The Toxicity and Accumulation of Metals in Crop Plants

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Abstract

Metals are ubiquitously present in the environment and are crucial for life on earth. This is because several metals perform life saving biological functions. However, there are other metals, which are non-essential. The entry of toxic metals into plants causes physiological and biochemical disturbances and also affects molecular responses. The growth and development of plants are affected that ultimately reduces the yield and quality of plant produce. Another aspect of this issue is that through plant produce, metals gain entry into humans and cause several ailments including cancer. Hence, the concentration of toxic metals in plants and plant based food products needs to be regulated effectively. The present chapter gives an overview of metal toxicity to plants and the status of metal accumulation in various crop plants, fruits, vegetables, etc.

Keywords

Arsenic · Cadmium · Food · Grains · Metals

3.1 Introduction

The elements having metallic properties and atomic number of higher than 20 are referred to as heavy metals. However, metals have been categorized according to their preferential binding to different binding ligands available and their reactivity as

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K. Mishra et al. (eds.), *Sustainable Solutions for Elemental Deficiency and Excess in Crop Plants*, https://doi.org/10.1007/978-981-15-8636-1_3

class A, B and intermediate (Nieboer and Richardson 1980). Metals include both essential metals [zinc (Zn), iron (Fe), nickel (Ni), cobalt (Co), copper (Cu), etc.] and toxic metals [cadmium (Cd), lead (Pb), arsenic (As), chromium (Cr), mercury (Hg), etc.] depending on their requirement for normal growth and metabolism by plants (Pilon et al. 2009; Afonne and Ifediba 2020). Toxic metals are actually a great threat to the natural ecosystem and ultimately to the environment. Thus proper steps should be taken for saving and correcting the soil ecosystem by removing the excess concentration of heavy metals such as Cd, Pb, Cr, Hg, As, etc. by the number of physico-chemical methods and also through proper legislation (Wuana and Okieimen 2011; Li et al. 2019). Some plant species of *Cynodon, Phragmites, Typha Pteris, Thalspi,* etc. are reported to accumulate high amounts of toxic metals. Such species are often referred to as hyperaccumulators. Due to their hyperaccumulation characteristic, they may be used for removing toxic metals from the contaminated environment (Rascio and Navari-Izzo 2011).

One of the major sources of various heavy metals in the environment is agricultural chemicals, such as fertilizers and pesticides, fungicides, weedicides, etc., which are used to increase and protect grain yield in almost all the major crops. With the increasing population, the need for crop production has also increased manifold and this has necessitated even extensive use of various chemicals in agriculture (Ray et al. 2013). Chemical fertilizers are also used in areas where essential nutrients are present in deficient amounts so as to overcome the deficiency of essential elements. In order to overcome a number of plant diseases, frequent use of pesticides and fungicides is practiced while weedicides are needed to clear the field of weeds for optimum crop growth. However, various agricultural chemicals contain some toxic metals such as Cd, As, Pb, Cr, etc. as contaminant and therefore cause metal contamination in the field (Antoniadis et al. 2019; Afonne and Ifediba 2020; Shukla et al. 2020).

Agricultural soils may also get contaminated through erosion and sediment deposition from contaminated land, landfill site leachate, livestock manure, sewage sludge based amendments, wastewater reuse, and fly ash deposition (Dwivedi et al. 2007; Rai et al. 2019). Other sources of metals are discharges of municipal and domestic sewages, and industrial wastes dumped into waterways, i.e., river, ponds, lakes, and sea. There are several industries like batteries, chip manufacturing, steel, electroplating, textiles, leather, e-waste, etc. which are the sources of a number of metals in the environment (Wuana and Okieimen 2011; Li et al. 2019; Rai et al. 2019). Mining processes and automobile emissions as well as coal use in electricity generation are also the sources of several metals. Particular matter emission from vehicular and industrial pollution results in soil and plant deposition ultimately (Rai et al. 2019). Apart from this, natural geological processes like volcanic eruptions and biogeochemical weathering of rocks are an important source of metals in the environment. Arsenic contamination in Southeast Asian countries is mostly attributable to the natural weathering of rocks due to biogeochemical processes (Shukla et al. 2020).

