# Chapter 13
# Climate Change-Induced Heavy Metal (or Metalloid) Stress in Crop Plants and Possible Mitigation Strategies

**Navin Kumar, Shilpi Paul, and Shekhar Mallick**

**Abstract** Among the various changes which climate change would bring about, i.e., extreme weather, migration of population, shortage of food, and an outbreak of disease, the increase of heavy metal(loid)s in soils will also be another indirect effect as the soils would dry up. In such scenario, not only the productivity of crop plants would be compromised due to a changing environment, but also the food obtained will be having higher loads of heavy metal(loid)s. In addition, the plants would have to overcome the oxidative stress due to the excessive metal uptake. Abiotic stress due to toxic heavy metal(loid) like As, Cd, Pb, Hg, etc. remains an elusive and invisible challenge to the plants in general and crop plants in particular. Although plants has interconnected tolerance/s defense mechanisms, i.e., redox detoxification, glyoxalase, phytochelatin and metallothionein-mediated vacuolar sequestration, glutaredoxin-mediated pathways, under excess metal levels, the plant suffers from oxidative damage. The challenge becomes more acute under the extreme climatic conditions, demanding strategies to overcome such situations. Traditional breeding methods have a limited potential to improve plant genomes against environmental stresses, while the advent of recent biotechnological breakthroughs, i.e., genetically engineered varieties of different crops such as cotton, maize, rice, canola, and soybean and genome editing through CRISPER-Cas9, holds the answer. Several strategies can be adopted to achieve this, for example, engineering of tolerance pathways, like antioxidant enzymes, osmolyte accumulation, membrane-localized transporters, accumulation of essential elements, resistance against pests or pathogens and introgression of transporters and their overexpression, efficient nitrogen cycling, ascorbate-glutathione pathway, and regulation of stress-inducible phytohormones for climate-resilient crops. In view of these above views, this chapter comprises (i) metal/metalloid and their source of induction in the environment, (ii) mode of uptake by the plants, (iii) affected crops,

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(iv) metabolic pathways, (v) current investigations, (vi) mitigation strategies, (vii) and overall conclusion. Although climate change does not directly influence plant's heavy metal(loid) uptake, in the environment, every aspect is interconnected. This chapter attempts to comprehensively account for all the strategies known for countering excess heavy metal(loid) uptake in plants.

**Keywords** Heavy metal(loid)s · Abiotic stress · Climate change · Glyoxalase · Metallothionein · Asada cycle · Phytohormones · Dehydrins

## 1 Introduction

Human population is projected to increase to 9.8 billion by 2050 from the present 7.7 billion as of February 2019 (un.org), and this would be accompanied by equivalent urbanization of forest and arable land for industrialization and dwelling. These events would directly or indirectly govern the environmental changes both at the local level, i.e., extreme drought and water logging, and also at the global level, i.e., climate change and biodiversity shifts (Chakraborty et al. 2014; Roychowdhury 2014). In addition, according to UN intergovernmental panel on climate change (IPCC), global temperature is projected to increase by 1.8–4.0 °C by the end of the twenty-first century with the higher warming projected for high latitudes. At a global scale, regions which fall between the equator and the 30° north and south latitudes, mid-latitudes regions, i.e., North and South America, northern Europe, and northern and central Asia, are projected to experience increased precipitation, while others, including southern Africa and Asia and the Mediterranean, are expected to experience substantial droughts (Noyes et al. 2009).

Although the heavy metal(loid) pollution and climate change are two different aspects which may not appear to be interconnected, not many studies are available (Roychowdhury and Tah 2011; Basu et al. 2012). However, few studies appear to indicate that with the advent of global climate rise attributed for climate change, the release of metals from a bound state to the available state would rise and subsequently increase in the uptake in plants. In the Dommel catchment in the Netherlands, increase in the levels of Cd and Zn in surface waters has been projected in the discharge runoff toward the end of the twenty-first century as a result of breakthrough of Cd and Zn in the soil system by 820% and 570%, respectively (Wijngaard et al. 2017). In another study on four vegetables in Northwest China, temperature played a major role in the level of Cd, Pb, Cu, and Zn accumulation (Yu et al. 2013). The freshwater contaminations with, for example, heavy metal(loid)s would also further exacerbate due to the disposal of chemical wastes and industrial effluents and over demand of freshwater and absence of insufficient treatment technologies (Singh and Mosley 2003).

The mobility of heavy metal(loid)s in the soil and surface water is greatly governed by soil biogeochemical processes, including sorption/desorption, complexation, dissolution/precipitation, and uptake/release by biota, control, and thus its residence time in soils and water. The mineral-concentrated water and high temperature consequently increase the bioavailability of metal/metalloids to plants in general and crops in particular. The soil-solution partitioning in the soil is controlled by pH, redox potential, clay and soil organic matter (SOM) content, and the concentration of complex organic or inorganic ligands and its competing cations. Future climate scenario is projected to increase the global surface temperature which will eventually enhance evapotranspiration in certain regions, while certain regions will encounter heavy precipitation events (Seneviratne et al. 2012). During floods, the concentrations of heavy metal(loid) increase due to desorption or resuspension, while during droughts, eutrophication increases heavy metal(loid) concentrations possibly due to a decrease in dilution. The climate change also alters the physiological as well as metabolic responses in the crops; for example, the high temperature enhances root exudation of organic compounds which accounts for carbon loss by liberating organic compounds from mineral associations (Keiluweit et al. 2015). Additionally, the change in temperature could reduce the capacity to retain heavy metal(loid)s in soil, which enhances its bioavailability (Fritioff et al. 2005). Raising climate temperature could also affect uptake balance of cations and anions from the rhizosphere (Marschner 2011; Hasanuzzaman et al. 2013). This process would likely decrease the pH of the pore water in the rhizosphere. In addition, the enhanced plant transpiration may enhance the metals/metalloids uptake (Qaderi et al. 2012; Yin et al. 2013). The metals such as $Zn^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $Co^{2+}$, and $Ni^{2+}$ are essential micronutrients for plants development. The divalent metal cations are the prime centers of different enzymes, transcription factors, and the regulatory mechanisms, which are involved in the metal ion homeostasis in plants. However, above the optimum level, these essential metals and nonessential toxic metals, such as $Hg^{2+}$, $Ag^{2+}$, $Cd^{2+}$, and $Pb^{2+}$, are toxic to the crops (Williams et al. 2000). In crops, the uptake of metals is facilitated by the selective transporters and some housekeeping proteins, which maintain the cellular metal(loid) homeostasis (González-Guerrero et al. 2016). On the other hand, above the optimum level, the accumulation of metal(loid)s in crops elevates the level of reactive oxygen species (ROS). The ROS such as superoxide ($O2^-$), hydrogen peroxide (H2O2), and singlet oxygen ($^1O2$), directly disrupting the structure of the biomolecules, resulted into the inhibition of physiological as well as the biochemical process in the crops (Foyer and Shigeoka 2011). Owing to these toxic manifestations, crop growth and yields are reported to reduce. To counter this oxidative stress, plant adopts different stress ameliorative strategies. Antioxidants system (comprising of enzymatic and nonenzymatic antioxidants) directly counters the elevated level of ROS (Das and Roychoudhury 2014). Simultaneously, the biosynthesis of diverse cellular biomolecules also regulates the tolerance response in the crops. Compounds such as polyamines, mugineic acids, organic acids, phytochelatins (PC), dehydrins, and metallothioneins are involved in stress amelioration either by scavenging the ROS or sequestering the toxic cations itself. Certain cellular secondary metabolites, such as flavonoid and phenolic compounds, and amino acids, such as cysteine and proline, are also reported to take part in defense mechanism. Phytohormones such as salicylic acid, jasmonic acid, abscisic acid, auxin, and ethylene are elevated against metals/metalloids stress (Kumar et al. 2019; Ghasemzadeh and Ghasemzadeh 2011; Al-Whaibi 2011; Suzuki et al. 2006). On the other hand, during metal/metalloid stress, the reduced state of cell slightly changes to the oxidizing state where cellular level of reducing agents such as glutaredoxin (GRX), glutathione (GSH), and ascorbic acid elevates to maintain cellular reduced environment (Foyer and Noctor 2011). In this chapter, we briefly describe the different strategies adopted by the plants involved in the stress ameliorative response against metal/metalloid stress, which could possibly be explored for developing climate-resilient crops.

