Heavy Metal and Their Regulation in Plant System: An Overview

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Abstract

Unplanned industrialization and improper waste disposal have resulted in the release of enormous quantities of inorganic toxicants like metal, metalloids, and radionuclides in the biosphere. Since, metals are non-biodegradable and tend to bioaccumulate via food chain, they pose threat to human health. Indiscriminate disposal of industrial waste to the environment causes adverse impact on ecosystem. Plants growing on metal-contaminated sites display several disturbances related to physiology and biochemical process like gaseous exchange, CO_2 fixation, respiration, nutrient absorption, etc. These disturbances subsequently cause reduction in plant growth and lower biomass production. Although being an essential micronutrient, some heavy metals at lower concentrations are vital for plant growth; however, at higher concentrations they become very toxic. To cope up with the metal toxicity, plants have developed various mechanisms like immobilization, exclusion, chelation, and compartmentization. Plants have distinct cellular mechanism such as chelation and vacuolar compartmentization of metals to withstand the metal toxicity. Phytochelatins, the thiol peptides, potentially chelate metals and form complexes in cytoplasm; subsequently these metal-thiol complexes are sequestrated into vacuole via ATP-binding cassette transporters (ABC transporters). In the last couple of

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decades, the role of phytochelatin synthetase (PCS) and phytochelatins (PCs) in metal detoxification has been proven. In present scenario, there is a great need of sound and intensified research for better understanding of metal toxicity and its metabolism in plants to maintain our ecological harmony.

Keywords
Heavy metals • Toxicity • Contamination • Metabolism

2.1 Introduction

Accelerated industrialization and modernization throughout the world has led to the emergence of various luxurious facilities and goods; however, such industrialization and modernization also releases a considerable amount of undesirable xenobiotic or toxic wastes to various components of environment, i.e., soil, air, and water (Adriano 1992; McIntyre 2003; Kumar et al. 2013). Even the most pristine environment like the Arctic Circle and Antarctic has not been spared by the globally transported xenobiotics (AMAP 2002). Although environmental pollution is a natural process, the human activities like improper waste management practices, landfill operations, mining, the use of chemical fertilizers, application of sewage sludge, etc. have accelerated the level, rate, and types of contamination to soil, air, and water. Further, application of sewage sludge and discharge of industrial effluent containing inorganic chemicals like heavy metals to agricultural lands intensifies the problem of soil pollution. The problem of contamination turns to be more complex when the effluents are discharged directly because of the heterogeneity in the quality and quantity of discharged effluents (Srivastava et al. 1994; Kara 2005; Singh et al. 2010).

Heavy metals (e.g., Cr, Cd, As, Fe, Ni, Pb, Hg, Zn, etc.) are an important class of environmental pollutants, and many of these are highly toxic in soluble forms. Since, heavy metals are non-biodegradable in nature and persist in soil for a long time, they tend to bioaccumulate in ecological food chain through uptake at primary producer level and subsequently via consumption at secondary and tertiary levels (Sakakibara et al. 2011; Bauddh and Singh 2012; Lu et al. 2014; al. 2016). Therefore, removal of the metals and other contaminants is an important concern and a major policy priority globally.

Chemically, the term heavy metal refers to any metallic element with a specific gravity greater than 5 (Venugopal and Luckey 1978). Heavy metals are naturally found in dispersed form in rock. However, industrialization and urbanization have increased the heavy metals in biosphere. Further, the major availability of heavy metals is in the soil and aquatic system, and relatively a smaller portion is available in the atmosphere in the form of particulate or vapors. Plants growing on land contaminated with heavy metals display several disturbances related to physiology and biochemical processes like gaseous exchange, CO_2 fixation, respiration, nutrient absorption, etc. These disturbances subsequently cause reduction in plant growth and lower biomass production. The toxicity due to heavy metals in plants varies with several factors, viz., plant species, concentration of the metal and its chemical form, soil composition, and pH (Nagajyoti et al. 2010).

