

Heavy metals, occurrence and toxicity for plants: a review

P. C. Nagajyoti · K. D. Lee · T. V. M. Sreekanth

Received: 31 March 2010 / Accepted: 13 July 2010 / Published online: 28 July 2010
© Springer-Verlag 2010

Abstract Metal contamination issues are becoming increasingly common in India and elsewhere, with many documented cases of metal toxicity in mining industries, foundries, smelters, coal-burning power plants and agriculture. Heavy metals, such as cadmium, copper, lead, chromium and mercury are major environmental pollutants, particularly in areas with high anthropogenic pressure. Heavy metal accumulation in soils is of concern in agricultural production due to the adverse effects on food safety and marketability, crop growth due to phytotoxicity, and environmental health of soil organisms. The influence of plants and their metabolic activities affects the geological and biological redistribution of heavy metals through pollution of the air, water and soil. This article details the range of heavy metals, their occurrence and toxicity for plants. Metal toxicity has high impact and relevance to plants and consequently it affects the ecosystem, where the plants form an integral component. Plants growing in metal-polluted sites exhibit altered metabolism, growth reduction, lower biomass production and metal accumulation. Various physiological and biochemical processes in plants are affected by metals. The contemporary investigations into toxicity and tolerance in metal-stressed plants are prompted by the growing metal pollution in the environment. A few metals, including copper, manganese, cobalt, zinc and chromium are, however, essential to plant metabolism in trace amounts. It is

only when metals are present in bioavailable forms and at excessive levels, they have the potential to become toxic to plants. This review focuses mainly on zinc, cadmium, copper, mercury, chromium, lead, arsenic, cobalt, nickel, manganese and iron.

Keywords Heavy metals · Environment · Toxic effects · Plants · Anthropogenic activities

Introduction

Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons. The term “heavy metals” refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech Water Treatment and Air Purification 2004). “Heavy metals” in a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3 , or 5 times or more, greater than water (Hawkes 1997). However, chemical properties of the heavy metals are the most influencing factors compared to their density. Heavy metals include lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn), chromium (Cr), iron (Fe), arsenic (As), silver (Ag) and the platinum group elements. Environment is defined as totally circumstances surrounding an organism or group of organisms especially, the combination of external physical conditions that affect and influence the growth, development and survival of organisms (Farlex Incorporated 2005). The environment is considered in food, and the less tangible, through no less important, the communities we live in (Gore 1997). A pollutant is any substance in the environment, which causes objectionable

P. C. Nagajyoti
Institute of Environmental & Industrial Medicine (IEIM),
Hanyang University, Seoul, South Korea

K. D. Lee · T. V. M. Sreekanth (✉)
Department of Nanomaterial Chemistry, Dongguk University,
Gyeongju, Republic of Korea
e-mail: sreekanth@dongguk.ac.kr; tvmsreekanth@gmail.com

effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Such a substance has to be present in the environment beyond a set or tolerance limit. Hence, environmental pollution is the presence of a pollutant in the environment air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment.

Heavy metals are largely found in dispersed form in rock formations. Industrialization and urbanization have increased the anthropogenic contribution of heavy metals in biosphere. Heavy metals have largest availability in soil and aquatic ecosystems and to a relatively smaller proportion in atmosphere as particulate or vapors. Heavy metal toxicity in plants varies with plant species, specific metal, concentration, chemical form and soil composition and pH, as many heavy metals are considered to be essential for plant growth. Some of these heavy metals like Cu and Zn either serve as cofactor and activators of enzyme reactions e.g., informing enzymes/substrate metal complex (Mildvan 1970) or exert a catalytic property such as prosthetic group in metalloproteins. These essential trace metal nutrients take part in redox reactions, electron transfer and structural functions in nucleic acid metabolism. Some of the heavy metal such as Cd, Hg and As are strongly poisonous to metal-sensitive enzymes, resulting in growth inhibition and death of organisms.

An alternative classification of metals based on their coordination chemistry, categorizes heavy metals as class B metals that come under non-essential trace elements, which are highly toxic elements such as Hg, Ag, Pb, Ni (Nieboer and Richardson 1980). Some of these heavy metals are bioaccumulative, and they neither break down in the environment nor easily metabolized. Such metals accumulate in ecological food chain through uptake at primary producer level and then through consumption at consumer levels. Plants are stationary, and roots of a plant are the primary contact site for heavy metal ions. In aquatic systems, whole plant body is exposed to these ions. Heavy metals are also absorbed directly to the leaves due to particles deposited on the foliar surfaces.

Essential heavy metals

Some of heavy metals (Fe, Cu and Zn) are essential for plants (Table 1) and animals (Wintz et al. 2002). The availability of heavy metals in medium varies, and metals such as Cu, Zn, Fe, Mn, Mo, Ni and Co are essential micronutrients (Reeves and Baker 2000), whose uptake in excess to the plant requirements result in toxic effects (Monni et al. 2000; Blaylock and Huang 2000). They are also called as trace elements due to their presence in trace (10 mg kg^{-1} , or mg L^{-1}) or in ultra trace ($1 \text{ } \mu\text{g kg}^{-1}$, or $\text{ } \mu\text{g L}^{-1}$) quantities in the environmental matrices.

Table 1 Range of a few environmentally important heavy metals in plants (Misra and Mani 1991)

Elements	Land plants ($\mu\text{g g}^{-1}$ dry wt)
As	0.02–7
Cd	0.1–2.4
Hg	0.005–0.02
Pb	1–13
Sb	0.02–0.06
Co	0.05–0.5
Cr	0.2–1
Cu	4.15
Fe	140
Mn	15–100
Mo	1–10
Ni	1
Sr	0.30
Zn	8–100

The essential heavy metals (Cu, Zn, Fe, Mn and Mo) play biochemical and physiological functions in plants and animals. Two major functions of essential heavy metals are the following: (a) Participation in redox reaction, and (b) Direct participation, being an integral part of several enzymes.

Copper is an essential heavy metal for higher plants and algae, particularly for photosynthesis (Mahmood and Islam 2006; Chatterjee et al. 2006). Cu is a constituent of primary electron donor in photosystem 1 of plants. Because Cu can readily gain and lose an electron, it is a cofactor of oxidase, mono- and di-oxygenase (e.g., amine oxidases, ammonia monooxidase, ceruloplasmin, lysyl oxidase) and of enzymes involved in the elimination of superoxide radicals (e.g., superoxide dismutase and ascorbate oxidase). Several enzymes contain Zn, such as carbonic anhydrase, alcohol dehydrogenase, superoxide dismutase and RNA polymerase. Zinc is required to maintain the integrity of ribosome. It takes part in the formation of carbohydrates and catalyzes the oxidation processes in plants. Zinc also provides a structural role in many transcription factors and is a cofactor of RNA polymerase.

Nickel is recognized as another essential micronutrient for living organisms and is a component of the enzyme urease, which is essential for its functioning and thereby good health in animals. Manganese plays an important role in reactions of enzymes like mallic dehydrogenase and oxalosuccinic decarboxylase. It is also needed for water splitting at photosystem II and for superoxide dismutase. In plants, Co complex is found in the form of vitamin B₁₂. Iron is an essential element in many metabolic processes and is indispensable for all organisms. It is a component of heme-containing protein such as hemoglobin, myoglobin

and cytochrome, and innumerable non-heme iron-containing proteins with vital functions in many metabolic processes. Iron and copper are found as components of protein and catalyze redox reactions.

Nature of heavy metals

No organic life can develop and survive without the participation of metal ions. Current research has revealed that life is as much inorganic as organic. Generally, the term trace element is rather loosely used in current literature to designate the elements which occur in small concentrations in natural biologic systems. The growing public concern over the deteriorating quality of the environment has led to a generalized usage when referring to trace elements. Thus, for all practical purposes, other terms such as “trace metals”, “trace inorganics”, “heavy metals”, “micro elements” and “micronutrients” have been treated as synonyms with the term trace elements. The elementary constituents of plant, animal and human life may be classified as major and trace elements, the latter group comprising both essential and non-essential elements (including toxic elements).

Source of contamination

There are different sources of heavy metals in the environment such as (1) natural sources, (2) agricultural sources, (3) industrial sources, (4) domestic effluent, (5) atmospheric sources and (6) other sources.

Heavy metal pollution can originate from both natural and anthropogenic sources. Activities such as mining and smelting operations and agriculture have contaminated extensive areas of world such as Japan, Indonesia and China mostly by heavy metals such as Cd, Cu and Zn (Herawati et al. 2000), Cu, Cd and Pb in North Greece (Zanthopolous et al. 1999), in Albania (Shallari et al. 1998) and Cr, Pb, Cu, Ni, Zn and Cd in Australia (Smith 1996). Heavy metals originate within the Earth’s crust; hence their

natural occurrence in soil is simply a product of weathering process.

Natural sources of heavy metals

The most important natural source of heavy metals is geologic parent material or rock outcroppings (Table 2). The composition and concentration of heavy metals depend on the rock type and environmental conditions, activating the weathering process. The geologic plant materials generally have high concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb. However, class-wise the heavy metal concentrations vary with in the rocks. Soil formation takes place mostly from sedimentary rock, but is only a small source of heavy metals, since it is not generally or easily weathered. However, many igneous rocks such as olivine, augite and hornblende contribute considerable amounts of Mn, Co, Ni, Cu and Zn to the soils. Within the class of sedimentary rocks, shale has highest concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb followed by limestone and sand stone.

Volcanoes have been reported to emit high levels of Al, Zn, Mn, Pb, Ni, Cu and Hg along with toxic and harmful gases (Seaward and Richardson 1990). World wide data on emission of heavy metals from natural sources are particularly scanty, but a summary of literature survey has been prepared (Table 3) (Pacyna 1986). Wind-blown dusts and volcanic eruptions are of particulate relevance to ecosystem inventories and budgets of heavy metals. Wind dust, which arises from desert region such as Sahara, has high levels of Fe and lesser amounts of Mn, Zn, Cr, Ni and Pb (Ross 1994). Marine aerosols and forest fires also exert a major influence in the transport of some heavy metals in many environments. While the long range transport of dusts, particularly from the Sahara, has received considerable recent attention, (SCOPE 1974), the transport of dusts originating in Asia and elsewhere to the Pacific, Arctic and Antarctic has also been investigated (Davidson et al. 1985). Some major eruptions have more far-reaching

Table 2 Range of heavy metal concentrations (ppm) in igneous and sedimentary rocks (Cannon et al. 1978)

Metals	Basaltic igneous	Granite igneous	Shales and Clays	Black shales	Sand stone
As	0.2–10	0.2–13.8	–	–	0.6–9.7
Cd	0.006–0.6	0.003–0.18	0.0–11	<0.3–8.4	–
Cr	40–600	2–90	30–590	26–1,000	–
Co	24–90	1–15	5–25	7–100	–
Cu	30–160	4–30	18–120	20–200	–
Pb	2–18	6–30	16–50	7–150	<1–31
Mo	0.9–7	1–6	–	1–300	–
Ni	45–410	2–20	20–250	10–500	–
Zn	48–240	5–140	18–180	34–1,500	2–41

Table 3 Worldwide emissions of heavy metals from natural sources (Pacyna 1986)

Sources	Global production	Annual emission (kg × 10 ⁶)								
		Cd	Co	Cu	Cr	Hg	Mn	Ni	Pb	Zn
Windblown dust	6–1,100	0.25	4	12	5	0.03	425	20	10	25
Volcanogenic particles	6.5–150	0.5	1.4	4	3.9	0.03	82	3.8	6.4	10
Forest wild fires	2–200	0.01	–	0.3	–	0.1	–	0.6	0.5	0.5
Vegetation	75–1,000	0.2	–	2.5	–	–	5	1.6	1.6	10
Sea salt	300–2,000	0.002	–	0.1	–	0.003	4	0.04	0.1	0.02
Total		0.96	5.4	18.9	8.9	0.16	516	26	18.6	45.52

effects e.g., emissions from Mount Etna, Sicily include 10×10^6 kg per year⁻¹ of Cd, as well as Cr, Cu, Mn and Zn (Climino and Ziino 1983). The activity of this volcano also significantly enhanced the Hg content of plants and soil in the surrounding area (Barghiani et al. 1987).