## 2 Antioxidants Against Metals/Metalloids Stress

The antioxidants system contains several enzymatic and nonenzymatic compounds, i.e., glutathione, ascorbic acid, α-tocopherol, carotenoids, and phenolic compounds, to counter oxidative stress induced by the elevated accumulation of metals/metalloids (Fig. 13.1). In the enzymatic antioxidant system, superoxide dismutase (SOD) is considered first line of defense, which converts O2⁻ to less reactive and decomposable H2O2. Superoxide dismutase activity varies quite widely with metal(loid)s accumulation in different plants. In *Arabidopsis*, genes encoding the three classes of SOD (FeSOD, MnSOD, Cu/ZnSOD) respond to metal(loid)s differentially at the transcript level (Abercrombie et al. 2008). Transcripts for genes encoding a chloroplastic and a cytosolic Cu/ZnSOD induced more than twofold by metalloid exposure, while transcripts for a FeSOD were downregulated about fivefold (Abercrombie et al. 2008). Hydrogen peroxide produced in a plant cell is neutralized by enzyme

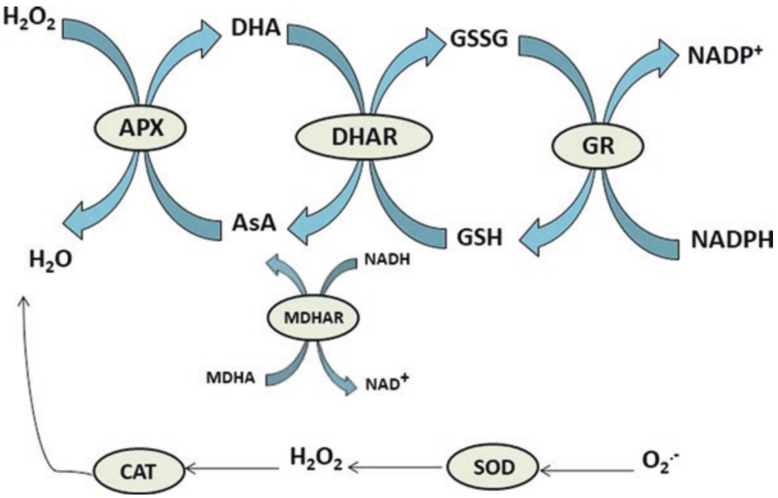

**Fig. 13.1** The schematic diagram of enzymatic antioxidant defense mechanism

action such as catalase (CAT), ascorbate peroxidase (APX), glutathione peroxidase (GPX), etc. (Mittler 2002; Roychowdhury et al. 2018, 2019). In addition to enzymes, plants have a two-component system for regulating the balance of H2O2, broadly ROS, within cells. Nonenzymatic antioxidants include GSH, PC, ascorbate, carotenoids, and anthocyanin. Their accumulation enhances upon metal(loid) exposure (Schmöger et al. 2000; Song et al. 2010).

The second component of the two-component $H_2O_2$ neutralizing system consists of series of enzymes, viz., monodehydroascorbate reductase, dehydroascorbate reductase, and GSH reductase. These enzymes recycle the oxidized GSH and ascorbate for donating electron for H2O2 reduction. The enzymes involved in the recycling of oxidized GSH and ascorbate are also often induced upon exposure of plants to metalloid. Thus, the interdependent ascorbate-GSH cycle has an important role in maintaining ROS balance in plants (Foyer and Noctor 2011) even during metalloid exposure (Tripathi et al. 2012).

## 3 GABA Shunt Against Metals/Metalloids Stress

In plant, γ-aminobutyric acid (GABA) is a multifunctional, nonproteinogenic amino acid involved in signaling acting as metabolic intermediates. γ-aminobutyric acid was primarily discovered in the potato tubers (Steward 1949).

In plant cytoplasm, GABA is produced by evolutionarily conserved three-step pathway, viz., “GABA shunt” (Fig. 13.2). The GABA shunt is composed of a three-enzyme pathway, viz., cytosolic glutamate decarboxylase (GAD), mitochondrial GABA transaminase (GABA-T), and succinic semialdehyde dehydrogenase (SSADH) (Bouche and Fromm 2004). A TCA intermediate, i.e., succinate, synthesis is inhibited during oxidative stress. The two enzymes of TCA cycle, i.e., succinyl CoA ligase and α-ketoglutarate dehydrogenase, are oxidative stress sensitive, hence inhibit the synthesis of succinate. Thus, this step is bypassed through GABA shunt pathway (Bouche and Fromm 2004). The regulation of this conserved metabolic pathway seems to have particular significance in plants. Several experimental observations exhibited that the GABA shunt rapidly activates against the biotic and abiotic stress (Bown and Shelp 2016). GABA shunt does not only fulfill the intermediate of TCA cycle but is also associated with the various physiological responses: regulation of cytosolic pH, carbon flux into TCA cycle, nitrogen metabolism, deterrence toward insects, osmoregulation, and signaling (Ramesh et al. 2015). A study reported that the *ssadh* mutant of *Arabidopsis thaliana* was hypersensitive to the environmental stress Bouché et al. (2003). Kumar et al. (2017) also reported that the accumulation of arsenic enhances the level of GABA to counter stress through GABA shunt pathway.

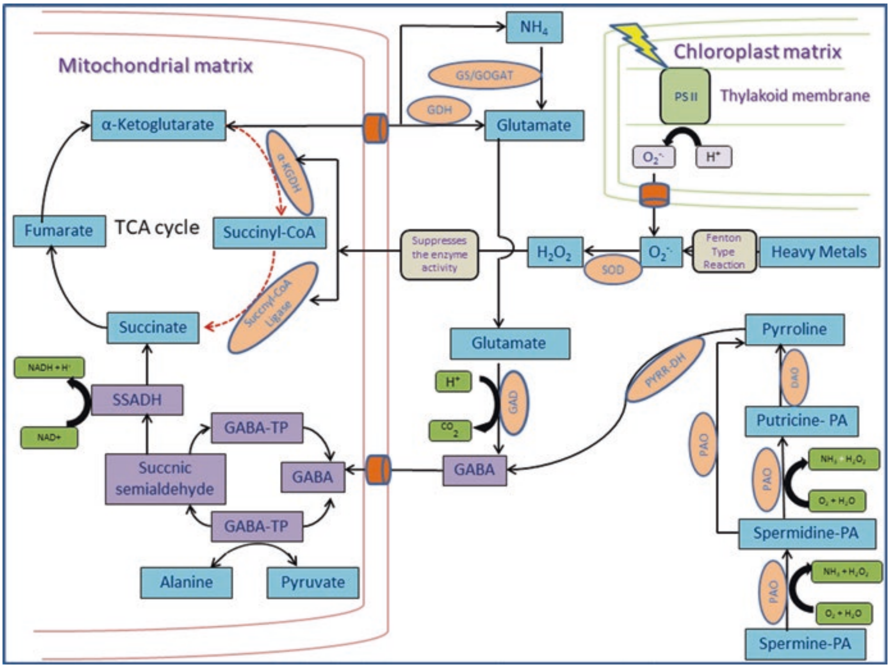

**Fig. 13.2** The γ-aminobutyric acid (GABA) shunt pathway and its regulation in plants

## 4 Nitric Oxide Against Metal/Metalloid Stress

Nitric oxide (NO) is a gaseous free radical with a relatively short half-life (3–5 s) in a biological system, which is involved in the stress ameliorative activity. In plants, NO is synthesized through different pathways such as via nitrate reductase (NR), plasma membrane-bound nitrite: NO reductase (Ni-NOR), xanthine oxidoreductase (XOD), and arginine-dependent and polyamine-mediated synthesis (Stöhr et al. 2001; Rockel et al. 2002; Tun et al. 2006; Parankusam et al. 2017) (Fig. 13.3). The various abiotic stresses such as metalloids, drought, low and high temperatures, and UV and ozone exposure induce generation of ROS (Neill et al. 2002; Vranová et al. 2000). ROS causes several oxidative destructive processes both physiologically and morphologically; however, at the same time, it also activates various signaling pathways (Neill et al. 2002). Thus, maintenance of appropriate ROS levels is prerequisite for survival of plant. In fact, NO interacts with ROS in various ways and might serve antioxidant function during various stresses (Beligni and Lamattina 1999). Nitric oxide may directly act as an ROS scavenger being a free radical and can react with other free radicals such as ROS, or it may activate the antioxidant gene expression or may activate antioxidant enzymes. Modulation by NO against superoxide

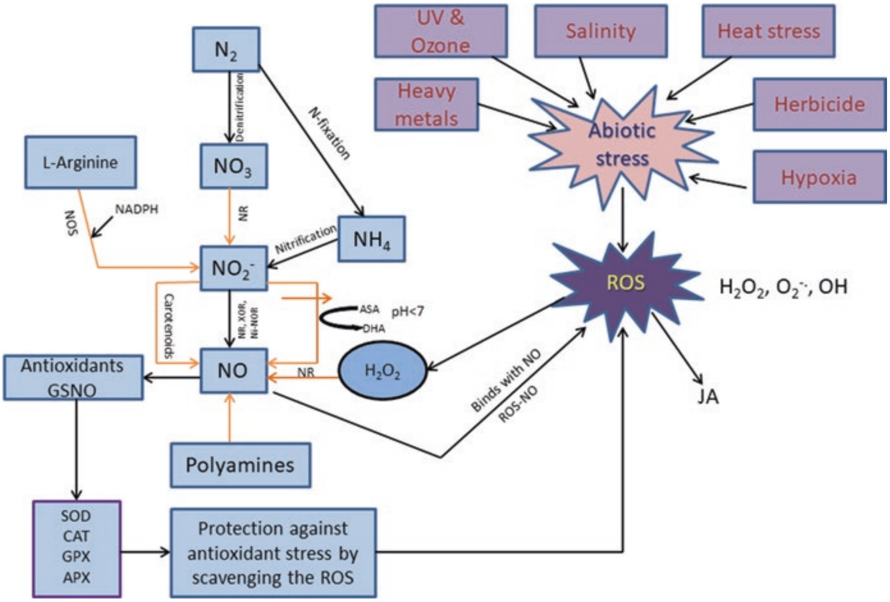

**Fig. 13.3** Schematic diagram showing the crosstalk between NO and RS and their interregulatory mechanism

formation illustrates its potential antioxidant role. On the other hand, excess NO can result in nitrosative stress, so a favorable balance of ROS/NO is important.

Heavy metal(loid)s contamination affects the overall performance of plant growth across all agroclimatic zones worldwide. Nitric oxide plays a crucial role in resistance against heavy metal(loid) stress in plants (Table 13.1). The detoxification and antioxidative properties of NO is also found in soybean cell cultures under cadmium (Cd) and Cu stress (Singh et al. 2008). Hu et al. (2007) also reported that NO improved wheat seeds germination and alleviated oxidative stress against Cu toxicity by enhancing the activity of SOD and CAT and correspondingly decreasing in the lipoxygenase activity and lipid peroxidation. Nitric oxide was reported to have the ability to reduce Cu-induced toxicity. Nitric oxide is most likely mediated through the modulation in the activities of antioxidant enzymes (CAT, POD, and AXP) involved in H2O2 detoxification and in the maintenance of cellular redox couples (GR) and contents of molecular antioxidants particularly nonprotein thiol, ascorbate, and its redox status (Tewari et al. 2008). Nitric oxide protects plants against $Al^{+3}$-induced oxidative stress, and increased root elongation was correlated with a decrease in $Al^{+3}$ accumulation in root apices (Wang and Yang 2005). Sun et al. (2015) reported that nitrate reductase (NR)-mediated early NO burst could be responsible in protecting roots of wheat against Al toxicity.