Owing to the widespread contamination of metals, most of the agricultural crops including cereals and vegetables are prone to metal toxicities. These plants absorb metals present in the soil and irrigation water and even through the air (Rai et al. 2019; Upadhyay et al. 2019; Shukla et al. 2020). The uptake and accumulation of metals vary from plant to plant. A number of plant dependent factors determine their potential for metal accumulation; for example root architecture (Srivastava et al. 2019), expression of a number of transporters involved in the uptake and transport of metals from root to shoot (Clemens and Ma 2016; Awasthi et al. 2017; Das et al. 2020), the ability of plant to transform metal species from one to other form like for As and Se (Chauhan et al. 2019; Srivastava and Shukla 2019; Guarino et al. 2020), the potential of plants to detoxify and tolerate metal stress, vacuolar sequestration of metals and metal homeostasis (Park et al. 2012; Peng and Gong 2014; Song et al. 2014). Apart from plant dependent features, the bioavailability of metal to plant determines its eventual accumulation in plants. There are a number of factors like pH, redox potential, soil porosity, soil type, water level, etc. which affect metal bioavailability to plants (Majumdar and Bose 2017, 2018; Upadhyay et al. 2019). In the case of As, it is known to be accumulated in very high levels in rice. One important factor responsible for such high As accumulation in rice is flooded cultivation that leads to the development of anaerobic conditions. This in turn results in the prevalence of reduced form of As, i.e., arsenite [As(III)] (Awasthi et al. 2017), which is efficienty taken up by highly expressed silicic acid transporters of rice plants. In aerobic conditions, prevailing during cultivation of wheat and other crops, As exists mainly in the oxidized form, arsenate [As(V)], whose uptake in plants is faces strong competition from phosphate and hence, crops other than rice show less As accumumulation. However, in aerobic conditions, divalent metals like Cd become more bioavailable (Yuan et al. 2019). Further, soil microbial activity, mycorrhizal inoculations in plants, and release of organic acids, nicotianamine, etc. by plants also alter metal bioavailability to plants and thus the uptake and accumulation of metals (Takahashi et al. 2003; Schwab et al. 2008; Poonam et al. 2017; Upadhyay et al. 2019). About 80% of land plants have mycorrhizal inoculation in their roots. Mycorrhiza make elements like phosphate available to plants and in return receive carbohydrates from plants (Poonam et al. 2017). Nicotianamine is well known to be excreted by a number of plants for enhancing the availability of Fe and for facilitating its uptake in chelated form (Ishimaru et al. 2010). Plant roots release a number of acids to the soil like citric acid, malic acid, oxalic acid to the soil that generates acidic pH in the rhizospheric zone around the roots (Schwab et al. 2008). This keeps most of the elements in free bioavailable form around roots and hence, metals are easily taken up by plants.

3.2 Accumulation of Toxic Metals in Crop Plants: Present Status

A number of studies from throughout the world have reported the accumulation of various toxic metals in higher than recommended ranges. These include market or field based survey experiments analyzing the level of various essential as well as toxic metals in crop plants, fruits, vegetables, etc. (Arora et al. 2008; Tosic et al.

2015; Rubio et al. 2018; Upadhyay et al. 2020). The permissible maximum level (mg/kg) is 0.2 mg/kg As and 0.4 mg/kg Cd in rice grains while 0.2 mg/kg Pb and 0.1 mg/kg Cd for other cereal grains. For leafy vegetables, the limit of Cd is 0.2 mg/kg while that of Pb is 0.3 mg/kg (FAO/WHO 2019; Afonne and Ifediba 2020). However, such limits have not been set for all types of foods for all metals. Hence, more research is needed to set guidelines for maximum permissible levels to ensure human safety in the future. A brief list of various toxic elements present in different food items is given in Table 3.1. Rice, wheat, and maize constitute some of the most important cereal grains, while potato and tomato are used widely among vegetables. The metal contamination of such widely used staple food items is alarming (Table 3.1). It is important to note that food products based on plant produce, fruits, grains, etc. are used for feeding babies and young children throughout the world (Upadhyay et al. 2020). Further, the status of metal exposure to humans is such that even breast milk is not safe and there are plenty of reports about infant exposure to toxic metals via breast milk (Rebelo and Caldas 2016). Mushrooms are very widely consumed owing to their nutritional properties and elemental levels. However, mushrooms are also known to accumulate various elements in the toxic range, e.g., As, Cd, Pb, etc. (Rashid et al. 2018). Hence, the level of toxic metals in crop plants is a prevalent problem throughout the world. The situation has been aggravated in the past few decades owing to ever-increasing metal contamination. The need of the hour is to develop easy low cost methods for routine analysis of metals in food items. This would also help in the determination of maximum allowable limits of metals in food items.

