

# Chapter 6

## Bioremediation of Metal Contaminated Soil for Sustainable Crop Production



M. L. Dotaniya, N. R. Panwar, V. D. Meena, C. K. Dotaniya, K. L. Regar, Manju Lata, and J. K. Saha

**Abstract** Heavy metal pollution is emerging with time and reduces the chances of healthy food production from natural resources. Heavy metals are toxic in nature and caused various types of malfunction in plant, animal, and human bodies. Some heavy metals are essential for plant growth in lower level; but higher level shows toxic effects on plant growth. Heavy metals are also having carcinogenic, mutagenic, malfunctioning, and teratogenic and mostly affected the neurological, liver, and kidney function. Increasing population with higher pace needs food from the fixed-cultivated land. It is a great challenge for the researcher and policy-maker in one side mitigating the food crisis without contamination of natural resources. The waste generation per capita increased with tremendous rate and vice versa freshwater resources shrinking. The needs of management for wastewater (WW) or metal-contaminated soil for the sustainable crop production in most of the developing countries. Various heavy metal remediation techniques are used for the removal of metals from environment. Among the techniques, bioremediation techniques are eco-friendly in nature, in situ, low cost, and energy saving. Phytoremediation techniques are green techniques with a wider scope of contamination removal. The climatic changes are also affecting the crop and soil production capacity; it needs more research in abiotic stress.

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## 6.1 Introduction

Sustainable crop production is a demand of today agriculture. From the old age, agricultural practices having an immense natural resources and less pressure for the food grain production across the globe. As the human and animal population is growing, the per capita pressure on natural resources is increasing with the pace of time. The fast industrialization, increasing burning of fossil fuels, poor management of natural resources, and low awareness among the peoples toward environment promote the pollution in natural resources. Indian population is growing higher in annual rate and needs 280 Mt food for fulfilling the hungry mouth of the country in 2020. If we consider at global level, it is much more than the potential capacity of natural resources. To mitigate the food crisis, we can follow (i) using the poor-quality natural resources, (ii) using high potential genetic crop varieties, and (iii) using sustainable management of natural resources. The use of poor-quality water for crop production reduced the soil fertility potential of soil and ultimately produced poor crop. This is also toxic in helping humans, due to the presence of various heavy metals. These metals in trace amount affected the living systems and physiological function and in higher level also caused death. In soil, the presence of heavy metals affected the plant nutrient transformation and enzymatic activities (Dotaniya et al. 2016f). The restriction of nutrient transformation reduced the plant nutrient supplying capacity of soil, as a result poor crop production.

Heavy metals are metal and metalloids having higher density compared to water (Dotaniya et al. 2016g). A metal having specific gravity of more than 5.0 or atomic number higher than 20 (calcium- Ca) is termed as heavy metal (Dotaniya et al. 2013e). It is the main group of inorganic contamination in a larger land, mostly due to application of sludge and sewage and municipal waste, through agricultural inputs, metallurgical industries, and mining (Rusan et al. 2007; Rajendiran et al. 2015; Lenka et al. 2016; Dotaniya and Saha 2017). These include metal and metalloids of chromium (Cr), cadmium (Cd), nickel (Ni), lead (Pb), mercury (Hg), arsenic (As), selenium (Se), and zinc (Zn). Apart from these, other heavy metals are also important, but these are having less account of human and plant health, *i.e.* aluminum, cobalt, and molybdenum. Among the heavy metals, few are necessary for the completion of biochemical cycles in plant, animal, and human systems (Ajay et al. 2012; Pingoliya et al. 2015). Heavy metals are also having the lowest level of concentration in soil, but they cause major effect on biotic life cycle (Dotaniya et al. 2014h; Meena et al. 2013a). Heavy metals are carcinogenic in nature; therefore, its decontamination from a system is necessary for sustainable crop production or a healthy environment.

## 6.2 Source of Heavy Metals

On the basis of heavy metal source and mode of dispersing into other systems are classified into the following groups. A list of heavy metal sources and its effect on human health are described in Table 6.1.

