



Chapter 4

Heavy metals accumulation in crop plants: Sources, response mechanisms, stress tolerance and their effects

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Abstract

Heavy metals are one of the major substances concerned with agricultural pollution. The heavy

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metals are highly toxic to plants and living life. Heavy metals play a vital role in nature as they are essential for the plant's normal growth. These heavy metals are also involved in redox reactions, transferring electrons, basic functions in nucleic acid metabolisms, and being an integral part of several enzymes as a direct participant. The availability at a certain concentration of these essential metals in growing medium is very important, but their excess concentration results in several toxic effects. Therefore, the present book chapter comprised the information for better understanding of heavy metal toxicity and their accumulation mechanism by the plants.

Keywords: Heavy metals, Metallothioneins, Phytochelatins, Toxic effects, Stress tolerance mechanisms, Uptake mechanisms

Introduction

Environmental contamination by significant metals could be a worldwide issue as a result of rising in urbanization, increment, and mining activities, etc. and leads to varied short- and long-run effects on the environment (Kumar *et al.*, 2015; Khanna *et al.*, 2018). Heavy metals such as Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn, etc. are highly toxic to the environment (soil and water) (Kumar *et al.*, 2016; 2017). Heavy metals can be defined as any metallic element with a specific gravity greater than five (g/cm^3) (Khanna *et al.*, 2018). The plants grown on soils with contaminated effluent (heavy metals) show several physiological changes in the biochemical process like nutrient accumulation, respiration, gaseous exchanges, etc. The substantial metal has poisonous quality because of overwhelming the stress in plants which vary with a few variables like plant species, the convergence of the substantial metal and its concoction structure and soil creation (Nagajyoti *et al.*, 2010).

Role and sources of heavy metals in plants

Different heavy metals play a vital role in nature as they are essential for the plant's normal growth. Important heavy metals such as Cu, Zn, Fe, Mn, Mo, and Ni play important roles in plant biochemistry and physiology (Zhuang *et al.*, 2009). As essential micronutrients, Cu and Zn are very important for normal plant growth as they either serve as an enzyme reaction cofactor and activator or exert a catalytic property in metalloproteins such as a prosthetic group. These crucial heavy metals also involve redox reactions, transferring electrons, basic functions in nucleic acid metabolisms, and being an integral part of several enzymes as a direct participant. The availability at a certain concentration of these essential metals in growing medium is very important, but their excess concentration results in several toxic effects (Nagajyoti *et al.*, 2010). Since synthetic and industrialization are the expanding source, these toxic metal contaminations go in the farming soil and water bodies. The heavy metals sources are discussed in Table 4.1 (Khanna *et al.*, 2018).

Table 4.1. Different sources of heavy metals in the agriculture and environment.

Sources	Heavy metals	References
Mining activities/smelting	Cr, Pb, Zn	Sumner (2000)
Geological and anthropic activities	Cr, Co and Ni, Cr, Pb, Zn	Facchinelli et al. (2001)
Sulfide mineral deposits	As	Nordstorm (2002)
Earth's crust	Cd, Hg, Pb, As	Järup (2003)
Phosphate fertilizers	Cd	Järup (2003)
Fossil fuels combustion, chemical industries, electroplating	Ni, As, Cr	Khodadoust et al. (2004)
Coal mining and steel processing industries	Zn	Greaney (2005)
Sewage, manures, sludge, limes	Cd	Yanqun et al. (2005)
Poultry waste, feed additives	As	Mukherjee et al. (2006)
Surface runoff from rain/snow	Hg	Kowalski et al. (2007)
Weathering of sedimentary rocks like sandstone and dolomite	Mn, Cr, As, Fe, Zn	Viers et al. (2007)
Industrial wastes	As	Tripathi et al. (2007)
Anthropogenic activities	Pb, Zn, Cu, Co, Ni, As	Jordanova et al. (2008)
Waste dumping	Cd, Pb, Cu	Zhuang et al. (2009)
Ores/mineral dissolution	Fe, Mn, Cr, Cd, Hg	Huffmeyer et al. (2009)
Pesticides	Hg, As, Cu, Zn	Arao et al. (2010)
Aerosols	As, Zn, Cd, Pb	Nagajyoti et al. (2010)
Atmospheric aerosols, windblown dust	Pb, Hg, Ni	Kang et al. (2011)
Industrial wastes and geological minerals	As	Murcott (2012)
Industrial waste pipes/additives	Cu	Mohod and Dhote (2013)
Volcanic emissions, forest fires, atmospheric deposition	Pb, Hg, Ni	Li et al. (2014)
Geological minerals	As, Cr, Pb, Mn	Kibria (2014)
Sewage irrigation	Cd, Pb, Cr, Hg	Su (2014)
Industrial pollution	As	Gillispie et al. (2015)
Geological processes and anthropogenic activities	Pb, As, Hg, Cd	Nkansah et al. (2016)
Metallic mining	Cd, Zn, Pb	Romero-Baena et al. (2017)
Chemical industries and geological minerals	Cd, Pb, Zn, As	Bech (2018)
Anthropogenic activities and industrialization	Cu, Cr, Zn, Ni	Adimalla (2019)
Smelting activities and agricultural industry, industrialization and urbanization	Ni, Cu, Cr, Mn, Zn, Fe	Doabi et al. (2019)
Geological and anthropogenic activities	Al, Fe, Mn, Si, As Cr, Hg, Ni	Kambunga et al. (2019)