2.2 Impact of Heavy Metals on Plant Growth and Development

Like all living creature, plants are also sensitive to both deficiency and excess of micronutrient including trace elements. Some heavy metals are essential in nature as they are required for normal growth of plant. Essential heavy metals like Cu, Zn, Fe, Mn, Mo, and Ni play important roles in biochemical and physiological functions in plants (Reeves and Baker 2000). Being essential micronutrients, Cu and Zn are very important for normal plant growth as they either serve as a cofactor and activators of enzyme reactions or exert a catalytic property such as prosthetic group in metalloproteins (Mildvan 1970). These essential heavy metals are also involved in redox reactions, electron transfer, basic functions in nucleic acid metabolisms, and, as direct participant, being integral part of several enzymes. The availability of these essential metals in growing medium at certain concentration is very important, but their excess concentration leads to several toxic effects (Blaylock and Huang 2000; Monni et al. 2000). Due to their presence in trace in environmental matrices, these heavy metals are also known as trace elements ($10 mgKg^{-1}$ or mgL^{-1} of metal in soil/aquatic medium) or ultra-trace element ($1 \mu gKg^{-1}$ or μgL^{-1} of metal in soil/aquatic medium). Besides these essential trace elements, another category of heavy metals, class B metals, that are considered as non-essential trace elements like Hg, Ag, Pb, Ni, etc. are very toxic in nature (Nieboer and Richardson 1980). In terrestrial system, plants are stationary, and the their roots are the main contact sites for trace metal ions, while in aquatic system, the entire plant body is exposed, and metal ions are absorbed directly due to particle deposition on leaves' surfaces.

2.2.1 Copper

Copper is considered as an essential micronutrient for plants and algae especially because of its crucial role in photosynthesis, CO_2, and ATP synthesis (Thomas et al. 1998; Chatterjee et al. 2006; Mahmood and Islam 2006). Copper is an important component of several proteins like plastocyanin of photosystem and cytochrome oxidase of respiratory electron transport chain (Demirevska-kepova et al. 2004). It is a primary electron donor in photosystem I. Copper plays a crucial role as a cofactor for enzymes involved in the elimination of superoxide radicals (superoxide dismutase and ascorbate oxidase) and also of oxidase and mono- and dioxyegenase (amine oxidases, ammonia monoxidase, ceruloplasmin, lysyl oxidase). Further, the toxicity due to the exposure of excess copper to plants has been well reported by several researchers (Moreno-Caselles et al. 2000; Singh and Tewari 2003; Keller et al. 2015). The presence of excess copper in soil displays cytotoxic role, induces stress, and causes damage to plants which leads to several deformities including retardation in plant growth and leaf chlorosis (Lewis et al. 2001; Adrees et al. 2015a, b). Excess of copper also generates ROS causing oxidative stress by damaging macromolecule disturbance in metabolic pathways (Hegedus et al. 2001; Habiba et al. 2015). In combination with Cd, Cu has been reported for its adverse effects on seed germination, length of seedling, and number of lateral roots (Neelima and Reddy 2002).

2.2.2 Cadmium

Cadmium is a non-essential heavy metal for plants. Cadmium has been ranked 7th among the top 20 toxins due to its great solubility in water and high toxicity (Yang et al. 2004). Cd has been reported as an extremely significant pollutant among the class of heavy metal pollutants (Das et al. 1997; Rizwan et al. 2016). Cadmium toxicity is easily identifiable in the form of stunt growth, chlorosis, browning of root tips, and finally plant death (Das et al. 1997; Wojciek and Tukiendorf 2004; Mohanpuria et al. 2007; Guo et al. 2008). Excess of Cd in growing soil can cause leaf chlorosis; however, it may be due to deficiency of iron and the interaction with toxic metals. Chlorosis may appear due to direct or indirect interaction with Fe present in leaves. The presence of excess cadmium in growing medium causes suppression in uptake of iron (Haghiri 1973). Cadmium induces the inhibition of root Fe(III) reductase which leads to deficiency of iron, severely affecting plant photosynthesis (Alcantara et al. 1994). Cd-induced chlorosis may be attributed to the changes in Fe/Zn ratio. It has been reported that Cd also interfere with the uptake, transport, and use of various essential elements like Ca, Mg, P, K, etc. and water (Das et al. 1997; Asgher et al. 2015). Further, Cd also inhibits the nitrate reductase activity which reduces the absorption of nitrate and its transport from roots to shoots (Hernandez et al. 1996). Cadmium has also been reported for its cytotoxic effects in the form of swelling, vacuolization, degeneration of mitochondria, inhibition in cell proliferation, and a low mitotic index (Silverberg 1976; Rosas et al. 1984; Khan et al. 2016). The chromosomal aberrations have been also reported in onions, beans, peas, and barley on exposure to excess Cd (Oehlkers 1953; Von Rosen 1954; Degreave 1981). Rosas et al. (1984), reported that the plant exposed to Cd at concentration of 1.5 to 10 mgL^{-1} for 24 h had caused physiological and genetical damages. They also reported that Cd inhibits the cell division and alters the chromosome. Further, they also mentioned that the inhibition of cell proliferation, shown by low mitotic index, was proportional to the concentration and time of exposure (Rosas et al. 1984). Moreover, exposure to Cd causes decrease in nitrogen fixation and primary ammonia assimilation in the root nodules (Balestrasse et al. 2003).