The contribution to ecosystem of elements from sea sprays and mists. Often transported many kilometers in land is widely recognized. Cu and Mn (Vermette and Bingham 1986) from such marine sources have been detected in rain water input to terrestrial environments. The natural process of ‘bubble bursting’ is a source of airborne Cd, Cu, Ni, Pb and Zn via sea salt particles (Pacyna 1986). Airborne emissions of heavy metals originate from forest and prairie fires (Ross 1994). Volatile heavy metals such as Hg and Se are part of carbonaceous matter produced during the fire. Natural vegetation emits heavy metals into the soil and atmosphere through leaching from leaves and stems, decomposition and volatilization. Many heavy metals have been detected in inland coastal areas due to sea sprays and aerosols produced in oceanic activities.

Agricultural sources of heavy metals

The inorganic and organic fertilizers (Fertilizer is a substance added to soil to improve plants growth and yield.) are the most important sources of heavy metals to agricultural soil include liming, sewage sludge, irrigation waters and pesticides, sources of heavy metals in the agricultural soils (Tables 4, 5). Others, particularly fungicides, inorganic fertilizers and phosphate fertilizers have variable levels of Cd, Cr, Ni, Pb and Zn depending on their sources. Cadmium is of particular concern in plants since it accumulates in leaves at very high levels, which may be consumed by animals or human being. Cadmium enrichment also occurs due to the application of sewage sludge, manure and limes (Nriagu 1988; Yanqun et al. 2005). Although the levels of heavy metals in agricultural soil are very small, but repeated use of phosphate fertilizer and the long persistence, time for metals, there may be dangerously high accumulation of some metals (Verkleji 1993).

Table 4 Heavy metal composition of typical uncontaminated soils and agricultural crops (Modified from Allaway 1968)

Heavy metals	Range in soil (ppm d.wt)	Range in agricultural crops(ppm d.wt)
Cd	0.01–0.7	0.2–0.8
Co	1–40	0.05–0.5
Cr	5–3,000	0.2–1.0
Cu	2–100	4–15
Fe	7,000–55,000	–
Mn	100–4,000	15–100
Mo	0.2–5	1–100
Ni	10–00	1.0
Pb	2–200	0.1–10
Zn	10–300	15–200

Animal manure enriches the soil by the addition of Mn, Zn, Cu and Co and sewage sludge by Zn, Cr, Pb, Ni, Cd and Cu (Verkleji 1993). The increase in heavy metal contamination of agricultural soil depends on the rate of application of the contributors with its elemental concentration and soil characteristics to which it is applied. Heavy metal accumulation in soil is also due to application of soil amendments such as compost refusing and nitrate fertilizers (Ross 1994). Liming increases the heavy metal levels in the soil more than the nitrate fertilizers and compost refuse. Sewage sludge is one of the most important sources of heavy metal contamination to the soil (Ross 1994) (Table 6). Several heavy metal-based pesticides (Pesticides kill unwanted pests) are used to control the diseases of grain and fruit crops and vegetables and are sources of heavy metal pollution to the soil (Verkleji 1993; Ross 1994). The orchards where these compounds have been used frequently resulted into contamination of orchard soil with high levels of heavy metals such as Cu, As, Pb, Zn, Fe, Mn and Hg (Ross 1994). Pesticides such as lead arsenate were used in Canadian orchards for more than six decades and were found to be enriched with Pb, As and Zn having greater consequences for food contamination. Continued irrigation of agricultural soil can lead to

Table 5 Guideline for safe limits of heavy metals

Sample	Standards	Cd	Cu	Pb	Zn	Mn	Ni	Cr
Agricultural soil ($\mu\text{g g}^{-1}$)	Indian standard (Awashthi 2000)	3–6	135–270	250–500	300–600	–	75–150	–
	WHO/FAO (2007)	–	–	–	–	–	–	–
	European union standards (EU 2002)	3	140	300	300	–	75	150

Table 6 Heavy metal concentrations ($\mu\text{g g}^{-1}$) in agricultural amendments (Modified from Ross 1994)

Metals	Agricultural amendments						
	Sewage sludge	Compost refuse	Farmyard manure	Phosphate fertilizers	Nitrate fertilizers	Lime	Pesticides
Cr	8.40–600	1.8–410	1.1–55	66–245	3.2–19	10–15	–
Ni	6–5,300	0.9–279	2.1–30	7–38	7–34	10–20	–
Cu	50–8,000	13–3,580	2–172	1–300	–	2–125	–
Zn	91–49,000	82–5,894	15–556	50–1,450	1–42	10–450	–
Cd	<1–3,410	0.01–100	0.1–0.8	0.1–190	0.05–8.5	0.04–0.1	–
Pb	2–7,000	1.3–2,240	0.4–27	4–1,000	2–120	20–1,250	11–26

accumulation of heavy metals such as Pb and Cd. The contamination of soil by heavy metals may also be from irrigation water sources such as deep wells, rivers, lakes or irrigation canals (Ross 1994).

Industrial sources of heavy metals

Industrial sources of heavy metals include mining, refinement (spoil heaps and tailings, transport of ores, smelting and metal finishing and recycling of metals). Mining operation emits different heavy metals depending on the type of mining (Table 7). For example, coalmines are sources of As, Cd, Fe, etc., which enrich the soil around the coalfield directly or indirectly. The utilization of Hg in gold mining and the mobilization of significantly high amounts of Hg from old mines have become a significant source of this pollutant to the environment (Lacerda 1997). This traditional practice had been nearly forgotten since 1960. Presently, it is rapidly spreading through out the tropics, particularly in Latin America and Asia involving over 10 million people (Lacerda 1997). High temperature processing of metals such as smelting and castings emit metals in particulate and vapor forms. Vapor form of heavy metals such as As, Cd, Cu, Pb, Sn and Zn combine with water in the atmosphere to form aerosols. These may be either dispersed by wind (dry deposition) or precipitated in rainfall (wet deposition) causing contamination of soil or water bodies. Contamination of soil and water bodies can also occur through runoff from erosion of mine wastes, dusts produced during the transport of crude ores, corrosion of metals and leaching of heavy metals to soil and ground water. Soil contamination of heavy metals occurs due to different types of processing in refineries. Energy-supplying power stations such as coal burning power

plants, petroleum combustion, nuclear power stations and high tension lines contribute many heavy metals such as Se, B, Cd, Cu, Zn, Cs and Ni to the environment (Verkleji 1993). Other industrial sources include processing of plastics, textiles, microelectronics, wood preservation and paper processing. Contamination of plants growing beneath the power line with high concentration of Cu is reported to be toxic to the grazing animals (Kraal and Ernst 1976).

Domestic effluents

These waste waters probably constitute the largest single source of elevated metal values in rivers and lakes. Domestic effluents may consists of (1) untreated or solely mechanically treated waste waters (2) substances which have passed through the filters of biological treatment plants (3) waste substances passed over sewage outfalls and discharged to receiving water bodies often end up into the sea from coastal residential areas (Table 7).

The use of detergents creates a possible pollution hazard, since common house hold detergent products can affect the water quality. Angino et al. (1970) found that most enzyme detergents contained trace amounts of the elements Fe, Mn, Cr, Co, Zn, Sr and B.

With regard to pollution resulting from urbanized areas, there is an increasing awareness that urban runoff presents a serious problem of heavy metal contamination. A statistical summary by Bradford (1997) revealed that urban storm water runoff has long been recognized as a major source of pollutants to surface waters. Studies by Bolter et al. (1974) indicate that lead is leached by humic and other acids, thus increasing its availability for runoff rather than seepage into the upper soil layer.

Table 7 Occurrence of metals or their compounds in effluents from various industries

Industry	Metals																																
	Al	Ag	As	Au	Ba	Be	Bi	Cd	Co	Cr	Cu	Fe	Ga	Hg	In	Mn	Mo	Os	Pb	Pd	Ni	Sb	Sn	Ta	Ti	Tl	U	V	W	Zn			
Mining operations and ore processing	X	X						X						X	X	X			X								X	X					
Metallurgy and electroplating		X	X			X	X	X		X	X			X	X				X		X									X	X		
Chemical industries	X	X			X			X	X	X	X	X	X					X	X					X	X	X	X					X	
Dyes and pigments	X	X						X			X	X							X						X	X							
Ink manufacturing									X		X	X		X							X												
Pottery and poccelain			X							X													X					X					
Alloys						X							X		X			X		X				X									
Print					X					X								X	X					X								X	
Photography		X		X				X		X							X				X							X					
Glass			X		X				X													X			X							X	
Paper mills	X									X	X			X							X		X		X	X						X	
Leather training	X	X			X					X	X	X		X																			X
Pharmaceuticals	X										X	X	X	X				X						X									
Textiles	X	X			X			X			X	X		X				X				X	X										
Nuclear technology					X			X							X													X					
Fertilizers	X	X						X		X	X	X		X		X					X	X											X
Chlor-alkali production	X	X						X		X		X	X	X		X					X			X									X
Petroleum refining	X	X						X		X		X	X	X					X		X												X

Atmospheric sources

Natural and man-made processes have been shown to result in metal containing airborne particulates. Depending on prevailing climatic conditions, these particulates may become wind-blown over great distances; nonetheless, they are subjected to the fate that they are ultimately returned to the lithosphere as precipitations by rain or snowfall. Additional sources of atmospheric metal enrichment, such as the high temperature anthropogenic sources, are of special importance on a global scale. Geothermal sources, such as volcanic eruptions, have caused significant atmospheric pollution (Eshleman et al. 1971).

Other sources

Other sources of heavy metals include refuse incineration, landfills and transportation (automobiles, diesel-powered vehicles and aircraft). Two main anthropogenic sources that contaminate the soil are fly ash produced due to coal burning and the corrosion of commercial waste products, which add Cr, Cu, Pb and galvanized metals (primarily Zn) into the environment (Al-Hiyaly et al. 1988). Coal burning adds heavy metals such as Cd, Hg, Mn, Ni, Al, Fe and Ti into the soils (Verkleji 1993). Oil burning contributes V, Fe, Pb and Ni to the environment. Metal emission during the transportation of vehicles includes Ni and Zn from tires, Al from catalyst, Cd and Cu primarily from diesel engines and Ni and Zn from aerosol emissions. Lubricants,

which are antiwear protectants for vehicles, emit Cd, Cr, Hg, Ni, Pb and Zn, particularly incase of inefficient engines. The burning of leaded gasoline has been an important source of Pb in the environment. Incinerations of municipal wastes generate significant concentrations of Zn, Pb, Al, Sn, Fe and Cu.

Heavy metal emission

Heavy metals can be emitted into the environment by both natural and anthropogenic activities. The major causes of emission are the anthropogenic sources specifically mining operations (Nriagu 1989). In some cases, even long after the mining activities have ceased, the emitted metals continue to persist in the environment. Peplow (1999) reported that hard rock mines operate from 5–15 years until the minerals are depleted, but metal contamination that occurs as a consequence of hard rock mining persist for hundreds of years after the cessation of mining operations. Apart from mining operations, mercury is introduced to the environment through cosmetic products as well as manufacturing processes like making of sodium hydroxide.

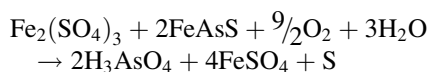
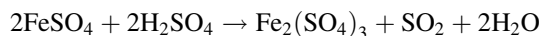
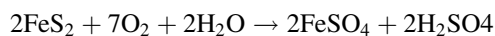
Heavy metals are emitted both in elemental and in compound (organic and inorganic) forms. Anthropogenic sources of emission are the various industrial point sources including former and present mining sites, foundries and smelters, combustion by-products and traffics (UNEP/GPA 2004). Cadmium is released as a by-product of zinc (and

occasionally lead) refining; lead is emitted during its mining and smelting activities, from automobile exhausts (by combustion of petroleum fuels treated with tetraethyl lead antiknock) and from old lead paints; mercury is emitted by the degassing of the earth's crust. Generally, metals are emitted during their mining and processing activities (Lenntech Water Treatment and Air Purification 2004).