### 6.2.1 Geogenic

Such type of sources includes the heavy metal toxicity from its origin of soils from rocks. The produced toxicity of heavy metals is in soil or in groundwater (Dotaniya et al. 2014h, 2016c). With the help of various soil and crop management practices, contaminated soil can be used for crop or forest plant cultivation. The As toxicity in Bangladesh and West Bengal of India is a good example of geogenic source of As metal. The weathering of natural rocks, erosion, and volcanic eruptions are major sources of geogenic activities. Few pockets across the globe have geogenic sources of heavy metals, and with the anthropogenic activities, it is dispersed in other natural ecosystems (Dotaniya et al. 2016d).

**Table 6.1** Source and effect of heavy metals on human health (Singh et al. 2011)

Metals	Major source	Effect on human health
<b>Arsenic</b>	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis, poisoning
<b>Cadmium</b>	Welding, electroplating, pesticides, fertilizers, Cd and Ni batteries, nuclear fission plant	Renal dysfunction, lung disease, lung cancer, bone defects, increased blood pressure, kidney damage, gastrointestinal disorder, cancer
<b>Lead</b>	Paint, pesticide, smoking, automobile emission, mining, burning of coal	Mental retardation of children, developmental delay, congenital paralysis, sensory neural deafness, acute and chronic damage of the nerve system, liver, kidney, gastrointestinal tract
<b>Mercury</b>	Pesticides, batteries, paper industry	Tremors, gingivitis, minor psychological changes, spontaneous abortion, damage to nervous system, protoplasm poisoning
<b>Chromium</b>	Mines, minerals, leather industry	Damage to the nervous system, fatigue, irritability
<b>Zinc</b>	Refineries, brass manufacture, metal plating, plumbing	Zinc fumes have a corrosive effect on the skin and cause damage to nervous membrane
<b>Copper</b>	Mining, pesticide production, chemical industry, metal piping	Liver and kidney damage, stomach and intestinal irritation

### 6.2.2 *Anthropogenic Sources*

These heavy metals are extracted from point sources or from geogenic sites for utilization in different activities. The contamination in the environment may be due to natural as well as anthropogenic activities. The activities of mining, smelting, and electroplating and other industrial units are discharging significant amount of metals into natural systems. The leather industries are using chromium sulfate and discharging noteworthy amount of Cr into effluent. This effluent is used for the cultivation of crops and other agricultural purposes, mostly in water-scarce areas. Dotaniya et al. (2014c) reported that long-term application of leather industrial effluent for crop production accumulated ~25–30% more Cr in soil than tube well-irrigated fields. Similarly, other industries like Pb, Hg, Cr, Ni, Cd, Zn, As, and Se are also contributing a meaning amount of metals into natural ecosystems. Apart from these, various heavy metals are used for preservation of wood and other household activities (Ahmad et al. 2016; Parewa et al. 2014).

Sewage water or biosolids for the cultivation of vegetable in peri-urban areas of megacities are also a source of heavy metal accumulation in soil (Dotaniya et al. 2013f, 2016h). Due to progressive industrial developmental activities and increasing population growth, huge volume of domestic sewage water is being produced in megacities. On an average ~90% of generating wastewater (WW) at the global level is left untreated, causing extensive water contamination, especially in developing countries. Here the WW means industrial effluent, household WW, and sewage effluent (Meena et al. 2015a). It is cheaper to dispose such effluent in this way and provides water and nutrients to crop (Saha et al. 2010). Therefore, Indian agriculture is encountering the problems of irrigation water scarcity and rising cost of fertilizers; domestic sewage water generated from cities is the better option to successfully use irrigation. People are using WW for crop production and getting good yield due to the presence of organic matter and trace amounts in micronutrients; but in negative side, these WW channels are also contributing heavy metals into the soil and human body via food chain contamination (Rana et al. 2010; Meena et al. 2013a; Dotaniya et al. 2015a).