3.3 Metal Phytotoxicity and Stress Responses of Plants

The accumulation of non-essential metals as well as essential metals in excess causes a number of harmful effects in plants ranging from morphological, anatomical, physiological, biochemical, molecular, to metabolic changes. Some metals exist in different chemical species and the speciation of such metals affects their toxicity to plants. Chromium can exist as CrIII and CrVI and CrVI has been reported to be more toxic than CrIII (Chatterjee et al. 2011). Arsenic exists as inorganic [arsenate (AsV), arsenite (AsIII)] and organic [monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), etc.] (Upadhyay et al. 2020). Similarly, selenium (Se) and mercury (Hg) exist in a variety of different inorganic and organic species (Chauhan et al. 2019). Several metals exist as monovalent and divalent states like Cu and Fe and are redox active. The different chemical species of metal have variable toxicity in plants and humans and hence, a basic mechanism of metal tolerance is the conversion of more toxic metal species to less toxic ones.

Transporters maintaining physiological concentration of heavy metals include zinc-iron permease (ZIP) heavy metal transporter ATPase, natural resistant associated macrophage protein (NRAMP) cation diffusion facilitator (CDF) and ATP binding cassette (ABC) transporter which are found at the plasma membrane and on the tonoplast membrane of cell (Park et al. 2012; Singh et al. 2015; Clemens

Table 3.1 Reported concentrations/content of toxic metals in cereals, vegetables, fruits, mushrooms, and baby food products from various locations

Name of plant/food	Country/ location	Concentration of metal (mg/kg dry weight, dw)	References
Cereals			
Wheat grains (field collection)	India	1.04 (Cd), 13.97 (Co), 4.53 (Cr), 6.08 (Cu), 16.98 (Pb), 50.87 (Zn)	Sharma et al. (2018)
Rice grains (field collection)	India	0.99 (Cd), 15.21 (Co), 19.98 (Cr), 69.89 (Cu), 17.13 (Pb), 35.71 (Zn)	Sharma et al. (2018)
Maize grains (field collection)	India	1.09 (Cd), 15.13 (Co), 2.48 (Cr), 43.87 (Cu), 18.28 (Pb), 39.17 (Zn)	Sharma et al. (2018)
Mustard seeds (field collection)	India	1.05 (Cd), 13.46 (Co), 2.45 (Cr), 7.61 (Cu), 16.34 (Pb), 59.33 (Zn)	Sharma et al. (2018)
Wheat grains (normal Se and high Se fields collection)	India	High Se mean–Normal Se mean 106.50.18 (Se), 6.775–9.34 (Al), 0.010–0.020 (As), 0.030–0.040 (Cd), 0.002–0.004 (Hg), 0.175–1.230 (Ni), 0.110–2.120 (Pb)	Skalnaya et al. (2017)
Rice grains (normal Se and high Se fields collection)	India	High Se mean–Normal Se mean 21.41–0.25 (Se), 4.135–5.150 (Al), 0.170–0.110 (As), 0.008–0.040 (Cd), 0.002–0.002 (Hg), 0.120–1.330 (Ni), 0.080–1.820 (Pb)	Skalnaya et al. (2017)
Maize grains (normal Se and high Se fields collection)	India	High Se mean–Normal Se mean 24.43–0.380 (Se), 1.8353.320 (Al), 0.007–0.010 (As), 0.005–0.030 (Cd), 0.008–0.002 (Hg), 0.155–2.370 (Ni), 0.070–1.960 (Pb)	Skalnaya et al. (2017)
Mustard seeds (normal Se and high Se fields collection)	India	High Se mean–Normal Se mean 121.0–1.090 (Se), 109.5–47.87 (Al), 0.070–0.020 (As), 0.080–0.070 (Cd), 0.007–0.002 (Hg), 0.7402.070 (Ni), 0.255–2.190 (Pb)	Skalnaya et al. (2017)
Rice grains (market collection of 10 types of rice)	Bangladesh	Maximum 1.616 (Cd), 0.01 (Cr), 0.08 (Pb), 0.70 (As), 1.63 (Mn)	Real et al. (2017)
Rice (*Oryza sativa*)	Pakistan	3.17 (Cr), 0.44 (As), 0.16 (Cd), 0.28 (Pb)	Nawab et al. (2017)
Kidney beans (*Phaseolus vulgaris*)	Pakistan	2.04 (Cr), 0.06 (As), 0.07 (Cd), 0.33 (Pb)	Nawab et al. (2017)
Chick peas (*Cicer arietinum*)	Pakistan	2.27 (Cr), 0.10 (As), 0.06 (Cd), 0.29 (Pb)	Nawab et al. (2017)
Rice grains	Turkey	0.232 (Cd), 0.15 (Co), 1.71 (Cu), 6.9 (Mn), 0.034 (Mn), 12.0 (Zn)	Sofuoglu and Sofuoglu (2017)
Bulgur (prepared from wheat grains)	Turkey	0.008 (Cd), 0.016 (Co), 3.72 (Cu), 14.1 (Mn), 0.023 (Mn), 14.7 (Zn)	Sofuoglu and Sofuoglu (2017)
Rice grains	India	0.29–0.95 (As)	Upadhyay et al. (2019)