2.2.3 Zinc

Zinc is considered as an essential micronutrient for plants because at optimal concentration it is essential for normal functioning of cell metabolism as well as for plant growth (Dhankhar et al. 2012; Broadley et al. 2007). It plays crucial role as a cofactor in many physiological processes such as metabolism of several biomolecules, gene expression and regulation, enzyme activation, protein synthesis, and reproductive development (Cakmak 2000). However, accumulation of Zn in plant at higher concentration (>300μgg^{-1} in dry weight) causes physiological alteration and growth inhibition (Foy et al. 1978). High level of exposure of Zn in growing medium inhibits several plant metabolic functions, results in stunted growth, and causes senescence. Zn toxicity restricts the growth of roots and shoots (Choi et al. 1996; Fontes and cox 1998). At high concentration, it also causes chlorosis in premature leaves, which can extend to older leaves on prolonged high exposure. Excess of Zn also causes deficiency of other essential elements, viz., Mn and Cu, in shoots which hinders the transfer of these essential micronutrients from root to shoot. The possible reason for this hindrance of transfer of these micronutrients is the concentration of Fe and Mn in plant grown in Zn-rich media is greater in root than the shoot (Ebbs and Kochian 1997).

2.2.4 Arsenic

Arsenic (As) is a metalloid and considered as a nonessential and toxic element for plants (Zhao et al. 2009). Mobility and availability of As in soil depends upon its ionic form. As(III) is very toxic in nature but less mobile than As(V). Arsenate, i.e., As(V), is the most stable form found in the soil, and hence its availability for plant is greater than As(III). The availability and mobility of As in soil highly depends on soil pH. As commonly forms complexes with calcium at high pH (pH 6–8) while it frequently binds with iron at low pH (pH 4) (Fayiga and Ma 2006). Further, the presence of Fe and MnO in soil also increases the availability and mobility of As (Zavala and Duxbury 2008). In plants, it mainly accumulates in roots and to very less extent in shoots. Generally, plants uptake arsenic as As(V) and translocate it via the xylem along with water and minerals as As(III)-S compound (Wang et al. 2002). Chemically, As(V) is analog to PO_4^{3+} and hence competes with PO_4^{3+} uptake in root and interferes metabolic processes like ATP synthesis, oxidative phosphorylation, and transport across the plasma membrane through phosphate transport channels (Meharg and Macnair 1992; Tripathi et al. 2007; Stoeva and Bineva 2003). The presence of excess As in growing medium causes physiological changes, interference with metabolic processes, growth inhibition, ultimate reduction in crop productivity, and finally death (Miteva 2002; Stoeva et al. 2004; Anjum et al. 2016). Arsenic toxicity may be seen as a consequence of binding of As with sulfhydryl (SH) group of protein, leading to inhibition of protein activity or structural disruption, or replacing the essential element resulting in deficiency effects (Assche and Clijsters 1990; Delnomdedieu et al. 1994; Kumar et al. 2015). Arsenic may also stimulate the formation of free radicals and reactive oxygen species like $O_2^{\bullet -}$, $OH^{\bullet}$, and H_2O_2 which are strong oxidizing agents and cause oxidative damage to biomolecules like lipids and protein and finally cell death (Dietz et al. 1999; Molassiotis et al. 2006; Gunes et al. 2009).