One of the major sources of heavy metal contamination in soil and water bodies is through agricultural crop production inputs. In recent years, there has been increasing concern toward the health hazards through heavy metal contamination via food chain contamination (Dotaniya et al. 2014g). Fertilizers contain heavy metals as impurities; in this respect rock phosphate is a highly potential source. The contaminated soil or contamination through fertilizer impurities came into human and animal body and caused various types of malfunctions (Dotaniya et al. 2012a). The application of rock phosphate or its products during crop production in soil always implies the addition of a significant amount of Pb and Cd into the soils. The analysis of Pb and Cd from phosphatic fertilizers suggested that low-grade and

straight fertilizers have more chance of contamination than high analysis and mixed fertilizers (Dotaniya et al. 2014h; Singh 2002). During the application of phosphatic fertilizers for crop production accumulated heavy metal concentration on the surface of the soil and is easily available to plants (Meena et al. 2015b, c; Dominguez-Nunez et al. 2016; Dotaniya et al. 2016g). The surface retention of heavy metals has more chances to contaminants in the water bodies during rains and via soil erosion.

In soils with coarser textures and acidic reaction, having greater chances of heavy metal availability and mobility than finer texture (contain more amount of clay) and with the alkaline reaction medium for plants. It is very interesting that less than 6% of annual deposition of Cd in the soil of the European Economic Community comes, due to the use of phosphate fertilizers, with a further 2% from phosphoric acid manufacture industries. Whereas, two third is contributed from solid wastes and excrement, aerial deposition, and use of pigments and stabilizers (Roberts 2014).

### 6.3 Geo-accumulation Indexes

The heavy metal contamination in soil is due to wider sources and whether these soils are heavy metal contamination or not. In this index the metal concentration with respect to uncontaminated soil is used for the cultivation of toxicity. Geo-accumulation index ( $I_{geo}$ ) is widely used for assessing heavy metal contamination in sediments (Ball and Izbicki 2004; Chabukdhara and Nema 2012), dust (Kong et al. 2011), and trace metal pollution in agricultural soils (Wei and Yang 2010). The geo-accumulation index was calculated using the following formula described by Muller (1969):

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}$$

where  $I_{geo}$  stands for the geo-accumulation index,  $C_n$  is the soil trace metal concentration ( $\text{mg kg}^{-1}$ ), and  $B_n$  geochemical baseline concentration ( $\text{mg kg}^{-1}$ ), *i.e.* the mean trace metal concentration in the uncontaminated soils. The soil sample with  $I_{geo} \leq 0$  indicates unpolluted and classified under class I. Similarly,  $I_{geo}$  values 0–1, 1–2, 2–3, 3–4, 4–5, and >5 indicate unpolluted to moderate polluted (class II), moderate polluted (class III), moderate to heavily polluted (class IV), heavily polluted (class V), heavily to extremely polluted (class VI), and extremely polluted (class VII), respectively.

## 6.4 Metal Transfer Factors

The contaminated soil or water is used for the cultivation of food crops and the transfer of heavy metal soil to the human body via food chain contamination. To calculate the heavy metal toxic effect in the human body, the metal transfer factor and hazard quotient (HQ<sub>gv</sub>) are calculated for the safe utilization of metals through dietary intake. The metal transfer factor showed the heavy metal concentration in edible part of leafy vegetables. It is a simple ratio between metal concentrations in the plant part (on dry weight basis) from soil. The DTPA extractable concentration of heavy metals in soil is considered for computation of metal transfer factor. Risk assessment of heavy metal is calculated with the help of hazard quotient for the intake of leafy vegetables like palak, mustard, and coriander; those growing in effluent irrigated soil were computed with the help of Pierzynski et al. (2000).

$$\text{HQ}_{\text{gv}} = \frac{\text{add}}{\text{RfD}}$$

where HQ<sub>gv</sub> is the hazard quotient to a human from consumption of green vegetables; add the average daily dose (mg metal per kg body weight per day) and RfD the reference dose. The values of RfD for Zn, Ni, Cd, Pb, and Cr were used as 0.3, 0.02, 0.001, 0.0035, and 0.003 mg kg<sup>-1</sup> body weight day<sup>-1</sup>, respectively (IRIS 2015). For Cu, value of provisional maximum tolerable daily intake is 0.5 mg kg<sup>-1</sup> body weight day<sup>-1</sup> (WHO 1982), and the same is used as RfD (Alam et al. 2003). Daily intake of green vegetable was considered as 0.2 kg<sup>-1</sup> person day<sup>-1</sup>, which is recommended amount from a nutritional point of view (Hassan and Ahmed 2000). A factor of 0.085 was used to convert the fresh to dry weight of these green vegetables. Average body weight for an adult was considered as 70 kg (USEPA 1991). Average daily dose (add) was computed using following relationship:

$$\text{add} = \frac{\text{mc} \times \text{cf} \times \text{di}}{\text{bw}}$$

where mc is the metal concentrations in plant (mg kg<sup>-1</sup>) on dry weight basis, cf the fresh to dry weight conversion factor, di the daily intake of green vegetable (kg), and bw the body weight (kg). Assessment of risk as computed here is not complete since metal accumulation to soil organisms, groundwater, and surface water direct uptake of soil by human and animal are some of the other risks which have not been considered here.

