Chapter 1
Impact of Heavy Metal Contamination on Quality Environs

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1.1 Introduction

Industrialization and technical progression have put enhancing load of heavy metals (HMs) on the environs by discharging huge magnitude of perilous waste (Table 1.1). HMs and organic pollutants have wreaked severe harm to the environment. The upsurge of HMs in "soils and waters" prolonged severe global health problems. These toxic substances (HMs) cannot be despoiled into non-hazardous forms, but remain in the biotic and abiotic systems. Environmental contamination with HMs has amplified ahead of the safe limits and is unfavorable to both flora and fauna (Tak et al. 2013; Gaur et al. 2014; Dixit et al. 2015). The highest tolerable concentrations of some HMs in water, as declared by the "Comprehensive Environmental Response Compensation and Liability Act (CERCLA), USA" are presented in Table 1.2. The examples of "common HMs include Pb, As, Cr, Ni, Zn, Cd, Cu, and Hg" (Wuana and Okieimen 2011). HM contamination at present is a foremost environmental concern because metal ions stick within the environment owing to their non-degradable character. The "toxicity and bioaccumulation" potential of HMs in the environment is a severe danger to all the biota (Rashid et al. 2019). Unlike organic pollutants, HMs cannot be wrecked by "chemical or biological" processes, but can

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Table 1.1 Different sources of HMs pollution in soil environs (Nriagu and Pacyna 1988; Su et al. 2014)

Source	As	Cd	Cr	Cu	Hg	Pb	Zn
	per year (1000 t/a)						
Crop cultivation and food processing	0.0–0.07	0.01–0.3.3	5.0–85.50	2.5–40.0	0.01–2.0	1.4–30	10–145
Farmyard fertilizer	1.0–4.0	0.21–1.3	15.0–55.0	14–80	0.01–0.23	2.9–19.5	14–315
Logging and timber	0.1–3.2	0.01–2.4	2.5–15.0	3.3–52	0.01–1.9	6.9–7.9	11–70
Domestic waste	0.10–0.60	0.9–8.0	7.0–35.0	13–40	0.02–0.30	20–58	18–89
Macrobiotic wastes	0.01–0.30	0.01–0.03	0.12–0.50	0.04–0.61	0.00	0.03–1.5	0.12–2.7
Metallurgy waste	0.011–0.24	0.02–0.09	0.7–2.6	0.95–7.6	0.01–0.09	3.9–10.99	3.0–16
Coal residue	7.0–12.0	1.7–12.5	150.0–460.0	93–335	0.40–50	50–235	110–479
Chemical fertilizers	0.01–0.22	0.02–0.35	0.04–0.41	0.05–0.58	0.00	0.40–2.5	0.3–1.3
Goods and services	34–42	0.8–1.8	315–622	395–790	0.60–0.79	189–389	299–599
Aerosol deposition	8.5–20.0	2.2–8.4	5.1–38	14–36	0.63–4.3	202–263	49–135

Table 1.2 Heavy metal concentration limits in water and soils

HM (mg/L) limit in water as per the standards of CERCLA						
Ar	Cd	Cr	Pb	Hg	Ag	References
0.01	0.05	0.01	0.015	0.002	0.05	Chaturvedi et al. (2015)
HMs (mg/kg) limit in soils as per Indian standards						
Cd	Cu	Ni	Pb	Zn	Nagajyoti et al. (2010)	
3–6	135–270	75–150	250–500	300–600		