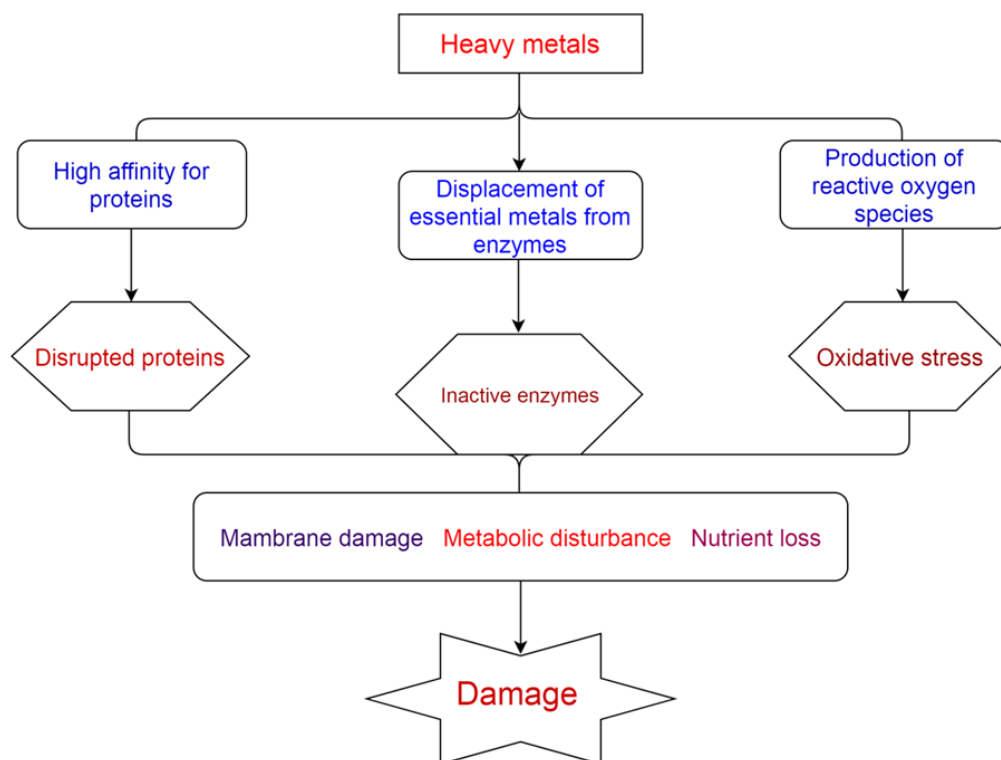


Figure 4.1. Summary of heavy metals induced toxicity mechanism in plants (Adopted from: Kumar et al., 2016).

These heavy metals are also known as trace elements (10mg/Kg or mg/L in soil/aquatic medium) or ultra-trace elements (1µg/Kg or µg/L in soil / aquatic medium) because of their presence in the soil environment. In addition to these essential trace elements, another category of heavy metals, Class B metals, considered to be non-essential trace elements such as Hg, Ag, Pb, and Ni, etc., are in nature very toxic. The mechanism of heavy metal-induced toxicity in plants is summarized in Figure 4.1. In a terrestrial system, plants are stationary and their roots are the main contact sites for trace metal ions, while the entire plant body is exposed in the aquatic system and metal ions are absorbed directly from the surfaces of the leaves due to particle deposition (Kibria, 2014). Plants are stationary, and plant roots for heavy metal ions are the main contact site. Because of this contact, due to the deposition of particles containing these metals, plants absorb heavy metals primarily through roots and also through the leaf surfaces. Those plants that are grown in aquatic systems face greater toxicity as the whole plant body is exposed to toxic ions in this type of plant. Some heavy metals are considered essential elements for plants (Fe, Cu, Mo, and Zn). Two key functions of essential heavy metals in cells are involvement in redox reactions and being an integral part of enzymes. Heavy metals such as Cu, Mo, Zn, etc.

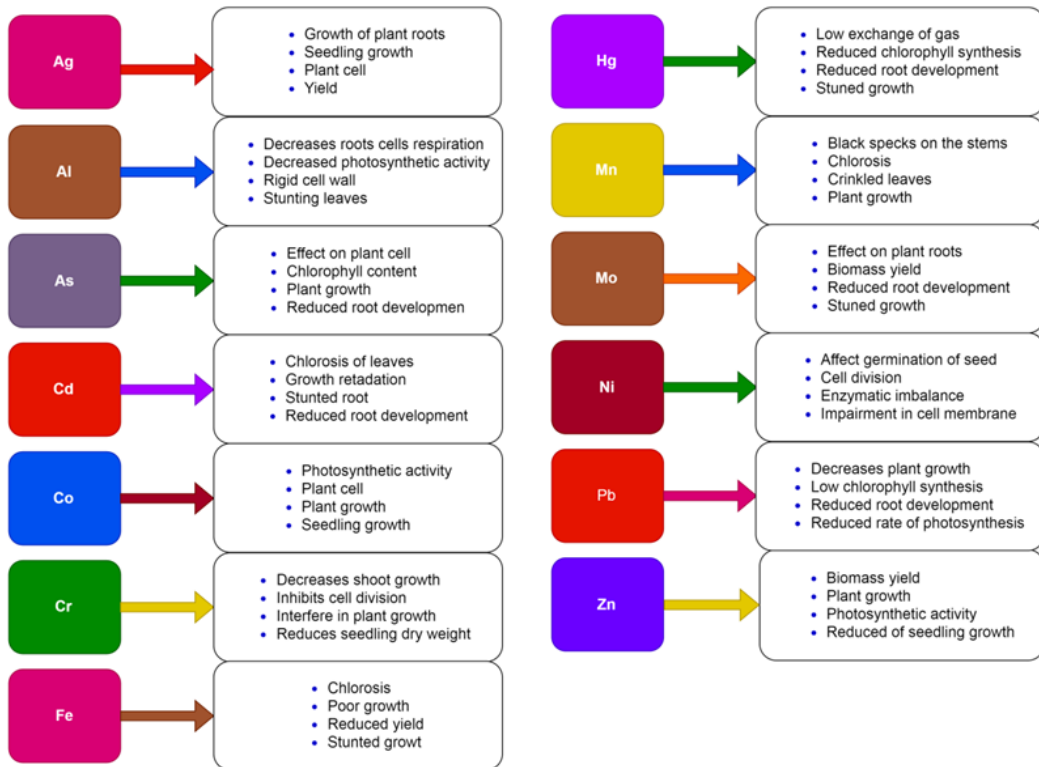


Figure 4.2. Heavy metal toxicity symptoms in plants (Adopted from: Kumar and Aery, 2016).