## **6.5 Effect of Heavy Metals on Plant, Human, and Animals**

### **6.5.1 Lead**

Mental retardation, developmental delay, congenital paralysis, sensory neural deafness, acute and chronic damage of the nerve system, liver, kidney, gastrointestinal in human. In the present context, use of nanomaterial for the removal of Pb from water bodies is a major area of research at the top of the global issues. Use of titanium oxide and hematite nanoparticles is the foremost, for the 100% recovery of the Pb ions. This efficiency is also affected by the pH and contact time, which is  $\leq 6$  and  $\geq 60$  min, respectively, for the typical optimum conditions for Pb removal of water bodies. The recovery percent is also affected by adsorbent dose for the adequate surface area and number of adsorption sites (Bhatia et al. 2016; Masood and Bano 2016).

### **6.5.2 Mercury**

It is also a toxic is associated with kidney damage. Hair fall in early age is a symptom of Hg toxicity. Apart from these, tremors, gingivitis, minor psychological changes, spontaneous abortion, damage to the nervous system, and protoplasm poisoning are also happening due to Hg toxicity. It is mostly in Hg industries' WW utilization for fish and crop production.

### **6.5.3 Arsenic**

This heavy metal problem aggravated mostly as chronically in Bangladesh, India, Chile, Mexico, Taiwan, and part of West Bengal of India. These countries are suffering due to geogenic concentration of As and also use of As-contaminated groundwater for consumptive use. The natural level of As in soil mostly ranges from 1 to 40 ppm, but use of pesticides or As-contaminated waste enhanced the level and caused toxicity (Tchounwou et al. 2004). Arsenic exposure much affected the mechanism of organs, including cardiovascular, renal, bronchitis, nervous, and also respiratory disease in human (Tchounwou et al. 2003). Many cases are reported in affected areas due to higher intakes of As through drinking water or via food chain contamination. The higher level caused the cancer of the kidney, gall bladder, and liver in major affected areas. The severity of ill effect on health of plant, animal, and

human health is closely related to the chemical form of As and time and level of dose. In the harmful effect situation, As (V) replaced the phosphate ions, which is key to many biochemical pathways in different organ systems. The inorganic trivalent arsenite is two to ten times more toxic than pentavalent arsenate for the human system. With the binding of the thiol or sulfhydryl groups on protein, As (III) can inactivate more than 200 enzymes (Hughes 2002).

#### **6.5.4 Cadmium**

In general, Cd poisoning occurs through inhalation of cigarette smoke and also ingestion of Cd-contaminated food materials. In other specific routes like people working in metal industries, working at a Cd-contaminated workplace and also eating or drinking with contaminated hand are the sources of Cd in the human body. Vegetables growing in Cd-contaminated WW nearby peri-urban areas of major cities are having more chances of metal contamination. Cadmium negatively affected the lung and bone and increased the blood pressure, and higher dose can cause cancer and mortality. In plant system, Cd reduced transportation of food material from root to shoot, by damaging the root tissues. The blackish-brown root or necrotic root is a clear-cut symptom of Cd toxicity in plants. The chronic inhalation exposure of Cd is associated with the malfunction or decrease in the pulmonary and olfactory functions (Mascagni et al. 2003). The level of Cd in the body is measured through the presence of Cd concentration in blood or urine. Both the blood and urine contaminated with Cd are higher in highly cigarette smokers.