2.2.5 Nickel

Nickel is considered as an essential element at lower concentration (0.01 to 5μgg^{-1}) for plants. The uptake of Ni from growing medium takes place mainly via passive diffusion and active transport. Plants passively absorb the soluble Ni compounds via cation transport system. The chelated Ni compounds are taken and transported via active-transported-mediated system using transport proteins like permeases. Moreover, the insoluble Ni compounds are absorbed in root cells through endocytosis and easily transported to shoots through the xylem via transpiration stream and can get accumulated in newly developed buds, fruits, and seeds. Ni is an essential component of several metalloenzymes such as superoxide dismutase, NiFe hydrogenases, methyl coenzyme M reductase, urease, acetyl Co-A synthase, carbon monoxide dehydrogenase, hydrogenases, and RNase-A. Further, the high exposure of Ni in growing medium affects the activities of amylases, proteases, and ribonucleases subsequently affecting the digestion and metabolization of food reserves in germinating seeds (Ahmad and Ashraf 2011). High concentration of Ni in growing medium causes alteration in physiological process and diverse toxicity symptoms such as chlorosis, necrosis, and wilting (Zornoza et al. 1999; Rao and Sresty 2000; Nakazawa et al. 2004). Plants growing in excess Ni medium show negative effects on photosynthesis, mineral nutrients, sugar transport, and water balance (Samarakoon and Rauser 1979; Tripathy et al. 1981; Parida et al. 2003; Sethy and Ghosh 2013). Decrease in uptake of water is an indicator of the increasing Ni toxicity in plants (Pandey and Sharma 2002; Gajewska et al. 2006). Ni toxicity has also been attributed for the impairment of nutrient balance, disturbance of lipid composition, and H-ATPase activity resulting in the cell membrane dysfunctions (Ros et al. 1992). Exposure of high level of Ni increases MDA concentration which might disturb membrane function and cytoplasmic ion balance, particularly K^+; the most mobile ion across the cell membrane.

2.2.6 Chromium

Chromium (Cr) is considered as a non-essential metal for plant. Chromium has been well reported for its toxicity to plant growth and development (Huffman and Alloway 1973; Vikram et al. 2011). On high exposure (1–5 mgL^{-1}), Cr causes chlorosis and alteration in several metabolic processes, *viz.*, growth inhibition and decline in the chlorophyll synthesis (Dube et al. 2003; Ahemad 2015). Some plants have been reported with potential to accumulate Cr without showing any symptoms of Cr toxicity. Chromium enters and accumulate in root cells by the symplastic pathway. Plants uptake chromium in its trivalent form, i.e., Cr(III) by passive mechanism, while uptake of Cr(VI) is inhibited by SO_4^{2-} and Ca^{2+} (Zayed and Terrey 2003). Hexavalent ions, i.e., Cr(VI), damage the root membranes due to their high oxidation power. Cr enters into plant roots by reduction and/or complexation with root exudates, which enhance the solubility and mobility via root xylem (Shanker et al. 2005; Bluskov et al. 2005). Although accumulation and mobilization of Cr inside the storage tissue depends on its ionic form, however, it accumulates mainly in roots and translocated poorly to shoots (James and Barlett 1983). Like cadmium, Cr(VI) also reduces the uptake of many essential elements like Fe, Mg, Mn, Ca, P, and K resulting in many negative effects on plant growth (Gardea-Torresdey et al. 2005; Peralta-Videa et al. 2009). Seed germination of *Phaseolus vulgaris* was reduced by 48 % on exposure of Cr(VI) at concentration of 500 ppm (Parr and Taylor. 1982). Reduction in seed germination was observed in seeds of *Medicago sativa* by 23 % at 40 ppm of Cr(VI) (Peralta et al. 2001). Adverse effect of Cr on photosynthesis has been also well documented (Assche and Clijsters 1983; Vikram et al. 2011). Chromium affects the photosynthesis in the form of reduction in photosynthetic pigments and inhibition in photophosphorylation, electron transport, and enzyme activities (Clijsters and Assche 1985; Vikram et al. 2011). Furthermore, it also causes disorganization of ultrastructure of chloroplasts, which are the primary site for photosynthesis (Vazques et al. 1987; Ahemad 2015).

