Chapter 5
Plants Response and Tolerance to Arsenic-Induced Oxidative Stress

Anindita Mitra, Soumya Chatterjee, and Dharmendra K. Gupta

Abstract Arsenic (As) is a toxic metalloid of global concern derived from natural, geothermal, and anthropogenic sources. Arsenic has deleterious effects in all forms of life including plants. Between the two inorganic forms, the highly oxidized pentavalent arsenate (As^V) is prevalent in the aerobic environment, while the highly reduced trivalent arsenite (As^{III}) is the predominant form in an anaerobic environment. The main route of As^V uptake in plants is through the phosphate transporters, while As^{III} and methylated As species enter through nodulin 26–like intrinsic protein (NIP) or aquaglyceroporins. After entering into the plant cell As can severely impede plant metabolism which leads to various physiological disorder. Subsequently, growth of the plants is subdued, and it results in delaying or restraining accrual of biomass and induces loss of fertility, yield, and fruit production. Exposure to inorganic As in plants promotes oxidative stress by generating reactive oxygen species (ROS) during their conversion from As^V to As^{III}. Plants have a well-organized antioxidant defense system to combat As stress. In plants, As intoxication triggers the activation of enzymatic antioxidants like superoxide dismutase (SOD), ascorbate peroxidase (APX), catalase (CAT), glutathione reductase (GR), glutathione *S*-transferase (GST), and glutathione peroxidase (GPX); synthesis of nonenzymatic antioxidants, such as ascorbate and γ-Glu-Cys-Gly-tripeptide glutathione (GSH); and accumulation of anthocyanin in the leaves. As tolerance in plants is achieved by the production of phytochelatin following As exposure which is derived from GSH. This chapter aims to provide current updates about the molecular mechanism involved in uptake of the inorganic and organic species of As, their translocation, and the As-induced stress in plants with a special emphasis on oxidative stress.

A. Mitra (✉)
Bankura Christian College, Bankura, West Bengal, India

S. Chatterjee
Defence Research Laboratory, Defence Research and Development Organization (DRDO), Ministry of Defence, Tezpur, Assam, India

D. K. Gupta
Gottfried Wilhelm Leibniz Universität Hannover, Institut für Radioökologie und Strahlenschutz (IRS), Hannover, Germany

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5.1 Introduction

Arsenic (As) is a toxic metalloid. Naturally, it exists in four oxidation states (-III), (0), (+III), and (+V) (Rathinasabapathi et al. 2006). Mostly available chemical forms of As having diverse physicochemical properties are: arsenite (As^{III}), arsenate (As^{V}), trimethylarsine (TMA), dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), arsenosugars, arsenocholine (AsC), arsenobetaine (AsB) (Panda et al. 2010). Due to various factors including dumping of industrial wastes and dust from smelters, As contamination in soils is indiscriminate in many parts of the world (Chatterjee et al. 2017a). Depending on the redox status, inorganic arsenite or arsenate is primarily present in soil solution, which is the most phytoavailable form (Meharg and Hartley-Whitaker 2002). Among the inorganic As species, trivalent state of As is most toxic in comparison to the pentavalent state (Gupta and Chatterjee 2017), whereas the organic As has less toxicity than inorganic species (Chung et al. 2014). As^{V} is present in aqueous solution in the form of H_3AsO_4, $H_2AsO_4^{-}$, $HAsO_4^{2-}$, and AsO_4^{3}, whereas As^{III} exists in reducing form, for example, H_3AsO_3 in anaerobic groundwater (Panda et al. 2010). Arsenic may also associate in nature with several other metals like copper, cobalt, nickel, silver, and lead (Gupta et al. 2017).

Arsenic concentration usually varies from noncontaminated soil to contaminated soils from 10 mg kg^{-1} to 30,000 mg kg^{-1}, respectively (Adriano 1986; Vaughan 1993). Terrestrial plants grown in noncontaminated soil show less than 10 mg As kg^{-1} in tissues, but a typical threshold of 40 mg kg^{-1} of As has been reported from different tissues of crop plants (Matschullat 2000). High-affinity phosphate transporters help plants to readily take up arsenate (being an analogue of phosphate) from the soil (Meharg and Macnair 1992). Incorporation of As to the food chain via the groundwater-soil-plant system due to the use of high As contaminated groundwater in agriculture and bioaccumulation of As in crop plants are potentially hazardous to public health (Rahman et al. 2008; Patra et al. 2004).

Arsenic has no known biological function in plants. The exposure of plants to a higher level of As^{III} and As^{V} induces the production of reactive oxygen species (ROS) (Gupta et al. 2013a). Transformation of arsenate to arsenite within plant cell produces ROS directly through Haber–Weiss reactions (Mascher et al. 2002, Mithöfer et al. 2004). Heavy metal interaction with the antioxidant system generates oxidative stress in plants (Srivastava et al. 2004), either indirectly through disruption of electron transport chain (Qadir et al. 2004), creating disorders in the essential elemental metabolisms, or directly through ROS-mediated cellular damages, enhanced lipid peroxidation, and membrane leakage (Dong et al. 2006). Arsenic-induced negative effect in plant development is a well-known fact (Islam et al. 2015), where significant interspecific variation and also among cultivars within the same species (like, *Oryza sativa*) are reported (Lei et al. 2013; Lemos Batista et al. 2014; Begum et al. 2016). Shorter length and lower biomass, mainly in roots, accompanied by oxidative stress of a plant, signify arsenic triggered stress symptoms (Abercrombie et al. 2008; Shri et al. 2009; Talukdar 2011; Upadhyay 2014).