serve as cofactor and activator of various enzyme reactions and play a vital role in the formation of enzymes / substrate metal complexes or as a catalytic property as a prothesis group in metalloenzymes participate in electron transport and structural functions in nucleic acid metabolism (Nagajyoti *et al.*, 2010). Figure 4.2 shows the toxic effects of some heavy metals. Metals pollution is a worldwide issue for soil and water environment. The adverse effect of heavy metals on the growth and activities of soil microbes may also indirectly affect plant growth (Kumar *et al.*, 2016).

Heavy metal interference with ionic homeostasis and enzyme activity affects single-organ physiological processes (such as root nutrient uptake) followed by multiple processes such as germination, photosynthesis, respiration, plant water balance, metabolism, and reproduction. Indeed, visible symptoms of toxicity to heavy metals include chlorosis, necrosis, senescence, and wilting, stunted growth, low production of biomass, limited seed numbers, and eventually death. The plants that grow under heavy metal stress must spend more energy on their survival, which would otherwise have been available for their other process. This deficiency in the amount of energy required may result in the overall decrease in the growth of the plant in such hostile metal-stressed environment (Kumar and Aery, 2016).

Mechanisms of heavy metal chelation in crop plants

Chelation is a kind of molecular chemical bonding of metal ions. Heavy metal chelation is the plant's main approach to detoxify and tolerate high heavy metal concentrations. The ligand binds through the donor atoms to a heavy metal ion, chelation happens. Ligands are components that relate to the central metal ion's electronic orbitals and form secondary valence bonds that result in a complex molecule. High production of various metal chelating molecules *viz.*; organic acids, phytochelatins, metallothioneins (MTs), phytosiderophores, and ferritin or overexpression of metal transporter proteins coding genes increases the tolerance and accumulation of heavy metals in plant tissue (Verkleij *et al.*, 2003; Kumar *et al.*, 2016). In the process of chelating heavy metals, heavy metals approach the rhizosphere. It takes place both outside the body of the plant and within the cell of the plant. Several organic acids present in roots exudate the extracellular chelation of heavy metals, whereas different organic acids, amino acids, and peptides are responsible for intracellular heavy metal chelation within the plant cell. Metal-binding proteins and peptides are preferably metal precisely so that only toxic metals (e.g., Cd, Hg, Pb, and Cr) are appropriated and important metals such as Zn, Cu, etc. are discounted (Ryu *et al.*, 2003; Yang *et al.*, 2005). Chelators can be classified as natural and synthetic chelating agents. The plants produce various types of ligands that contain such compounds as citric acid and malic acid, amino acids, and S-containing compounds that form metal complexes. Because these ligands play a major role as detoxifying influences and are used to inhibit heavy metal persistence in plants. Citrate is Ni's chief ligand in *Thlaspi vaingense* leaves (Krämer *et al.*, 2000), while citrate and acetate bind Cd in *Solanum nigrum* leaves (Sun *et al.*, 2006). In addition, a large proportion of Zn is complexed with malate in *Arabidopsis halleri* and Cd in *Thlaspi caerulescens* (Sarret *et al.*, 2002). In Se hyperaccumulator plants, the main detoxification strategy is to protect against selenoamino acids, primarily selenocysteine (Se-Cys), resulting from the assimilation of selenite in leaf chloroplasts. Al-induced release of organic anions such as malate, oxalate, or citrate that chelate Al³⁺ in the rhizosphere and present its entry into the root of a number of plant species (wheat, maize, buckwheat, rye, taro, snap bean) has been shown (Sors *et al.*, 2009).

Metallothioneins (MTs) are a family of small, extremely conserved, cysteine-rich metal-binding proteins that are important for zinc and copper homeostasis, oxidative stress protection, and toxic heavy metal buffering. Metallothioneins are classified into three types as (I) metallothioneins are mammal-related polypeptides consisting of 61 amino acids and lacking aromatic amino acids or histidines. (II) MTs are from *Candida albicans*, yeast or cyanobacteria (Winge *et al.*, 1985); similar chelators of this class are *Saccharomyces cerevisiae* metallothioneins, which contribute to high plant copper tolerance (Kagi, 1991). (III) MTs are distinct polypeptides consisting of units of π -glutamylcysteinyl. Metallothioneins (MTs) are cysteine-rich (more than 30% of all amino acids), metal-binding, low-molecular-mass (2–16 kDa) proteins that play a crucial role in metal detoxification and absorption. MTs have a unique property of binding d-block metal ions through the 20 cysteinyl groups that abound in their component structure. Phytochelatins are MTs of the Third