2.2.7 Lead

Lead (Pb) is a non-essential and one of the most ubiquitously distributed toxic elements in the soil. Plant gets lead mainly from soil and aerosol (Sharma and Dubey 2005). In plants, roots have greater ability to accumulate Pb; however, its subsequent translocation to aerial parts is highly restricted (Lane and Martin 1977). It was also reported that lead could be translocated and accumulated in leaves in a concentration-dependent manner (Miller and Koeppe 1971). Further, the extent of Pb uptake by plant from aerial sources, through leaves, depends on the ability and specific leaf morphology (Godzik 1993). Availability of lead in soil highly depends on soil conditions like soil pH, particle size, and cation exchange capacity. Moreover, the availability and uptake of Pb is also affected by some other factors such as root surface area, root exudation, mycorrhization, and degree of transpiration (Davies 1995). Absorption of Pb from soil increases with the increase in pH from 3 to 8.5, while at pH 5.5 to 7.5, its solubility is controlled by phosphate or carbonate ions (Sharma and Dubey 2005). Plants' root absorbs the Pb through apoplastic pathway or via Ca^{2+} permeable channels (Rudakova et al. 1988; Pourrut et al. 2011). After uptake, it accumulates primarily in root cells, due to the blockage by the Casparian strips inside the endodermis. Further, lead is also trapped by the negative charges that exist on the roots' cell wall (Seregin and Ivaniov 1997, 2001). At root surface, Pb binds to carboxyl groups of mucilage uronic acids which restrict the Pb uptake into the root and form an important barrier to protect root system (Morel et al. 1986). Plant growing in Pb-contaminated medium exerts several adverse effects. Accumulation of lead in plants exerts several deleterious effects on morphological, physiological, and biochemical function of plants, either directly or indirectly. When Pb enters inside the cells, it causes toxicity by altering cell membrane permeability, by reacting with active groups of metabolic enzymes, by replacing essential ions, and by complex formation with phosphate group of ADP or ATP. Lead toxicity causes inhibition of enzyme activities, disturbed mineral nutrition, water imbalance, hormonal disturbances, inhibition of ATP production, lipid peroxidation, change in membrane permeability, and DNA damage by overproduction of reactive oxygen species (ROS) (Sharma and Dubey 2005; Pourrut et al. 2011; Sethy and Ghosh 2013). Further, high concentration of Pb in growing medium causes inhibition of seed germination, root and stem elongation, and leaf expansion (Morzck and Funicclli 1982; Gruenhage and Jager 1985). The extent of inhibition of root elongation depends on the concentration and ionic composition of lead and pH of the growing medium (Gruenhage and Jager 1985).

2.2.8 Manganese

Manganese (Mn) is an essential element for plant with a key role in various physiological processes particularly in photosynthesis and as an enzyme antioxidant cofactor. In plant cell, it exists as a cation in several complexes and can form metalloproteins in which Mn is tightly bound, probably to produce an appropriate protein conformation. Deficiency of Mn also affects the photosynthesis by affecting water-splitting system of photosystem II, which provides necessary electrons for photosynthesis (Buchanan et al. 2000). Mn deficiency occurs mostly in severely weathered sandy and organic soil having pH more than 6 (Alloway 2008). Mn has low phloem mobility, resulting in typical leaf symptoms of Mn deficiency which initially develops into premature leaves. In biological system Mn exists in many states preferably as II, III, and IV. In soil divalent state, i.e., Mn(II), is the most soluble form, while Mn(III) and Mn(IV) are very less soluble (Guest et al. 2002). The bioavailability of Mn in soil is influenced by soil pH and redox potential of Mn. Lower pH (<5.5) and increased redox potential of Mn increase the amount of soluble Mn(II) in soil (Kogelmann and Sharpe 2006; Watmough et al. 2007). Higher soil pH (up to 8) favors chemical autoxidation of Mn(II) causing the formation of MnO_2, Mn_2O_3, Mn_3O_4, and Mn_2O_7 which are normally unavailable (Ducic and Polle 2007; Humphries et al. 2007). Moreover, high pH also causes adsorption of Mn on soil particles, thereby decreasing their bioavailability to plants (Fageria et al. 2002). Mn is transported from root to aerial parts via the transpiration stream and accumulates in leaves which did not re-mobilize to other aerial parts through the phloem (Loneragan 1988). Accumulation of high concentration of Mn in leaves causes reduced rate of photosynthesis (Kitao et al. 1997a, b). Mn toxicity causes necrotic brown spots on leaves which start from the lower leaves and progresses with the time toward upper leaves (Horiguchi 1988; Wu 1994). Furthermore, with the time, the number and size of necrotic spots increase, resulting in necrotic lesions, leaf browning, and finally death (Elamin and Wilcox 1986a, b). Mn toxicity has also been attributed for the crinkled leaf, chlorosis, and browning of the youngest leaf, petiole, and stem tissues (Wu 1994; Bachman and Miller 1995). Probably, Mn-induced iron deficiency is the possible reason for chlorosis in younger leaves (Horst 1988). Mn toxicity is also associated with the brown coloring and sometimes cracks in roots (Bot et al. 1990a, b; Foy et al. 1995). Accumulation of Mn in leaves inhibits synthesis of chlorophyll by blocking iron, a concerning process resulting in the decrease in photosynthesis (Clarimont et al. 1986).