Plants have evolved several mechanisms to combat As-induced stress such as suppression of high-affinity phosphate/arsenate transporter and to bind the metal to extracellular exudates and cell wall constituents thereby reducing uptake, sequestration of metals in the vacuole, complexation of metalloids by different substances, activation or modification of plant metabolism, and synthesis of antioxidant enzymes (Duquesnoy et al. 2010). Antioxidative defense is achieved either by nonenzymatic antioxidants with low molecular mass (like GSH, glutathione, and ascorbate (AsA)) and enzymatic antioxidants like ascorbate peroxidase (APX), superoxide dismutase (SOD), glutathione reductase (GR), and catalase (CAT) (Finnegan and Chen 2012; Sharma 2012; Talukdar 2013a).

Although a number of reports are available on the morphological and physiological mechanism of As uptake and accumulation in plants, however, oxidative information on stress induced by As and related defense mechanisms are still poorly recognized. The present chapter is an attempt to focus on oxidative stress in plants induced by As and antioxidant defense mechanisms relating to As uptake, translocation, and phytochelatin (PC)-mediated As detoxification mechanism.

5.2 Uptake of Different Arsenic Species by Plant

5.2.1 Arsenate Uptake

The pathways of As uptake in plants have been extensively investigated by several authors (Tripathi et al. 2007; Zhao et al. 2009, 2010; Mitra et al. 2017a). Physiological and electrophysiological studies revealed that as the oxyanion structure of arsenate (As^V) is analogous to inorganic phosphate (Pi), both are transported through shared transporter in higher plants (Meharg et al. 1994; Gupta et al. 2011). During uptake of each phosphate ($H_2PO_4^-$)/arsenate ($H_2AsO_4^-$) molecule, two protons ($2H^+$) are co-transported across the membrane (Ullrich-Eberius et al. 1989). Although hundreds of phosphate transporters are recognized in higher plants, the PHT1 family of Pi transporter present in the roots is likely to be involved in As^V transport (Ullrich-Eberius et al. 1989; Wu et al. 2011). Studies reported that Pht protein transports As^V in As hyperaccumulators (Wang et al. 2002; Tu and Ma 2003; Cesaro et al. 2015), As-tolerant non-hyperaccumulators (Meharg and Macnair 1992; Bleeker et al. 2003), and also in As-sensitive non-accumulators (Esteban et al. 2003). However, different phosphate transporters present in hyperaccumulator plants show greater affinity for As^V than non-accumulator species of plants (Wang et al. 2002; Poynton et al. 2004). Double mutant *Arabidopsis thaliana*, for two high-affinity Pht1 isoform Pht 1;1 and Pht 1;4, was found to be resistant for arsenate than wild-type plants, which strongly supports the role of Pht 1;1 and Pht 1;4 in arsenate transport (Shin et al. 2004). Magnitude of phytotoxicity was greater following increasing uptake in soil with low levels of Pi as PHT transporters have higher affinity for phosphate than arsenate; therefore, As^{V} may outcompete Pi for entry through the root (Meharg et al. 1994). This can be overcome by applying larger amounts of phosphates that compete with arsenate at root surfaces to decrease uptake and phytotoxicity (Tu and Ma 2003; Titah et al. 2013). Some of the As-tolerant plants species such as *Holcus lanatus* and *Cytisus striatus* can grow in soil with higher As concentration without exhibiting any toxicity, which can be achieved by restricting the inflow of As by constitutive suppression of high-affinity phosphate/As^{V} transporter (Meharg and Macnair 1992; Bleeker et al. 2003).

5.2.2 Arsenite Uptake

In reducing environment, like swampy areas, arsenite (As^{III}) is the predominant As species (Marin et al. 1993; Chatterjee et al. 2017b). In plants, members of nodulin 26–like intrinsic proteins (NIPs) commonly known as aquaporins are known to involve in As^{III} transport through the root cells (Isayenkov and Maathuis 2008; Ma et al. 2008; Mitra et al. 2014). Additionally, NIPs also facilitate the transport of multiple uncharged solutes including glycerol, urea, ammonia, boric acid, and silicic acid, hence called aquaglyceroporins (Wallace et al. 2006) but impermeable to water (Bienert et al. 2008). The other three plant aquaporins comprise tonoplast intrinsic protein (TIPs), plasma membrane intrinsic protein PIP), and small basic intrinsic protein (SIPs) (Chaumont et al. 2005; Maurel et al. 2008). In contrast to arsenate, arsenite uptake is repressed by glycerol and antimonite instead of phosphate (Zhao et al. 2009). Aquatic macrophytes take up As either through phosphate transporter by active transport or passively through aquaglyceroporins and/or physicochemically adsorb in the root (Rahman and Hasegawa 2011; Mitra and Chatterjee 2016).

Ma et al. (2008) have isolated an arsenite transporter OsNIP 2;1, also known as *Lsi1* in the rice root, which primarily transports silicon. Efflux of arsenite directed from the root toward xylem is mediated by another arsenite transporter *Lsi2* also described by Ma et al. (2008). Role of *Lsi2* gene was confirmed from the observation of *Lsi2* mutant rice species in which As^{III} accumulation was found much lower in the shoots or xylem sap in comparison to those xylem sap of wild species (Ma et al. 2008). Recently, two transporters OSNIP 3;3 and HvNIP1;2 have been reported to involve in As^{III} transport in the yeast cell (Katsuhara et al. 2014).