Environmental pollution by heavy metals is very prominent in areas of mining, and old mine sites and pollution reduces with increasing distance away from mining sites (Peplow 1999). These metals are leached out and in sloppy areas are carried by acid water downstream or run off to the sea. Through mining activities, water bodies are most emphatically polluted (Garbarino et al. 1995; INECAR 2000). The potential for contamination is increased when mining exposes metal-bearing ores rather than natural exposure of ore bodies through erosion (Garbarino et al. 1995), and when mined ores are dumped on the earth surfaces in manual decreasing processes. Through rivers and streams, the metals are transported as either dissolved species in water or an integral part of suspended sediments, (dissolved species in water have the greatest potential of causing the most deleterious effects). They may then be stored in river bed sediments or seep into the underground water thereby contaminating water from underground sources, particularly wells, and the extent of contamination will depend on the nearness of the well to the mining site. Wells located near mining sites have been reported to contain heavy metals at levels that exceed drinking water criteria (Garbarino et al. 1995; Peplow 1999). The tolerance limits of some heavy metals are shown in Table 8.

Chemistry of heavy metal pollution

Mining activities and other geochemical process often result in the generation of acid mine drainage (AMD), a phenomenon commonly associated with mining activities. It is generated when pyrite (FeS₂) and other sulfide minerals in the aquifer and present and former mining sites are exposed to air and water in the presence of oxidizing bacteria, such as *Thiobacillus ferrooxidans*, and oxidized to produce metal ions, sulfate and acidity (Ogwuegbu and Muhanga 2005).

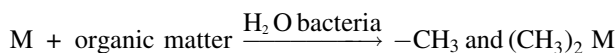


Literature survey shows that heavy metals (M) at mining sites are leached and carried by acidic water downstream. They can be acted upon by bacterial activity and methylated

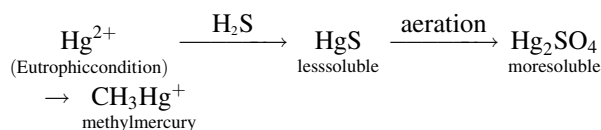
Table 8 Indian standards for heavy metals in soil, food and drinking water (Awashthi 2000)

Heavy metal	Soil (mg/kg)	Food (mg/kg)	Water (mg/L)
Cd	3–6	1.5	0.01
Cr	–	20	0.05
Cu	135–270	30	0.05
Fe	–	–	0.03
Ni	75–150	1.5	–
Pb	250–500	2.5	0.1
Zn	300–600	50	5.0
As	–	1.1	0.05
Mn	–	–	0.1

to yield organic forms, such as monomethyl mercury and dimethylcladium. This conversion is effected by bacteria in water, in the presence of organic matter, according to the following simplified equation



In the non-biological conversions, the following reactions have been identified for mercury



These organic forms have been reported to be very toxic and adversely affect water qualities by seepage to pollute under ground water source. Low pH values do not need to be established for some metals to be released from mine wastes at adverse concentration, because near neutral pH (pH 6–7) have been established for some metals, such as Zn, Cd, and As (INECAR 2000; Lenntech Water Treatment and Air Purification 2004). Factors such as downstream distances from the mining sites, colloid loads, pH perturbations and dilution ultimately control the quality of water sources.

Factors influencing heavy metal uptake

Anthropogenic activities greatly influence the availability of heavy metals in the environment. Heavy metals interfere with physiological processes such as gaseous exchange, CO₂ fixation, respiration and nutrient absorption. Heavy metal uptake is not linear in response to the increasing concentrations. Many factors influence the uptake of metals and include the growing environment, such as temperature, soil pH, soil aeration, Eh condition (particularly of aquatic environment) and fertilization, competition between the plant species, the type of plant its size, the root system, the availability of the elements in the soil or foliar deposits,

the type of leaves, soil moisture and plant energy supply to the roots and leaves (Yamamoto and Kozlowski 1987). As far as the growing environment is concerned the increase in pH, i.e., the environment becoming more alkaline, and decrease in Eh (redox potential), i.e., the environment becoming more reducing, result in decrease in availability of heavy metals, or metals in general to plants (Misra and Mani 1991). However, under a given environmental condition, the uptake of a metal by a plant can be estimated from the biological absorption coefficient.

$$\text{BAC} = [\text{Mp}]/[\text{Ms}]$$

where [Mp] is concentration of the element in the plant, and [Ms] is its concentration in the soil (Fergusson 1990). However, in field conditions, the relationship works best only when the concentration of the metal in the soil is not too high (Shaw and Panigrahi 1986).

Because of the influence of environmental factors and the type of plant itself, the levels of heavy metals in plants (both terrestrial and aquatic) vary widely (Wong 1996). The range of heavy metals observed in plants is presented in Table 1. If the other facts are constants, the uptake of a metal by different plant species may be compared.

Effects of heavy metals on plants

Like all living organisms, plants are often sensitive both to the deficiency and to the excess availability of some heavy metal ions as essential micronutrient, while the same at higher concentrations and even more ions such as Cd, Hg, As are strongly poisonous to the metabolic activities. Researches have been conducted throughout the world to determine the effects of toxic heavy metals on plants (Reeves and Baker 2000; Fernandes and Henriques 1991). Contamination of agricultural soil by heavy metals has become a critical environmental concern due to their potential adverse ecological effects. Such toxic elements are considered as soil pollutants due to their widespread occurrence and their acute and chronic toxic effect on plants grown of such soils.

Zinc effects on plants

Zinc (Zn) is an essential micronutrient that affects several metabolic processes of plants (Cakmak and Marshner 1993) and has a long biological half-life. The phytotoxicity of Zn and Cd is indicated by decrease in growth and development, metabolism and an induction of oxidative damage in various plant species such as *Phaseolus vulgaris* (Cakmak and Marshner 1993) and *Brassica juncea* (Prasad et al. 1999). Cd and Zn have reported to cause alternation in catalytic efficiency of enzymes in *Phaseolus vulgaris*

(Van Assche et al. 1988; Somasekharaiah et al. 1992) and pea plants (Romero-Puertas et al. 2004). Concentrations of Zn found in contaminated soils frequently exceed to those required as nutrients and may cause phytotoxicity. Zn concentrations in the range of 150–300 mg/kg have been measured in polluted soils (Devries et al. 2002; Warne et al. 2008). High levels of Zn in soil inhibit many plant metabolic functions, result in retarded growth and cause senescence. Zinc toxicity in plants limited the growth of both root and shoot (Choi et al. 1996; Ebbs and Kochian 1997; Fontes and Cox 1998). Zinc toxicity also causes chlorosis in the younger leaves, which can extend to older leaves after prolonged exposure to high soil Zn levels (Ebbs and Kochian 1997). The chlorosis may arise partly from an induced iron (Fe) deficiency as hydrated Zn^{+2} and Fe^{+2} ions have similar radii (Marschner 1986). Excess Zn can also give rise to manganese (Mn) and copper (Cu) deficiencies in plant shoots. Such deficiencies have been ascribed to a hindered transfer of these micronutrients from root to shoot. This hindrance is based on the fact that the Fe and Mn concentrations in plants grown in Zn-rich media are greater in the root than in the shoot (Ebbs and Kochian 1997). Another typical effect of Zn toxicity is the appearance of a purplish-red color in leaves, which is ascribed to phosphorus (P) deficiency (Lee et al. 1996).

Cadmium effects on plants

The regulatory limit of cadmium (Cd) in agricultural soil is 100 mg/kg soil (Salt et al. 1995). Plants grown in soil containing high levels of Cd show visible symptoms of injury reflected in terms of chlorosis, growth inhibition, browning of root tips and finally death (Sanita di Toppi and Gabbrielli 1999; Wojcik and Tukiendorf 2004; Mohanpuria et al. 2007; Guo et al. 2008). The inhibition of root Fe(III) reductase induced by Cd led to Fe(II) deficiency, and it seriously affected photosynthesis (Alcantara et al. 1994). In general, Cd has been shown to interfere with the uptake, transport and use of several elements (Ca, Mg, P and K) and water by plants (Das et al. 1997). Cd also reduced the absorption of nitrate and its transport from roots to shoots, by inhibiting the nitrate reductase activity in the shoots (Hernandez et al. 1996). Appreciable inhibition of the nitrate reductase activity was also found in plants of *Silene cucubalus* (Mathys 1975). Nitrogen fixation and primary ammonia assimilation decreased in nodules of soybean plants during Cd treatments (Balestrasse et al. 2003). Metal toxicity can affect the plasma membrane permeability, causing a reduction in water content; in particular, Cd has been reported to interact with the water balance (Costa and Morel 1994). Cadmium treatments have been shown to reduce ATPase activity of the plasma membrane fraction of wheat and sunflower roots (Fodor et al. 1995). Cadmium

produces alterations in the functionality of membranes by inducing lipid peroxidation (Fodor et al. 1995) and disturbances in chloroplast metabolism by inhibiting chlorophyll biosynthesis and reducing the activity of enzymes involved in CO₂ fixation (De Filippis and Ziegler 1993).

Copper effects on plants

Copper (Cu) is considered as a micronutrient for plants (Thomas et al. 1998) and plays important role in CO₂ assimilation and ATP synthesis. Cu is also an essential component of various proteins like plastocyanin of photosynthetic system and cytochrome oxidase of respiratory electron transport chain (Demirevska-kepova et al. 2004). But enhanced industrial and mining activities have contributed to the increasing occurrence of Cu in ecosystems. Cu is also added to soils from different human activities including mining and smelting of Cu-containing ores. Mining activities generate a large amount of waste rocks and tailings, which get deposited at the surface. Excess of Cu in soil plays a cytotoxic role, induces stress and causes injury to plants. This leads to plant growth retardation and leaf chlorosis (Lewis et al. 2001). Exposure of plants to excess Cu generates oxidative stress and ROS (Stadtman and Oliver 1991). Oxidative stress causes disturbance of metabolic pathways and damage to macromolecules (Hegedus et al. 2001). Copper toxicity affected the growth of *Alyssum montanum* (Ouzounidou 1994) and Cd of cucumber (Moreno-Caselles et al. 2000) and *Brassica juncea* (Singh and Tewari 2003). Copper and Cd in combination have affected adversely the germination, seedling length and number of lateral roots in *Solanum melongena* (Neelima and Reddy 2002).

Mercury effects on plants

The large input of mercury (Hg) into the arable lands has resulted in the widespread occurrence of mercury contamination in the entire food chain. Hg is a unique metal due to its existence in different forms e.g., HgS, Hg²⁺, Hg⁰ and methyl-Hg. However, in agricultural soil, ionic form (Hg²⁺) is predominant (Han et al. 2006). Hg released to the soil mainly remains in solid phase through adsorption onto sulfides, clay particles and organic matters. Increasing evidence has shown that Hg²⁺ can readily accumulate in higher and aquatic plants (Kamal et al. 2004; Wang and Greger 2004; Israr et al. 2006). High level of Hg²⁺ is strongly phytotoxic to plant cells. Toxic level of Hg²⁺ can induce visible injuries and physiological disorders in plants (Zhou et al. 2007). For example, Hg²⁺ can bind to water channel proteins, thus inducing leaf stomata to close and physical obstruction of water flow in plants (Zhang and Tyerman 1999). High level of Hg²⁺ interfere the

mitochondrial activity and induces oxidative stress by triggering the generation of ROS. This leads to the disruption of biomembrane lipids and cellular metabolism in plants (Messer et al. 2005; Cargnelutti et al. 2006).