(continued)

Table 3.1 (continued)

Name of plant/food	Country/ location	Concentration of metal (mg/kg dry weight, dw)	References
Maize grains	Egypt	0.03–0.55 (Pb), 0.009–0.112 (Cd)	El-Hassanin et al. (2020)
Vegetables			
Spinach (*Spinacia oleracea*)	India	10 (Zn), 2.9 (Cr), 0.09 (Cu), 3.2 (Ni), 0.13 (Co), 3.1 (Pb)	Chary et al. (2008)
Amaranth (*Amaranthus graecizans*)	India	8 (Zn), 2.4 (Cr), 1.4 (Cu), 3.1 (Ni), 0.09 (Co), 2.9 (Pb)	Chary et al. (2008)
Brinjal (*Solanum melongena*)	India	4.5 (Zn), 1.1 (Cr), 0.7 (Cu), 3.1 (Ni), 3.0 (Pb)	Chary et al. (2008)
Ladies finger (*Abelmoschus esculentus*)	India	3.7 (Zn), 1.4 (Cr), 0.6 (Cu), 2.4 (Ni), 3.6 (Pb)	Chary et al. (2008)
Coriander leaves (*Coriandrum sativum*)	India	5.4 (Zn), 2.1 (Cr), 1.2 (Cu), 2.7 (Ni), 0.03 (Co), 2.7 (Pb)	Chary et al. (2008)
Mint leaves (*Mentha spicata*)	India	6.5 (Zn), 1.4 (Cr), 1.1 (Cu), 2.4 (Ni), 2.2 (Pb)	Chary et al. (2008)
Radish (*Raphanus sativus*)	India	117 (Fe), 22.5 (Zn), 12.8 (Mn), 5.96 (Cu)	Arora et al. (2008)
Spinach (*Spinacia oleracea*)	India	309 (Fe), 33.1 (Zn), 69.4 (Mn), 16.5 (Cu)	Arora et al. (2008)
Turnip (*Brassica rapa*)	India	197 (Fe), 29.3 (Zn), 18.2 (Mn), 16.1 (Cu)	Arora et al. (2008)
Carrot (*Daucus carota*)	India	216 (Fe), 46.4 (Zn), 17.4 (Mn), 16.8 (Cu)	Arora et al. (2008)
Cauliflower (*Brassica oleracea*)	India	215 (Fe), 40.2 (Zn), 41.3 (Mn), 5.23 (Cu)	Arora et al. (2008)
Tomato (*Solanum lycopersicum*)	Bangladesh	Maximum 0.001 (Cd), 0.02 (Cr), 0.025 (Pb)	Real et al. (2017)
Red Amaranth (*Amaranthus gangeticus*)	Bangladesh	Maximum 0.001 (Cd), 0.044 (Pb)	Real et al. (2017)
Cauliflower (*Brassica oleracea*)	Bangladesh	Maximum 0.016 (Cr)	Real et al. (2017)
Kochu (*Colocasia antiquorum*)	Bangladesh	Maximum 0.072 (As)	Real et al. (2017)
Potato (*Solanum tuberosum*), agricultural field	Bangladesh	0.68 (Cr), 1.3 (Ni), 2.4 (Cu), 0.07 (As), 0.10 (Cd), 0.43 (Pb)	Islam et al. (2015)
Green Amaranth (*Amaranthus hybridus*), agricultural field	Bangladesh	1.3 (Cr), 3.2 (Ni), 2.9 (Cu), 0.15 (As), 0.32 (Cd), 1.2 (Pb)	Islam et al. (2015)[a]
Red Amaranth (*Amaranthus gangeticus*), agricultural field	Bangladesh	1.5 (Cr), 3.6 (Ni), 2.6 (Cu), 0.12 (As), 0.25 (Cd), 0.97 (Pb)	Islam et al. (2015)[a]