Type. Heavy metals such as Cd, Zn, Hg, Ag, and Pb, especially in animal and plant species, induce the production of metallothionein. Cd is the best metallothionein activator, followed by other metals such as Ag, Bi, Pb, Zn, Cu, Hg, and Au Kagi (1991). In tobacco plants with transgenic coding for the polyhistidine cluster combined with yeast metallothionein, Cd uptake increased significantly. The introduction of a tobacco metallothionein gene also enhances tolerance to certain heavy metals such as Cd, Zn, and Ni (Macek *et al.*, 2002; Pavlíková *et al.*, 2004). Phytochelatins are glutathione oligomers formed by the phytochelatin synthase enzyme. In plants, fungi, nematodes and all algae groups, including cyanobacteria, phytochelatins are found. Phytochelatins act as chelators and are important for detoxification of heavy metals. PC2 is abbreviated by PC11. Phytochelatins are the well-known plant heavy metal chelators, especially from the Cd tolerance perspective. Phytochelatin's common structure is $(\gamma\text{-Glu-Cys})_n\text{X}$, where X is Gly, α -Ala, Ser, or Glu, and n is the number of peptides= 2-11. Most common PC forms have 2-4 peptides. Phytochelatins are synthesized in cytosol glutathione-derived peptides and are reported in a variety of plant species including monocots, dicots, gymnosperms, and algae (Cobbett and Goldsbrough, 2002). Plants exposed to Cd stress had 2.7-3 times more total phytochelatins than plants grown without Cd of the same lines. Phytochelatins form PC-metal (loid) complexes which are transported into vacuoles, thereby helping to reduce cytosol toxic metals (Guo *et al.*, 2012). Some synthetic chelators are also known beyond the aforementioned natural chelators. The practice of ethylenediaminetetraacetate (EDTA) among synthetic chelators has been more intensive (Grčman *et al.*, 2001). EDTA binds to and unloads heavy metal ions. High mobility and much easier to pass through the plasma membrane is an uncharged ion. EDTA application enhanced Pb accumulation in *Brassica juncea* (L.) Czern, 1000-10,000 times higher than control plants. In some cases, phytoremediation has recently used ethylenediamine disuccinate (EDDS) (a structural isomer of EDTA) to improve metal accumulation (Grčman *et al.*, 2003; Luo *et al.*, 2005).

Response of plants towards different heavy metals

The toxic heavy metals are also a serious fear of living organisms and plants as they are highly persistent and present in the soil ecosystem for a long time. The plant roots are the key contact sites for exposure to toxic heavy metals in terrestrial plants. For aquatic plants, the entire plant body is visible in the growing medium to the metal present. The growing medium includes crucial and non-essential metals that become toxic on excess, resulting in growth and development inhibition and even plant death (Figure 4.3). Plants have changed some effective and accurate mechanisms to deal with heavy metal stress in order to survive. The adaptive mechanism that plants have developed to cope with metal stress includes immobilization, exclusion of plasma membranes, restriction of absorption and transport, synthesis of specific heavy metal transporters, induction of stress proteins, chelation and sequestration by specific ligands, etc. (Clemens, 2001; Dalcorsio *et al.*, 2008; Adrees *et al.*, 2015). There are two simple ways to keep a low

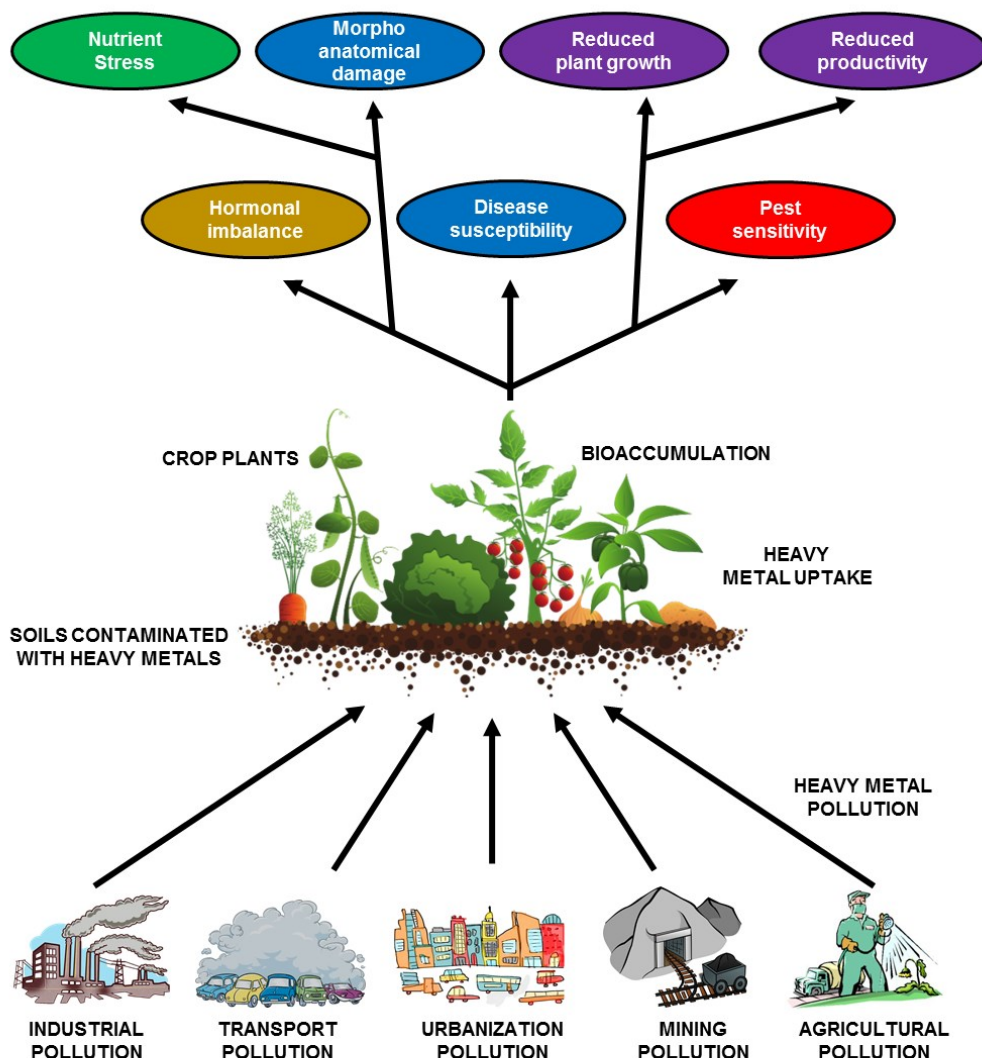


Figure 4.3. Response of crop plants toward different kind of environmental pollutions.