Chromium effects on plants

Chromium (Cr) compounds are highly toxic to plants and are detrimental to their growth and development. Although some crops are not affected by low Cr ($3.8 \times 10^{-4} \mu\text{M}$) concentrations (Huffman and Allaway 1973a, b), Cr is toxic to most higher plants at $100 \mu\text{kg}^{-1}$ dry weight (Davies et al. 2002). Since seed germination is the first physiological process affected by Cr, the ability of a seed to germinate in a medium containing Cr would be indicative of its level of tolerance to this metal (Peralta et al. 2001). Seed germination of the weed *Echinochloa colona* was reduced to 25% with 200 μM Cr (Rout et al. 2000). High levels (500 ppm) of hexavalent Cr in soil reduced germination up to 48% in the bush bean *Phaseolus vulgaris* (Parr and Taylor 1982). Peralta et al. (2001) found that 40 ppm of Cr(VI) reduced by 23% the ability of seeds of Lucerne (*Medicago sativa* cv. Malone) to germinate and grow in the contaminated medium. Reductions of 32–57% in sugarcane bud germination were observed with 20 and 80 ppm Cr, respectively (Jain et al. 2000). The reduced germination of seeds under Cr stress could be a depressive effect of Cr on the activity of amylases and on the subsequent transport of sugars to the embryo axes (Zeid 2001). Protease activity, on the other hand, increases with the Cr treatment, which could also contribute to the reduction in germination of Cr-treated seeds (Zeid 2001). Decrease in root growth is a well-documented effect due to heavy metals in trees and crops (Tang et al. 2001). Prasad et al. (2001) reported that the order of metal toxicity to new root primordia in *Salix viminalis* is $\text{Cd} > \text{Cr} > \text{Pb}$, whereas root length was more affected by Cr than by other heavy metals studied. Chromium stress is one of the important factors that affect photosynthesis in terms of CO₂ fixation, electron transport, photophosphorylation and enzyme activities (Clijsters and Van Assche 1985). In higher plants and trees, the effect of Cr on photosynthesis is well documented (Van Assche and Clijsters 1983). However, it is not well understood to what extent Cr-induced inhibition of photosynthesis is due to disorganization of chloroplasts' ultra structure (Vazques et al. 1987), inhibition of electron transport or the influence of Cr on the enzymes of the Calvin cycle. Chromate is used as a Hill reagent by isolated chloroplast (Desmet et al. 1975). The more pronounced effect of Cr(VI) on PS I than on PS II activity in isolated chloroplasts has been reported by Bishnoi et al. (1993a, b) in peas. Nevertheless, in whole plants, both the photosystems were affected. Chromium stress can induce three

possible types of metabolic modification in plants: (i) alteration in the production of pigments, which are involved in the life sustenance of plants (e.g., chlorophyll, anthocyanin) (Boonyapookana et al. 2002) (ii) increased production of metabolites (e.g., glutathione, ascorbic acid) as a direct response to Cr stress, which may cause damage to the plants (Shanker et al. 2003b) and (iii) alterations in the metabolic pool to channelise the production of new biochemically related metabolites, which may confer resistance or tolerance to Cr stress (e.g., phytochelatins, histidine) (Schmfgger 2001). Induction and activation of superoxide dismutase (SOD) and of antioxidant catalase are some of the major metal detoxification mechanisms in plants (Shanker et al. 2003a). Gwozdz et al. (1997) found that at lower heavy metal concentrations, activity of antioxidant enzymes increased, whereas at higher concentrations, the SOD activity did not increase further and catalase activity decreased.

Lead effects on plants

Lead (Pb) is one of the ubiquitously distributed most abundant toxic elements in the soil. It exerts adverse effect on morphology, growth and photosynthetic processes of plants. Lead is known to inhibit seed germination of *Spartiana alterniflora* (Morzck and Funicelli 1982), *Pinus helipensis* (Nakos 1979). Inhibition of germination may result from the interference of lead with important enzymes. Mukherji and Maitra (1976) observed 60 μM lead acetate inhibited protease and amylase by about 50% in rice endosperm. Early seedling growth was also inhibited by lead in soya bean (Huang et al. 1974), rice (Mukherji and Maitra 1976), maize (Miller et al. 1975), barley (Stiborova et al. 1987), tomato, egg plant (Khan and Khan 1983) and certain legumes (Sudhakar et al. 1992). Lead also inhibited root and stem elongation and leaf expansion in *Allium* species (Gruenhagen and Jager 1985), barley (Juwarkar and Shende 1986) and *Raphanus sativas*. The degree to which root elongation is inhibited depends upon the concentration of lead and ionic composition and pH of the medium (Goldbold and Hutterman 1986). Concentration-dependent inhibition of root growth has been observed in *Sesamum indicum* (Kumar et al. 1992). A high lead level in soil induces abnormal morphology in many plant species. For example, lead causes irregular radial thickening in pea roots, cell walls of the endodermis and lignification of cortical parenchyma (Paivoke 1983). Lead also induces proliferation effects on the repair process of vascular plants (Kaji et al. 1995). Lead administered to potted sugar beet plants at rates of 100–200 ppm caused chlorosis and growth reduction (Hewilt 1953). In contrast, there was no visual symptoms of lead toxicity in alfalfa plants exposed to 100 mg/mL (Porter and Cheridan 1981). Low amounts

of lead (0.005 ppm) caused significant reduction in growth of lettuce and carrot roots (Baker 1972). Inhibitory effects of Pb^{2+} on growth and biomass production may possibly derive from effects on metabolic plant processes (Van Assche and Clijsters 1990). The primary cause of cell growth inhibition arises from a lead-induced stimulation of indol-3 acetic acid (IAA) oxidation. Lead is also known to affect photosynthesis by inhibiting activity of carboxylating enzymes (Stiborova et al. 1987). High level of Pb also causes inhibition of enzyme activities (Sinha et al. 1988a, b), water imbalance, alterations in membrane permeability and disturbs mineral nutrition (Sharma and Dubey 2005). Pb inhibits the activity of enzymes at cellular level by reacting with their sulfhydryl groups. High Pb concentration also induces oxidative stress by increasing the production of ROS in plants (Reddy et al. 2005)

Arsenic effects on plants

Arsenate (As) is an analog of phosphate (P) and competes for the same uptake carriers in the root plasmalemma of plants (Meharg and Macnair 1992). The As tolerance has been identified in a number of plant species (Meharg 1994; Sharples et al. 2000). The As tolerance in grasses results from suppression of a high-affinity P/As uptake system (Meharg and Macnair 1992). This suppression reduces As influx to a level at which plant can easily detoxify it, presumably by constitutive mechanisms (Meharg 1994). The As tolerance is achieved by a single gene encoding for the suppressed P/As transport (Meharg and Macnair 1992). Despite this clear understanding of the process controlling decrease in As uptake, tolerant grasses still assimilate As, albeit at much lower rate compared with non-tolerant. Nevertheless, assimilation over the life history of plants growing on contaminated soil can result in a very high As concentration, e.g., 3,470 mg/g As in *Agrostis tenuis* and 560 mg/g As in *Holcus lanatus* (Porter and Peterson 1975). The As also undergoes transformation within plant cells to other less phytotoxic As species (Meharg 1994). In phytoplankton and macro algae, As is converted to arsenite, dimethylarsinic acid (DMA) and mono methyl arsenic acid (MMA). Such methylated forms of As are then metabolized to organo phospholipids and arsenosugars (Phillips 1990). Previously, terrestrial plants have been documented only for the presence of arsenate and arsenite (arsenate ion; arsenite is a chemical compound containing an arsenic oxoanion where arsenic has oxidation state +3 arsenic atom in arsenate has a valency of 5) (Meharg 1994; Van den Broeck et al. 1998). However, a later study on a range of terrestrial plants has also reported low concentrations of methylated As species such as MMA and DMA (Koch et al. 2000).

Cobalt effects on plants

Cobalt (Co) naturally occurs in the earth's crust as cobaltite [CoAsS], erythrite [Co₃(AsO₄)₂] and smaltite [CoAs₂]. Plants can accumulate small amount of Co from the soil. The uptake and distribution of Co in plants is species-dependent and controlled by different mechanisms (Kukier et al. 2004; Li et al. 2004; Bakkaus et al. 2005). Very little information is available regarding the phytotoxic effect of excess Co. Phytotoxicity study of Co in barley (*Hordeum vulgare* L.), oilseed rape (*Brassica napus* L.) and tomato (*Lycopersicon esculentum* L.) has recently shown the adverse effect on shoot growth and biomass (Li et al. 2009). In addition to biomass, excess of Co restricted the concentration of Fe, chlorophyll, protein and catalase activity in leaves of cauliflower. Further, high level of Co also affected the translocation of P, S, Mn, Zn and Cu from roots to tops in cauliflower. In contrast to excess Cu or Cr, Co significantly decreased water potential and transpiration rate. While diffusive resistance and relative water content increased in leaves of cauliflower upon exposure to excess Co (Chatterjee and Chatterjee 2000).

Nickel effects on plants

Nickel (Ni) is a transition metal and found in natural soils at trace concentrations except in ultramafic or serpentinitic soils. However, Ni²⁺ concentration is increasing in certain areas by human activities such as mining works, emission of smelters, burning of coal and oil, sewage, phosphate fertilizers and pesticides (Gimeno-Garcia et al. 1996). Ni²⁺ concentration in polluted soil may range from 20- to 30-fold (200–26,000 mg/kg) higher than the overall range (10–1,000 mg/kg) found in natural soil (Izosimova 2005). Excess of Ni²⁺ in soil causes various physiological alterations and diverse toxicity symptoms such as chlorosis and necrosis in different plant species (Zornoza et al. 1999; Pandey and Sharma 2002; Rahman et al. 2005), including rice (Das et al. 1997). Plants grown in high-Ni²⁺-containing soil showed impairment of nutrient balance and resulted in disorder of cell membrane functions. Thus, Ni²⁺ affected the lipid composition and H-ATPase activity of the plasma membrane as reported in *Oryza sativa* shoots (Ros et al. 1992). Exposure of wheat to high level of Ni²⁺ enhanced MDA concentration (Pandolfini et al. 1992). Moreover, Gonnelli et al. (2001) reported an increase in MDA concentration of Ni²⁺-sensitive plants compared to a Ni²⁺-tolerant saline. Such changes might disturb membrane functionality and ion balance in the cytoplasm, particularly of K⁺, the most mobile ion across plant cell membrane. Other symptoms observed in Ni²⁺-treated plants were related with changes in water balance. High uptake of Ni²⁺ induced a decline in water content of dicot

and monocot plant species. The decrease in water uptake is used as an indicator of the progression of Ni²⁺ toxicity in plants (Pandey and Sharma 2002; Gajewska et al. 2006).

Manganese effects on plants

Accumulation of excessive manganese (Mn) in leaves causes a reduction of photosynthetic rate (Kitao et al. 1997a, b). Mn is readily transported from root to shoot through the transpiration stream, but not readily remobilized through phloem to other organs after reaching the leaves (Loneragan 1988). Necrotic brown spotting on leaves, petioles and stems is a common symptom of Mn toxicity (Wu 1994). This spotting starts on the lower leaves and progresses with time toward the upper leaves (Horiguchi 1988). With time, the speckles can increase in both number and size resulting in necrotic lesions, leaf browning and death (Elamin and Wilcox 1986a, b). General leaf bronzing and shortening of internodes has been documented in *Cucumis sativus* (cucumber) (Crawford et al. 1989). Another common symptom is known as “crinkle-leaf”, and it occurs in the youngest leaf, stem and petiole tissue. It is also associated with chlorosis and browning of these tissues (Wu 1994; Bachman and Miller 1995). Roots exhibiting Mn toxicity are commonly brown in color (Le Bot et al. 1990; Foy et al. 1995) and sometimes crack (Foy et al. 1995). Chlorosis in younger leaves by Mn toxicity is thought to be caused through Mn-induced Fe deficiency (Horst 1988). Excess Mn is reported to inhibit synthesis of chlorophyll by blocking a Fe-concerning process (Clari-mont et al. 1986). Manganese toxicity in some species starts with chlorosis of older leaves moving toward the younger leaves with time (Bachman and Miller 1995). This symptom starts at the leaf margins progressing to the interveinal areas and if the toxicity is acute, the symptom progresses to marginal and interveinal necrosis of leaves (Bachman and Miller 1995). In the only research on Mn toxicity of Australian native trees, *Eucalyptus gummiifera* (red blood wood) displayed small, chlorotic leaves that were often distorted in shape and death of terminal buds (Winterhalder 1963).

Iron effects on plants

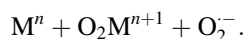
Iron as an essential element for all plants has many important biological roles in the processes as diverse as photosynthesis, chloroplast development and chlorophyll biosynthesis. Iron is a major constituent of the cell redox systems such as heme proteins including cytochromes, catalase, peroxidase and leghemoglobin and iron sulfur proteins including ferredoxin, aconitase and superoxide dismutase (SOD) (Marschner 1995).