be altered to less toxic. Most of the HMs are lethal at small concentrations and are accomplished of “entering the food chain,” where they hoard and impose damage to “living organisms.” All metals have the potential to reveal detrimental impacts at elevated concentrations and “the toxicity of each metal depends on the amount available to organisms’, viz. the absorbed dose, the route, and the duration of exposure” (Mani and Kumar 2014). Owing to the lethal impacts of these toxic substances, there are increasing environmental and human well-being issues and ensuing requirement for expediting the wakeful and responsiveness in order to treat the contaminated environs. Therefore, it is essential to eliminate or trim down HM pollution in order to avert or diminish polluting the environment. To attain this, “bioremediation should be employed in order to increase metal stability, which in turn decreases the bioavailability of HMs” (Abbas et al. 2014; Akcil et al. 2015; NdeddyAka and Babalola 2016). Bioavailability of HMs establishes the "physiological and toxic effects" of a metal on biota (Olaniran et al. 2013). Bioremediation is a futuristic technique applied for HM elimination and/or resurgence from contaminated environs. The method utilizes intrinsic biological systems to exterminate perilous pollutants by way of employing the microbes and plants to reinstate contaminated environs to their original state (Mani and Kumar 2014; Akcil et al. 2015; Dixit et al. 2015). Microbial remediation by way of applying microbes to execute reduction of HMs in the soils has gained vital position in the field of treating the disturbed environs (Su et al. 2014). Microbes have amazing "metabolic pathways" which consume diverse noxious substances as a source of food for "growth and development, through respiration, fermentation, and cometabolism." Owing to their distinctive destructive enzyme package for a specific pollutant, hence, developed varied mechanisms for sustaining "homeostasis and resistance" to HMs in any ecosystem (Brar et al. 2006; Wei et al. 2014). Most of the HMs destroy "microbial cell membranes," but microbes can build up protection mechanisms that support them in eradicating the lethal effect. Thus, the reaction of microbes to HM contamination is of significance for restoration of degraded environs. The chapter provides insights into the sources and deleterious impacts of HMs on different environs.

1.2 HMs Effluence in Different Environs

Naturally occurring HMs are present in the complexes, which are not quickly accessible for plants. They are on average occurring in insoluble compounds, like in "mineral structures," or in "precipitated or complexes" unavailable for plants' life. HMs present in nature have enormous adsorption ability in soils and hence are not readily obtainable for biota. The adsorption capacity between HMs and soil in nature is massive in relation to man-made sources (Singh et al. 2018). The natural processes by which HMs bring into the environs are: "erosion, volcanic eruptions, and the weathering of minerals." HMs released from man-made cause have elevated "bioavailability" due to their soluble and transferable imprudent forms. The man-made sources comprise "alloy fabrication, automobiles, battery manufacturing, coating, galvanization, explosive manufacturing, discharge of untreated sewage, leather tanning, pesticides, phosphate fertilizer, photographic materials, printing pigments and dyes, and wood preservation" (Fulekar et al. 2009; Dixit et al. 2015; Singh et al. 2018; Bhat et al. 2018) (Table 1.2). The HMs accumulated in soil and then transferred to the food chain depend upon the concentration of HMs in soil, pollution load, and potential of uptake by plants (Bolan et al. 2014). According to D'Amore et al. (2005), "the geochemical cycle of HMs results in the increase of HMs in the environment, which could cause risk to all life forms, when they are greater than permissible limits." Metal extraction from ore is the chief source of HMs contamination in soil environs, and the restoration of these disturbed environs may possibly take long durations. Drawing out of metals and "ore processing" are chief sources of HM contamination in soil environs, and the restoration of disturbed environs from mining activities may possibly take some decades. These activities yield huge quantities of pollutants, which are habitually dumped without treatment and contaminate freshwater environs via "chemical run-off and particulates" that accrue in freshwater sources (Adler et al. 2007).