concentration of metal ions in the cytoplasm by preventing toxic metal from being transported across the plasma membrane, the cellular mechanism for heavy metal tolerance. It can be achieved either by increasing metal ion binding to the cell wall or by pumping the metal out of the cell through active efflux pumps. Another process is to detoxify toxic metal ions by inactivating them through chelation or altering toxic metal ion to a lower toxic concentration (Tong *et al.*, 2004). Plants are highly capable of solubilizing and absorbing various types of soil nutrients by helping to generate chelating agents and change pH and redox reactions (oxidation

and reduction reaction). They also have extremely precise mechanisms for different nutrients or metals being translocated and accumulated. These processes also complete heavy metal uptake and translocation, the physical and chemical properties of which are similar to those of vital compounds (Tangahu *et al.*, 2011; Kumar *et al.*, 2017). A plant's accumulation of metals is significantly affected by a number of factors such as plant structure, plant life cycle, plant vigor, soil pH, root system depth, temperature, partial oxygen pressure, carbohydrate level, respiration rate, nutrient interface and microbial presence, etc. (Chen *et al.*, 2006). Plants can precipitate heavy metals strongly by changing the rhizosphere's pH or by excreting anions such as PO_3^{-4} . The root surface can bind many heavy metals during the adsorption process. These heavy metals (Cd, Ni, Pb, and Sr) concentrate rapidly in plant root tissues (Hossain *et al.*, 2012). The generally plants could be classified into three categories as excluders, accumulators and indicators based on the mechanism of action for survival under stress conditions as suggested by Baker (1981).

Hyperaccumulation of heavy metal is the process by which plants accumulate metals in excess of 0.1-1% of the dry weight. Baker and Brooks (1989) gave this term to define plants containing more than 1000 mg/g nickel in leaves. Baker *et al.* (2000) reported that plants that accumulate more than 100 mg Cd /Kg (0.01 %) or more than 500 mg Cr /Kg (0.05 %) in dry plant leaf tissue could be considered as hyperaccumulator species. A plant with hyperaccumulator can accumulate and tolerate enormous quantities of pollutants from metals. Some plant species have the capacity to grow in the soil, are contaminated with heavy metals and have the capacity to accumulate high quantities of metals in soil-containing metals as an ecological adaptation (Lombi *et al.*, 2002). The main methods involved in the hyperaccumulation of toxic metals in plants include bio-activation of heavy metals in the rhizosphere by means of root microbe interfaces, improved activity of metal conveyor proteins in the cell membranes, detoxification of metals by limiting them to apoplasts, chelation of heavy metals in the cytoplasm by several ligands and sequestration of metals into the vacuole by means of several ligands.

Silver (Ag)

Silver (Ag) concentration in the Earth's crust and soil averages approximately 0.06 and 0.13 mg/Kg. It is used primarily in photographic industries and is also useful in other areas such as batteries, coins, jewelry, silverware, catalysts, brazing, and soldering of electronics. Therefore, silver toxicity depends on the concentration of active free silver ions (Ag^+), found primarily in the aqueous stage. Several processes in medium and water characteristics reduce silver toxicity by preventing free Ag^+ formation or by avoiding binding Ag^+ to organisms' reactive surfaces. For a long time, the toxic effects of Ag on plants grown on the ground have not been reported (Khanna *et al.*, 2018). Ratte (1999) reported that about 5 mg/Kg Ag in shoots and about 1500 mg/Kg in bush bean roots significantly reduced yields without any symptoms of toxicity Wallace *et al.* (1977) reported that Ag in the nutrient medium at a very low concentration (10 $\mu\text{g/L}$) stimulated the growth of grass roots. He speculated that some cations (e.g., Ag, Co, and Cu) could indirectly change cell metabolism, leading to a higher cell growth rate. The Ag replaces K^+ sites in

membranes and prevents the roots from absorbing other cations. High Ag concentrations (up to 1 $\mu\text{M/L}$) significantly decrease growth and protein content, while sunflower enzyme urease activity is increased (Krizkova *et al.*, 2008).

Aluminum (Al)

Aluminum is the third richest element in the crust of the Earth, occurring at around 8%. It has some useful features that allow us to use it in various industries such as electrical, metallurgical, transportation, packaging, and chemical manufacturing. The various aluminum residences are often used in the manufacture of paper, sugar refining, water purification, wood preservation, leather tanning and textiles for water resistance (Kumar and Aery, 2016). As insoluble aluminosilicates and oxides, Al is present in the soil. In the initial phases of plant growth, it is easily accumulated by plant roots and translocated within the plant, but then drops sharply with advancing maturity. The concentration of other elements (P and Ca) in the rhizosphere affects the accumulation of Al.