Although most mineral soils are rich in iron, the expression of iron toxicity symptoms in leaf tissues occurs only under flooded conditions, which involves the microbial reduction of insoluble Fe^{3+} to soluble Fe^{2+} (Becker and Asch 2005). The appearance of iron toxicity in plants is related to high Fe^{2+} uptake by roots and its transportation to leaves and via transpiration stream. The Fe^{2+} excess causes free radical production that impairs cellular structure irreversibly and damages membranes, DNA and proteins (Arora et al. 2002; de Dorlodot et al. 2005). Iron toxicity in tobacco, canola, soybean and *Hydrilla verticillata* are accompanied with reduction of plant photosynthesis and yield and the increase in oxidative stress and ascorbate peroxidase activity (Sinha et al. 1997).

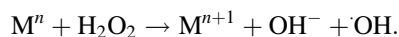
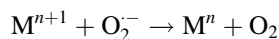
Mechanisms of plants to cope with metal toxicity

Activation of reduced forms of oxygen and associated biochemical damage

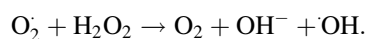
Oxygen free radicals are produced when molecular oxygen accepts electrons from other molecules, and many intracellular reactions reduce oxygen to superoxide (O_2^-) or hydrogen peroxide (H_2O_2). Although these molecules are not very reactive, they can form hydroxyl radicals ($\cdot\text{OH}$), which are probably responsible for most of the oxidative damage in biological systems (Cadenas 1989; Halliwell and Cutler 1990). The one electron reduction of molecular oxygen to the superoxide radical is thermodynamically unfavorable (Illan et al. 1976), but can nevertheless take place by interaction with another paramagnetic centre. Transition metals such as iron and copper (M) have frequently unpaired electrons and are, therefore, very good catalysts of oxygen reduction, following the reaction:



In aqueous solutions at neutral pH, O_2^- can generate H_2O_2 , which can subsequently decompose to produce $\cdot\text{OH}$ by the Haber–Weiss reaction, copper or iron (M) being again involved as follow:



These reactions are usually summarized as



When iron is the transition metal in the Haber–Weiss reaction, it is called the Fenton reaction. Hydroxyl radicals ($\cdot\text{OH}$) produced by the Haber–Weiss reaction can oxidize biological molecules, leading to major cellular damages,

and ultimately to cell death. Hydroxyl radicals can be produced in close proximity to DNA, adding or removing H atoms to DNA bases or the DNA backbone, respectively (Pryor 1988). Their action could be responsible for 10^4 – 10^5 DNA base modifications per cell per day (Ames et al. 1991). Fe^{2+} ions either complexed to a phosphate residue or coordinated with ring nitrogens, or free in solution are involved in these hydroxyl radical-mediated DNA alterations (Luo et al. 1994).

Metal ions, through Haber–Weiss reaction, also play an important role in the oxidative modifications of free amino acids and proteins, and this aspect has been reviewed by Stadtman (1993). Histidine, arginine, lysine, proline, methionine and cysteine residues are the most common sites of oxidation in proteins, and their major oxidation products have been identified. Frequently, only one amino acid residue in a given protein is modified by oxidation. These modifications correspond to site-specific processes, amino acid residues at metal binding sites being specific targets. A major consequence of oxygen free radical damage to proteins is to target them for degradation by proteases (Roseman and Levine 1987). Release of Fe^{2+} from [4Fe-4S] clusters of some dehydratases such as aconitases is also another important aspect of protein oxidation (Goldstein and Czapski 1986).

Finally, oxygen and transition metals (in particular iron) are implicated in lipid peroxidation, and biological membranes rich in polyunsaturated fatty acids are extremely susceptible to these reactions. Ascorbic acid is known to quench lipid peroxy and alkoxy radicals in the aqueous phase. However, ascorbate can also function as a prooxidant by reducing Fe^{3+} or Cu^{2+} , allowing the metal-catalyzed transition of lipid hydro peroxides to radical species (Scholz et al. 1990).

Genotoxicity

Metal binding to the cell nucleus causes promutagenic damage including DNA base modifications, inter- and intra-molecular cross-linkage of DNA and proteins, DNA strand breaks, rearrangements and de-purination. Chemical reactions driving this damage, and the resulting mutations, are characteristics of an oxidative DNA attack (Kasprzak 1995). Metal-mediated production of reactive oxygen species in the DNA vicinity generates principally the promutagenic adduct 8-oxoG (7,8-dihydro-8-oxoguanine) that could mispair with adenine in the absence of DNA repair, resulting in C to T transversion mutations (Cunningham 1997).

Although oxidative damage explains most of the mechanisms involved in metal-mediated carcinogenicity and acute toxicity, other pathways also have to be

considered. DNA methylation aberration has been shown to play an important role in tumorigenesis (Zingg and Jones 1997). Cell treatment with carcinogenic nickel can cause chromatin condensation through competition with magnesium ions. This condensed chromatin is hypermethylated, leading to silencing of putative anti-oncogenic gene expression, thus driving treated cells to a carcinogenic state (Lee et al. 1995).

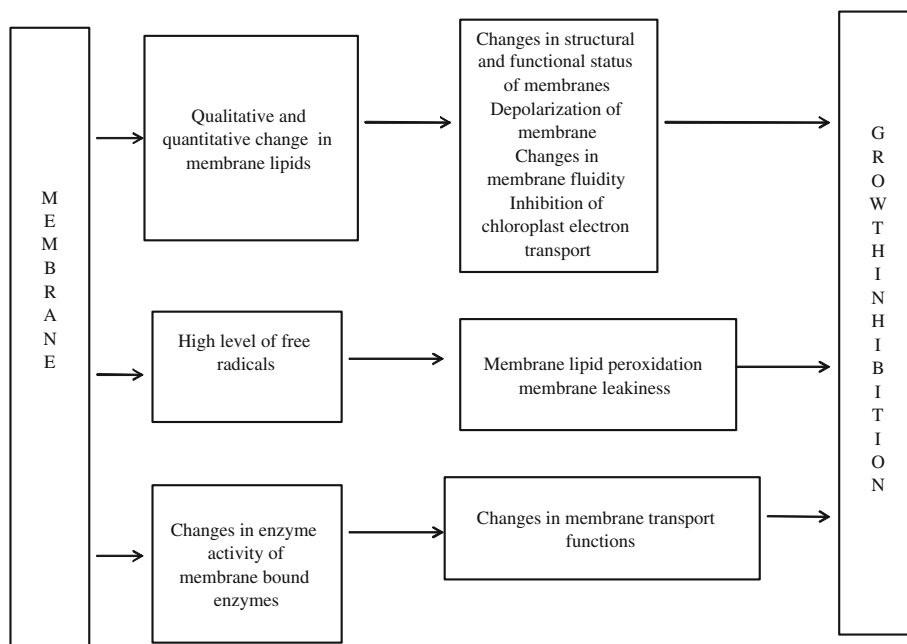
Most of the cellular and molecular aspects of metal toxicity in plants are unknown, even though deleterious effects on crop production have long been recognized. Preliminary observations on putative metal genotoxic effects in plant are scarce. At the organ level, this symptom is common to numerous metals (Punz and Sieghardt 1993). Nickel accumulation in maize root apex reduces meristem mitotic activity, and this could be due to the lack of integrity of root meristems (L’Huillier et al. 1996). Concentration- and time-dependant cadmium, copper and nickel clastogenic effects were observed in *Helianthus annuus* (Chakravarty and Srivastava 1992). Taken together, these observations suggest that genotoxic effects could be in part responsible for metal phytotoxicity, deserving more work to elucidate the underlying mechanisms.

Effects on antioxidant activity

Heavy metal toxicity is reported to increase the activity of enzymes such as, glucose-6-phosphate dehydrogenase and peroxidase in the leaf of plants grown in polluted soil (Fig. 1) (Van Assche and Clijsters 1987). Metal ions play an important role in the antioxidant network, as these are essential cofactors of most antioxidant enzymes. For

example, all isoforms of super oxide dismutase (SOD) contain bound heavy metal ions. Cu and Zn constitute the cofactor of the Cu/Zn-SOD associated with chloroplast, glyoxisomes contain Mn-SOD. Fe-SOD has been found in the chloroplast of some plants. Metals are involved in the direct or indirect generation of free radicals (FR) and reactive oxygen species (ROS) in the following ways: 1. direct transfer of electron in single electron reduction, 2. disturbance of metabolic pathways resulting in an increase in the rate of FR and ROS formation, 3. inactivation and down regulation of the enzymes of the antioxidative defense system and 4. depletion of low molecular weight antioxidants (Aust et al. 1985). The ROS produced in leaf cells are removed by complex enzymes catalase (CAT), ascorbate peroxidases (APX), glutathione peroxidases (GP_x), superoxide dismutase (SOD) and glutathione reductases (GR) of antioxidant systems (Fig. 2). Heavy metals induced oxidative damage in senescing oat leaf cells (Luna and Gonzalez 1994), primary leaves of mung bean (Weckex and Clijsters 1997) and in wheat leaves (Panda and Patra 2000). Proline is known to play a role in the detoxification of active oxygen in *Brassic juncea* and *Cajanus cajan* under heavy metal stress (Alia Prasad and Pardha Saradhi 1995). Accumulation of proline has been observed in various plant species subjected to heavy metal stress (Shah and Dubey 1998). It is reported that antioxidant enzyme activities increase under Zn stress in *Brassica juncea* (Prasad et al. 1999). Verma and Dubey (2003) have reported that with increase in the level of Pb treatment, antioxidant enzymes such as guaiacol peroxidase, SOD, APX and GR activities increased compared to control in rice plants. It has been further suggested that SOD and GR

Fig. 1 Heavy metal–induced membrane changes play a major role in plant growth (Prasad and Hagemeyer 1999)



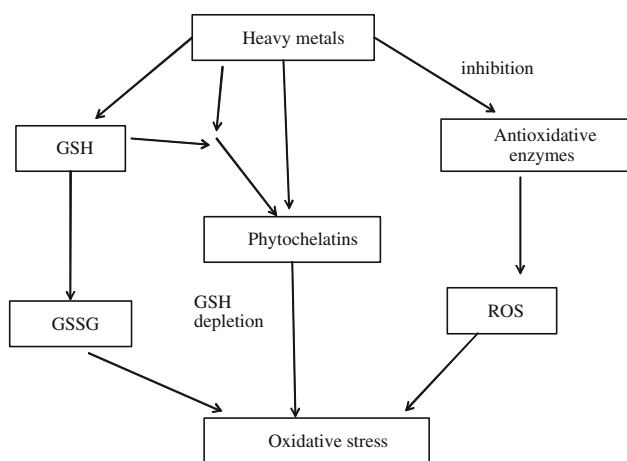


Fig. 2 Heavy metal-induced oxidative stress and related cellular processes (Prasad and Hagemeyer 1999)

play a pivotal role in combining oxidative stress in rice plants and Pb toxicity.

Thus, it is evident from the several research reports that judicious use and presence of heavy metals have toxic effects on plants, animals and other living organisms and affects the same after certain limits. Therefore, it is well needed to intensify the research programmes for better understanding of heavy metal toxicity on plants and allied areas to maintain the ecological harmony of the globe.