(continued)

Table 3.1 (continued)

Name of plant/food	Country/ location	Concentration of metal (mg/kg dry weight, dw)	References
Bottle gourd (*Lagenaria siceraria*), agricultural field	Bangladesh	0.67 (Cr), 3.2 (Ni), 3.2 (Cu), 0.83 (As), 0.09 (Cd), 0.41 (Pb)	Islam et al. (2015)[a]
Tomato (*Solanum lycopersicum*), agricultural field	Bangladesh	0.63(Cr), 0.81 (Ni), 1.6 (Cu), 0.21 (As), 0.07 (Cd), 0.21 (Pb)	Islam et al. (2015)[a]
Pumpkin (*Cucurbita maxima*), agricultural field	Bangladesh	0.67 (Cr), 2.1 (Ni), 2.7 (Cu), 0.22 (As), 0.06 (Cd), 0.20 (Pb)	Islam et al. (2015)[a]
Bean (*Phaseolus vulgaris*), agricultural field	Bangladesh	0.82(Cr), 0.89 (Ni), 2.1 (Cu), 0.11 (As), 0.08 (Cd), 0.95 (Pb)	Islam et al. (2015)[a]
Lentil (*Lens culinaris*), agricultural field	Bangladesh	0.68 (Cr), 1.7 (Ni), 1.9 (Cu), 0.75 (As), 0.03 (Cd), 0.31 (Pb)	Islam et al. (2015)[a]
Tomato (*Solanum lycopersicum*)	Pakistan	1.98 (Cr), 0.14 (As), 0.18 (Cd), 0.11 (Pb)	Nawab et al. (2017)
Potato (*Solanum tuberosum*)	Pakistan	2.19 (Cr), 0.15 (As), 0.15 (Cd), 0.41 (Pb)	Nawab et al. (2017)
Pea (*Pisum sativum*)	Pakistan	2.23 (Cr), 0.12 (As), 0.06 (Cd), 0.40 (Pb)	Nawab et al. (2017)
Ladyfinger (*Abelmoschus esculentus*)	Pakistan	2.72 (Cr), 0.21 (As), 0.27 (Cd), 0.57 (Pb)	Nawab et al. (2017)
Onion (*Allium cepa*)	Pakistan	2.73 (Cr), 0.25 (As), 0.05 (Cd), 0.39 (Pb)	Nawab et al. (2017)
Mushrooms			
Lactarius deliciosus	Spain	0.16 (Cr), 1.64 (Cu), 18.2 (Al), 0.006 (Cd), 0.08 (Pb)	Rubio et al. (2018)[a]
Pholiota nameko	Spain	0.10 (Cr), 1.73 (Cu), 19.3 (Al), 0.002 (Cd), 0.08 (Pb)	Rubio et al. (2018)[a]
Lentinula edodes	Spain	0.15 (Cr), 1.53 (Cu), 16.8 (Al), 0.009 (Cd), 0.09 (Pb)	Rubio et al. (2018)[a]
Pleurotus ostreatus	Spain	0.17 (Cr), 1.99 (Cu), 18.1 (Al), 0.004 (Cd), 0.1 (Pb)	Rubio et al. (2018)[a]
Agaricus bisporus	Spain	0.07 (Cr), 1.54 (Cu), 18.2 (Al), 0.002 (Cd), 0.07 (Pb)	Rubio et al. (2018)[a]
Pleurotus highking	Bangladesh	0.56 (As), 0.35 (Cd), 0.27 (Cr), 14.2 (Cu), 0.40 (Pb), 0.126 (Hg)	Rashid et al. (2018)
Pleurotus ostreatus	Bangladesh	0.45 (As), 0.41 (Cd), 0.30 (Cr), 13.2 (Cu), 0.22 (Pb), 0.124 (Hg)	Rashid et al. (2018)
Agaricus bisporus	India	0.05 (Cr), 0.05 (Ni), 0.05 (As), 13.61 (Fe), 0.05 (Pb), 3.85 (Zn)	Sinha et al. 2019
Fruits			
Walnut (production areas, field)	China	0.056 (Pb), 0.015 (As), 0.007 (Cd), 0.184 (Cr), 0.0005 (Hg)	Han et al. (2018)