5.2.3 Uptake of Organic Species of Arsenic

Organic forms of As such as MMA^{V} and DMA^{V} are in very small proportion in soil and may derive from the previous application of arsenical pesticides and herbicides or may be synthesized by the microorganism. The organic As compounds are less efficiently taken up by plants than that of inorganic As species (Carbonell-Barrachina et al. 1998; Raab et al. 2007). Very little information is available about the mechanism involved in the uptake and transport of methylated As species by plants. In aquatic plants, As^{III} is transported passively through aquaglyceroporin channel in the form of dimethylarsinic acid (DMAA) and monomethyl arsinic acid (MMAA) (Rahman and Hasegawa 2011). The aquaporin *OsLsi1* is involved in the uptake of MMA^V, and the loss of function in rice *OsLsi1*led to an 80% reduction in MMA^V uptake and 50% for DMA^V compared to wild species (Li et al. 2009). Although rate of uptake of MMA^V and DMA^V by plant roots occurs very slowly than that of arsenate or arsenite (Abbas and Meharg 2008; Li et al. 2016), greater mobility of MMA^V and DMA^V was found within the plant tissue than that of inorganic As species (Li et al. 2009; Carey et al. 2010,2011). Involvement of *OsLsi1* was confirmed in the uptake of organic As species, but no role is played by *OsLsi2* in plants in the efflux of the MMA^V and DMA^V (Li et al. 2009).

5.3 Translocation of Arsenic

Arsenic hyperaccumulators have greater mobility of As relating to translocation from roots toward shoots in comparison to non-hyperaccumulator. The less efficient translocation of As directing toward shoot from root tissue in non-hyperaccumulators is indicative of the low ratios of shoot As to root As concentrations (Burlo et al. 1999) and thereby justifying the phenomenon that the reduction of arsenate to arsenite occurs rapidly in roots, following complexation with thiols and insulation within the root vacuoles. In *A. thaliana* knocked out *AtACR2* gene (arsenate reductase) using RNAi leads to increased accumulation of As in the shoots (Dhankher et al. 2006). Blocking *AtACR2* leads to more arsenate available for xylem transport to the shoots from root via the phosphate transport pathway. Among all As species, DMA is translocated more proficiently from roots to shoots, although root uptake is less efficient compared to other As species (Raab et al. 2007). The inorganic form in which As is transported from root to shoot is questionable. Some authors reported that arsenite prevalently exists in the xylem sap, accounting for 60–100% of the total As (Zhao et al. 2009). *A. thaliana* mutant for phosphate transporter, defective in xylem loading of phosphate but showed no effect on As distribution to the shoots (Quaghebeur and Rengel 2004), suggests that As is not loaded into the xylem as phosphate analogue arsenate. Duan et al. (2005) also support that majority of the transported As is in arsenite form as AR activity was solely confined within the roots. In contrary, a number of reports showed that arsenate is present in the xylem as it is being loaded by PHT protein, into the xylem vessels (Catarecha et al. 2007; Zhao et al. 2010; Mendoza-Cózat et al. 2011; Wu et al. 2011). However, methylated As is detected very meager amount in xylem sap as DMA was found in xylem sap of cucumber (*Cucumis sativus*) and tomato plants only at <4% of the total As (Mihucz et al. 2005; Xu et al. 2007).

5.4 Arsenic-Induced Oxidative Stress in Plants

Arsenic exposure leads to abiotic stress which emanates to oxidative stress at cellular level by producing reactive oxygen species (ROS) (i.e., singlet oxygen, $^1O_2$; superoxide, $O_2^{\bullet -}$; hydrogen peroxide, H_2O_2; hydroxyl radical, $OH^{\bullet}$) that surpass the pace of their metabolism (Gill and Tuteja 2010; Mallick et al. 2011). Arsenic induces ROS production by blocking the activity of key enzyme system along with electron drainage during As^{V} to As^{III} conversion (Sharma 2012). The reduction of As^{V} is succeeded by methylation of inorganic As, a redox-directed process that may also give rise to ROS (Zaman and Pardini 1996). Methylated As species such as dimethylarsinic acid (DMA) causes iron-dependent oxidative stress which is based on iron released from ferritin. DNA damage takes place by reactive oxygen species which are generated directly from DMA^{3+} (Shi et al. 2004). ROS induces chain like peroxidation of polyunsaturated fatty acid in membrane lipids, damaging the proteins, amino acids, nucleotides, and nucleic acids (Noctor et al. 2016; Moller et al. 2007). Malondialdehyde (MDA), a product of lipid peroxidation resulting from membrane damage, is considered as an indicator of oxidative stress (Shri et al. 2009). Lipid peroxidation also increases thiobarbituric acid-reacting substances (TBARS) and H_2O_2 content in *H. lanatus* (Hartley-Whitaker et al. 2001), *Trifolium pratense* (red clover) (Mascher et al. 2002), *Vigna radiata* (mung bean) (Singh et al. 2007), and *Oryza sativa* (rice) (Shri et al. 2009). In *Pteris vittata* and *Sphagnum nemoreum*, As exposure leads to alteration of chloroplast membrane structure and subsequent rupture and enlargement of thylakoid membranes (Simola 1997; Li et al. 2006). Elevated and nonmetabolized cellular H_2O_2 is responsible for severe damages to biomolecules such as cellular lipids and proteins and consequent interruption of key cellular functions (Gill and Tuteja 2010; del Río 2015).