#### **6.5.5 Chromium**

It is a carcinogenic metal. Occupational exposure is a major concern for the Cr-induced disease in industrial worker due to hexavalent Cr (Guertin 2005). Long-term exposure can cause kidney and liver damage and damage to circulatory and nerve tissue. It is estimated that 33 tons of total Cr is released annually into the environment, which is a matter of health concern. The US Occupational Safety and Health Administration (OSHA) fixed a safe level  $5 \mu\text{g m}^{-3}$  for 8 h working at the industrial work place. This level also may still pose a carcinogenic risk in the human body. In crop plants Cr reduced the germination rate and root and shoot growth in wheat (Dotaniya et al. 2014d) and pigeon pea (Dotaniya et al. 2014f).



## 6.6 Heavy Metal Chemistry in Soil

### 6.6.1 Lead

It is bluish gray, a constituent of the earth's crust ranging from 10 to 67 mg kg<sup>-1</sup>, and belonging to group IV and period 6 in the periodic table. It has atomic number 82 and density 11.4 g cm<sup>-3</sup> with atomic mass 207.2. It is naturally occurring, but due to massive anthropogenic activities like burning of fossil fuels, metallic mining and industrial waste disposal spread the Pb concentration into the environment. The application of Pb in day-to-day life is more prominent mostly in industrial and domestic equipment. In nature, it is found in combination with other elements like sulfur (Pbs, PbSO<sub>4</sub>) and oxygen (PbCO<sub>3</sub>) (USDHHS 1999). In nature, ionic form of Pb, Pb(II), and various types of oxide and hydroxide as well as lead metal oxyanion complexes are in the general form of Pb, which is mainly contributed in soil, surface, and groundwater across the global length and width. The most common stable form of Pb is Pb(II); it is forming mononuclear and polynuclear oxides and hydroxides in major soil groups (GWR TAC 1997).

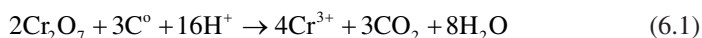
Lead ranked fifth place after Fe, Cu, Al, and Zn in the list of industrial production of metal and metalloids. Major part of Pb is used in batteries, solders and pipes, electric cable covers, bearing, tire manufacturing, pigmentation, plumbing, X-ray shielding, and caulking. Very high concentration of Pb in soil affected the soil process and is necessary to produce toxic response. It is fixed in soil by hydrolysis and polymerization mechanisms. Some of the metals commonly alloyed with Pb are (1) in storage batteries, antimony; (2) Ca and Sn in maintenance-free storage electric batteries; (3) in solder and anode work, silver metal; (4) as anodes in electrowinning process with Sr and Sn; and (5) tellurium during the process of pipe and sheet in chemical installation as well as nuclear shielding (Manahan 2003). The fraction of Pb from these metal industries is released into effluent and reached ultimately soil and water bodies. Soil factors such as high-cation exchange capacity, alkaline pH, high organic matter, and P-content in the soil antagonize Pb uptake by plants. The various types of soil also affected the availability of Pb metal for plant availability and also affected the soil critical limit for toxicity. It implies that if wastes rich in phosphorus (P) and organic matter (such as, sewage water and sludge) are applied to the soil, very little hazards due to Pb are expected.

### 6.6.2 Chromium

Chromium is the 21<sup>st</sup> most abundant element in the earth's crust (Dotaniya et al. 2014h). It occurs in nature in bound forms that constitute 0.1–0.3 mg kg<sup>-1</sup> of the earth's crust. It has several oxidation states ranging from Cr(–II) to Cr(+VI). It

exists predominantly in the Cr<sup>+3</sup> and Cr<sup>+6</sup> oxidation states. The most stable oxidation state of Cr is Cr(III), and under most prevailing environmental conditions Cr(VI) is rapidly reduced to Cr(III). The intermediate states of +IV and +V are metastable and rarely encountered (Lokhande et al. 2011). The Cr(III) is strongly adsorbed on soil particles, whereas Cr(VI) is weakly adsorbed and is readily available to plant uptake or leaching to groundwater (James and Bartlett 1983). Plants do not accumulate a significant amount of Cr from soil in high concentrations. Thus, plants can tolerate higher amounts of Cr present in soil due to accumulation by long-term application of sewage or sludge.

When the Cr was applied through hexavalent for soil, with the soil constituents, it is rapidly converted into nontoxic form of Cr(III) as insoluble hydroxides or oxides. Suitable conditions for Cr(VI) reduction occur where organic matter is present and act as an electron donor, and Cr(VI) reduction is enhanced in acidic rather than alkaline soils mentioned in Eq. 1 (Bartlett and Kimble 1976; Bolan et al. 2003).