(continued)

Table 3.1 (continued)

Name of plant/food	Country/ location	Concentration of metal (mg/kg dry weight, dw)	References
Walnut (supermarket)	Serbia	0.150 (Pb), 0.157 (Cr)	Tosic et al. (2015)
Walnut (supermarket)	Chile	0.009 (Pb), 0.064 (As), 0.0014 (Cd), 0.083 (Cr)	Kafaoglu et al. (2014)
Walnut (supermarket)	Spain	0.705 (Cd), 1.454 (Cr)	Moreda-Pineiro et al. (2016)
Banana (*Musa acuminata*)	Pakistan	2.55 (Cr), 0.15 (As), 0.07 (Cd), 0.35 (Pb)	Nawab et al. (2017)
Tangerine (*Citrus tangerina*)	Pakistan	2.58 (Cr), 0.12 (As), 0.06 (Cd), 0.33 (Pb)	Nawab et al. (2017)
Apple (*Malus domestica*)	Pakistan	2.18 (Cr), 0.10 (As), 0.06 (Cd), 0.32 (Pb)	Nawab et al. (2017)
Guava (*Psidium guajava*)	Pakistan	2.19 (Cr), 0.06 (As), 0.04 (Cd), 0.05 (Pb)	Nawab et al. (2017)
Pineapple	Nigeria	0.057 (As), 0.00005 (Hg), 0.00011 (Cu)	Ezeonyejiaku and Obiakor (2017)[a]
Orange	Nigeria	0.044 (As), 0.00002 (Hg), 0.00011 (Cu)	Ezeonyejiaku and Obiakor (2017)[a]
Guava	Nigeria	0.020 (As), 0.0009 (Hg), 0.0002 (Cu)	Ezeonyejiaku and Obiakor (2017)[a]
Baby foods/food items			
Porridge (fish and vegetables)	Spain	0.10 (As), 0.006 (Pb), 0.16 (Cu), 2.66 (Fe), 0.30 (Mn)	Skrbic et al. (2016)
Infant and follow-on formula	Spain	2.76 (Cu), 187.77 (Fe), 0.24 (Mn)	Skrbic et al. (2016)
Porridge (corn and rice)	Serbia	0.56 (Cu), 164.85 (Fe), 2.01 (Mn)	Skrbic et al. (2016)
Porridge (grains and honey)	Serbia	1.07 (Cu), 207.63 (Fe), 4.58 (Mn)	Skrbic et al. (2016)
Infant and follow-on formula	Serbia	1.47 (Cu), 79.13 (Fe), 0.14 (Mn)	Skrbic et al. (2016)
Crisped rice	UK	0.21 (As)	Sun et al. (2009)
Puffed rice	UK	0.24 (As)	Sun et al. (2009)
Rice noodles	UK	0.12 (As)	Sun et al. (2009)
Rice crackers	UK	0.28 (As)	Sun et al. (2009)
Rice malt	UK	0.21 (As)	Sun et al. (2009)