**Table 13.1** Impact of nitric oxide on various metals/metalloids stress

| Stress | NO donor | Plants | Stress effect on | | | Impact of NO on abiotic stress-induced changes in antioxidant properties | | | | | | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | H2O2 | NO | Antioxidant | H2O2 | MDA | SOD | CAT | APX | GR | |
| 0.25, 0.5 m M As | 0.25 mM SNP | *Triticum aestivum* | + | | ± | ↓ | ↓ | | ↑ | ↔ | ↑ | Hasanuzzaman and Fujita (2013) |
| 0.025 mM As | 0.1 mM SNP | *Festuca arundinacea* | + | + | + | ↓ | ↓ | ↑ | ↑ | ↑ | | Jin et al. (2010) |
| 0.0250.5 mM As | 0.05 mM SNP | *Oryza sativa* | + | – | + | ↓ | ↓ | ↓ | ↓ | ↓ | | Singh et al. (2008) |
| 0.05 mM Cu | 0.1 mM SNP | *Panax ginseng* | + | + | – | ↓ | ↓ | ↑ | ↑ | ↑ | ↑ | Tewari et al. (2008) |
| 0.025 mM Cd | 5 mM SNP | *Brassica juncea* | + | + | + | | ↓ | ↓ | ↓ | ↓ | | Verma et al. (2013) |
| 5 mM Cd | 0.1 mM SNP | *Oryza sativa* | + | | + | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | Hsu and Kao (2007) |
| 0.5 mM Cd | 0.1 mM SNP | *Helianthus annuus* | | | ± | | ↓ | ↓ | ↓ | | ↓ | Laspina et al. (2005) |

Arrows indicate up-, down-, or no regulation. +, −, ±, and = indicate up-, down-, differential, or no regulation

## 5 Role of Polyamines Against Metals/Metalloids Stress

Polyamines (PAs) are low-molecular-weight, aliphatic polycations compound, which are found in all the livings organisms (Chen et al. 2018; Kumar et al. 2019). Three abundant PAs, i.e., putrescine (Put), spermine (Spm), and spermidine (Spm), play a vital role in stress tolerance. In plants, PAs are biosynthesized mainly via two enzymes activity, i.e., ornithine decarboxylase (ODC) and arginine decarboxylase (ADC) (Vera-Sirera et al. 2010; Pegg and Casero 2011; Gupta et al. 2013) (Fig. 13.2). Stress-derived changes in the levels of cellular PA provide clues on their possible implication in plants stress amelioration. Several studies show that PAs could ameliorate the metals/metalloids stress toxicity by (i) maintaining integrity of plant cell membrane, (ii) reversal of growth inhibition due to abiotic stress, (iii) modulation in the expression of osmotically responsive genes, (iv) reduction of superoxide radical and H2O2 levels, (v) reduction in the accumulation of $Na^+$ and $Cl^-$ ions in different organs, and (vi) increasing activities of antioxidant enzymes (Tang and Newton 2005; Ndayiragije and Lutts 2006; Wang et al. 2007; Yiu et al. 2009; Zhang et al. 2009; Hussain et al. 2011; Alcázar et al. 2010; Kumar et al. 2019). To prove the role of PAs against the abiotic stress, the isolated ethyl methanesulfonate (EMS) mutants of *Arabidopsis* with reduced ADC activity exhibited reduced accumulation of PAs and less tolerance compared with the wild type of plants (Watson et al. 1998; Kasinathan and Wingler 2004). Similarly, the ADC2 knockout mutant exhibited no obvious phenotypic change under normal growth conditions and was more sensitive to metal stress, which can be partially reversed by uptake of Put (Urano et al. 2009). This suggests that ADC2 is a key gene and Put derived from the ADC pathway in providing stress tolerance. In another report, mutant of acl5/spms was found to be sensitive against abiotic stress such as drought, salinity, and metalloids which recovered upon the application of Spm (Yamaguchi et al. 2006, 2007). These studies revealed that the PAs are important molecule involved in stress management in the plants.

## 6 Role of Glutaredoxins Against Metals/Metalloids Stress

Glutaredoxins (GRXs) are universal, oxidoreductase enzymes with molecular mass between 10 and 15 kDa (Fomenko and Gladyshev 2002). Glutaredoxin/glutathione/glutathione reductase (GRX/GSH/GR) is mainly involved in maintaining the redox state of the cell. Glutaredoxins regulate the activity of proteins or enzyme through reversible glutathionylation or reduction of disulfide bonds (-S-S-) in order to maintain conformational integrity throughout the oxidative stress (Rouhier et al. 2008; Meyer et al. 2009). Glutaredoxins uses GSH and NADPH as a cofactor, generated through NADPH-dependent GSH reductase (GR) system (Rouhier et al. 2008; Zaffagnini et al. 2008) (Fig. 13.4).

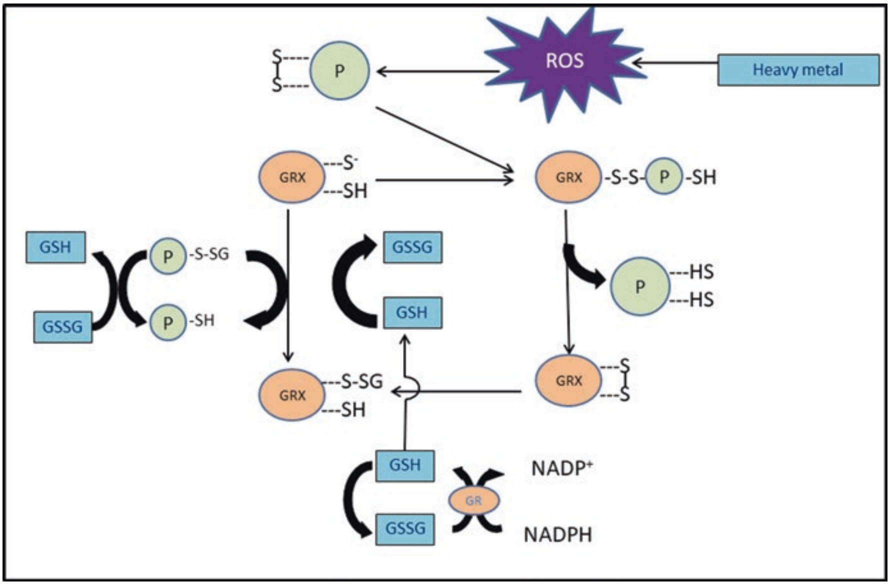

**Fig. 13.4** Schematic model of redox activity of glutaredoxin under oxidative stress. (*P* protein, *GSSG* oxidized glutathione, *GSH* reduced glutathione, *GRX* glutaredoxin)

In plants, GRXs consist of a large family of genes, and others remain to be explored on the basis of mode of function under normal and metals/metalloids stress conditions (Jozefczak et al. 2012). A study reported that GRX gene (*PvGRX5*) from As-tolerant fern *Pteris vittata* when integrated in *E. coli* exhibited tolerance against 10 mM As(V) treatments (Sundaram et al. 2008, 2009; Sundaram and Rathinasabapathi 2010). Tomato (*Lycopersicon esculentum*) plants silenced with *SlGRX1* gene showed susceptibility toward metal(loid) stress, whereas, overexpressed gene in *Arabidopsis* provides tolerance against these stresses (Guo et al. 2010). Rice GRX (*OsGrx*) protects glutamine synthetase toward metal stresses (Lee et al. 2002). The role of GRXs in the mitigation of metalloids is well recognized in the prokaryotic as well as mammalian system (Ning et al. 2018). However, in plants, the GRXs are mostly reported against cadmium stress (Li 2014). A study reported that exposure of arsenic enhanced the expression of four GRX genes (*Os01g26912*, *Os02g40500, Os02g40500*) in rice plants, indicating GRXs are directly/indirectly involved in the amelioration of As-induced stress (Rai et al. 2011).

## 7 Role of Glyoxalase System Against Metals/Metalloids Stress

The glyoxalase system is an important pathway of cellular metabolism, which involves in the methylglyoxal (MG) detoxification. Various stresses such as heavy metal(loid)s, salinity, drought, and high temperature drastically increase the rate of glycolysis, which leads to the MG formation (Hoque et al. 2016). Removal of phosphoryl group by β-elimination from the unstable triose phosphates emphasizes the formation of MG. Methylglyoxal is a genotoxic agent, and at higher concentration, it directly disrupts the structure of the proteins through the formation of advanced glycation end products (AGEs). It also damages DNA structure and, consequently, enhances cell death (Borysiuk et al. 2018).

In plants, MG is eliminated by the two-glyoxalase pathway containing glyoxalase I (Gly I) and glyoxalase II (Gly II) (Sankaranarayanan et al. 2017) (Fig. 13.5). In condition where reduced glutathione (GSH) is abundant, MG is converted into hemithioacetal (HTA), where Gly-I enzyme converts HTA into S-D-lactoyl-glutathione (SLG). Further, the toxic SLG is detoxified through Gly-II, converting SLG to nontoxic D-lactate, where the GSH is also freed by the compound and gets back to the normal cellular metabolism (Yadav et al. 2008). There are several studies showing the increase in activities of Gly-I and Gly-II, conferring tolerance against heavy metal(loid)s in plants. Overexpression of the glyoxalase pathway in transgenic tobacco and rice plants has been found to prevent an increase of ROS and MG under stress conditions by maintaining GSH homeostasis and antioxidant enzyme levels (Yadav et al. 2005; Singla-Pareek et al. 2006, 2008). The specific activity of glyoxalase I (Gly I) was increased along with the other antioxidant enzyme activities in *Vigna radiata* plants in response to Cd stress (1 mM, 48 h) (Hossain et al. 2010).