References

- Alcantara E, Romera FJ, Canete M, De La Guardia MD (1994) Effects of heavy metals on both induction and function of root Fe(III) reductase in Fe-deficient cucumber (*Cucumis sativus* L.) plants. *J Exp Bot* 45:1893–1898
- Al-Hiyaly SA, McNeilly T, Bradshaw AD (1988) The effect of zinc concentration from electricity pylons-evolution in replicated situation. *New Phytol* 110:571–580
- Alia Prasad KVS, Pardha Saradhi P (1995) Effect of zinc on free radical and proline in *Brassica juncea* and *Cajanus cajan*. *Phytochem* 39:45–47
- Allaway WH (1968) Agronomic control over the environmental cycling of trace elements. *Adv Agron* 20:235–274
- Ames BA, Shingenaga MK, Park EM (1991) Oxidative damage and repair: chemical, biological and medical aspects. In: Elmsford (ed) Pergamon Press, New York, pp 181–187
- Angino EE, Magnuson LM, Waugh TC, Galle OK, Bredfeldt J (1970) Arsenic in detergents-possible danger and pollution hazard. *Sci* 168:389–392
- Arora A, Sairam RK, Srivastava GC (2002) Oxidative stress and antioxidative system in plants. *Cur Sci* 82:1227–1338
- Aust SD, Marehouse CE, Thomas CE (1985) Role of metals in oxygen radical reactions. *J Free Radi Biol Med* 1:3–25
- Awashthi SK (2000) Prevention of Food Adulteration Act no 37 of 1954. Central and State Rules as Amended for 1999. Ashoka Law House, New Delhi
- Bachman GR, Miller WB (1995) Iron chelate inducible iron/manganese toxicity in zonal geranium. *J Plant Nutri* 18:1917–1929

- Baker WG (1972) Toxicity levels of mercury lead, copper and zinc in tissue culture systems of cauliflowers lettuce potato and carrot. *Can J Bot* 50:973–976
- Bakkaus E, Gouget B, Gallien JP, Khodja H, Carrot H, Morel JL, Collins R (2005) Concentration and distribution of cobalt in higher plants: the use of micro-PIXE spectroscopy. *Nucl Instr Meth B* 231:350–356
- Balestrasse KB, Benavides MP, Gallego SM, Tomaro ML (2003) Effect on cadmium stress on nitrogen metabolism in nodules and roots of soybean plants. *Func Plant Biol* 30:57–64
- Barghiani C, Gloffre D, Bargali R (1987) Mercury content in *Pinus* Sp of the Mt. Etna volcanic area, in heavymetals in the environment, Vol 2. Lindberg JE, Hutchinson TC (eds). New Orleans.51
- Becker M, Asch F (2005) Iron toxicity in rice—conditions and management concepts. *J Plant Nutr Soil Sci* 168:558–573
- Bishnoi NR, Chugh LK, Sawhney SK (1993a) Effect of chromium on photosynthesis, respiration and nitrogen fixation in pea (*Pisum sativum* L) seedlings. *J Plant Physiol* 142:25–30
- Bishnoi NR, Dua A, Gupta VK, Sawhney SK (1993b) Effect of chromium on seed germination, seedling growth and yield of peas. *Agri Eco Environ* 47:47–57
- Blaylock MJ, Huang JW (2000) Phytoextraction of metals. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals-using plants to clean up the environment. Wiley, New York, pp 53–70
- Bolter E, Wixson BG, Butherus DL, Jennett JC (1974) Distribution of heavy metals in soils near an active lead smelter. In: Fed kenheuer PJ (ed) Issue confronting Min. Ind. Ann. Meet. Sect. Aime 47th. Department. of Cond. Cont. Ext. University of Minneapolis. Minneapolis, 73
- Boonyapookana B, Upatham ES, Kruatrachue M, Pokethitiyook P, Singhakaew S (2002) Phytoaccumulation and phytotoxicity of cadmium and chromium in duckweed *Wolffia globosa*. *Int J Phytoremed* 4:87–100
- Bradford WI (1997) Urban storm water pollutant loadings a statistical summary through. *JWPCF* 49:610–613
- Cadenas E (1989) Biochemistry of oxygen toxicity. *Annu Rev Biochem* 58:79–110
- Cakmak I, Marshner H (1993) Effect of zinc nutritional status on superoxide radical and hydrogen peroxide scavenging enzymes in bean leaves. In: Barrow NJ (ed) Plant nutrition-from genetic engineering field practice. Kluwer, The Netherlands, pp 133–137
- Cannon HL, Connally GG, Epstein JB, Parker JG, Thornton I, Wixson G (1978) Rocks: geological sources of most trace elements. In: report to the workshop at south seas plantation Captiva Island, FL, US. *Geochem Environ* 3:17–31
- Cargnelutti D, Tabaldi LA, Spanevello RM, Jucoski GO, Battisti V, Redin M, Linares CEB, Dressler VL, Flores MM, Nicoloso FT, Morsch VM, Schetinger MRC (2006) Mercury toxicity induces oxidative stress in growing cucumber seedlings. *Chemosph* 65:999–1106
- Chakravarty B, Srivastava S (1992) Toxicity of some heavy metals in vivo and in vitro in *Helianthus annuus*. *Mutat Res* 283:287–294
- Chatterjee J, Chatterjee C (2000) Phytotoxicity of cobalt, chromium and copper in cauliflower. *Environ Pollut* 109:69–74
- Chatterjee C, Rajeev Gopal, Dube BK (2006) Physiological and biochemical responses of French bean to excess cobalt. *J Plant Nutri* 29:127–136
- Choi JM, Pak CH, Lee CW (1996) Micronutrient toxicity in French marigold. *J Plant Nutri* 19:901–916
- Clarimont KB, Hagar WG, Davis EA (1986) Manganese toxicity to chlorophyll synthesis in tobacco callus. *Plant Physiol* 80:291–293
- Clijsters H, Van Assche F (1985) Inhibition of photosynthesis by heavy metals. *Photosynth Res* 7:31–40

- Climino G, Ziino M (1983) Heavy metal pollution part VII emissions from Etna volcanic. *Geophy Res Lett* 10:31–38
- Costa G, Morel JL (1994) Water relations, gas exchange and amino acid content in Cd-treated lettuce. *Plant Physiol Biochem* 32:561–570
- Crawford TW, Stroehlein JL, Kuehl RO (1989) Manganese and rates of growth and mineral accumulation in cucumber. *J Am Soc Horti Sci* 114:300–306
- Cunningham RP (1997) DNA repair: caretakers of the genome? *Curr Biol* 7:576–579
- Das P, Samantaray S, Rout GR (1997) Studies on cadmium toxicity in plants: a review. *Environ Pollut* 98:29–36
- Davidson CI, Santhanam S, Fortmann RC, Olson MP (1985) Atmospheric transport and deposition of trace elements onto the Greenland ice sheet. *Atmos Envi* 19:2065–2082
- Davies FT, Puryear JD, Newton RJ, Egilla JN, Grossi JAS (2002) Mycorrhizal fungi increase chromium uptake by sunflower plants: influence on tissue mineral concentration, growth, and gas exchange. *J Plant Nutr* 25:2389–2407
- de Dorlodot S, Lutts S, Bertin P (2005) Effects of ferrous iron toxicity on the growth and mineral composition of an inter specific rice. *J Plant Nutr* 28:1–20
- De Filippis LF, Ziegler H (1993) Effect of sublethal concentrations of zinc, cadmium and mercury on the photosynthetic carbon reduction cycle of *Euglena*. *J Plant Physiol* 142:167–172
- Demirevska-Kepova K, Simova-Stoilova L, Stoyanova Z, Holzer R, Feller U (2004) Biochemical changes in barley plants after excessive supply of copper and manganese. *Environ Exp Bot* 52:253–266
- Desmet GA, de Ruyter GA, Rigoet A (1975) Absorption and metabolism of Cr(VI) by isolated chloroplasts. *Phytochem* 14:2585–2588
- Devries W, Loftis S, Tipping E, Meili M, Groenenberg JE, Schutze G (2002) Impact of soil properties on critical concentrations of cadmium, lead, copper, zinc and mercury in soil and soil solution in view of ecotoxicological effects. *Rev Environ Contam Toxicol* 191:47–89
- Ebbs SD, Kochian LV (1997) Toxicity of zinc and copper to *Brassica* species: implications for phytoremediation. *J Environ Qual* 26:776–781
- Elamin OM, Wilcox GE (1986a) Effect of magnesium and manganese nutrition on muskmelon growth and manganese toxicity. *J Am Soc Horti Sci* 111:582–587
- Elamin OM, Wilcox GE (1986b) Effect of magnesium and manganese nutrition on watermelon growth and manganese toxicity. *J Am Soc Horti Sci* 111:588–593
- Eshleman A, Siegel SM, Siegel BZ (1971) Is mercury from Hawaiian volcanoes a natural source of pollution? *Nature* 223:471–475
- European Union (2002) Heavy metals in wastes, European commission on environment <http://www.ec.europa.eu/environment/waste/studies/pdf/heavymetalsreport.pdf>
- Farlex Incorporated (2005) Definition: environment, the free dictionary, Farlex Inc. Publishing, USA (<http://www.thefreedictionary.com/>)
- Fergusson JE (1990) The heavy elements: chemistry, environmental impact and health effects. Pergamon, Oxford
- Fernandes JC, Henriques FS (1991) Biochemical, physiological and structural effects of excess copper in plants. *Bot Rev* 57:247–273
- Fodor A, Szabo-Nagy A, Erdei L (1995) The effects of cadmium on the fluidity and H⁺-ATPase activity of plasma membrane from sunflower and wheat roots. *J Plant Physiol* 14:787–792
- Fontes RLS, Cox FR (1998) Zinc toxicity in soybean grown at high iron concentration in nutrient solution. *J Plant Nutr* 21:1723–1730
- Foy CD, Weil RR, Coradetti CA (1995) Differential manganese tolerances of cotton genotypes in nutrient solution. *J Plant Nutr* 18:685–706
- Gajewska E, Sklodowska M, Slaba M, Mazur J (2006) Effect of nickel on antioxidative enzymes activities, proline and chlorophyll contents in wheat shoots. *Biol Planta* 50:653–659
- Garbarino JR, Hayes H, Roth D, Antweider R, Brinton TI, Taylor H (1995) Contaminants in the Mississippi River, U.S. Geological Survey Circular 1133, Virginia (<http://www.pubs.usgs.gov/circ/circ1133/>)
- Gimeno-Garcia E, Andreu V, Boluda R (1996) Heavy metals incidence in the application of inorganic fertilizers and pesticides to rice farming soils. *Environ Pollu* 92:19–25
- Goldbold DJ, Hutterman A (1986) The uptake and toxicity of mercury and lead to spruce (*Picea abies*) seedlings. *Wat air Soil Pollu* 31:509–515
- Goldstein S, Czapski C (1986) The role and mechanism of metal ions and their complexes in enhancing damage in biological systems or in protecting these, systems from the toxicity of O₂⁻
- Gonnelli C, Galardi F, Gabbriellini R (2001) Nickel and copper tolerance in three Tuscan populations of *Silene paradoxa*. *Physiol Planta* 113:507–514
- Gore A (1997) Respect the land, our precious olant. *Time Magaz* 150:8–9
- Gruenhage L, Jager IJ (1985) Effect of heavy metals on growth and heavy metals content of *Allium Porrum* and *Pisum sativum*. *Angew Bot* 59:11–28
- Guo J, Dai X, Xu W, Ma M (2008) Over expressing GSHI and AsPCSI simultaneously increases the tolerance and accumulation of cadmium and arsenic in *Arabidopsis thaliana*. *Chemosphere* 72:1020–1026
- Gwozdz EA, Przymusinski R, Rucinska R, Deckert J (1997) Plant cell responses to heavy metals: molecular and physiological aspects. *Acta Physiol Plant* 19:459–465
- Halliwell B, Cutleridge JMC (1990) Role of free radicals and catalytic metal ions in human disease: an overview. *Methods Enzymol* 186:1–85
- Han FX, Su Y, Monts DL, Waggoner AC, Plodinec JM (2006) Binding distribution, and plant uptake of mercury in a soil from Oak Ridge, Tennessee, USA. *Sci Total Env* 368:753–768
- Hawkes JS (1997) Heavy metals. *J Chem Edu* 74:1369–1374
- Hegedus A, Erdei S, Horvath G (2001) Comparative studies of H₂O₂ detoxifying enzymes in green and greening barley seedlings under cadmium stress. *Plant Sci* 160:1085–1093
- Herawati N, Suzuki S, Hayashi K, Rivai IF, Koyoma H (2000) Cadmium, copper and zinc levels in rice and soil of Japan, Indonesia and China by soil type. *Bull Environ Contam Toxicol* 64:33–39
- Hernandez LE, Carpena-Ruiz R, Garate A (1996) Alterations in the mineral nutrition of pea seedlings exposed to cadmium. *J Plant Nutr* 19:1581–1598
- Hewilt EJ (1953) Metal inter-relationships in plant nutrition. *J Exp Bot* 4:59–64
- Horiguchi T (1988) Mechanism of manganese toxicity and tolerance of plants. IV. Effects of silicon on alleviation of manganese toxicity of rice plants. *Soil Sci Plant Nutri* 34:65–73
- Horst J (1988) Beschreibung der Gleichgewichtslage des ionenaustauschs an schwach sauren harzen mit hilfe eines models der oberflächenkomplexbildung, doctoral thesis, University of Karlsruhe, Kfk report 4464
- Huang CV, Bazzaz FA, Venderhoef LN (1974) The inhibition of soya bean metabolism by cadmium and lead. *Plant Physiol* 34:122–124
- Huffman EWD Jr, Allaway HW (1973a) Chromium in plants: distribution in tissues, organelles, and extracts and availability of bean leaf Cr to animals. *J Agric Food Chem* 21:982–986
- Huffman EWD Jr, Allaway WH (1973b) Growth of plants in solution culture containing low levels of chromium. *Plant Physiol* 52:72–75