Differential modulation in the antioxidant system occurs in the plant under As stress as reported from several studies (Dwivedi et al. 2010; Tripathi et al. 2012). Activated antioxidant system and increased levels of PC production in different plants like *Hydrilla verticillata* and *C. demersum* suggest that specific proteins are responsive to As stress (Srivastava et al. 2007; Mishra et al. 2008; Dave et al. 2013a). Similarly, enhanced activities of antioxidative enzymes such as superoxide dismutase, APX, peroxidase (POD), and GR indicate As exposure generates oxidative stress (Shri et al. 2009; Dave et al. 2013b). The first line of defense in higher plants includes activation of CAT, SOD isozymes, and the AsA-GSH cycle in response to As stress. To mitigate the negative effects of excess ROS, the plant defense system functions in a coordinated manner under adverse environmental circumstances in the different cell compartments and organs (Airaki et al. 2015). However, following exposure to higher As level, ROS production reaches too high that the antioxidant defense mechanisms may be devastated, leading to cellular damage which ultimately leads to cell death (Van Breusegem and Dat 2006).

5.5 Arsenic-Induced Metabolic Alterations in Plants

The potential of As^V to substitute for Pi and the aptness to bind and alter the activities of fundamental enzymes and hazardous effects of ROS have a direct and significant effect on plant metabolism. Arsenic vulnerability leads to changes in the levels of various compounds like starch and sugars and modulates the activities of the key enzymes of interrelated metabolic pathways like RNase, protease, and leucine aminopeptidase in plants (Mishra and Dubey 2006; Choudhury et al. 2010). Productivity was severely hindered due to significant disruption of carbohydrate metabolism in plants growing in As-contaminated soil and may be due to the rise in the level of soluble sugars in the tissues, especially sucrose and hexoses, the end products of the photosynthesis (Mishra and Dubey 2013). A comparative transcriptomic analysis revealed variation in the lipid metabolism and phytohormone signaling in plants under $As^{(III)}$ stress (Yu et al. 2012).

To encounter the ROS generated by the As exposure, plants need to produce sufficient metabolites, and such response predominantly impacts on carbon, nitrogen, and sulfur metabolism of plants (Finnegan and Chen 2012). Promoting accumulation of AsA is the main effect of As^V on plant carbon metabolism to reinforce protection against ROS (Srivastava et al. 2005; Singh et al. 2006; Khan et al. 2009). However, genomic analysis on carbon metabolism proved no changes in transcriptional profiles as observed both in *Arabidopsis* and *Oryza sativa* (Abercrombie et al. 2008; Norton et al. 2008; Chakrabarty et al. 2009). Exposure to As^V, As^{III}, and MMA^{III} are able to interfere the photosynthetic process in different ways like decrease in chlorophyll content (Duman et al. 2010; Gupta et al. 2013b) or Photosystem II activity (Stoeva and Bineva 2003) which may perturb photosynthetic electron flow across the membrane of thylakoid sinking the efficiency to produce ATP and NADPH, both of which are essential to fuel the carbon fixation reactions.

Arsenic exposure has the potential to strongly reduce the nitrogen fixation in alfalfa roots as observed when alfalfa growing in As-contaminated soil had less than half of the total number of root nodules formed in the absence of As (Carrasco et al. 2005; Pajuelo et al. 2008). Transcriptomic analysis by Lafuente et al. (2010) reported that As^{III} exposure prevents the gene expression required for early nodule development. As a result, soil contaminated with As shows lower potential for N_2 fixation in ecosystem involving legume-rhizobium symbiosis as evidenced from alfalfa. Considerable changes in the amino acid pool have been reported to occur after As exposure (Dwivedi et al. 2010; Pavlík et al. 2010). A number of the study reported that the RuBisCo, an abundant protein having the capacity to store nitrogen, can be a target for disruption in As^V treated plants (Duquesnoy et al. 2009; Ahsan et al. 2010; Bona et al. 2010). Thus, As exposure that accompanies lower protein content in plants may be due to As-induced diminution in carbohydrate metabolism that would deter the biosynthesis of amino acids (Finnegan and Chen 2012).

The major As detoxification pathway, that is, binding of As with the thiol group of GSH and PC, indicates the crucial importance of sulfur metabolism regulating plant survival in As-contaminated soils. Adequate supplies of the GSH building blocks Glu, Cys, and Gly are required immediately after As exposure. According to Munoz-Bertomeu et al. (2009), cysteine is the limiting substrate for GSH biosynthesis in Arabidopsis. Decreasing cysteine pool following As exposure (Sung et al. 2009) signifies that higher Cys biosynthesis is needed to support GSH and PC generation that is also steered from sulfur metabolism (Finnegan and Chen 2012). Plants that overproduce the enzymes mediating GSH and PC biosynthesis were found to maintain higher levels of nonprotein thiols than wild species (Guo et al. 2008). Sulfur is acquired from the soil in the form of sulfate to sustain biosynthesis of GSH and PC at high rate. Both species of As induces the expression of sulfur transporter genes. Norton et al. (2008) observed that in rice subsequent to As^{V} treatment upregulation of five sulfate transporter genes, but Sung et al. (2009) reported that in *Arabidopsis* at least one gene is upregulated. Similarly, As^{III} treatment in *B. juncea* and rice seedlings at least one sulfate transporter gene was found to be upregulated (Chakrabarty et al. 2009; Srivastava et al. 2009). However, Takahashi et al. (2011) suggested that small number of transporters may be adequate to direct the mobility of sulfate from the soil toward the plants root.