From the global research side, many researchers find out the effect of organic matter or organic-rich soil amendments for the reduction of Cr toxicity by transforming Cr(VI) to Cr(III) (Dotaniya et al. 2015b). Losi et al. (1994) reported that addition of cattle manure reduced the potential Cr toxicity from Cr(VI) to nontoxic Cr(III) in soil. The presence of organic matter supplies the C and protons and also stimulated the growth of soil microorganisms, which mediated and facilitated the Cr reduction process Cr(VI) to Cr(III) (Losi et al. 1994).

### 6.6.3 Cadmium

It is one of the toxic metals in nature located in transition element category. It is having atomic number 48 with density 8.65 g cm<sup>-3</sup>. In nature, it exists as Cd(II) ion. It is having similarity with essential element of Zn, which is essentially required for plant and animal systems for potential growth. In Zn deficiency conditions, plant take up Cd as a substitution of Zn and may affect the metabolism of plants (Campbell 2006). Cadmium is one of the most toxic elements not having any well-known essential physiological functions in plant and human. At low concentration in soil, it is toxic to a number of plants. Accumulation of Cd varies with plant species, varieties, and plant part under consideration and soil properties. Cadmium has a tendency to accumulate more in a leafy part rather than in fruits and grains/seeds. Factors such as soil pH, applied fertilizers, presence of other heavy metals, temperature, and soil organic matter have a profound influence on Cd uptake by plants. Although incidence of *itai-itai* disease in the Jintsu Valley of Japan occurred because of the high Cd content of rice, reducing soil conditions hinder the uptake of Cd by rice. Anaerobic conditions during the grain filling stage depress the Cd content of grains (Singh 2002). Most common use of Cd in Ni-Cd electric batteries is for

rechargeable or storage for secondary purpose, due to high output, durability, low wearing and tearing, and larger tolerance to physical and electrical fluctuations. Cadmium is also utilized for better corrosive resistance coating in most of marine equipment, *i.e.* vessels and vehicles.

#### 6.6.4 Nickel

It is a transitional metal having atomic number 28 and atomic weight 58.69. It is much affected by the soil-water pH. In most of the low-pH regions, nickelous ion, Ni(II), is found; whereas in neutral to slightly higher-pH soils, nickelous hydroxide, Ni(OH)<sub>2</sub>, precipitates as a stable compound. This stable compound is readily soluble in acid environment and formed Ni(III) and in high alkaline conditions formed nickelite ion, HNiO<sub>2</sub>, which is soluble in water. In very oxidizing and the alkaline environment, Ni found in the form of stable nickel-nickelic oxide, Ni<sub>3</sub>O<sub>4</sub>, is easily soluble in acid solvents. In highly acidic condition, various types of Ni oxides, *i.e.* nickelic oxide and nickel peroxide, Ni<sub>2</sub>O<sub>3</sub>, are converted into Ni<sup>2+</sup> ions (Wuana and Okieimen 2011). Nickel content in the range of 50–100 mg g<sup>-1</sup> (dry weight basis) is indicative of its toxicity to plants. Nickel behaves largely like essential plant nutrient Zn in the soil-plant system, but it forms stronger chelates with soil organic matter, thereby showing closeness to Cu. Possibility of Ni toxicity to plants cannot be ruled out when industrial or municipal wastes with high Ni concentrations are applied to agricultural lands. Nevertheless, like Zn and Cu, phytotoxicity of Ni appears to provide an effective barrier against Ni toxicity to human population and animals.

#### 6.6.5 Mercury

It is also one of the toxic metals in the human and animal systems. It belongs to the same group of Zn and Cd in the periodic table with atomic number 80 and mass 200.6. It is liquid in nature and mostly recovered during ore processing (Smith et al. 1995). In the environment, its major contribution through combustion of coal and release from manometers located at gas or oil pipelines. Mostly in the environment it is present in mercuric (Hg<sup>2+</sup>), mercurous (Hg<sub>2</sub><sup>2+</sup>), elemental (Hg<sup>0</sup>), and also in alkylated form as methyl or ethyl mercury. Mercury is more toxic in alkylated form, because these are soluble in water and volatile in air (Smith et al. 1995). In most cases the form of Hg depends on the redox potential and pH of the existing environment. For example, under oxidizing condition, Hg<sup>2+</sup> and Hg<sub>2</sub><sup>2+</sup> are more stable, whereas under reducing conditions, organic or inorganic Hg may be converted to elemental Hg and then again converted to alkylated forms by a biotic or abiotic process of nature. Mercury(II) formed strong complex with the organic and inorganic ligands present in the environment, which is easily soluble in oxidized aquatic systems (Bodek et al. 1988; Wuana and Okieimen 2011). In the uncontaminated