Aluminum in the soil can inhibit the growth of plants at a level as low as 1 mg/Kg (Rana and Aery, 2000). The root tip, which turns brown, shows the earliest symptoms of Al toxicity. The damage is limited to the root tip's active growth of tissues. In particular, the distal part of the root apex transition zone is highly sensitive to Al toxicity (Kumar and Aery, 2016). This extensive damage to the root structure leads to the reduced and damaged root system and the absorption of limited water and mineral elements. This will result in the plant's deformed growth. Aluminum is known to affect other nutrients such as Ca, Mg, P, and K intake, transportation, and functions. The reduced absorption of nutrients leads to deficiencies in nutrients. The application of Al to plants can block the uptake of many cations such as Ca^{2+} , Mg^{2+} , K^+ , and NH_4^+ by interrelating directly with several different channel proteins (Pineros *et al.*, 2001).

Cadmium (Cd)

The usual Cd content is 0.1 and 0.41 mg/Kg, respectively, in the Earth's crust. Most cadmium is used in the production of batteries (Ni-Cd and Ag-Cd). It is also used in relatively large quantities as pigments (yellow), coatings and stabilizers. Cd is also used for alloys and is used as a stabilizer for various plastics due to certain distinctive physical and chemical characteristics (Kumar and Aery, 2016). Commonly, Cd is considered to be one of the most harmful metals that adversely affect all living organism biological processes including humans, animals, and plants. Although, plants are considered a non-essential heavy metal. Due to its high water solubility and high toxicity, cadmium was ranked 7th among the top 20 toxins (Prasad, 1995). Cadmium has been described among the class of heavy metal pollutants as a very important pollutant. The toxicity of cadmium can be easily identified in the form of stunt growth, chlorosis, root tip browning, and ultimately plant death (Kumar *et al.*, 2016). Excess Cd in growing soil may cause leaf chlorosis, but it may be due to iron deficiency and toxic metal interaction. Due to direct or indirect interaction with Fe in leaves, chlorosis may appear. It is also found that the presence of excess

cadmium in soils causes suppression in the uptake of iron by plants (Kumar *et al.*, 2016).

Cobalt (Co)

Cobalt has cobaltite, smaltite, and erythrite in the minerals. Like many other metals, Co-contaminated soil pollution is largely due to mining and smelting, sewage sludge dispersal, and fertilizer use, which can pose an environmental risk (Bakkaus *et al.*, 2005). It is, therefore, necessary to evaluate the possibility of adverse effects of Co on the terrestrial ecosystem. Some studies on Co toxicity to soil microbes and invertebrates have been conducted. But the literature on the toxicity and risk of Co to higher plants is limited. Some studies found that when given in high doses, Co is relatively toxic to plants. Cobalt uptake and distribution in plants is dependent on species and controlled by various mechanisms. Root absorption of Co^{2+} involves active transportation across cell membranes, even though the molecular mechanisms remain unknown. Although low mobility of Co^{2+} in plants restricts its transportation from roots to shoots, its distribution may involve organic complexes (Lock *et al.*, 2007).

Chromium (Cr)

Chromium (Cr) is Earth's 7th most abundant component and 21st in the crust, with an average concentration of 100 mg/Kg. It is used primarily for stainless steel, pigments, metal finishing, and preservatives of wood, chemicals, and chromate plating. For paints, varnishes, glazes, inks, and paper, chromium is usually used in the production of green tints. Significant amounts of Cr compounds are also used in leather tanning. Dyestuffs and leather tanning are the main source of Cr pollution in the environment when waste is discharged directly into aquatic bodies. (Aery and Kumar, 2016). Cr is considered a non-essential metal for the plant and plant growth and development has been well reported for its toxicity. Plants use inactive mechanisms to absorb chromium in its trivalent form, i.e. Cr(III), while Cr(VI) is inhibited by SO_4^{2-} and Ca^{2+} (Vikram *et al.*, 2011).

Due to their high oxidation power, hexavalent ions, i.e. Cr(VI), damage the root membranes. Cr enters plant roots through root exudates reduction and/or complexation, enhancing solubility and mobility through root xylem (Shanker *et al.*, 2005). However, Cr's accumulation and mobilization within the storage tissue depends on its ionic state, it accumulates mainly in roots and is poorly translocated to shoots. Like cadmium, Cr(VI) also reduces the uptake of many essential elements such as Fe, Mg, Mn, Ca, P, and K resulting in many negative plant growth effects (Peralta-Videa *et al.*, 2009).

Iron (Fe)

Iron plays an important role in animals, plants and as well as microbes. Plants mostly get Fe from the plant's rhizospheric zone. While iron is one of the largest abundant metals in the crust of the earth, it is very low to obtain plant roots. Iron through the Fenton reaction is very reactive and toxic. Thus, plants control Fe homeostasis tightly and react to both Fe deficiency and Fe excess.

Plant's ability to respond to the availability of Fe ultimately affects human nutrition in terms of both crop yield biomass and concentration of Fe in edible tissues. Thus, illuminating the mechanisms of Fe absorption and transportation is essential for the breeding of crops that are additional nutrient-rich and more tolerant of Fe-limited soils. Iron is primarily accumulated by plants, solubilizing Fe^{3+} and then reducing it to Fe^{2+} for absorption or transportation into the root (Kumar et al., 2016). Iron plays an important role in many plant forms of physiology and biochemistry. It assists as a component of many vital enzymes such as the electron transport chain's cytochromes and is therefore essential for a wide range of biological activity. Iron is involved in chlorophyll synthesis in plants and is vital for maintaining the construction and function of chloroplast (Rout and Sahoo, 2015).