5.6 Enzymatic Antioxidative System

5.6.1 Superoxide Dismutase

Superoxide dismutases or SODs are metalloenzymes that play key roles in protecting cells from oxidative stress by catalyzing the dismutation of $O_2{\bullet}-$ to H_2O_2 (Li et al. 2017). Superoxide dismutase enzyme requires metals as cofactors. SOD associated with Cu/Zn is found in the cytosol, plastid, peroxisomes, and root nodules. Mn-SOD is confined in the mitochondria, and Fe-SOD is localized in the plastids. In maize root, the proteomic analysis reveals Cu/Zn SOD as one of the highly responsive enzymes to As which is involved in cellular homeostasis during redox disturbance (Requejo and Tena 2005). SOD activity was found to significantly increase in response to As toxicity as evidenced from As hyperaccumulator and sensitive fern species (Srivastava et al. 2005), in maize (Mylona et al. 1998) and in the grass *H. lanatus* (Hartley-Whitaker et al. 2001); in contrast, high concentration of As inhibits the accumulation of SOD mRNA, thus reducing its activity (Gong et al. 2005; Gunes et al. 2009). The inhibition of SOD activity in response to high As exposure could be attributed to inactivation of the enzyme by H_2O_2 produced in different cellular compartments where SOD neutralizes $O_2^{\bullet -}$ (Khan et al. 2009). ROS- detoxifying enzymes are induced during abiotic stress but are also susceptible to oxidative damage (Dietz et al. 1999). Hydrogen peroxide itself is a highly reactive oxidizing agent that undergoes detoxification by CAT and the AsA–GSH cycle, both regulates H_2O_2 level (Shigeoka et al. 2002; Fig. 5.1). The equilibrium between

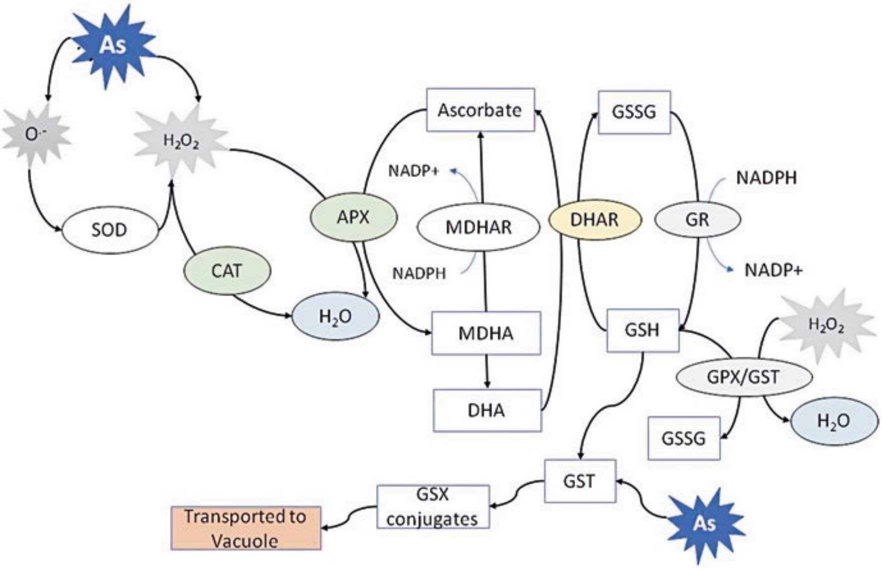

Fig. 5.1 Antioxidant defense system in plants after As exposure including enzymatic and nonenzymatic antioxidants (modified from Hasanuzzaman et al. 2012). As, arsenic; SOD, superoxide dismutase (in peroxisomes and plastids); *CAT* catalase (in mitochondria, peroxisomes, cytosol), *APX* peroxidase (in mitochondria, peroxisomes, cytosol, chloroplast), *MDHA* monodehydroascorbate, *DHA* dehydroascorbate, *DHAR* DHA reductase, *GSH* glutathione, *GSSG* glutathione disulfide, *GR* glutathione reductase (in chloroplast, mitochondria, cytosol), *GPX* glutathione peroxidase (in cytosol, chloroplasts, mitochondria, peroxisome, apoplast), *GST* glutathione sulfo-transferases (in cytosol)

the activity level of SOD and enzymes involved in AsA–GSH cycle and sequestration of metal ions promotes to maintain the steady-state level of O_2 and H_2O_2 and play crucial role by inhibiting formation of the ROS via the metal-dependent Haber–Weiss or Fenton reactions (Mittler 2002).