environment, its concentration in plant part seldom exceeds 500 parts per billion (ppb). In naturally contaminated areas, i.e., near Hg-bearing deposits, its level can be as high as 3500 ppb. Many agricultural crop inputs are having significant amounts of Hg like fungicide Ceresan M. Mercury is strongly held by the soil particles at various adsorption sites for the element never approaches saturation before another toxic element becomes hazardous. The Hg content in the aboveground part of plants is very low except Hg seed treatment or its addition to soil.

Most of the cases, Hg toxicity was reported in aquatic food chains compared to intensive agriculture. For the removal of Hg from solution, sorption to soil, sediment- and humic-containing material is playing a valuable mechanism. Increasing the pH of the system increases the sorption mechanism. Removal of Hg from solution may be recovered by coprecipitation with sulfides, and under low oxygen conditions, anaerobic microorganisms especially sulfur-reducing bacteria converted organic and inorganic forms of Hg to alkylated form. In anaerobic conditions, elemental Hg also transformed into demethylation of methyl-Hg or by reduction of Hg(II) in environment. In high acidic condition,  $\text{pH} < 4$  preferred the formation of methyl mercury; and higher pH range favors precipitation of  $\text{HgS(s)}$ .

### 6.6.6 Arsenic

Arsenic is classified under the metallic group of VA and period 4 in the periodic table associated with other minerals widely, mainly as  $\text{As}_2\text{O}_3$ . It has atomic number 33 and atomic mass 75 and exists in various forms of oxidation (i.e., -III, 0, III, V). In most of the aerobic environment, As(V) is the dominant species in the form of arsenate ( $\text{AsO}_4^{3-}$ ) in the different protonation states like  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$ . It is recovered during the ore processing of Cu, Pb, Zn, Ag, and Au. Arsenic builds up in the natural soil environment through natural processes of weathering of As-bearing rocks or As-contaminated groundwater used for crop production as a means of irrigation. Apart from these are anthropogenic activities such as mining operations, burning of coal, smelting of base metal ores, and application of As-containing agricultural inputs. The concentration of As in world soils varied widely. In common, soils overlying sulfide ore deposits or derived from shales and granites and those surrounding geothermal activity have high As contents. Arsenate and other anionic forms of As act as a chelates and precipitated with the presence of cations (Bodek et al. 1988). In West Bengal, water samples from about 55% tube wells have been found to contain As in a concentration greater than  $10 \mu\text{g L}^{-1}$ , which is the maximum permissible limit of the World Health Organization (Chowdhury et al. 1999). The soils being irrigated with As-contaminated waters have already started showing the presence of 6–10 mg  $\text{kg}^{-1}$  of EDTA extractable As. Arsenic retention by soil is mainly performed by the adsorption mechanism rather than the precipitation of sparingly soluble As compounds.