- Illan YA, Crapski C, Meisel D (1976) The one-electron transfer redox potentials of free radicals. 1. The oxygen/superoxide system. *Biochem Biophys Acta* 430:209–224
- Institute of Environmental Conservation and Research INECAR (2000) Position paper against mining in Rapu-Rapu, Published by INECAR, Ateneo de Naga University, Philippines (<http://www.adnu.edu.ph/Institutes/Inecar/pospaper1.asp>)
- Israr M, Sahi S, Datta R, Sarkar D (2006) Bioaccumulation and physiological effects of mercury in *Sesbania drummonii*. *Chemosphere* 65:591–598
- Izosimova A (2005) Modelling the interaction between calcium and nickel in the soil-plant system. *FAL Agric Res Special issue* 288:99
- Jain R, Srivastava S, Madan VK, Jain R (2000) Influence of chromium on growth and cell division of sugarcane. *Ind J Plant Physiol* 5:228–231
- Juwarkar AS, Shende GB (1986) Interaction of Cd-Pb effect on growth yield and content of Cd, Pb in barley. *Ind J Environ Heal* 28:235–243
- Kaji T, Suzuki M, Yamamoto C, Mishima A, Sakamoto M, Kozuka H (1995) Severe damage of cultured vascular endothelial cell monolayer after simultaneous exposure to cadmium and lead. *Arch Environ Contam Toxicol* 28:168–172
- Kamal M, Ghalya AE, Mahmouda N, Cote R (2004) Phytoaccumulation of heavy metals by aquatic plants. *Environ Intern* 29:1029–1039
- Kasprzak KS (1995) Possible role of oxidative damage in metal-induced carcinogenesis. *Cancer Invest* 13:411–430
- Khan S, Khan NN (1983) Influence of lead and cadmium on growth and nutrient concentration of tomato (*Lycopersicon esculentum*) and egg plant (*Solanum melongena*). *Plant Soil* 74:387–394
- Kitao M, Lei TT, Koike T (1997a) Effects of manganese toxicity on photosynthesis of white birch (*Betula platyphylla var. japonica*) seedlings. *Physiol Plant* 101:249–256
- Kitao M, Lei TT, Koike T (1997b) Effects of manganese in solution culture on the growth of five deciduous broad-leaved tree species with different successional characters from northern Japan. *Photosynth* 36:31–40
- Koch I, Wang L, Olsson CA, Cullen WR, Reimer KJ (2000) The predominance of inorganic arsenic species in plants from Yellowknife, Northwest Territories, Canada. *Environ Sci Tech* 34:22–26
- Kraal H, Ernst W (1976) Influence of copper high tension lines on plants and soil. *Environ Pollu* 11:131–135
- Kukier U, Peters CA, Chaney RL, Angle JS, Roseberg RJ (2004) The effect of pH on metal accumulation in two *Alyssum* species. *J Environ Qual* 33:2090–2102
- Kumar G, Singh RP, Sushila (1992) Nitrate assimilation and biomass production in *Seasamum indicum* (L.) seedlings in lead enriched environment. *Wat Soil Pollu* 215:124–215
- Lacerda LD (1997) Global mercury emissions from gold and silver mining. *Water Air Soil Pollu* 97:209–221
- Le Bot J, Kirkby EA, Beusichem ML (1990) Manganese toxicity in tomato plants: effects on cation uptake and distribution. *J Plant Nutri* 13:513–525
- Lee YW, Klein CB, Kargacin B, Salnikow K, Kitahara J, Dowjat K, Zhitkovich A, Christie NT, Costa M (1995) Carcinogenic nickel silences gene expression by chromatin condensation and DNA methylation: a new model for epigenetic carcinogens. *Mol Cell Biol* 15:2547–2557
- Lee CW, Choi JM, Pak CH (1996) Micronutrient toxicity in seed geranium (*Pelargonium × hortorum* Baley). *J Am Soc Horti Sci* 121:77–82
- Lenntech Water Treatment and Air Purification (2004) Water treatment. Lenntech, Rotterdamseweg, Netherlands (<http://www.excelwater.com/thp/filters/Water-Purification.htm>)
- Lewis S, Donkin ME, Depledge MH (2001) Hsp 70 expression in *Enteromorpha intestinalis* (Chlorophyta) exposed to environmental stressors. *Aqua Toxicol* 51:277–291
- L'Huillier L, d'Auzac J, Durand M, Michaud-Ferriere N (1996) Nickel effects on two maize (*Zea mays*) cultivars: growth, structure, Ni concentration, and localization. *Can J Bot* 74:1547–1554
- Li Z, McLaren RG, Metherell AK (2004) The availability of native and applied soil cobalt to ryegrass in relation to soil cobalt and manganese status and other soil properties. *N Z J Agri Res* 47:33–43
- Li HF, Gray C, Mico C, Zhao FJ, McGrath SP (2009) Phytotoxicity and bioavailability of cobalt to plants in a range of soils. *Chemosphere* 75:979–986
- Loneragan JF (1988) Distribution and movement of manganese in plants. In: Graham RD, Hannam RJ, Uren NC (eds) *Manganese in soils and plants*. Kluwer, Dordrecht, pp 113–124
- Luna CM, Gonzalez CA (1994) Trippi VS (1994) Oxidative damage caused by an excess of copper in oat leaves. *Plant Cell Physiol* 35:11–15
- Luo Y, Han Z, Chin SM, Linn S (1994) Three chemically distinct types of oxidants formed by iron mediated Fenton reactions in the presence of DNA. *Proc Natl Acad Sci USA* 91:12438–12442
- Mahmood T, Islam KR (2006) Response of rice seedlings to copper toxicity and acidity. *J Plant Nutri* 29:943–957
- Marschner H (1986) *Mineral nutrition of higher plants*. Academic Press, London, p 674
- Marschner H (1995) *Mineral nutrition of higher plants*, 2nd edn. Academic Press, Toronto
- Mathys W (1975) Enzymes of heavy metal-resistant and non-resistant populations of *Silene cucubalus* and their interactions with some heavy metals in vitro and in vivo. *Physiol Plant* 33:161–165
- Meharg AA (1994) Integrated tolerance mechanisms-constitutive and adaptive plant-response to elevated metal concentrations in the environment. *Plant Cell and Envi* 17:989–993
- Meharg AA, Macnair MR (1992) Suppression of the high affinity phosphate uptake system; a mechanism of arsenate tolerance in *Holcus lanatus* L. *J Exp Bot* 43:519–524
- Messer RL, Lockwood PE, Tseng WY, Edwards K, Shaw M, Caughman GB, Lewis JB, Wataha JC (2005) Mercury (II) alters mitochondrial activity of monocytes at sublethal doses via oxidative stress mechanisms. *J Biomed Mat Res B* 75: 257–263
- Mildvan AS (1970) Metal in enzymes catalysis. In: Boyer DD (ed) *The enzymes*, vol 11. Academic Press, London, pp 445–536
- Miller JE, Hassete JJ, Koppe DE (1975) Interaction of lead and cadmium of electron energy transfer reaction in corn mitochondria. *Physiol Plant* 28:166–171
- Misra SG, Mani D (1991) *Soil pollution*. Ashish Publishing House, Punjabi Bagh
- Mohanpuria P, Rana NK, Yadav SK (2007) Cadmium induced oxidative stress influence on glutathione metabolic genes of *Camella sinensis* (L.). *O Kuntze. Environ Toxicol* 22:368–374
- Monni S, Salemma M, Millar N (2000) The tolerance of *Empetrum nigrum* to copper and nickel. *Environ Pollut* 109:221–229
- Moreno-Caselles J, Moral R, Pera-Espinosa A, Marcia MD (2000) Cadmium accumulation and distribution in cucumber plants. *J Plant Nutri* 23:243–250
- Morzck E Jr, Funicelli NA (1982) Effect of lead and on germination of *Spartina alterniflora* Losiel seeds at various salinities. *Environ Exp Bot* 22:23–32
- Mukherji S, Maitra P (1976) Toxic effects of lead growth and metabolism of germinating rice (*Oryza sativa* L.) seeds mitosis of onion (*Allium cepa*) root tip cells. *Ind J Exp Biol* 14:519–521
- Nakos G (1979) Lead pollution: fate of lead in soil and its effects on *Pinus haplenis*. *Plant Soil* 50:159–161