1.3 Ecotoxicity of HMs

Although some HMs play imperative functions in the "physiological, biochemical, and metabolic processes" of all biota, working as co-factors for various enzymes, "micronutrients, regulators of osmotic pressure, and stabilization of molecules, the majority of them have no known biological function in living organisms and are toxic when generated in excess" (Fashola et al. 2016). The ill effects of HMs are the capacity of a HM to cause detrimental effects on living creatures. This "depends on the HM bioavailability and the absorbed dose" (Rasmussen et al. 2000; Mehmood et al. 2019). The danger produced by HMs to the healthiness of biota is further affected by their endlessly relentless nature in the environs. The toxic effects of HMs worsened in the mediums having acidic pH and low nutrient content, and "when the soil structure is poor, especially in mining environments" (Mukhopadhyay and Maiti 2010). In acidic mediums, HMs lean to produce metal ions, with extra H^+ vacant to inundate metal adsorbing sites, which implies that at higher H^+ concentrations, "the adsorbent surface is further positively charged, thus reducing the attraction between adsorbent and metal cations" (Olaniran et al. 2013). In this way, HM becomes more "bioavailable," thus mounting the grave effects to flora and fauna. In basic medium, metal ions substitute H^+ to produce new group complexes, ^-OH metal complexes. These complexes are soluble in some cases (Cd, Ni, Zn), while those of Cr and Fe are insoluble (Olaniran et al. 2013). The "solubility and bioavailability" of HMs are capable of being influenced by a slight change in the pH values. Slight alteration in the composition of soils, viz. organic matter (OM) content and nutrients, further tighten the effects of HMs toxicity. It has been observed so far that the soils which contain low OM relatively have high concentration of HMs and vice versa. OM content has a forceful impact on "cation exchange capacity (CEC), buffer capacity," as well as on the availability of HMs. Thus, "metals present in organic soils contaminated with a combination of HMs are less mobile and less bioavailable to microorganisms and plants, than metals present in mineral soils" (Olaniran et al. 2013). Hotness of environs also has a pivotal role in the adsorption of HMs. Temperature has two main impacts on the adsorption route. Firstly, rising temperature will enhance the pace of "adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles," since fluid gumminess diminishes as temperature rises. Secondly, temperature alters the impacts on the immovability of the metal ions primarily located in solution; immovability of the "microorganism metal complex" relies on the bioactive absorption sites, "microbial cell wall configuration and ionization of chemical moieties on the cell wall" (Arjoon et al. 2013). An "increase in the sorption capacity of lead, from 0.596 to 0.728 mg/g, was obtained when the temperature was raised from 25 to 40 °C" (Arjoon et al.

2013). Introduction to HMs (Pb and Hg) can affect the improvement of autoimmunity, having consequent effects on joint disorders, viz. "rheumatoid arthritis, kidney diseases, circulatory and nervous system disorders," and the detrimental to human fetal brain. Exposure to Pb and Hg in kids diminishes intelligence, impaired improvement, and enhanced risks of cardio disorders. Cadmium is known to be "carcinogenic and mutagenic and can disrupt the endocrine system, harm the bones and respiratory organs, and impinge on the balance of calcium in living organism" (Mani and Kumar 2014). Chromium damages normal hairs and causes baldness, headaches, diarrhea, gastric disorders, and queasiness in humans (Table 1.3). HM infected soils reduce plant growth because of toxic effects, follow-on ecological, "evolutionary, and nutritional troubles" (Abdul-Wahab and Marikar 2012). The HMs contamination in plants fluctuates, depending on the plant variety, involvement of specific metals, and absorption of metal, chemical state of metal, and soil structure and pH (Nagajyoti et al. 2010). Rise in HMs in plant tissues distresses or hampers nutrient uptake, "homoeostasis, growth, and development" (Chibuike and Obiora 2014; Sankarammal et al. 2014; Fashola et al. 2016). They interrupt metabolic functions, such as "physiological and biochemical processes, biochemical lesions, cell organelles destruction, chlorosis, delayed germination, induced genotoxicity, inhibition of photosynthesis and respiration, loss of enzyme activities, oxidative stress" (Salem et al. 2000; Nagajyoti et al. 2010; Dixit et al. 2015), "premature leaf fall, reduced biomass, reduced crop yield" (Fashola et al. 2016) "senescence, stunted growth, wilting, and can even cause the death of plants" (Wang et al. 2012; Ali et al. 2013; Fashola et al. 2016; Ayangbenro and Babalola 2017) (Table 1.3). HM toxicity "affects microbial population size, diversity, and activity, as well as their genetic structure" (Wang et al. 2012; Ali et al. 2013; Fashola et al. 2016; Ayangbenro and Babalola 2017). It affects "the morphology, metabolism, and growth of microorganisms by altering the nucleic acid structure, disrupting the cell membranes, causing functional disturbance, inhibiting enzyme activity and oxidative phosphorylation, and causing lipid peroxidation, osmotic balance alteration, and protein denaturation" (Chibuike and Obiora 2014; Fashola et al. 2016; Xie et al. 2016).