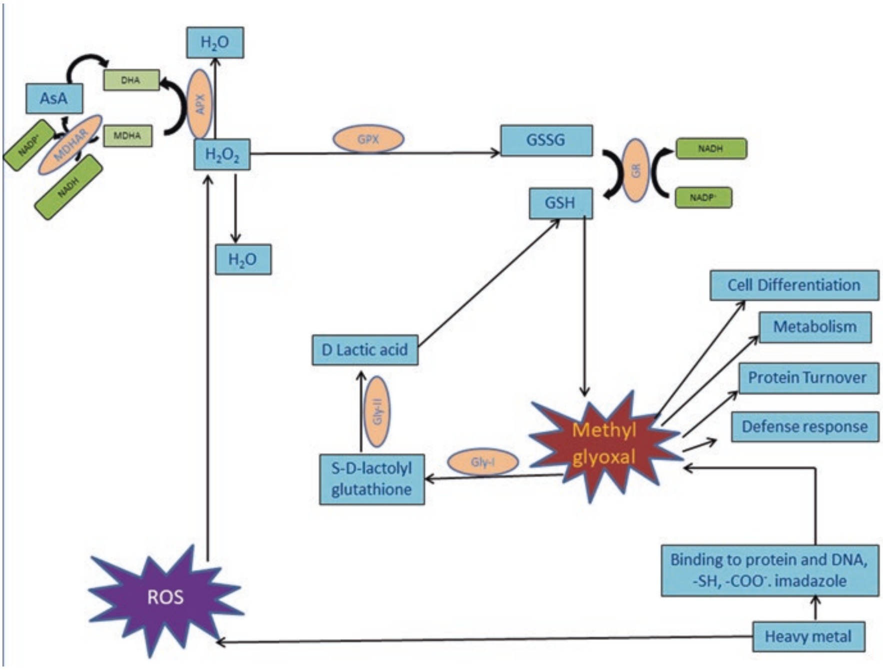

**Fig. 13.5** Schematic diagram showing pathways of glyoxalase in detoxification of methylglyoxal generated against oxidative stress

## 8 Dehydrins

Dehydrins (DHNs), also known as the group 2 or D-11 family of late embryogenesis abundant (LEA) proteins, are widely distributed in the plant kingdom which accumulates under environmental stresses, viz., drought, low temperature, and salinity. Dehydrins are hydrophilic, thermostable, stress-responsive proteins and contain high-charged amino acids belonging to late embryogenesis abundant (LEA) family (Hasanuzzaman et al. 2015). Dehydrins contain conserved lysine-rich motifs known as K-segments consisting of 15-amino acid motif sequence present in 1–11 copies near to the C-terminus of dehydrin (EKKGIMDKIKEKLPG) (Fig. 13.6).

Apart from the K-segment, dehydrins can possess other conserved sequential motifs: the tyrosine-rich Y-segment (consensus (V/T)D(E/Q)YGNP) near to the N-terminus and the serine-rich S-segment (Kosová et al. 2010). S-segment is formed by a stretch of 4–10 phosphorylable serine-rich tract which is proposed to be related to the nuclear transport of dehydrins. Dehydrins form an amphiphilic helix which interacts with the membranes or proteins to prevent inactivation under dehydration (Liu et al. 2017a, b). According to the number and combination of these three conserved domains, a "YnSnKn" nomenclature scheme within the dehydrin family has been developed (Close 1996). Recently, antioxidative activity has also been attrib-

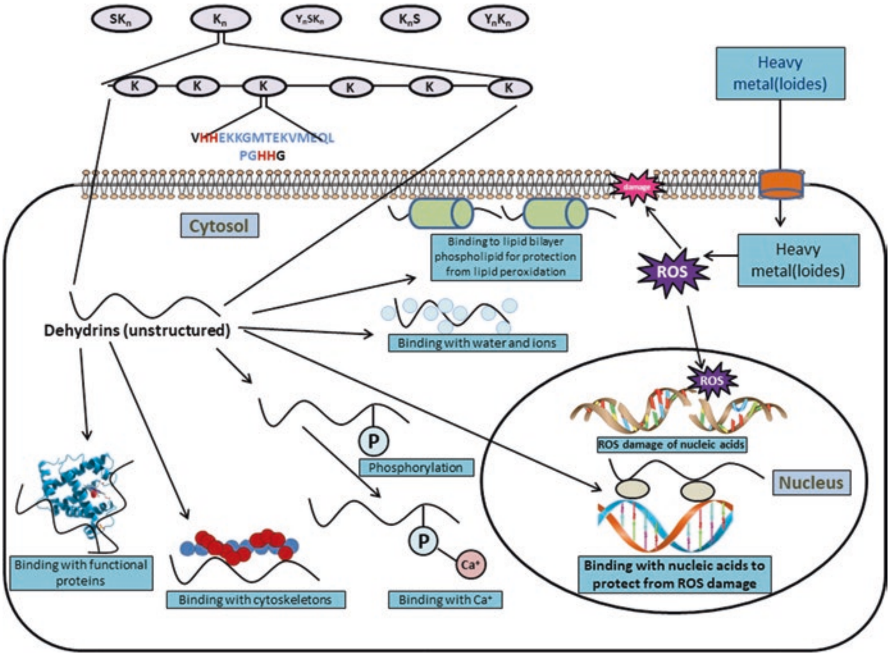

**Fig. 13.6** Generalized schematic illustration of various functions of dehydrins in plant cell

uted to dehydrins, since the environmental stresses which induce the accumulation of dehydrins also produce ROS, inducing oxidative stress in plants (Sun and Lin 2010). The localization of dehydrins in subcellular components also strengthens the role of dehydrins playing role in antioxidative activity. Dehydrins are reported to occur in (i) nucleus to possibly stabilize chromosome against ROS (Carjuzaa et al. 2008; Egerton-Warburton et al. 1997; Hara et al. 2009), (ii) in vicinity of plasma membrane to protect the lipid peroxidation (Danyluk et al. 1998), and (iii) in mitochondria and chloroplast (Borovskii et al. 2000; Mueller et al. 2003) to protect the cellular machinery from H2O2 being generated from PS-II (Salin 1991). Dehydrins are also known as responsive to ABA (RAB) proteins, synergistically elevating with ABA. Various stress related to dehydration (e.g., osmotic stress, drought, salinity, and heat) enhances the level of DHNs (Fig. 13.6). The limited studies indicate the role of DHNs in the amelioration of metals/metalloids stress. In a study, the expression of two DHN genes of *Brassica juncea*, i.e., *Bj*DHN2 and *Bj*DHN3, was found to enhance with heavy metal(loid)s accumulation. The overexpression of *Bj*DHN2 and *Bj*DHN3 in transgenic plants exhibits heavy metal(loid)s tolerance (Xu et al. 2008). Similarly, the overexpression of *DREB* transcription factor (plays a crucial role in abiotic stress tolerance) in plants exhibited the enhanced expression of DHNs such as RD29A, COR15a, and RD29B, which also enhanced the tolerance against heavy metal(loid)s stress (Ban et al. 2011; Yu et al. 2018). On the other hand, DHNs can stabilize the free transition metal ions by chelating them with motifs, reducing oxidative stress (Svensson et al. 2002). A study using metal ion affinity chromatography (IMAC) shows CuCOR15 dehydrin has the capability to chelate and immobilize $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ ions. The chelation capacity of dehydrin indicates it could be an in vivo tool for metal tolerance in plants. In tobacco plants, the overexpression of maize dehydrin gene, i.e., *Zm*DHN13, correlated with the tolerance to oxidative stress (Liu et al. 2017a, b). Dehydrins are reported to accumulate against heavy metal(loid)s. Expression of a bean dehydrin gene *Pv*SR3 was upregulated by H2O2 and heavy metal(loid)s, which are known to catalyze the production of toxic ROS. There are also report of radical scavenging ability of a citrus dehydrin (CuCOR19) owing to high content of amino acid glycine (Gly), histidine (His), and lysine (Lys)—residues which are susceptible to oxidative modification (Dean et al. 1997). Catalytic metals, such as Fe and Cu, mainly exist as cofactors in many enzymes and proteins in plants under normal growth conditions. These metals can be released as free ions when plants are exposed to environmental stresses, producing highly toxic radicals via the Haber-Weiss or the Fenton reactions (Mittler 2002). Owing to the high His content, having strong metal-binding domains like His-His pairs and His-X3His motifs, plant dehydrins can be suggested to be ion-sequestering antioxidative proteins.

## 9 Heavy Metal(loid)s Chelation: Metallothioneins and Phytochelatins

Chelation of the toxic/excess metals in the cytosol by high-affinity ligands is a unique and efficient strategy for heavy metal(loid) detoxification and tolerance. In addition to organic acids and amino acids, two classes of peptides, viz., metallothioneins (MTs) and phytochelatins (PCs), are predominant in heavy metal(loid) detoxification by chelation. Phytochelatins are family of metal-ligating peptides synthesized non-translationally, having the general structure of ($\gamma$-Glu-Cys)n-Gly where $n = 2–11$. The PCs are synthesized using GSH as substrate and PC synthase enzyme, which is induced by the presence of metals (Cobbet 2000; Goldsborough 2000). The reported metals which are ligated with the PCs and sequestered in vacuoles are Cd, Zn, and As. Ligated metal-PC complex are transported across the tonoplast membrane into the vacuole through ABC and CAX transporters. Metallothioneins are low-molecular-mass cysteine-rich polypeptides encoded by a family of genes which can bind with heavy metal(loid)s and play a role in their intracellular sequestration. MT were discovered 57 years ago as a Cd-binding protein in horse kidney. MT genes and proteins have been reported from many prokaryotic (bacteria) and eukaryotic organisms (plants, invertebrates, and vertebrates) which are induced in the presence of metals and also play a role in its detoxification and intracellular metal ions homeostasis (Robinson et al. 1993; Cobbett and Goldsbrough 2002; Roychowdhury et al. 2018, 2019). The two metal-binding, cysteine-rich domains in MTs give these metalloproteins their characteristic dumbbell conformation (Fig. 13.7).