5.6.2 Catalase

Catalase is another H_2O_2 scavenger, located mainly in peroxisomes, glyoxisome, cytosol, mitochondria, and root nodules (Shugaev et al. 2011; Sharma et al. 2012; Su et al. 2014). This tetrameric, heme-containing enzyme degrades hydrogen peroxide promptly into water and molecular oxygen without utilizing cellular reducing supplements, thereby, protecting the cell by removing hydrogen peroxide by saving energy (Sharma 2012). Following As exposure, an upsurge of CAT activities was found in *Zea mays* (Mylona et al. 1998). As-tolerant Chinese brake fern (*P. vittata*) displays higher degree of CAT activity than As-susceptible slender brake fern (*P. ensiformis*) and Boston fern (*Nephrolepis exaltata*) (Srivastava et al. 2005). In contrast, As-induced deterioration of CAT has also been reported by Singh et al. (2007) in *Vigna radiata* (mung bean) and in moss, *Taxithelium nepalense*. The association of a heme prosthetic group with CAT has been established by the irreversible inhibition of CAT by cyanide, azide, and hydroxylamine, all of which are hemeprotein inhibitors (Anjum et al. 2016). In addition, existence of a thiol group close to the active center of CAT contributing in the CAT-mediated reactions has been proven from the inhibition of CAT by thiol inhibitors like aminotriazole and mercaptoethanol.

5.6.3 Ascorbate Peroxidase

An alternative mechanism to detoxify H_2O_2 by peroxidase through AsA-GSH pathway is found in higher plants that require AsA as a reductant to reduce hydrogen peroxide into water (Fig. 5.1; Mehlhorn 1990). APX are class I heme-peroxidases, which function as active scavengers of H_2O_2 in higher plants and prevail as cAPX or cytosolic isoforms, mit APX or mitochondrial isoforms, and also in microbodies as mAPX, including peroxisomal and glyoxysomal isoforms, and ch APX or chloroplastic isoforms (Miyake and Asada 1996; Yadav et al. 2014; Anjum et al. 2016). Isoforms are unlike in their molecular weight, stability, and substrate specificity optimal pH and have been refined and characterized from several plant species including *Pisum sativum* (Caverzan et al. 2012), *Camellia sinensis* (Chen and Asada 1989), *Gossypium hirsutum* (Bunkelmann and Trelease 1996), *Cucumis sativus* (Battistuzzi et al. 2001), *Nicotiana tabacum* (Madhusudhan et al. 2003), *Oryza sativa* (Sharma and Dubey 2004), *Olea europaea* (Lopez-Huertas and del Rio 2014), and *Ziziphus mauritiana* (Yadav et al. 2014). APX catalyzes the reduction of hydrogen peroxide into water and two molecules of monodehydroascorbate (MDHA; Noctor and Foyer 1998). APX activity has been upregulated after As exposure as observed in maize (Miteva and Peycheva 1999), beans (Stoeva et al. 2005), mung bean (Singh et al. 2007), and rice seedling (Shri et al. 2009).

5.6.4 Glutathione Reductase

Glutathione reductase (GR, NADPH: oxidized glutathione oxidoreductase) is another key component of ROS scavenging system, located predominantly in chloroplast but also in mitochondria and cytosol in a small amount (Gill and Tuteja 2010). Glutathione reductase reduces glutathione disulfide (GSSG) to GSH using NADPH as reducing equivalent (Fig. 5.1), and thus conserves the cellular redox levels by retaining a high ratio of intracellular GSH/GSSG and AsA/dehydroascorbate (AsA/DHA) during oxidative stress (Anjum et al. 2012). Two genes, namely GR1 and GR2, have been distinguished to encode GR in plants; both are expressed in plastids and mitochondria (Jozefczak et al. 2012). A range of biotic and abiotic stress factors such as heavy metals and metalloids affect the activity of GR in plants (Anjum et al. 2010, 2011a, b; Gill and Tuteja 2010). Unfortunately, there is paucity of reports about the active role of GR in higher plants during oxidative stress induced by As. It is found in rice seedlings that higher level of GSH required during As-induced oxidative stress is achieved by the activation of GR (Shri et al. 2009). Similar reports, that is, elevated level of GR activity has been observed in roots of *P. vittata*, *P. ensiformis*, and *Nephrolepis exaltata* after As exposure (Srivastava et al. 2005).

5.6.5 Glutathione Peroxidases

Glutathione peroxidase (GPX) belongs to large peroxidase family with broad substrate specificity, localized in cytosol, chloroplasts, mitochondria, peroxisome, and apoplast of plant cell, and catalyzes the reduction of H_2O_2, organic and lipid hydroperoxides consuming GSH pool as a reducing substrate, thereby protecting the cells from ROS (Anjum et al. 2010, 2011b). Some authors opined that, plant GPXs are actually peroxiredoxins (Prx) as they can use both GSH and thioredoxin (Trx) as electron donor, but Trxs act as more efficient reductants (Herbette et al. 2002; Iqbal et al. 2006; Navrot et al. 2006; Noctor et al. 2011). Millar et al. (2003) identified a family of protein isoforms called AtGPX1–AtGPX7 in *Arabidopsis* among which AtGPX1and AtGPX7 are present in chloroplast providing antioxidant protection and synchronizes salicylate, and ROS triggered plant immune responses (Chang et al. 2009). The other GPXs isoforms are found in the cytosol, mitochondria, and the endoplasmatic reticulum (Milla et al. 2003). Arsenate stress induced to increase the GPX activity in dose-dependent manner as observed in mung bean and in rice (Singh et al. 2007; Singh et al. 2015). A study carried out in *P. vittata* reported that a rise in GPX activity has occurred up to 20 mg kg^{-1} As and then declined with the increasing As concentration (Cao et al. 2004).