1.4 Effects of HMs on Soil Structure

Soil is the key recipient of HMs via a range of man-made activities. HMs "may persist in soil for a considerably long time" (Adriano et al. 2004). They change the composition and activity of essential soil micro- and meso-fauna groups (Xie et al. 2016). Above permissible limit concentrations of HMs in soil environs caused high ecotoxicity soil toxicity (Su et al. 2014). Chander et al. (1995) have reported that the HM contamination reduced the enzyme activities manifolds. Marques et al. (2009) have determined that the HMs consist of "exchangeable ions" that are "absorbed by inorganic solids on the surface." Metals that are present previously in the soil environs cause no pollution; however, HMs that are added in the soils via anthropo-

Table 1.3 Deleterious effects of HMs on different biota

		Impacts on			
HMs	Source	Humans	Plants	Microorganisms	References
As	"Atmospheric deposition, mining, pesticides, rock sedimentation, smelting"	"Brain damage, cardiovascular and respiratory disorder, conjunctivitis, dermatitis, skin cancer"	"Damages cell membrane, inhibition of growth, inhibits roots extension and proliferation, interferes with critical metabolic processes, loss of fertility, yield, and fruit production, oxidative stress, physiological disorders"	"Enzyme deactivation"	Bissen and Frimmel (2003), Abdul-Wahab and Marikar (2012), Finnegan and Chen (2012), Ayangbenro and Babalola (2017), Mushtaq et al. (2018)
Cd	"Fertilizer, mining, pesticide, plastic, refining, welding"	"Bone disease, coughing, emphysema, headache, hypertension, itai-itai, kidney diseases, lung and prostate cancer, lymphocytosis, microcytic hypochromic anemia, testicular atrophy, vomiting"	"Chlorosis, decrease in plant nutrient content, growth inhibition, reduced seed germination"	"Damages nucleic acid, denatures protein, inhibits cell division and transcription, inhibits carbon and nitrogen mineralization"	Nagajyoti et al. (2010), Sebogodi and Babalola (2011), Chibuike and Obiora (2014), Sankarammal et al. (2014), Fashola et al. (2016), Ayangbenro and Babalola (2017)
Cr	"Dyeing, electroplating, paints production, steel fabrication, tanning, textile"	"Bronchopneumonia, chronic bronchitis, diarrhea, emphysema, headache, irritation of the skin, itching of respiratory tract, liver diseases, lung cancer, nausea, renal failure, reproductive toxicity, vomiting"	"Chlorosis, delayed, senescence, wilting, biochemical lesions, reduced biosynthesis germination, stunted growth, oxidative stress"	"Elongation of lag phase, growth inhibition, inhibition of oxygen uptake"	Cervantes et al. (2001), Barakat (2011), Mohanty et al. (2012), Ayangbenro and Babalola (2017)

(continued)

Table 1.3 (continued)