- Neelima P, Reddy KJ (2002) Interaction of copper and cadmium with seedlings growth and biochemical responses in *Solanum melongena*. *Envi Pollu Technol* 1:285–290
- Nieboer E, Richardson DHS (1980) The replacement of the non-descript term heavy metals by a biologically and chemistry significant classification of metal ions. *Environ Pollut Series B* 1:3–26
- Nriagu JO (1988) A silent epidemic of environmental metal poisoning? *Environ Pollut* 50:139–161
- Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. *Nature* 338:47–49
- Ogwuegbu MOC, Muhanga W (2005) Investigation of lead concentration in the blood of people in the copperbelt province of Zambia. *J Environ* 1:66–75
- Ouzounidou G (1994) Change in chlorophyll fluorescence as a result of copper treatment: dose response relations in *Silene* and *Thlaspi*. *Photosynthetica* 29:455–462
- Pacyna JM (1986) Atmospheric trace elements from natural and anthropogenic sources. In: Nriagu JO, Davidson CI (eds) *Toxic metals in the atmosphere*, Chap 2. Wiley, New York
- Paivoke H (1983) The short term effect of zinc on growth anatomy and acid phosphate activity of pea seedlings. *Ann Bot* 20:307–309
- Panda SK, Patra HK (2000) Does chromium (III) produce oxidative stress in excised wheat leaves? *J Plant Biol* 27:105–110
- Pandey N, Sharma CP (2002) Effect of heavy metals Co^{2+} , Ni^{2+} , and Cd^{2+} on growth and metabolism of cabbage. *Plant Sci* 163:753–758
- Pandolfini T, Gabbriellini R, Comparini C (1992) Nickel toxicity and peroxidase activity in seedlings of *Triticum aestivum* L. *Plant Cell Environ* 15:719–725
- Parr PD, Taylor FG Jr (1982) Germination and growth effects of hexavalent chromium in Orocol TL (a corrosion inhibitor) on *Phaseolus vulgaris*. *Environ Int* 7:197–202
- Peplow D (1999) Environmental impacts of mining in Eastern Washington. Center for Water and Watershed studies fact sheet, University of Washington, Seattle
- Peralta JR, Gardea Torresdey JL, Tiemann KJ, Gomez E, Arteaga S, Rascon E (2001) Uptake and effects of five heavy metals on seed germination and plant growth in alfalfa (*Medicago sativa*) L. *B. Environ Contam Toxicol* 66:727–734
- Phillips DJH (1990) Arsenic in aquatic organisms: a review of emphasizing chemical speciation. *Aqua Toxicol* 16:151–186
- Porter JR, Cheridan RP (1981) Inhibition of nitrogen fixation in alfalfa by arsenate, heavy metals, fluoride and simulated acid rain. *Plant Physiol* 68:143–148
- Porter EK, Peterson PJ (1975) Arsenic accumulation by plants on mine waste (United Kingdom). *Environ Pollut* 4:365–371
- Prasad MNV, Hagemeyer J (1999) Heavy metal stress in plants. Springer, Berlin, pp 16–20
- Prasad KVSK, Pardha saradhi P, Sharmila P (1999) Concerted action of antioxidant enzyme and curtailed growth under zinc toxicity in *Brassica juncea*. *Environ Exp Bot* 42:1–10
- Prasad MNV, Greger M, Landberg T (2001) *Acacia nilotica* L. bark removes toxic elements from solution: corroboration from toxicity bioassay using *Salix viminalis* L. in hydroponic system. *Int J Phytoremed* 3:289–300
- Pryor WA (1988) Why is the hydroxyl radical the only radical that commonly adds to DNA? hypothesis: it is a rare combination of high electrophilicity, high thermo chemical reactivity, and a mode of production that occurs near DNA. *Free Radi Biol Med* 4:219–223
- Punz WF, Sieghardt H (1993) The response of roots of herbaceous plant species to heavy metals. *Environ Exp Bot* 33:85–98
- Rahman H, Sabreen S, Alam S, Kawai S (2005) Effects of nickel on growth and composition of metal micronutrients in barley plants grown in nutrient solution. *J Plant Nutri* 28:393–404
- Reddy AM, Kumar SG, Jyotsnakumari G, Thimmanayak S, Sudhakar C (2005) Lead induced changes in antioxidant metabolism of horsegram (*Macrotyloma uniflorum* (Lam.) Verdc.) and bengalgram (*Cicer arietinum* L.). *Chemosphe* 60:97–104
- Reeves RD, Baker AJM (2000) Metal-accumulating plants. In: Raskin I, Ensley BD (eds) *Phytoremediation of toxic metals: using plants to clean up the environment*. Wiley, New York, pp 193–229
- Romero-Puertas MC, Rodriguez-Serrano M, Corpas FJ, Gomez M, Del Rio LA, Sandalio LM (2004) Cadmium-induced subcellular accumulation of O_2^- and H_2O_2 in pea leaves. *Plant Cell Env* 27:1122–1134
- Ros R, Cook David T, Picazo Carmen Martinez-Cortina Isabel (1992) Nickel and cadmium-related changes in growth, plasma membrane lipid composition, ATPase hydrolytic activity and proton-pumping of rice (*Oryza sativa* L. cv. Bahia) Shoots. *J Exp Bot* 43:1475–1481
- Roseman IE, Levine RL (1987) Purification of a protease from *Ochelichia coli* with specificity for oxidized glutamine synthetase. *J Biol Chem* 262:2101–2110
- Ross SM (1994) Toxic metals in soil–plant systems. Wiley, Chichester, p 469
- Rout GR, Sanghamitra S, Das P (2000) Effects of chromium and nickel on germination and growth in tolerant and non-tolerant populations of *Echinochloa colona* (L.). *Chemosphere* 40:855–859
- Salt DE, Blaylock M, Kumar NPBA, Dushenkov V, Ensley D, Chet I, Raskin I (1995) Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. *Biotechn* 13:468–474
- Sanita di Toppi L, Gabbriellini R (1999) Response to cadmium in higher plants. *Environ Exp Bot* 41:105–130
- Schmfer MEV (2001) Phytochelatin: complexation of metals and metalloids, studies on the phytochelatin synthase. PhD Thesis, Munich University of Technology (TUM), Munich
- Scholz RW, Graham KS, Wynn MK (1990) Interaction of glutathione and α -tocopherol in the inhibition of lipid peroxidation of rat liver microsomes. In: Eddy CC, Hamilton GA, Madyastha KM (eds) *Biological oxidation systems*. Academic Press, San Diego, pp 841–867
- SCOPE (1974) Saharan Duct. Scientific committee on problems of the environment. Wiley, New York
- Seaward MRD, Richardson DHS (1990) Atmospheric sources of metal pollution and effects on vegetation. In: Shaw AJ (ed) *Heavy metal tolerance in plants evolutionary aspects*. CRC Press, Boca Raton, pp 75–94
- Shah K, Dubey RS (1998) Effect of cadmium on proline accumulation and ribonuclease activity in rice seedlings: role of proline as a possible enzyme protectant. *Biol Plant* 40:121–130
- Shallari S, Schwartz C, Hasko A, Morel JL (1998) Heavy metals in soils and plants of serpentine and industrial sites of Albania. *Sci Total Environ* 19(209):133–142
- Shanker AK, Sudhagar R, Pathmanabhan G (2003a) Growth Phytochelatin SH and antioxidative response of Sunflower as affected by chromium speciation. In: 2nd international congress of plant physiology on sustainable plant productivity under changing environment, New Delhi
- Shanker AK, Djanaguiraman M, Pathmanabhan G, Sudhagar R, Avudainayagam S (2003b) Uptake and phytoaccumulation of chromium by selected tree species. In: Proceedings of the international conference on water and environment held in Bhopal, India
- Sharma P, Dubey RS (2005) Lead toxicity in plants. *Braz J Plant Physiol* 17:35–52
- Sharples JM, Meharg AA, Chambers SM, Cairney JWG (2000) The symbiotic solution to arsenic contamination. *Nature* 404:951–952

- Shaw BP, Panigrahi AK (1986) Uptake and tissue distribution of mercury in some plant species collected from a contaminated area in India: its ecological importance. *Arch Environ Contam Toxicol* 15:439–466
- Singh PK, Tewari SK (2003) Cadmium toxicity induced changes in plant water relations and oxidative metabolism of *Brassica juncea* L. plants. *J Environ Biol* 24:107–117
- Sinha SK, Srinivastava HS, Mishra SN (1988a) Nitrate assimilation in intact and excised maize leaves in the presence of lead. *Bull Environ Contam Toxicol* 41:419–422
- Sinha SK, Srinivastava HS, Mishra SN (1988b) Effect of lead on nitrate reductase activity and nitrate assimilation in pea leaves. *Bot Pollu* 57:457–463
- Sinha S, Guptha M, Chandra P (1997) Oxidative Stress induced by iron in *Hydrilla verticillata* (i.f) Royle: response of antioxidants. *Ecotoxicol Environ Safe* 38:286–291
- Smith SR (1996) Agricultural recycling of sewage sludge and the environment. CAB International, Wallingford, UK
- Somasekharaiyah BV, Padmaja K, Prasad ARK (1992) Phytotoxicity of cadmium ions on germinating seedlings of mung bean (*Phaseolus vulgaris*): involvement of lipid peroxidase in chlorophyll degradation. *Physiol Plant* 85:85–89
- Stadtman ER (1993) Oxidation of free amino acids and amino acid residues in proteins by radiolysis and by metal-catalysed reactions. *Annu Rev Biochem* 62:797–821
- Stadtman ER, Oliver CN (1991) Metal-catalyzed oxidation of proteins. *Physiological consequences*. *J Biol Chem* 266:2005–2008
- Stiborova M, Pitrichova M, Brezinova A (1987) Effect of heavy metal ions in growth and biochemical characteristic of photosynthesis of barley and maize seedlings. *Biol Plant* 29:453–467
- Sudhakar C, Simalabai L, Veeranaveyuler K (1992) Lead tolerance of certain legume species grown on lead or tailing. *Agri Eco Environ* 41:253–261
- Tang SR, Wilke BM, Brooks RR, Tang SR (2001) Heavy-metal uptake by metal tolerant *Elsholtzia haichowensis* and *Commelina communis* from China. *Commun Soil Sci Plant Anal* 32:895–905
- Thomas F, Malick C, Endreszl EC, Davies KS (1998) Distinct responses to copper stress in the halophyte, *Mesembryanthemum crystallinum*. *Physiol Plant* 102:360–368
- United Nations Environmental Protection/Global Program of Action (2004) Why the marine environment needs protection from heavy metals, Heavy Metals 2004, UNEP/GPA Coordination Office (<http://www.oceansalts.org/unatlas/uses/uneptextsph/wastesph/2602gpa>)
- Van Assche F, Clijsters H (1983) Multiple effects of heavy metals on photosynthesis. In: Marcelle R (ed) Effects of stress on photosynthesis. Nijhoff/Junk, The Hague 7, pp 371–382
- Van Assche F, Clijsters H (1987) Enzymes analysis in plants as a tool for assessing phytotoxicity on heavy metal polluted soils. *Med Fac Landouw Rijksuniv Gent* 52:1819–1824
- Van Assche F, Clijsters H (1990) Effects of metals on enzyme activity in plants. *Plant Cell Environ* 13:195–206
- Van Assche F, Cardinaels C, Clijsters H (1988) Induction of enzyme capacity on plants as a result of heavy metal toxicity, dose response relations in *Phaseolus vulgaris* L. treated with cadmium. *Environ Pollut* 6:103–115
- Van den Broeck K, Vandecasteele C, Geuns JMC (1998) Speciation by liquid chromatography-inductively coupled plasma-mass spectrometry of arsenic in mung bean seedlings used as a bio-indicator for arsenic contamination. *Anal Chim Acta* 361:101–111
- Vazques MD, Ch Poschenrieder, Barcelo J (1987) Chromium (VI) induced structural changes in bush bean plants. *Ann Bot* 59:427–438
- Verkleji JAS (1993) The effects of heavy metals stress on higher plants and their use as bio monitors. In: Markert B (ed) Plant as bioindicators: indicators of heavy metals in the terrestrial environment. VCH, New York, pp 415–424
- Verma S, Dubey RS (2003) Lead toxicity induces lipid peroxidation and alters the activities of antioxidant enzymes in growing rice plants. *Plant Sci* 164:645–655
- Vermette SJ, Bingham VG (1986) Trace elements in Frobisher Bay rain water. *Arctic* 39:177–179
- Wang Y, Greger M (2004) Clonal differences in mercury tolerance, accumulation, and distribution in willow. *J Environ Qual* 33:1779–1785
- Warne MS, Heemsbergen D, Stevens D, McLaughlin M, Cozens G, Whatmuff M, Broos K, Barry G, Bell M, Nash D, Pritchard D, Penney N (2008) Modeling the toxicity of copper and zinc salts to wheat in 14 soils. *Environ Toxicol Chem* 27:786–792
- Weckex JEJ, Clijsters HMM (1997) Zn phytotoxicity induces oxidative stress in primary leaves of *Phaseolus vulgaris*. *Plant Physiol Biochem* 35:405–410
- WHO/FAO (2007) Joint FAO/WHO food standard programme codex Alimentarius commission 13th session. Report of the thirty-eight session of the codex committee on food hygiene. Houston, ALINORM 07/30/13
- Winterhalder EK (1963) Differential resistance of two species of *Eucalyptus* to toxic soil manganese levels. *Aust J Sci* 25:363–364
- Wintz H, Fox T, Vulpe C (2002) Responses of plants to iron, zinc and copper deficiencies. *Biochem Soc Trans* 30:766–768
- Wojcik M, Tukiendorf A (2004) Phytochelatin synthesis and cadmium localization in wild type of *Arabidopsis thaliana*. *Plant Growth Regul* 44:71–80
- Wong JWC (1996) Heavy metal contents in vegetables and market garden soils in Hung Kong. *Environ Technol* 17:407–414
- Wu S (1994) Effect of manganese excess on the soybean plant cultivated under various growth conditions. *J Plant Nutri* 17:993–1003
- Yamamoto F, Kozlowski TT (1987) Effect of flooding, tilting of stem, and ethrel application on growth, stem anatomy, and ethylene production of *Acer platanoides* seedlings. *Scand J For Res* 2:141–156
- Yanqun Z, Yuan L, Jianjun C, Haiyan C, Li Q, Schratz C (2005) Hyper accumulation of Pb, Zn and Cd in herbaceous grown on lead-zinc mining area in Yunnan, China. *Environ Int* 31:755–762
- Zanthopolous N, Antoniou V, Nikolaidis E (1999) Copper, zinc, cadmium and lead in sheep grazing in North Greece. *Bull Environ Contam Toxicol* 62:691–699
- Zeid IM (2001) Responses of *Phaseolus vulgaris* to chromium and cobalt treatments. *Biol Plant* 44:111–115
- Zhang WH, Tyerman SD (1999) Inhibition of water channels by HgCl₂ in intact wheat root cells. *Plant Physiol* 120:849–857
- Zhou ZS, Huang SQ, Guo K, Mehta SK, Zhang PC, Yang ZM (2007) Metabolic adaptations to mercury-induced oxidative stress in roots of *Medicago sativa* L. *J Inorg Biochem* 101:1–9
- Zingg JM, Jones PA (1997) Genetic and epigenetic aspects of DNA methylation on genome expression, evolution, mutation and carcinogenesis. *Carcinogenesis* 18:869–882
- Zornoza P, Robles S, Martin N (1999) Alleviation of nickel toxicity by ammonium supply to sunflower plants. *Plant Soil* 208:221–226