Class I MTs are widespread in vertebrates containing 20 highly conserved cysteine, while class II MTs include all those from plants and fungi as well as from nonvertebrate animals which do not follow any strict arrangement of Cys residues. However, due to lack of scientific consensus, phytochelatins are considered as class III metallothioneins. Following the discovery of PCs as a Cd-binding ligand in plants, MT proteins were discovered as Zn-binding proteins from wheat embryos in plants (Lane et al. 1987). This provided the evidence that in plants, in addition to PCs, MTs also play a role in metal(loid) binding and homeostasis (Fig. 13.8). MTs are involved in Cu tolerance and homeostasis in plants: Some plant MTs are functional copper-binding proteins, and expression of some MT genes is induced by copper.

## 10 Heavy Metal(loid) Transporters

Plants require six macronutrients (Ca, K, Mg, N, P, S) and eight micronutrients (B, Cl, Cu, Fe, Mo, Mn, Ni, Zn), and absence of any one of these elements does not allow transition through a full life cycle. For example, Fe is a key component of heme proteins for a range of enzymes (e.g., cytochromes, catalase, and Fe-S pro-

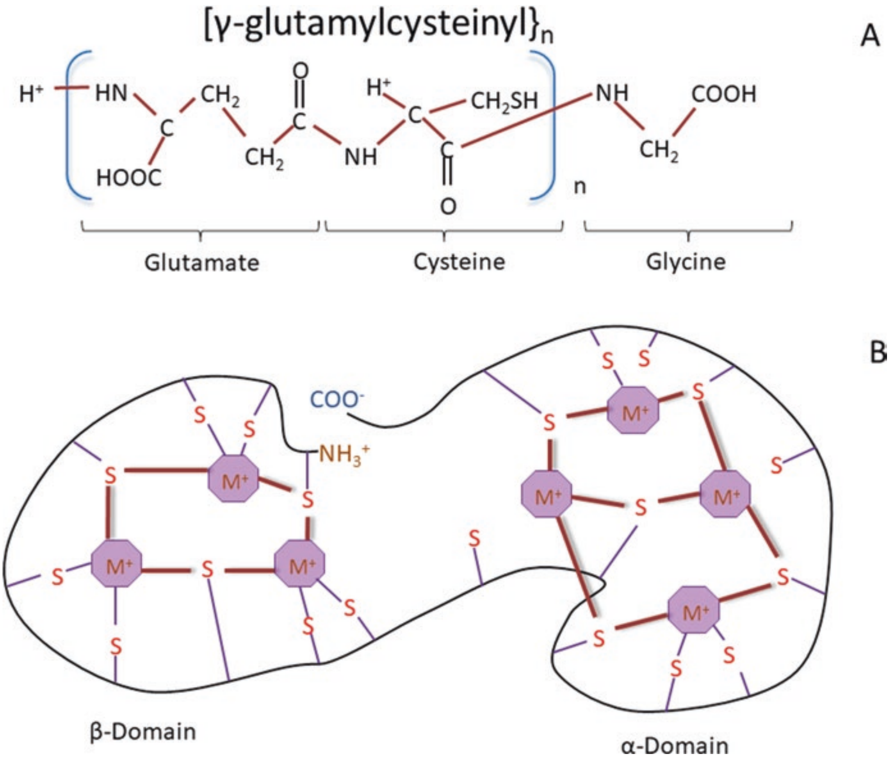

**Fig. 13.7** Schematic structure of (**a**) phytochelatin and (**b**) metallothionein proteins that have been classified based on the arrangement of their cysteine (Cys) residues

teins such as ferredoxin), Cu is key cofactor for certain electron transfer proteins in photosynthesis (e.g., plastocyanin) and respiration (e.g.. cytochrome C oxidase) and lignification (laccase), while Mn is less redox active but is also involved in photosynthesis (e.g., O2 evolution). Zn is non-redox active but has a key structural and/or catalytic role in many proteins and enzymes. Although essential, these metals can be toxic when present in excess as they can produce ROS through Fenton-type reaction.

$$\mathbf{Fe^{2+} + H_2O_2 \ \text{intermediate complex} \ Fe^{3+} + OH^{\bullet} + OH^{-}}$$

Cation/s transport across the plant plasma membrane is governed by an electrochemical gradient of protons generated due to the pumping of protons out of the cell by $H^+$-ATPases, creating an electrochemical potential (ECP) across the plasma membrane (PM). Using this ECP, several other transporters can efflux and influx cations across the PM. Modern genetic and molecular techniques such as sequence comparison and functional complementation of yeast mutants have identified a wide range of transition metal transporter gene families in plants (Fig. 13.9). These

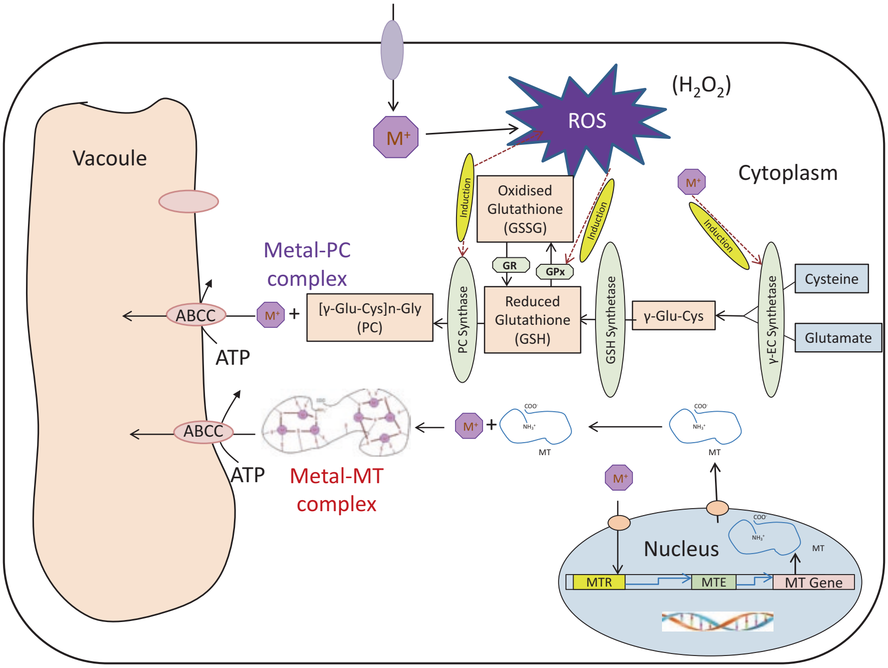

**Fig. 13.8** Schematic diagram showing pathway of phytochelatin and metallothionein induction by heavy metal(loid) [M+] in a plant cell

include the heavy metal(loid) (or CPx-type) ATPases, natural resistance-associated macrophage proteins (Nramps), cation diffusion facilitators (CDFs), ZIP family (ZRT, IRT-like protein), the cation antiporters, YSL (yellow-stripe-like) transporter, NAS (nicotianamine synthase), SAMS (S-adenosylmethionine synthetase), FER (ferritin Fe (III) binding), CDF (cation diffusion facilitator), and IREG (iron-regulated transporter) family (Hall and Williams 2003; Guerinot 2000; Williams et al. 2000; Talke et al. 2006; van de Mortel et al. 2006; Kramer et al. 2007; Memon and Schroder 2009; Maestri et al. 2010).

In plants, ZIPs have been identified in both dicots and monocots, such as 18 ZIP genes in *Arabidopsis* and 16 from rice (Ivanov and Bauer 2017). In *Arabidopsis, IRT1*is expressed against Fe deficiency and plays a role in Mn/Zn transport. A few studies have also implied that ZIPs may be involved in Cd transport. Among the transport of major trace cations, the uptake of Fe is of particular interest as there are two different strategies between non-graminaceous plants (strategy I) and graminaceous plants (strategy II) Briat and Lobreaux (1997) (Fig. 13.10).