HMs	Source	Impacts on			References
		Humans	Plants	Microorganisms	
Cu	"Copper polishing, mining, paint, plating, printing operations"	"Abdominal pain, anemia, diarrhea, headache, liver and kidney damage, metabolic disorders, nausea, vomiting"	"Chlorosis, oxidative stress, retard growth"	"Disrupts cellular function, inhibits enzyme activities"	Salem et al. (2000), Nagajyoti et al. (2010), Dixit et al. (2015), Fashola et al. (2016), Ayangbenro and Babalola (2017)
Hg	"Batteries, coal combustion, geothermal activities, mining, paint industries, paper industry, volcanic eruption, weathering of rocks"	"Ataxia, attention deficit, blindness, deafness, decreases rate of fertility, dementia, dizziness, dysphasia, gastrointestinal irritation, gingivitis, kidney problem, loss of memory, pulmonary edema, reduced immunity, sclerosis"	"Affects antioxidative system, affects photosynthesis, enhances lipid peroxidation, induced genotoxic effect, inhibits plant growth, yield, nutrient uptake, and homeostasis, oxidative stress"	"Decreases population size, denatures protein, disrupts cell membrane, inhibits enzyme function"	Wang et al. (2012), Ali et al. (2013), Fashola et al. (2016), Ayangbenro and Babalola (2017)
Pb	"Coal combustion, electroplating, manufacturing of batteries, mining, paint, pigments"	"Anorexia, chronic nephropathy, damage to neurons, high blood pressure, hyperactivity, insomnia, learning deficits, reduced fertility, renal system damage, risk factor for Alzheimer's disease, shortened attention span"	"Affects photosynthesis and growth, chlorosis, inhibits enzyme activities and seed germination, oxidative stress"	"Denatures nucleic acid and protein, inhibits enzyme activities and transcription"	Nagajyoti et al. (2010), Wuana and Okieimen (2011), Mupa (2013), Fashola et al. (2016), Ayangbenro and Babalola (2017)
Zn	"Brass manufacturing, mining, oil refinery, plumbing"	"Ataxia, depression, gastrointestinal irritation, hematuria, icterus, impotence, kidney and liver failure, lethargy, macular degeneration, metal fume fever, prostate cancer, seizures, vomiting"	"Affects photosynthesis, inhibits growth rate, reduced chlorophyll content, germination rate, and plant biomass"	"Death, decrease in biomass, inhibits growth"	Chibuike and Obiora (2014), Gumpu et al. (2015), Ayangbenro and Babalola (2017)

genic activities alter drastically quality characteristics of soils (Ramos et al. 1994). The existence of HMs in soil environs also impacts the pH of the soil (Harter 1983), OM, compactness and category of charge in soil microcell, degree of coordination with type of ligand and soil, soil comparative active surface sites (Norvell 1984), and "soil soluble concentrations" (Marques et al. 2009). HMs tempt noxious effects on soil microorganisms, and the level of effect changes with relation to physico-chemical attributes, viz. "pH, temperature, clay minerals, OM, ions, and metal compounds" (Bååth 1989). They also decrease the decomposition of OM in the soil and disturb the nutrient recycling (Su et al. 2014).

1.5 Effects of HMs on Plant Life Cycle

HM accretion above the acceptance point in plants also has undesirable effects on the plants. The plant turns extremely toxic, and it possibly will die. However, a few plants bear HMs toxicity up to the permissible limits. Two characteristics of plant HM interaction are as follows: (1) "metal-induced impairment of plant development" and (2) "resistive adaptation of plants to metal toxicity through modified metabolism" (Cheng 2003). HMs can interact with the bio-physiological processes that are vital to plant development (Chibuike and Obiora 2014). HM infected plants may possibly reveal decreased yield production, which accordingly impacts the food chain. "Cytoplasmic enzyme inhibition and cell structure injuries with oxidative stress occur when the plant is contaminated with a HM" (van Assche and Clijsters 1990; Jadia and Fulekar 2009). An example of "an indirect toxic effect is the replacement of essential nutrients at the cation exchange sites of plants" (Taiz and Zeiger 2002). For example, Zaier et al. (2010) reported that "the water content of *Brassica juncea* plants remarkably decreases under Pb toxicity, although this species is considered tolerant." Servilia et al. (2005) "demonstrated that plants exposed to HM exhibit stunted growth, deformation, reduced physicochemical activities, and overall alteration of cellular metabolism." Hg, As, Pb, Cd, and Cr are ranked among the most toxic metals that display considerable effects on plants (Tchounwou et al. 2012).