Fe is accumulated primarily by plants, solubilizing Fe^{3+} and then reducing it to Fe^{2+} for absorption or root transport. Fe is transferred as ferric citrate or iron(III) chelate form from roots to shoots and transported to active growing shooting regions. Iron is a crucial mineral for plants that is essential for the biological redox system, and it is also a vital component of numerous enzymes that play significant roles in plant physiology and biochemistry. It acts as a cofactor of key enzymes involved in plant hormone synthesis and is involved in many reactions to electron transfer (Jeong et al., 2008). Because of their immovability, plants are exposed to varying changes in iron obtainability from the environment. Therefore, it is believed that either malnutrition or extra volumes of this component generate oxidative stress (Abdel-Kader, 2007), which leads to numerous nutritional disorders affecting plant physiology. The toxicity of reactive oxygen species depends on the presence of a Fenton catalyst, such as iron or copper ions, which leads to extremely reactive OH^{\cdot} radicals in the presence of Fenton. The reactive toxic oxygen species cause damage to DNA proteins, lipids, chlorophyll, and nearly every other organic essential of living cells (Becker and Asch, 2005).

Mercury (Hg)

The average concentration of Hg in the Earth's crust is 0.07 mg/Kg; while it ranges from 0.58 to 1.8 mg/Kg in multi-group soils around the world, and the average global mean is estimated to be 1.1 mg/Kg. Mercury used primarily in gold mining, batteries, paints, pesticides, impregnation of wood, and electrical products. Because of its enormous use, this metal is accumulated at various sites and is reflected as a global pollutant (Kabata-Pendias, 2011). Plants take up mercury directly depends on its quantities in the soil. As the volume of Hg in the soil increased, there was an increase in plant concentration of Hg. While an extreme portion of Hg is found in roots, a significant fraction of Hg was also stored in leaves and grains. Not only is mercury accumulated from the soil by plants, but it is also immersed in progressively released Hg vapor from the soil (Israr et al., 2006).

Stunted plant growth, reduced root development, and photosynthetic activity inhibition are the major common symptoms of Hg toxicity. It is also responsible for a various metabolic activity like a failure; photosynthesis, synthesis of chlorophyll, gas exchange, and respiration. The higher root

accumulation of Hg inhibits plant uptake of K^+ . It is also observed, however, that lower volume of Hg stimulates K^+ uptake. It is known that the toxicity of volatilized elemental Hg is the most serious for plants. By increasing the production of ethylene, Hg vapor induces processes related to senescence, and the most active toxicant is elemental Hg, not its ionic form. More than developed plants, young plants are more sensitive to Hg-saturated air. Mercury has a strong affinity with multiple proteins and enzyme amino acids. It appears that its binding nature to sulfhydryl groups is the key reaction to plant metabolism disruption (McNear *et al.*, 2012). The association of Hg with Se in soybean root molecules of high molecular weight. In addition, improved antioxidant enzyme activity is observed in some cases when mercury is applied to growth media (Zhou *et al.*, 2008).

Manganese (Mn)

Mn is a common metal in the crust of the earth and its occurrence in soils is primarily the result of the parent material. In recent times, however, the severe anthropogenic has focused on increasing manganese content and obtainability in many soils. Mine tailings and metal smelters, long-term and heavy use of sewage sludge (biosolids) or other organic changes in agricultural soils all result in an increase in manganese content or accessibility (Kumar *et al.*, 2016). Mn is a vigorous plant component that interferes in several metabolic activities, mostly in photosynthesis and as an antioxidant-cofactor enzyme. Several studies on the toxicity of manganese and translocation of Mn from soil to plant tissue in the form of Mn^{2+} have confirmed their significance under low pH and redox soil conditions. Mechanisms that can tolerate this toxicity are also recorded when Mn metal is inside the plant cell, making it vital to compartmentalize this metal in different plant tissue (leaves, roots, shoots, and leaf plant cells) (Millaleo *et al.*, 2010). Also recorded as a defense mechanism was the important role of the antioxidant process in the plant in relation to the high concentration of manganese. Excessive concentrations of manganese in plant tissues can change numerous developments, such as the activity of enzymes, absorption, translocation and use of other mineral elements (Ca, Mg, Fe and P), which can cause oxidative stress. The Mn injury threshold, as well as the tolerance of an extra of this metal, is highly dependent on the species of plants and cultivars or genotypes within a species (Ma *et al.*, 2015). Nutrient translocation in epidermal root cells via an active transport system and transported to the plants as a divalent cation Mn^{2+} . The roots characterize Mn accumulates as a biphasic process. The early and rapid uptake phase is reversible and non-metabolic, with freely exchanged rhizosphere Mn^{2+} and Ca^{2+} or other cations. In this first phase, Mn^{2+} seems to be adsorbed by the root-cell apoplastic places 'negatively charged cell wall ingredients (Humphries *et al.*, 2007). The second phase is slow, with less easy exchange of Mn^{2+} .

It is dependent on plant metabolism to incorporate it into the symplast, although the precise mechanisms are not clear (Humphries *et al.*, 2007). The study has studied that Mn binds to this protein in transgenic tobacco converted with a tomato plant root protein at its N-terminus (LeGlpI) with a metal binding side. This strongly refers to LeGlpI's contribution to manganese soil

uptake (Takahashi and Sugiura, 2001).

Molybdenum (Mo)

Mo is present in the lithosphere at an average concentration of up to 23 mg/Kg but may increase concentration (300 mg/Kg) in shales containing important organic matter. Mo is present as numerous different complexes in agricultural soils depending on the soil section's chemical speciation (Kaiser *et al.*, 2005). The strong relationship between Mo and Fe metabolisms is presumed because (i) the absorption mechanisms for Mo and Fe affect each other, (ii) the majority of molybdoenzymes also require the-containing organic reductions or organic oxidation groups such as the-sulfur groups or heme, (iii) Mo metabolism has enrolled mechanisms typical of iron-sulfur cluster synthesis, and (iv) both Mo cofactor synthesis and extra synthesis. Tomatsu *et al.* (2007); Bittner *et al.* (2014) the studied that Mo present in the soil are many forms in the soil such as molybdenite (MoS_2) or ferrimolybdate [$\text{Fe}_2(\text{MoO}_4)_3$], and its dissolved and plant-available form molybdate (MoO_4^{2-}). Plants take up molybdate from the soil by Mo transporters, such as MOT1 in *A. thaliana*.