2.3 Heavy Metal Tolerances

Roots are the primary contact sites in terrestrial plants with exposure to metal. In case of aquatic plants, the whole plant body is exposed to metal present in growing medium. The growing medium contains essential and non-essential metals which on excess become toxic resulting in inhibition of growth and development and even death of the plant. In order to survive, plants have evolved some efficient and specific mechanisms to deal with the heavy metal stress. The adaptive mechanism evolved by plants to cope up with metal stress includes immobilization, plasma membrane exclusion, restriction of uptake and transport, synthesis of specific heavy metal transporters, induction of stress proteins, chelation and sequestration by specific ligands, etc. (Cobbett et al. 2000; Clemens 2006; Dalcorso et al. 2008; Hossain et al. 2009; Hossain and Fujita 2009; Sharma and Dietz 2009; Hossain et al. 2012a, b; Adrees et al. 2015a, b). Cellular mechanism for metal tolerance involves two basic approaches to keep low concentration of toxic metal ions in cytoplasm by preventing metal from being transported across the plasma membrane. It can be achieved either by increasing binding of metal ions to cell wall or by pumping out the metal from cell by active efflux pumps. Another approach is detoxification of toxic metal ions by inactivation via chelation or conversion of toxic metal ion into less toxic forms (Zhu et al. 2004).

2.3.1 Cellular Exclusion of Heavy Metals

Cellular exclusion of heavy metals is an important adaptive system for plants to tolerate the heavy metal toxicity. A large fraction of heavy metals are found in the apoplastic space in plant roots. Tice et al. (1992), defined apoplastic and symplastic aluminum fraction in root tips of Al-intoxicated wheat (i.e., Al-sensitive and Al-tolerant wheat cultivars) and reported that at equal external Al concentrations, a sensitive wheat cultivar had more symplastic Al than a tolerant cultivar suggesting exclusion mechanism. They also suggested that the distribution of Al in two cultivars did not support a symplastic detoxification hypothesis, but the role of cytoplasmic exclusion remains disturbed. The transporter proteins are potentially involved in the cellular exclusion of toxic metal ions from the symplastic to apoplastic space. Further, cytoplasmic exclusion could be accomplished through selective permeability of plasma membrane, formation of a plant-induced pH barrier in the rhizosphere, immobilization of metal on the cell wall, or exudation of chelating ligands (Taylor 1991; Tice et al. 1992).

2.3.2 Heavy Metal Complexation at Cell Wall-Plasma Membrane

When a plant cell is exposed with heavy metals, the cell wall-plasma membrane interface accumulates large portion of heavy metals. Iwasaki et al. (1990), reported that about 60 % of the total root Cu was bound to the root cell walls and plasma membranes in Italian ryegrass (*Lolium multiflorum*) and red clover (*Trifolium pratense* L.). Exchange site present on the cell wall determines the cation exchange capacity (CEC). Masion and Bertsch (1997), reported that a sensitive wheat cultivar have low cell wall CEC concentration and show less tolerance to Al, while a tolerant cultivar have a high concentration of cell wall CECs and show high tolerance to Al. Further, the sensitive wheat cultivars showed a higher affinity for aluminum than tolerant cultivars which indicate that tolerance mechanism is based on the cell wall permeability.

