 2006).

6.2.2 Nonenzymatic Antioxidant Molecules

As an antioxidant, ascorbic acid is located in apoplast cytosol and vacuole. Ascorbic acid can manage ROS through the direct elimination of superoxide anions, hydrogen peroxide, and hydroxyl radicals (Sharma 2012). It also acts as a secondary antioxidant due to the maintenance of the reduction of another plant antioxidant α-tocopherol (Conklin 2001) or indirectly through the action of ascorbate peroxidase (Asada 1992). Glutathione is composed of the amino acids, glutamate, cysteine, and glycine. It is, directly and indirectly, demanding in defense and detoxification within the plant system. Glutathione also acts as a precursor for phytochelatin (PC) synthesis (Kneer and Zenk 1992; Zenk 1996; Pawlik-Skwronska 2001). It also binds with reactive oxygen species in the presence of enzyme glutathione *S*-transferases (GSTs). A cyclic pathway of glutathione reductase (GR) regulated glutathione to glutathione disulfide (GSSG) and again glutathione during detoxification of ROS in plant species (Hameed et al. 2014; Roychowdhury et al. 2018, 2019). Glutathione reductase is the enzyme that, in conjunction with NADPH, catalyzes the reduction of GSSG to GSH.

$$\mathrm{GSSG} + \mathrm{NADPH} - \mathrm{GSH} + \mathrm{NADP}^{+}$$

Glutathione reductase has been detected in bacteria, yeast, plants, and animals. It is essentially responsible for maintaining the GSH levels in the plant cell exposed to arsenic. Thus, the advancement of the experimental studies shows various avenues of research in the field of arsenic toxicity and tolerance in plant species. Some knowledge gaps and future prospects are still present like transporter for DMA and MMA, which are still unknown. The role of sulfur and silicon supply for mitigation of arsenic toxicity in field practices required more research.

7 Conclusion

Arsenic is an important stress factor which can damage cellular metabolism and can lead to death of the plant. It is a transition element found in the inorganic form of arsenate and arsenite. It can hinder the biological process due to the interaction and inhibition of thiol groups of enzymes. During the conversion of their oxidative state, arsenic produces reactive oxygen species due to an imbalance between generation and elimination of ROS that leads to rapid oxidation reaction in plant cells. Oxidative stress causes damage to cell membrane lipid bilayer, fragmentation of peptide chain, and altered electrical charge, DNA damage and mutation, base degradation, and single-strand breakage. To minimize the damaging effect of ROS, plants have enzymatic and nonenzymatic defense systems including metal binding phytochelatins. The biochemistry and toxicology of arsenic are still complicated in higher plants.

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