[a] Unit is mg/kg on fresh/wet weight basis

and Ma 2016). One of the major mechanisms of metal toxicity is the induced overproduction of reactive oxygen species (ROS) like superoxide radicals and hydrogen peroxide (H_2O_2) and consequently cause oxidative stress to plants (Chatterjee et al. 2011; Srivastava et al. 2011; Awasthi et al. 2017). This is due to the interference of redox active metals with redox reactions of cell and also owing to the conversion of non-redox active metals from one chemical form to other (Mylona et al. 1998). The excessive consumption of GSH as a reductant and other redox molecules like NADPH and NADH in the process disturbs redox balance and causes excessive ROS production (Mylona et al. 1998). ROS are highly reactive and attack various biomolecules in cells including lipids in membranes, proteins, and DNA and RNA (Srivastava et al. 2011). The damage to lipid structure in membranes and proteins has been observed through increased malondialdehyde (MDA) and carbonyl content, respectively, in a number of studies (Hartley-Whitaker et al. 2001; Srivastava et al. 2007; Chauhan et al. 2017; Awasthi et al. 2018). ROS also attack DNA and RNA and cause changes in nucleotides and consequently may induce mutations and affect normal functions. Other indirect mechanism of ROS production includes the role of ROS producing enzymes such as NADPH oxidases, glycolate oxidase, and ascorbate oxidase (Cuypers et al. 2009).

To deal with uncontrolled ROS production and to avoid oxidative stress, plants are equipped with a number of enzymatic and non-enzymatic antioxidants. These include superoxide dismutase (SOD), ascorbate peroxidase (APX), glutathione peroxidase, and catalase (CAT) among enzymes and ascorbate, glutathione (GSH), phenolics, and flavonoids among non-enzymatic molecules (Alscher et al. 2002; Shigeoka et al. 2002; Kováčik et al. 2011; Srivastava et al. 2016; Chauhan et al. 2017). SOD is considered to be the primary enzyme in the antioxidant defense of plants as it dismutates superoxide radicals to hydrogen peroxide, which is then broken down to water and oxygen by a number of peroxidises in cell (Alscher et al. 2002). One of the important pathways of ROS detoxification is ascorbate–glutathione cycle (Foyer and Noctor 2011) which involves both enzymes (APX, dehydroascorbate reductase, DHAR, monodehydroascorbate reductase, MDHAR, GR) and metabolites (ascorbate, glutathione) for ROS quenching.

The detoxification mechanisms include the production of metal binding peptides like GSH, phytochelatins, and metallothioneins (Zagorchev et al. 2013; Kumar and Trivedi 2016). The meal transporters and chelators overcome metal toxicity by chelating and sequestering them in plant vacuoles where essential and toxic metabolites are stored (Mendoza-Cózatl et al. 2011). Kumar et al. (2015) have reported the role of metal transporters and cys-rich metal binding peptides in As metal uptake, transport, and detoxification. The excessive consumption of GSH for metal detoxification and metal-induced effects on ascorbate and GSH metabolism in the presence of high metal concentration leads to uncontrolled ROS generation and toxicity to plants.

A number of biochemical parameters have been monitored and found to be modulated upon metal exposure. These include responses of a number of antioxidant enzymes, biosynthetic enzymes of metabolic pathways including carbon, nitrogen, sulfur, nucleotide metabolisms (Pathare et al. 2013; Srivastava et al. 2009, 2013a, b, 2019; Awasthi et al. 2018). Metallothioneins are found in certain eukaryotic organisms including fungi, invertebrates, mammals, and even some prokaryotes. These contain small cysteine rich, low molecular weight cytoplasmic binding proteins or polypeptides in family metallothioneins (Cobbett and Goldbrough 2002; Hassinen et al. 2011; Benatti et al. 2014). A five-carbon α-amino acid named proline, which behaves as a compatible and metabolic osmolyte, is a constituent of cell wall, an antioxidant, free radical scavenger, and macromolecules stabilizer (Liang et al. 2013; Emamverdian et al. 2015). An increase in antioxidant molecules such as ascorbate, peroxidase, dismutase, catalase, glutathione reductase, superoxide dismutase, vitamin C (ascorbic acid), vitamin E (α-Tocopherol), glutathione, carotenoids (β-carotein) provides a defense mechanism (Tiwari and Lata 2018). A study on effect of Cr on antioxidant potential of *Catharanthus roseus* varieties and production of their anticancer alkaloids such as vincristine and vinblastine revealed that Cr adversely affected foliar contents of total chlorophyll, Chl. a, and Chl. b in C. roseus. Growth performance was also found to be retarded due to Cr in excess amounts. However, this study also indicated the enhancement of two important anticancer alkaloids, i.e., Vincristine and Vinblastine under Cr stress (Rai et al. 2014). Cadmium at increasing concentration and exposure durations caused a reduction in protein, chlorophyll content, and biomass in *Bacopa monnieri*. However, it was observed that bacosite A and bacopside I contents were increased by Cd stress up to 10 μM Cd (Gupta et al. 2014). Similarly, exposure to As was found to cause growth reduction in *Ocimum* sp. and *Withania somnifera* (Siddiqui et al. 2013, 2015). It is also reported that the activity of antioxidant enzymes is directly related to the steady level of ROS in the cell and the augmentation of antioxidant defense plays an important part in the regulation of oxidative stress (Mishra and Tandon 2013).