5.6.6 Glutathione S-*transferase*

Glutathione *S*-transferases (GSTs) found in plant cytosol are major phase II, ROS-detoxifying enzymes (Sheehan et al. 2001) and dependent on GSH for catalyzing the conjugation of GSH via the sulfhydryl group to diversified electrophilic centers of hydrophobic compounds (Marrs 1996; Fig. 5.1). This reaction renders the compound more polar and facilitates its transport to vacuole or apoplast (Mylona et al. 1998). GSTs perform versatile roles where GSH serves as a co-substrate or coenzyme (Ghelfi et al. 2011). Like other antioxidant enzyme GST activity increases in plants after As exposure (Mylona et al. 1998; Srivastava et al. 2005; Norton et al. 2008; Mokgalaka-Matlala et al. 2009; Chakrabarty et al. 2009). As for example, upregulation of at least 10 GST genes has been observed in rice in response to As^V exposure, while not more than two GST genes are downregulated (Norton et al. 2008; Chakrabarty et al. 2009). However, no noticeable changes in GST transcript were found in response to As^{III} (Chakrabarty et al. 2009), focusing that two inorganic As forms have differential effects on cellular metabolism.

5.7 Nonenzymatic Antioxidants

5.7.1 Ascorbate

Ascorbate (AsA) is the most abundant antioxidant in plants, present in cytosol, apoplast, and in the stroma of chloroplast. Synthesis of AsA occurs in the cytosolic region chiefly from the transformation of d-glucose (Hasanuzzaman et al. 2012). AsA reacts with a range of ROS such as H_2O_2, O_2• −, and $^1O_2$ and is the most important reducing substrate for the removal of H_2O_2 (Singh et al. 2006) and restore membrane-bound carotenoids and α-tocopherol via the AsA-GSH cycle in plant cells (Sharma 2012). In the AsA-GSH cycle, two molecules of AsA (reduced) are utilized by APX to reduce H_2O_2 to water with the concomitant generation of oxidized form MDHA that immediately disproportionates into DHA and AsA (Gapper and Dolan 2006) by MDHAR or ferredoxin with the electron donor NADPH in the chloroplasts (Gapper and Dolan 2006). Recycling of AsA (reduced) from dehydroascorbate (DHA) is a GSH-dependent pathway catalyzed by dehydroascorbate reductase (DHAR) that consumes NADPH as a reducing agent. A report from the study by Singh et al. (2006) showed that following As exposure an upsurge of AsA (reduced) concentration and the ratio of AsA/DHA occurs in the fronds of As-hyperaccumulator *P. vittata* and As-sensitive *P. ensiformis*.

5.7.2 Glutathione

The potential detoxification mechanism found in plants for combating heavy metal induced phytotoxicity is by synthesizing low molecular weight thiols having high affinity for the toxic metals (Bricker et al. 2001). GSH is one of the vital low molecular weight tripeptide thiol associated with sulfur and found as reduced (GSH) and oxidized (GSSG) forms. GSH takes part in a slew of cellular processes including defense against ROS, sequestration and complexation of heavy metals, control of cell division, in budding, and in transport and storage of reduced sulfur (Vernoux et al. 2000; Cobbett and Goldsbrough 2002; Freeman et al. 2004; Ogawa et al. 2004; Foyer and Noctor 2005; Mullineaux and Rausch 2005). Formation of GSH involves two ATP-dependent enzymes namely γ-glutamylcysteine synthetase (GSH1) and GSH synthetase (GSH2). In the first reaction, synthesis of γ-glutamylcysteine (γ-EC) occurs through a peptide bonding between the carboxyl group of glutamate and the amino group of cysteine by the catalytic action of GSH1. In the second reaction, ligation between glycine residue and γ-EC is catalyzed by GSH2 to form GSH. GSH1 plays major role in the regulation of GSH biosynthesis (Yadav 2010).

During As detoxification, coupling of the reduction of arsenate to arsenite and NADPH oxidation occurs where GSH (reduced) is serving as the electron donor for arsenate reductase (Ellis et al. 2006). In plants, As is transported as oxyanion arsenate which is reduced to arsenite and sequestered as thiol–peptide complexes in vacuoles. Transgenic *A. thaliana* overexpressing both arsenate reductase (arsC) and GSH1 together showed substantially greater As tolerance than GSH1 transgenic and wild-type plants (Dhankher et al. 2002). One protective role of GSH in plants to As exposure is relieving from ROS. Supplementation of exogenous GSH and cysteine to plants under As stress reduced oxidative stress was observed, and the growth of rice seedlings was restored (Shri et al. 2009). Another important role of GSH is to serve as a precursor for the synthesis of phytochelatins a set of novel heavy metal-binding peptides.