2.3.3 Sequestration Within Vacuoles

Vacuole is commonly considered as the main storage cell organelle for metals in plant, and there is evidence that phytochelatin-metal complexes are driven into vacuole (Salt and Rauser 1995). There are several studies showing that the vacuole is the site for the accumulation of heavy metals (Ernst et al. 1992; De 2000). Once a plant cell is exposed to any toxic metal ions, it mechanizes various strategies to cope with the metal toxicity. Intracellular sequestration or vacuole compartmentalization is also one of them, in which toxic metals are transported either out of the cell sequestrated into vacuole, thereby removing it from the cytosol or other cellular compartments where sensitive metabolic activities take place (Clemens 2006; Dalcorso et al. 2010). In some hyperaccumulator plants, vacuole compartmentalization of metal is also a part of tolerance mechanism. It has been reported that the hyperaccumulator plants enhance their metal tolerance by compartmentalizing most of the intracellular metal present in leaves into vacuole (Kramer et al. 2000). Further, the two proton pumps, i.e., vacuolar proton-ATPase (V-ATPase) and vacuolar proton-phosphatase (V-Ppase), strengthen vacuolar uptake of most solutes. The uptake of metal ions can be catalyzed either by channels or by transporters. To date, a wide range of gene families have been identified which are probably involved in transition of metal ions uptake into cell, vacuole sequestration, remobilization of metal from vacuole, xylem loading, and unloading of metals. Several metal transporter proteins have been also reported, *viz*., zinc-regulated transporter (ZRT), iron-regulated transporter (IRT), ATP-binding cassette (ABC) transporters, the P-type metal ATPases, multidrug resistance-associated proteins (MRP), natural resistance-associated macrophage protein (NRAMP) family, ABC transporters of the mitochondria (ATM), cation diffusion facilitator (CDF) family of proteins, copper transporter (COPT) family proteins, yellow-stripe-like (YSL) transporter, Ca^{2+} cation antiporter (CAX), and pleiotropic drug resistance (PDR) transporters (Lee et al. 2005; Kramer et al. 2007; Chiang et al. 2006; Dubey 2011; Hossain et al. 2012a, b).

2.3.4 Metal Chelation by Phytochelatins

To protect themselves from toxicity of heavy metals, chelation of metal ions with high-affinity ligands is one of the prevailing mechanisms of metal detoxification

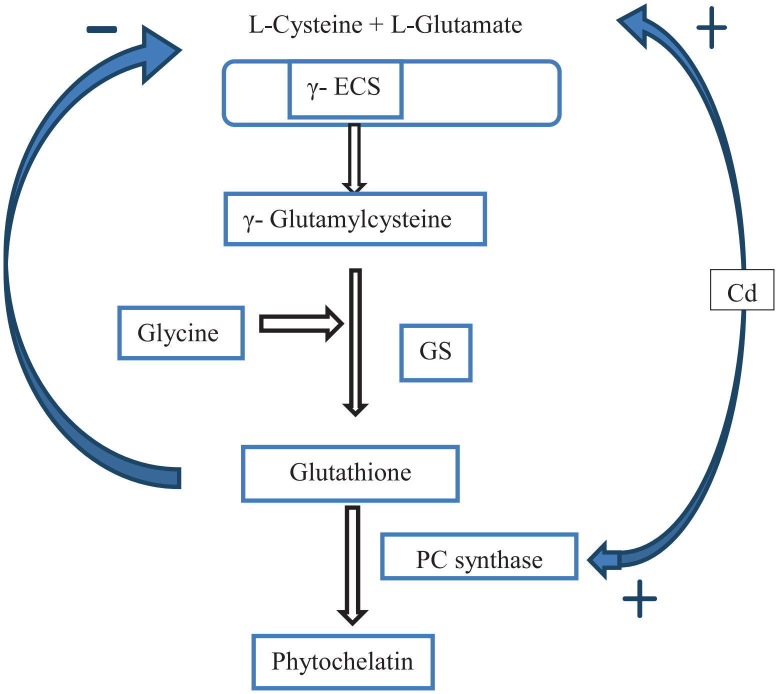

Fig. 2.1 Biosynthesis of phytochelatins in plants (Zenk 1996; Mejare and Bulow 2001)

and tolerance in plants. When a toxic metal enters in a plant cell, it may be scavenged by amino acids, organic acids, and tripeptide GSH or by specific metal-binding ligands. The two classes of peptides or metal-binding ligands are phytochelatins (PCs) and metallothioneins (MTs). The role of phytochelatins in metal detoxification and tolerance has been widely studied in plants (Zenk 1996; Cobbett 2000; Clemens 2001; Mishra et al. 2006). Phytochelatins are not present only in plant cells but have also been reported in fungi and other organism (Grill et al. 1987; Gekeler et al. 1988; Piechalak et al. 2002). Phytochelatins are small, cysteine-rich polypeptides which have potential to form complex with heavy metal ions via thiolate coordination. The general structure of phytochelatin is $(\gamma\text{-Glu-Cys})_n X$, in which X is Gly, γ-Ala, Ser, or Glu and n is the number of peptides = 2–11. Most of the common forms of PCs have 2–4 peptides. The biosynthesis of phytochelatins is activated in the presence of heavy metals; however, Cd has been reported as the strongest inducer (Grill et al. 1987). PCs are synthesized from glutathione (GSH; (γ-Glu-Cys-Gly)) and related compounds (Fig. 2.1). Their biosynthesis is catalyzed by the enzyme phytochelatin synthase (γ-glutamylcysteine dipeptidyl transpeptidase) which gets activated in the presence of metals (Tomaszewska et al. 1996; Vatamauniuk et al. 2000).