The strategy I plants rely on ferric reductase oxidase (FRO) to reduce the ferric chelates at the root PM and then consequently on the iron-regulated transporter (IRT) to absorb the generated $Fe^{2+}$ ions across the root PM. On the contrary, strategy II, used by graminaceous plants (e.g., barley, maize, and rice), depends on the bio-

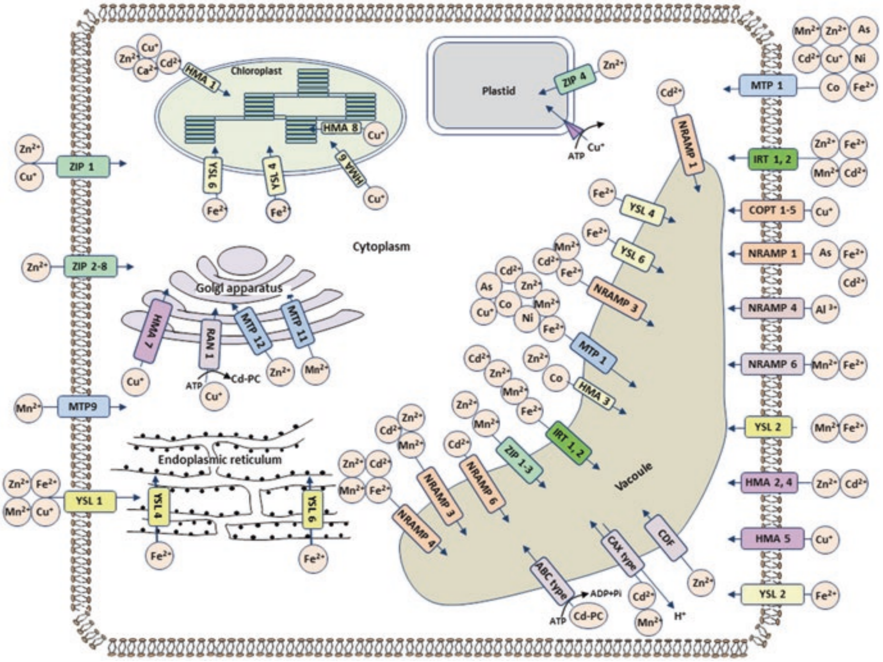

**Fig. 13.9** Schematic diagram of putative locations of different metal transporters in the plant cell. (Modified from Clemens 2001; Hall and Williams 2003; Ding et al. 2017)

synthesis and secretion of phytosiderophores (PS) such as mugineic acids (MAs) which mobilize $Fe^{3+}$ from the soil matrix. The secreted MAs into the rhizosphere solubilize $Fe^{3+}$ from the soil matrix, and the resulting Fe-PS complexes are taken up through yellow stripe (YS) and yellow stripe-like (YSL) transporters. Graminaceous plants, despite using strategy II, can also have ferrous transporters (IRT1, NRAMP) allowing the absorption of $Fe^{2+}$ in addition to its strategy II-based $Fe^{3+}$-MA uptake. Iron-regulated transporter (IRT1) is a member of a small gene family encoding a predicted protein of 339 amino acids, with eight transmembrane domains. Four histidine-glycine repeats constitute potential metal-binding domains between TM domains three and four. Five ZIP transporter genes have been reported for rice *Os*IRT1, *Os*IRT2, *Os*ZIP1, *Os*ZIP3, and *Os*ZIP4. *Os*IRT1 and *Os*IRT2 are ferrous iron transporters. *Os*ZIP1 is primarily associated with metal uptake and *Os*ZIP3 with overall Zn homeostasis in the cell, especially in leaves. COPT family transporter is known for the uptake of Cu in plants. They work as homo- or heterotrimer of a three-TM domain forming a channel for specific $Cu^{+}$ transport. The FRO present in the root PM facilitates the reduction of the unavailable $Cu^{2+}$ to $Cu^{+}$, consequently uptaken by COPT transporters. Similar to the reduction of $Cu^{2+}$ to $Cu^{+}$, $Mn^{3+}$ and $Mn^{4+}$ need to be reduced to $Mn^{2+}$ to be absorbed by IRT1 present in root PM. In addition, the NRAMP transporters can also transport Mn. In rice plants, both

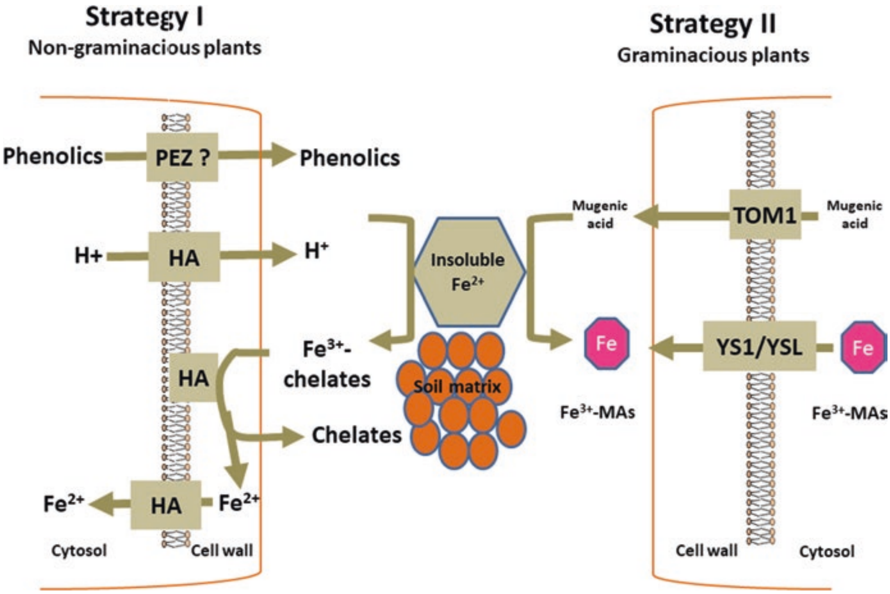

**Fig. 13.10** Schematic diagram showing strategies for Fe uptake in graminaceous and non-graminaceous plants

NRAMP1 and NRAMP 5 are reported to transport Mn. NRAMP transporters are a monomeric protein spanning 11 TM domains which transports a wide range of metals, i.e., $Fe^{2+}$, $Mn^{2+}$, $Co^{2+}$, and $Zn^{2+}$. Furthermore, $Cu^+$ transport is also mediated by members of the zinc-regulated transporter and iron-regulated transporter (ZRT-IRT)-like proteins (ZIP). These are a ubiquitous family of divalent metals transporters (primarily $Fe^{2+}$, $Zn^{2+}$, $Ni^{2+}$, Cd, and $Mn^2$) acting as homodimer where each monomer has eight TM domains. The metal specificity of the ZIP transporters is conferred by conserved histidine-rich cytosolic loops between three and four TM domains. Zn, $Mn^{2+}$, and $Cu^+$ uptake also takes place through YS and YSL family (e.g., *Zm*YS1 and *Hv*YSL2) are also involved in the transport of Zn-PS, Cu-PS, and Mn-PS complexes. YSL transporters (yellow stripe-like proteins) are phenotypes identified in maize containing a range of 11–16 TM regions and function across a $H^+$ symporter. Members of the YSL family can only be found in plants, although YSL belong to the larger OPT (oligopeptide transporter) family that is also present in fungi. YSL transporters do not use free metals as substrate but a complex of metals with nicotianamine (NA) or its derivatives. IRT1 also facilitates the transport of Ni as Ni-PS complexes (Pinto and Ferreira 2015). P1b-ATPases are a clade of the P-type superfamily of ATPases (which also includes the $Na^+/K^+$-ATPase or the $H^+$-ATPase which is a monomer with several TM domains from six to eight) where the last two cytosolic loops are enlarged and comprised the ATPase function domain (proximity to C-terminus) that drives transport of the metal. These transporters frequently have cytosolic metal-binding domains in N- and/or C-terminal with a regulatory function. P1b-ATPases are involved in long-distance $Cu^+$ and $Zn^{2+}$ transport in plants, as well as metal transport into organelle. CDF transporters (cation diffusion facilitator) is a homodimer facilitating the transport of divalent metals such as $Fe^{2+}$, $Zn^{2+}$, or $Mn^{2+}$, coupled to a $H^+$ antiporter. The monomer has six transmembrane domains with a His-rich region in the cytosol between the fourth and the fifth TM domain. There are three metal-binding domains in the protein (site I in the transmembrane region, site II in the membrane-cytosol interface, and site III in the C-terminal domain), but only I and III seem to be directly involved in transport.

## 11 Role of Phytohormones Against Metals/Metalloids Stress

Recent evidence suggests that phytohormones not only regulate the normal function of the plants but are also the key molecules in the plants which are elevated during the wide range of stresses. Several phytohormones such as abscisic acid (ABA), auxin, brassinosteroids, ethylene, gibberellic acid (GA), and cytokinins (CKs) have been reported to play a role during metal stress (Zhu et al. 2012; Masood et al. 2016; Bücker-Neto 2017).

Abscisic acid (ABA) plays a crucial role in plants, involving seed development and dormancy (Finkelstein 2013) and imparting tolerance to plants against adverse environmental conditions, and its signaling pathway is a central regulator of abiotic stress response in plants (Danquah et al. 2014). The metals Ni, Zn, and Cd reduce water potential and stomatal conductance in the plants where elevated level of ABA recovers the inhibition (Rucińska-Sobkowiak 2016). Abscisic acid is reported to play a role in increasing the growth of roots of aquatic plants *Typha latifolia* and *Phragmites australis* (Fediuc et al. 2005), in potato tubers (Stroinski et al. 2010), and in rice plants (Kim et al. 2014) against Cd exposure. Similarly, increase in ABA levels increased in wheat seeds when exposed to Hg, Cd, and Cu (Munzuro et al. 2008). The expression of genes involved in ABA synthesis, viz., 9-cis-epoxycarotenoid dioxygenase 2 (*Os*NCED2 and *Os*NCED3), in rice plant has been found to increase in coincidence with upregulation of four ABA signaling genes against As and Va stress (Huang et al. 2012). Although the mechanism underlying the ABA signaling pathway in response to heavy metal(loid)s exposure remains largely unexplored, the pathway involves pyrabactin resistance1 (PYR1)/PYR1-like (PYL)/regulatory components of ABA receptors (RCAR), PP2C, and SNF1-related protein kinase 2 (*Sn*RK2) (Fig. 13.11).

Abscisic acid is also known to induce transient mitogen-activated protein kinase (MAPK) kinase activity (Burnett et al. 2010). Elevated accumulation of Cd and Cu enhances MAPK activity and subsequently the level of ABA in plants to counter the stress (Yeh et al. 2004; Liu et al. 2018; Hsu and Kao 2003). Hence, there exists interrelationship between ABA and MAPK in countering heavy metal(loid)-induced stress. During stress, ABA also regulates the different genes expression involved in the late embryogenesis abundant (LEA) proteins, dehydrins, and stress-responsive proteins (Vaseva et al. 2010).