5.8 Role of Phytochelatin in Detoxification and Arsenic Tolerance

The most common method of detoxification of heavy metal/metalloid in plants is by synthesis of PC. PC is synthesized by the catalytic action of PC synthase (PCS) from GSH by transpeptidation of (γ-glutamyl-cysteinyl) n-glycine (Gasic and Korban 2007). PC has the capability of binding via sulfhydryl and carboxyl residues to a range of metals like Zn, Cu, Cd, as well as As (Gupta et al. 2013c). Studies support the occurrence of PCs throughout the plant kingdom, in gymnosperms, angiosperms, and bryophytes (Clemens 2006). As tolerance in As-non-hyperaccumulating plants is achieved through considerable increase in the production and procurement of GSH and phytochelatins (PC) following exposure (Schat et al. 2002; Grill et al. 2006). The presence of heavy metal ions and metalloid such as Pb, Cd, Hg, Ag, Cu, Zn, As, etc. is required for the constitutively expression of PCS gene (Vatamaniuk et al. 2004). The presence of As^{III}-GSH or As^{III}-PC complexes has been recognized in various plants such as Indian snakeroot (*Rauvolfia serpentina*), in perennial grass commonly known as Yorkshire fog (*H. lanatus*), *sunflower* (*Helianthus annuus*), *Indian mustard* (*B. juncea*), and in Cretan brake fern (*Pteris cretica*) (Pickering et al. 2000; Schmoger et al. 2000; Montes-Bayon et al. 2004; Raab et al. 2004). In sunflower plants (*H. annuus*), following As exposure, synthesis of 14 different As complexes have been reported including GS-As^{III}-PC_2, As^{III}-PC_3, As^{III}-$(PC_2)_2$, As^{III}-GS_3, and MMA-PC_2 (Raab et al. 2005). Schulz et al. (2008) reported that short chains of PCs instead of long chain dominate in As-tolerant plants. Study of cad1-3 mutant *A. thaliana*, lacking the functional enzyme for PC synthesis, ascertained the predictable role of PCs in As detoxification; the mutant was unable to produce functional PCs and was found to be more sensitive (10–20 fold) to arsenate than the wild-type plants (Ha et al. 1999). Finally, As is detoxified within root and shoot tissue vacuoles by sequestrating As^{III}-PC complexes (Tripathi et al. 2007) thus unable to interfere with the cellular metabolism (Mitra et al. 2017a). In rice leaves, PC-arsenite complexation restricts the mobility of As from leaves to grains (Mitra et al. 2017b). In *Arabidopsis*, ABC transporter MRP1/ABCC1 and MRP2/ABCC2 are involved in the transport of As^{III}-PC conjugates (Song et al. 2010). In rice, transcription-level upregulation of homologous ABCC2 transporter gene was found after As exposure

(Chakrabarty et al. 2009). A report of Mendoza-Cózat et al. (2011) has proven the presence of ABCC transporter in different plant species sharing homology with *Arabidopsis* ABCC1 and ABCC2 transporter. In non-hyperaccumulator plants, phytotoxicity is reduced by rapid formation of As-PC complexes and sequestration within vacuoles of root cells where acidic pH (5.5) is favorable to stabilize the complex following As uptake, thereby restricting the As transport from the root to shoot (Liu et al. 2010; Mendoza-Cózat et al. 2011). The predominating form in which As is transported from root to shoot is controversial. In sporophytes of *P. vittata*, As is directed to the shoot mainly as As^{V} form and accumulated in the fronds as As^{III} as reported by Zhao et al. (2003). In contrast, Duan et al. (2005) suggested that As is translocated mostly in reduced form (As^{III}) and thus supporting the restriction of AR activity within the roots. Dissimilar with non-hyperaccumulators, where most of As is detoxified by the formation of As-PC complexes, hyperaccumulators like *P. vittata* and *P. cretica* were found to store 60–90% of arsenic as arsenite (As^{III}) form in the vacuole of fronds (Pickering et al. 2006; Su et al. 2008) with little complexation with PC in the roots and fronds (Zhao et al. 2009).

5.9 Conclusion

In recent years, researchers are trying to decipher the As uptake and transport in plants through studying molecular and physiological mechanisms. In plant tissue, oxidative stress produced due to ROS production and disorders of antioxidant defenses have been considered a significant matter in As toxicity. In this chapter, an attempt has been made to compile the updated information about As toxicity specifically on oxidative stress and the antioxidant defense system in plants. Although As is a non-redox active metalloid, excessive ROS is produced during valency conversion and methylation in plant. Common manifestations of As-induced phytotoxicity are growth inhibition, shortening of roots (than shoots), and severe effects on anatomical structures, photosynthetic apparatus, and antioxidant defense activities are found. As a result, agricultural productivity worldwide is hugely affected by As. Therefore, an urgent need is to find As-tolerant plant variety to increase agriculture productivity in affected areas. ROS scavenging are vital for plant defenses, and overexpression of gene coding for ROS-detoxifying enzymes helps to increase tolerance against environmental abiotic stresses. Transgenic plants that overexpress gene coding for ROS-detoxifying enzymes may be a prospective item to grow plants with improved tolerance against As. Another way is to apply exogenous chemical protectants like glycinebetaine, proline, Se, and signaling molecules like NO to alleviate oxidative stress (Hasanuzzaman et al. 2011a, b; Hasanuzzaman and Fujita 2011). Meharg and Meharg (2015) reported that adequate silicon fertilization greatly boosts rice yield by alleviating biotic and abiotic stresses and improving grain quality through lowering the content of inorganic As. Nitric oxide (NO), the gaseous free radical, is a widespread intracellular messenger and has regulatory roles in plant physiological processes (Neill et al. 2002). Though the NO-mediated amelioration against As-induced oxidative stress appeared to be synchronized by modulating antioxidant enzyme activities, NO itself has the capacity to detoxify ROS directly (Talukdar 2013b). Therefore, an integrated approach by producing transgenic plants overexpressing genes related with antioxidant along with exogenous protectants may be implemented in order to achieve greater tolerance to As stress.

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