1.6 Effects of HMs on Human Health

HM pollution in different environs can unswervingly influence humans via suspended particulate matter inhalation or skin absorption (Table 1.3). HM pollution in soil has adverse impacts on humans and ecosystems via direct ingestion or makes contact with HM infected soils (McLaughlin et al. 2000; Ling et al. 2007). In the food chain, toxicity occurs in the order as depicted in Fig. 1.1.

Their contamination in soil also causes health disorders in humans via drinking polluted groundwater and eating of HM infected plants; this infectivity also causes

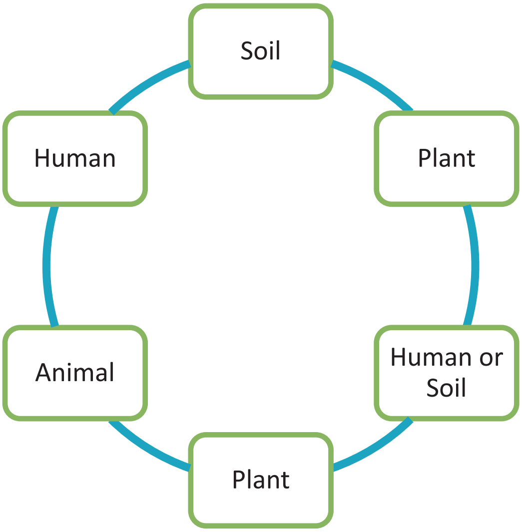

Fig. 1.1 Cyclic representation of heavy metal toxicity in food chain

disease in agricultural yield (Wuana and Okieimen 2011). Yabe et al. (2010) reported that "about 30% of Chinese children possess blood containing Pb levels in excess of the 100 g/L limit." Besides, he concluded that HM revelation occurs through "water, fish, soil, food crops, food animals, and toys" (Yabe et al. 2010). This revelation of HMs causes toxicity in children, which in turn can cause multi-organ disorders. Cd "emissions have increased remarkably in recent years, especially with its presence in household waste" (Järup 2003; Ogunkunle et al. 2013; Emenike et al. 2018). Another example of metal toxicity affecting human health is evident in a study conducted at the cement facility in Sagamu, Nigeria (Emenike et al. 2018). Findings revealed significant non-carcinogenic risks to children and adults who are 6–30 years old due to oral exposure to Cd and Cr from the facility (Emenike et al. 2018). Moreover, in Heshan Village, China, farmers were affected by As due to a As processing factory located in the village between 1951 and 1978 (Phoenix Satellite TV 2014). Since this period, "the surrounding environment has been highly polluted with high As levels" (Phoenix Satellite TV 2014). "Soil and water are highly contaminated with As above the prescribed level, and workers suffer from severe As poisoning" (Phoenix Satellite TV 2014). "The surrounding plant and crops die or become too toxic for consumption." According to the Phoenix Satellite TV (2014), "a total of 400 workers died due to As-induced cancer from 1951 to 2014."

1.7 Conclusion

Heavy metals release in the quality environment has wide range of negative significant impacts on different life forms from microscopic to macroscopic. These toxic substances are lethal at their low concentrations. Anthropogenic load has further magnified the HMs concentrations in the quality environs. There are multiple health issues caused due to the exposure of HMs on plants, animals, and microorganisms. Therefore primary conclusion is that the priority should be given to the reliable treatment technologies to remediate the HMs from contaminated substances prior to their final discharge and awareness about the sustainable management of different natural sources.

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