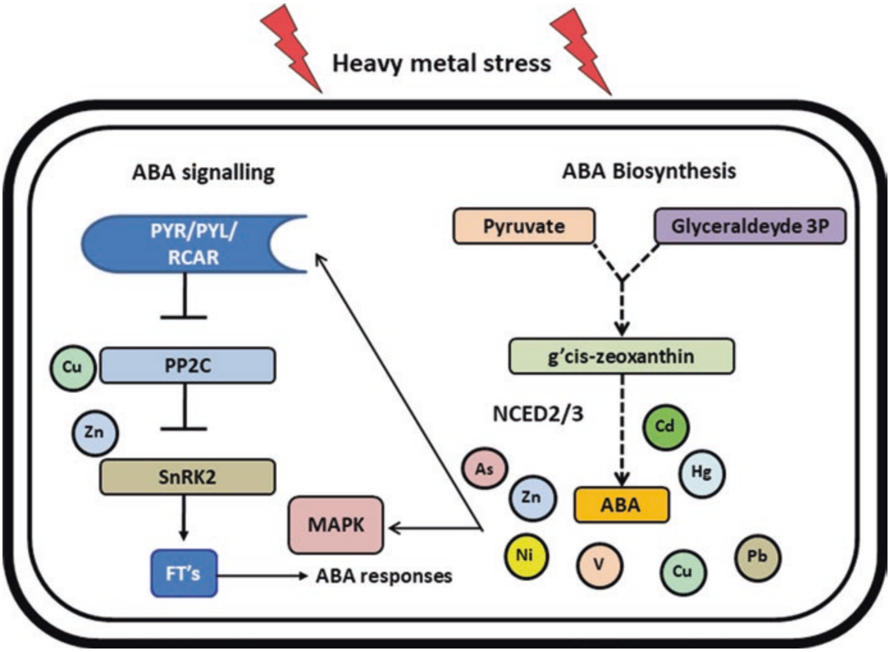

**Fig. 13.11** Schematic diagram of abscisic acid and heavy metal(loid)s interaction in plants. (Modified from: Bücker-Neto et al. 2017)

The involvement of ethylene (ET) has been reported in response to abiotic stress induced by several elicitors including heavy metal(loid)s (Maksymiec 2007; DalCorso et al. 2010; Khan et al. 2015). Ethylene is synthesized from methionine, which is converted to S-adenosylmethionine (SAM) by SAM synthetase. SAM, as a substrate, is capable of forming 1-aminocyclopropane-1-carboxylic acid (ACC) by ACC synthase (ACS) (Fig. 13.12). This is the rate-limiting step in the ethylene biosynthesis pathway and ultimately releases 5′-methylthioadenosine (MTA), which is recycled again to methionine via the "Yang cycle." However, in presence of $O_2$, ACC is degraded by ACC oxidase (ACO) forming ethylene, $CO_2$ and cyanide in plants (Yang and Hoffman 1984). The enzymes ACS and ACO are the two fundamental components of ET biosynthesis. Stress induced by heavy metal(loid) increases the expression of genes encoding these two proteins, resulting in higher ET production (Schellingen et al. 2014; Khan et al. 2015). ACS2 and ACS6 are phosphorylated by MAPKs, which in turn increase their stability and activity. The transcription factor WRKY33 protein binds directly to the W-boxes in the promoters of ACS2 and ACS6 genes in vivo; hence, WRKY33 activates ACS2 and ACS6 expression downstream of the MPK3/MPK6 cascade (Li et al. 2012). EIN2 gene is an important gene ethylene signaling pathway and acts as a transducer of ethylene and stress responses (Alonso et al. 1999). The transcript levels of EIN2 increase against Pb treatment in *Arabidopsis* seedlings (Cao et al. 2009).

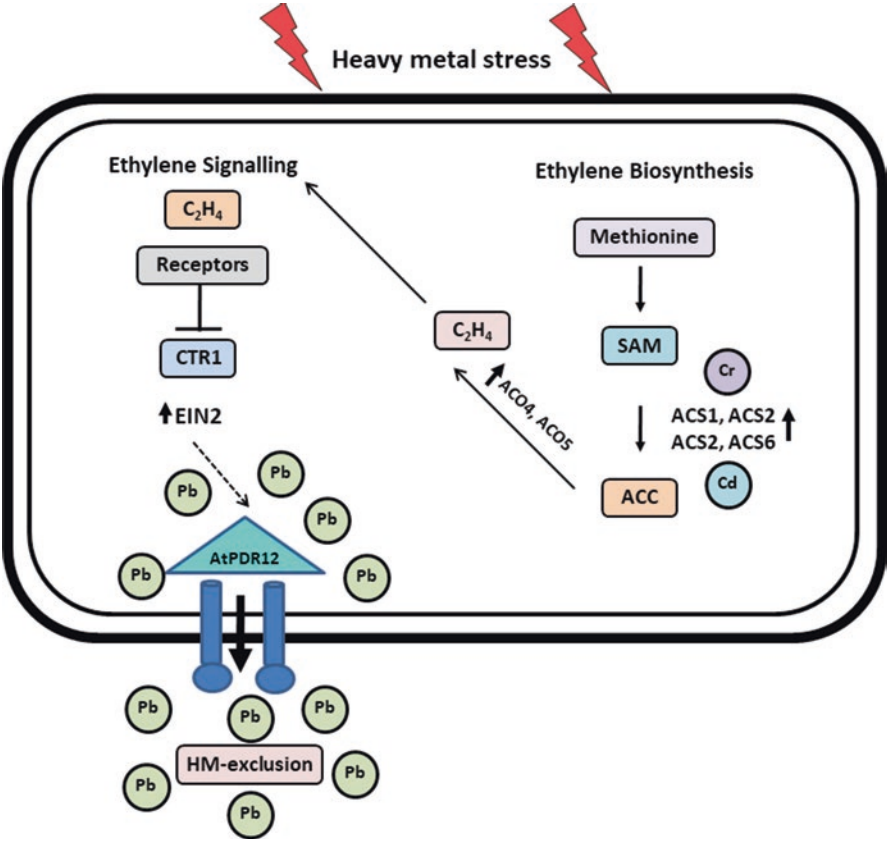

**Fig. 13.12** Schematic diagram illustrating the ethylene signaling against heavy metal(loid) stress. (Modified from: Bücker-Neto et al. 2017)

A study suggests that the Cd tolerance is related to the induction of ET biosynthesis (Cao et al. 2014). The *Arabidopsis thaliana* ein2-1 mutants (a gene involved in the ethylene biosynthesis) exposed to Al significantly enhance antioxidants enzymes, i.e., SOD and CAT activities, with respect to the WT plants. The study indicates that the elevated level of ET can ameliorate Al toxicity by regulating antioxidant enzymes in the plants (Zhang et al. 2014). Rice plants treated with Cr showed the enhanced expression of genes 1-aminocyclopropane-1-carboxylic acid synthase and 1-aminocyclopropane-1-carboxylic acid oxidase are involved in the ET biosynthesis, highlighting the role of ET in Cr tolerance (Steffens 2014; Trinh et al. 2014). The accumulation of Pb exhibited enhanced transcript levels of EIN2 in *Arabidopsis* seedlings, coinciding with the heavy metal(loid) tolerance (Cao et al. 2009). Another study also reported that *Arabidopsis* etr1-1 and ein3-3 mutants exhibited less sensitivity toward Li accumulation (Bueso et al. 2007).

The gibberellic acids (GAs) are the tetracyclic diterpenoid carboxylic acid compounds, in which the only GA1 functions as phytohormone (Sponsel and Hedden 2010).

The GAs regulate the seed germination, leaf expansion, development of fruits, and stem elongation (Salazar-Cerezo et al. 2018). A study reported that the GAs enhance the tolerance against heavy metal(loid)s in wheat by enhancing *Ta*MYB73 gene expression (He et al. 2011). The accumulation of Cd reported inducing iron-regulated transporter 1 (IRT1), which facilitates the uptake of Cd. The elevated level of GA against Cd toxicity was found to suppress the IRT1, thereby reducing the toxic manifestation in *Arabidopsis thaliana* (Zhu et al. 2012). The GA was also found to reverse the reduced growth and chlorophyll content in wheat seedlings exposed to Ni (Siddiqui et al. 2011). On the other hand, the GA is not restricted only to the regulation of genes expression and chlorophyll content; it also enhances the antioxidants against metal(loid) stress (Siddiqui et al. 2011). Several studies show that the elevated level of GA coincides with the enhanced peroxidase and CAT activity in plants (Wojtania et al. 2016).

Among the phytohormones, ABA, auxin, GA, ET, and cytokinins (CKs) are closely concurrent to the nitrogen metabolism. Cytokinins are the N6-prenylated derivative compound of the adenine, which regulates cell division, nutrient metabolism, and nodulation (Savelieva et al. 2018). CKs are mainly synthesized in the seeds, fruits, and roots (Matsuo et al. 2012). The accumulation of CKs has been reported to mitigate heavy metal(loid)s toxicity (Manara 2012). In plants, elevated accumulation of CKs was able to increase transpiration, which can stimulate photosynthesis rate, coinciding with reversal of plant biomass against heavy metal(loid)s stress (Cortleven and Schmülling 2015). During As toxicity, a CK receptor, cytokinin response-1 (CRE1), was downregulated and simultaneously induced the group 1 sulfate transporters. This indicates that the CKs are indirectly regulating the sulfur-related defense mechanism in the plants against As stress (Srivastava et al. 2009). In another study, depletion of CK was found to activate thiol compounds, which are directly involved in the defense mechanism against As stress in *Arabidopsis thaliana* (Mohan et al. 2016). It is reported that the Cd treatment inhibits the growth rate and net photosynthetic rate in plants. The adenosine-5′-phosphosulfate reductase (APR), an enzyme involved in the sulfate assimilation, was also reported to enhance with the elevated level of CKs in *Arabidopsis*, under the metal stress (Fu et al. 2018). The sulfur is an essential nutrient of the plants, which is also involved in the synthesis of defense mechanism compounds, such as cysteine, GSH, and GRX, against a wide range of stresses (Mallick et al. 2013). The studies indicate that the CKs may regulate genes expression, sulfur metabolism, and level of RNS to counter the metals/metalloids stress.