Displacement of essential metal ions or blocking of functional groups takes place due to the toxic metals. The disintegration of cytoplasmic membrane also takes place which in turn shows a negative effect on important functions such as photosynthesis, respiration, and also enzymatic activities (Emamverdian et al. 2015). Metal stresses affect various physiological processes of plants like leaf water potential, relative water content (RWC), water status, photosynthetic efficiency, respiration, and transpiration (Mobin and Khan 2007; Foyer and Noctor 2009). These processes affect plant growth and metabolism at a holistic level and eventually reduce the growth and halt optimum development of plants. Photosynthetic efficiency has been found to decrease upon metal stress in a number of plants. Photosynthesis is the crucial process to gain biomass and generate energy in the form of ATP. The reduced levels of ATP as well as negative effects on adenine and pyridine metabolisms have been found to correlate to the stress exerted by As in *Brassica juncea* (Srivastava et al. 2013a). Metal stresses also affect the water balance of plants that in turn has a profound impact on all biological processes (Barcelo and Poschenrieder 1990).

Various metal-induced effects on plants have also been monitored through changes in a number of genes, proteins, and metabolites in a number of omics studies with respect to various metals (Chakrabarty et al. 2009; Yu et al. 2012; Srivastava et al. 2013a, b, 2015; Chauhan et al. 2020). Such omics approaches provide extensive database to understand holistic responses of plants towards various metals in different concentration, time, tissue, and cell specific manner. These studies also shed insights into the role of a number of regulator factors like transcription factors, hormones, microRNAs, kinases, calcium signaling, etc. in the process of metal stress tolerance in plants (Rao et al. 2011; Zhou et al. 2012; Srivastava et al. 2013b; Chen et al. 2014; Raghuram et al. 2014; Steinhorst and Kudla 2014; Tang et al. 2014; Zhao et al. 2014; Bukhari et al. 2015; He et al. 2016; Jalmi et al. 2018).

Owing to such diverse effects on plant metabolism, crop production and produce quality are negatively affected under metal stress (Dwivedi et al. 2012). In rice, it has been found that As accumulation in rice grains affects grain quality, reduces the level of essential amino acids while increases that of non-essential amino acids, causes a decline in level of essential nutrient elements like Se Cu, etc. and also affects grain size and weight (1000 grain weight) (Dwivedi et al. 2012; Upadhyay et al. 2019). In the case of Cd and other metals also, a decline in the quality of crop produce and yield has been noticed in a number of studies (Huang et al. 2008).

Biotechnology can be a good tool in mitigating the problem of heavy metal toxicity in plants. Biotechnology in the form of transgenic plants and evolution of use of newer plants breeding techniques are able of getting a solution to overcome heavy metal toxicity problems by generating metal resistant varieties. Also, through proper use of microbes, heavy metal toxicity can be effectively controlled (Tiwari and Lata 2018). These aspects shall be discussed in depth in other chapters of the book.

3.4 Conclusions

In conclusion, the entry of toxic metals in plants is a serious issue. The metals entering into plants produce a variety of toxic responses and affect the normal growth and development of plants. The accumulation of toxic metals in crop plants affects the quality of their produce as well as yield. The presence of various toxic metals in various food crops and food products is a major concern throughout the world that threatens the health and safety of millions of people. The issue needs societal, governmental, and scientific measures to tackle it effectively and in a sustainable manner.

Acknowledgements SS would like to thank funding supports from Board of Research in Nuclear Sciences (BRNS) (35/14/15/2018-BRNS/10395) and ASEAN-India STI Cooperation, Science and Engineering Research Board (AISTC, SERB) (CRD/2018/000072) for supporting the ongoing research activities of the lab.

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