Metal binds to the constitutively PC synthase, thereby activating it to catalyze the conversion of glutathione to phytochelatin. Glutathione is the substrate of the phytochelatin which is synthesized from its constituent amino acids, i.e., L-cystein and

L-glutamate, in two consecutive steps. In the first step, i.e., the formation of γ-glutamylcysteine from L-cystein and L-glutamate is catalyzed by γ-glutamyl-cys synthetase (γ-ECS), while in second step glycine is added to γ-glutamylcysteine by glutathione synthetase (GS). The γ-glutamyl-cys synthetase is dependent on the availability of cysteine and feedback regulated by glutathione (Zenk 1996; Mejare and Bulow 2001).

Further, PCs form complexes with metal ions in cytosol and subsequently transport them into vacuole and protect plant cell from the toxic effects of metals (Salt and Rauser 1995).

2.3.5 Metal Chelation by Metallothioneins

Metallothioneins (MTs) are cysteine-rich (more than 30 % from all amino acids), metal-binding, low-molecular-mass proteins (2–16 kDa) that play a crucial role in detoxification and metabolism of metals. MTs have a unique property of binding d-block metal ions through the 20 cysteinyl groups which are abundant in their structural constituent. MTs were first reported by Margoshes and Vallee in 1957, from a horse renal cortex tissue (Margoshes and Vallee 1957). Metallothioneins have been well reported in bacteria, fungi, and plants (Lerch 1980; Kagi 1991; Murphy and Taiz. 1995; Suzuki et al. 2002; Ryvolova et al. 2011). On the basis of cysteine residue, plant MTs have been subcategorized into three classes, i.e., Cys-Cys, Cys-X-Cys, and Cys-X-X-Cys motifs (in which X denotes an amino acid). The biosynthesis of MTs (gene-encoded polypeptides) is induced by many factors including cytotoxic agents, hormones, and heavy metals (Kagi 1991; Yang et al. 2005; Zhou et al. 2006). Ahn et al. (2012) reported that there are three MT genes, *viz*., BrMT1, BrMT2, and BrMT3, in *Brassica rapa* which regulates the biosynthesis of MTs under the several metal stress condition. Furthermore, it has also been reported that MTs play an essential role as a Zn donor for several essential metalloproteins comprising matrix metalloproteinases and zinc fingers (Ryvolova et al. 2011).

2.4 Conclusions

Heavy metals/metalloids are important class of inorganic contaminants which enter into the soil and water through various natural and anthropogenic sources. Although some metals like Fe, Cu, Zn, Ni, etc. at required levels are essential for normal growth and metabolism of plants, however, their exposures at high concentration cause several negative impacts on the plant growth. Some metals such as As, Pb, Cr, Cd, etc. are non-essentials, and its contamination in growing medium causes various negative health effects. For terrestrial plants, roots are the primary contact sites exposed directly to the metal contaminants while, in case of aquatic plants, the whole plant body is exposed to metal present in growing medium. Metal contamination in growing environment causes disturbances in the physiological and biochemical processes of plants resulting in altered metabolism, growth reduction, lower biomass, chlorosis, necrosis, wilting, water imbalance, etc.

Heavy metals/metalloids differ in their affinity for O-, N-, and S-containing ligands depending on the physical and chemical properties of the heavy metals/metalloids ions. The metal toxicity is influenced by the binding ability of metals to various ligands present in metal biological system such as carboxylate ion, imidazole, sulfhydryl group, and aliphatic amine. In order to survive, plants have evolved many efficient and specific mechanisms to cope up with the metal stress. Adaptive mechanisms evolved by plants to deal with metal stress are immobilization, plasma membrane exclusion, restriction of uptake and transport, synthesis of specific heavy metal transporters, induction of stress proteins, chelation and sequestration by specific ligands, etc. Increasing research about the natural variation in the potential of plants to accumulate, tolerate, and detoxify heavy metals provides us wealthy information. Therefore, an extensive knowledge from various research domains will further increase our understanding about the fundamental mechanism involved in hyperaccumulation which allows us to find out that plants are more suitable for remediation of heavy metal-contaminated environment.

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