Auxin chemically known as indole-3-acetic acid (IAA) is an important phytohormone in several physiological aspects of plant growth and signaling in the stress tolerance mechanism. The expression of IAA in plants is tightly regulated by the degradation of AUX/IAA transcriptional repressors that are associated to ARFs (auxin-responsive factors) and thus inhibits the transcription of auxin-responsive genes ultimately regulating the plant physiology (Vanneste and Friml 2009) (Fig. 13.13). Evidence suggests that auxin reverses the inhibited shoot and root growth during heavy metal(loid) stress (Wang et al. 2015). Generally, the higher accumulation of metal(loids) such as As and Cd reduces root growth, which coin-

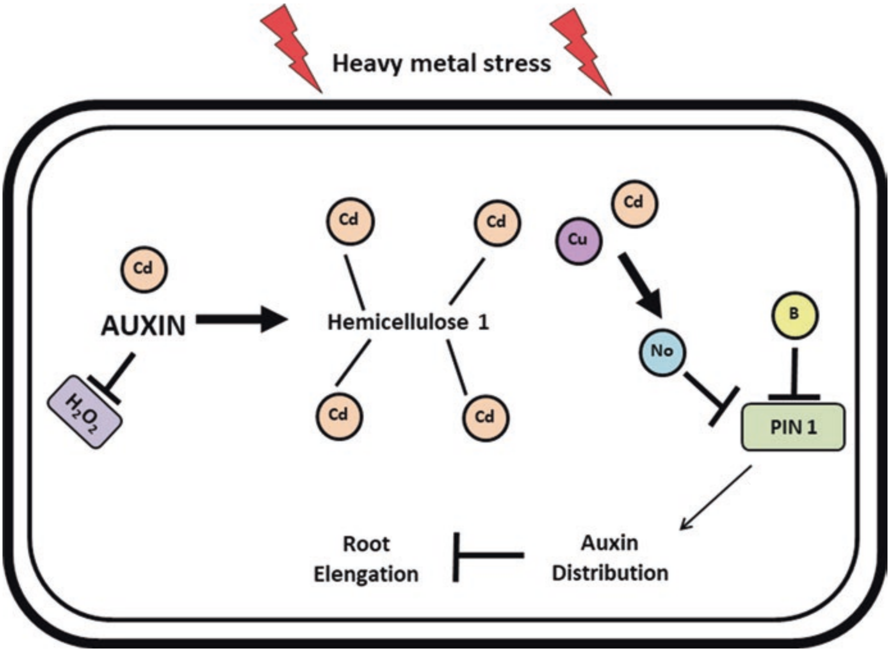

**Fig. 13.13** Schematic diagram illustrating the interactions between auxin and heavy metal(loid)s in plants. (Modified from: Bücker-Neto et al. 2017)

cides with the reduced level of auxin (Ronzan et al. 2018). It is reported that the hemicellulose-1 pays a crucial role in heavy metal(loid) stress tolerance. A recent study shows that the elevated level of auxin under Cd stress enhances the level of hemicelluloses, which restricts the heavy metal(loid)s movement within the root (Zhu et al. 2013). The accumulation of heavy metal(loid) enhances the level of auxin regulation via PINFORMED1 (PIN1) protein (an auxin efflux carrier for meristematic root growth under normal conditions) in plants (Bücker-Neto et al. 2017) and is involved in the hormone distribution under heavy metal(loid) stress. In *Arabidopsis thaliana*, the mutant lines of PIN1 (*pin1* DR5rev::GFP) exhibited no auxin activity in both the meristem and elongation zones compared to the normal lines (DR5rev::GFP) against Cu stress, indicating that PIN1 is involved in hormone distribution under heavy metal(loid) stress (Yuan et al. 2013). Evidences suggest that there exists interrelationship between ET and auxin. Ethylene induces the expression of genes involved in auxin biosynthesis and stimulates the auxin transport toward the elongation zone, thereby regulating root elongation (Ruzicka et al. 2007). Under boron (B) deficiency, *Arabidopsis* auxin, ethylene, and ROS participate together in signaling the reduction in root elongation (Camacho- Cristóbal et al. 2015). Generally, heavy metal(loid) stress leads to decrease in endogenous auxins levels. The level of three auxins (IAA, NAA, and IBA) was reported to reduce in *Brassica juncea* against As (Srivastava et al. 2013) and barley root tip against Cd (Zelinová et al. 2015). Nitric oxide (NO) also represses auxin transport to roots, which hinders its elongation (Yuan and Huang 2016).

Brassinosteroids (BRs) regulate several plant growth aspects, i.e., cell expansion and elongation, photomorphogenesis, flowering, male fertility, seed germination, vascular differentiation, plant architecture, stomata formation, and senescence, and it acts during abiotic stress. Phytotoxicity induced by heavy metal(loid)s is consequent upon ROS production in plants. Alternatively, antioxidant enzyme activities are also regulated by BRs (Cao et al. 2005); hence, BR-induced stress tolerance can be attributed to increased expression of antioxidant genes (Xia et al. 2009) (Fig. 13.14). Exogenous application of 24-epiBL has been found to ameliorate Ni stress in *Brassica juncea* by enhancing the activity of antioxidant enzymes (Kanwar et al. 2013), in wheat against Ni toxicity (Yusuf et al. 2011), and in *Raphanus sativus* and *Vigna radiate* (Yusuf et al. 2012), by elevation of different antioxidant enzyme activity. These reports suggest that BRs definitely play a role against amelioration of abiotic stress in general by elevating the antioxidant activity.

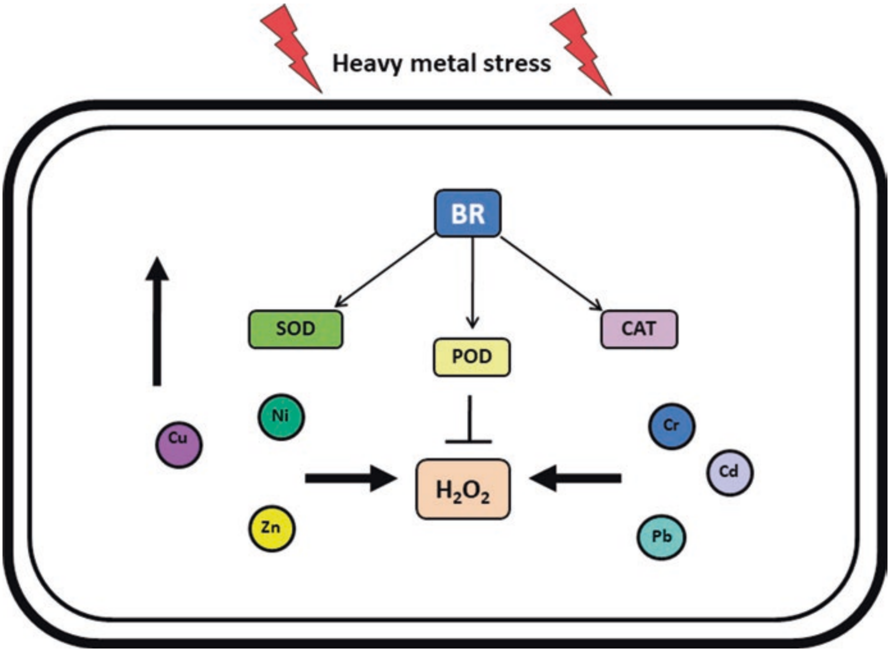

**Fig. 13.14** Diagram showing the brassinosteroids-induced stress tolerance in plants, under heavy metal(loid) exposure. (Modified from: Bücker-Neto et al. 2017)

## 12 Conclusion

The changing climate and demands of the population explosion misbalance the metals/metalloids in the environment, which consequently emphasizes the metals uptake in the crops. The uptake of metals/metalloids above optimum range leads to the toxic manifestation in the crops. Against metals/metalloids toxicity, a crop activates their mitigation strategies to provide tolerance. In the different mitigation strategies, the antioxidants system mainly counteracts the generation of ROS in the crop plants. Simultaneously, the NO also supports the mitigation strategies by nitrosylation process to activate antioxidants system proteins. Similarly, in the plants, phytohormones regulate the different signaling cascades, which involve in the different mitigation strategies. However, the GABA shunt pathway protects plants by synthesizing the TCA cycle intermediate, which inhibits during stress. Similarly, the PAs mainly protect plants by the preservation of bimolecular structure integrity and modulation in the expression of osmotically responsive genes. However, during oxidative stress, the GRXs are involved in the maintaining redox state of the cell. Simultaneously, the glyoxalase system detoxifies the MG, which synthesize during stress. On the other hand, DHNs stabilize the free transition metal ions by chelating them with their motifs. The regulation of the stress-responsive phytohormones, i.e., auxin, cytokinin, brassinosteroids, abscisic acid, and ethylene, can help not only in enabling crop plant to be resilient toward climate-induced stress, i.e., drought and high temperature, but also in overcoming the heavy metal(loid)-induced stress by regulating its uptake. Along with these mitigation strategies, specific agronomic practices using precise use of phytochemicals can help in growing crop plants in future climate change scenario.

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