Nickel (Ni)

Ni is a key component of several metalloenzymes such as superoxide dismutase, NiFe hydrogenases, M-reductase methyl coenzyme, urease, Co-A acetyl synthase, dehydrogenase carbon monoxide, hydrogenases, and RNase A. In addition, Ni's high exposure in growing medium affects the activities of amylases, proteases, and ribonucleases that subsequently affect the digestion and metabolization of food reserves in seed germination. Ni is considered at a lower concentration (0.01 to 5 μg) as a vital component for plants. Ni uptake from growing medium occurs primarily through passive diffusion and active transport. Through the cation transport system, plants passively absorb soluble Ni compounds.

The chelated Ni compounds are taken and translocated using transportation proteins such as permeases through an active-transported-mediated system (Ahmad and Ashraf, 2011). The high concentration of Ni in growing medium causes physiological process alteration and various symptoms of toxicity such as chlorosis, necrosis, and wilting. Plants growing in excess of Ni medium have negative effects on photosynthesis, mineral nutrients, transport of sugar, and balance of water. Reduction in water intake is an indicator of increasing Ni toxicity in plants. High-level Ni exposure increases MDA concentration that could disturb membrane function and cytoplasmic ion balance, especially K^+ ; the highest mobile ion in the cell membrane (Gajewska *et al.*, 2006; Sethy and Ghosh, 2013).

Lead (Pb)

The average content of lead (Pb) in the crust of the Earth is estimated at 15 mg/Kg. Two types of Pb are known in the terrestrial environment, i.e. primary and secondary. At the time of their formation, primary Pb is of geogenic activates and incorporated into minerals, while secondary

Pb is of radiogenic origin from uranium and thorium decline. The greatest use of lead is in the production of batteries of lead acid. In solders, alloys, cables, and chemicals, it is also used.

Lead (Pb) is a non-essential toxic element that is one of the most omnipresent in the soil. The plant is mainly produced from soil and aerosol (Sharma and Dubey, 2005). Roots are more able to accumulate Pb in plants; however, their subsequent translocation to aerial parts is highly restricted. The availability of lead in soil depends heavily on soil conditions such as soil pH, particle size and capacity for cation exchange.

In addition, some other factors such as root surface area, root exudation, mycorrhization, and degree of transpiration also affect the availability and uptake of Pb. Plants' root absorbs the Pb through the apoplastic pathway or via Ca^{2+} permeable channels (Pourrut *et al.*, 2011). It accumulates after take-up primarily in root cells due to the blockage inside the endodermis by the Casparian strips. In addition, lead is also trapped on the roots cell wall by the negative charges (Seregin and Ivaniov, 2001). The accumulation of lead in plants has several deleterious effects, either directly or indirectly, on the morphological, physiological and biochemical functions of plants. When Pb enters the cells, toxicity is caused by altering the permeability of the cell membrane, by reacting with active metabolic enzyme groups, by replacing essential ions, and by complex formation with the ADP or ATP phosphate group. Lead toxicity causes inhibition of enzyme activity, disturbed mineral nutrition, water imbalance, hormonal disturbance, inhibition of ATP production, lipid peroxidation, changes in membrane permeability and damage to DNA by overproduction of reactive oxygen species (ROS) (Sharma and Dubey 2005; Pourrut *et al.*, 2011; Sethy and Ghosh, 2013).

Zinc (Zn)

Zinc is considered a vital plant micronutrient because it is crucial for normal cell metabolism and plant growth at an ideal concentration (Dhankhar *et al.*, 2012). In many physiological processes such as multiple biomolecules metabolism, gene expression and regulation, enzyme activation, protein synthesis, and reproductive development, it plays an essential role as a cofactor. However, higher concentration accumulation of zinc in the plant ($> 300\mu\text{g}^{-1}$ in dry weight) causes physiological alteration and inhibition of growth (Cakmak, 2000). High zinc exposure in growing medium inhibits several metabolic functions of plants, leads to stunted growth, and causes senescence. Zn toxicity limits root and shoot growth (Fontes and Cox, 1998). It also causes chlorosis in premature leaves at high concentration, which may extend on prolonged high exposure to older leaves.

The excess of Zn also causes a deficiency in shoots of other essential elements such as Mn and Cu, which hinders the transfer from root to shoot of these essential micronutrients. The possible reason for this translocation interference of these micronutrients is that the iron and manganese concentration in a plant grown in zinc-rich media is greater in root than the shoot (Ebbs and Kochian, 1997).

Conclusion

Anthropogenic activities have contributed to continuously increasing the levels of different contaminants in agricultural soils. The present book chapter revealed that the heavy metals impose several toxic effects on the plant and adversely affect the growth as well as the development of plants. The integrated response adopted by plants toward metal stress, particularly in the form of antioxidant ability is the most important mechanism by which the crop plants tolerate towards the toxic metals. Sometimes, due to the ionic affinity of the metals with plant root enzymes they were taken by the vegetative parts of crops which create the health issues in the respective consumer. The efficient mitigation of such heavy metals should be done to minimize the heavy metal risk for both the plant and living beings by adopting eco-friendly approaches.

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