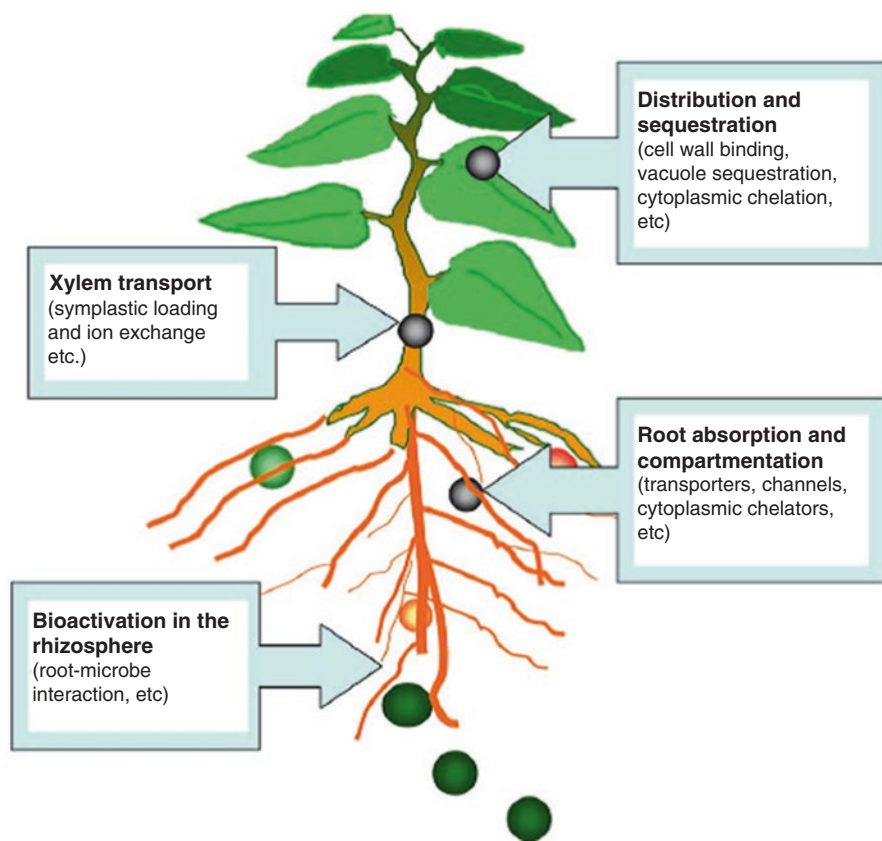
The toxicity of As depends on soil environment by the oxidation states and its presence with organic and inorganic combinations. The oxidation states of As metal are affected by pH and redox potential. The As mobility increases with increasing soil pH (Reed et al. 1995). The arsenates are very soluble, mobile, and toxic than the arsenates. The biological availability and phytotoxicity of As in soil increases on reduction of the As(III) state, which is facilitated on the flooding of the soils. The As uptake pattern is highly affected by crop, varieties, soil chemical environment, and some extent by climatic factors. The lowland rice is more susceptible to As toxicity than upland rice.

### 6.6.7 Zinc

It is an essential plant nutrient element and keeps the place in the period 4, group IIB, having atomic number 30 and mass 65.4. It is also a transitional metal, occurring naturally in soil systems. Fast industrialization or other anthropogenic activities like mining, coal, waste combustion, and use of steel processing activities enhance the Zn concentration in environment. The Zn availability varies with pH values. Increasing the soil pH decreased the availability of Zn in soil and reduced the concentration in soil solution toward plant uptake. In higher-pH condition, carbonate and bicarbonates are precipitated into unavailable forms and induced Zn deficiency in soils (Dotaniya and Meena 2013).

## 6.7 Cellular Mechanisms for Heavy Metals

Most of the heavy metals are toxic to plant systems except few. Largely heavy metals have low mobility in soils and have high adsorption with organic matter or silicate minerals. The plant uptake pattern is much affected by the presence of metal in soil and plant biochemical cycles. Hyperaccumulation in higher plant is a complex phenomenon and governed by various factors like (1) transport of heavy metals across the plasma membrane of root cells, (2) xylem loading and translocation in various part of plants, and (3) heavy metal detoxification and sequestration at the plant and cellular level (Lombi et al. 2002). The first hyperaccumulator plants were identified by the family of Brassicaceae and Fabaceae; and the list of plants crossed more than 400 (Halim et al. 2003). These plants have a particular gene for the hyperaccumulation of metal or metals (Yang et al. 2005). Many of the plants accumulated a particular metal, and a few plants are having the capacity to accumulate more than one metal. These metal accumulator mechanisms are not fully understood; but the capacity of plants toward metal uptake is accounted. The intracellular mechanism of heavy metal uptake has also helped to understand the various metal uptake phenomena in soil-plant dynamics. Some of the major processes influencing the accumulation rate in plants are defined in Fig. 6.1.



**Fig. 6.1** Major process involved in heavy metal hyperaccumulation by plants (Yang et al. 2005)

The hyperaccumulator plants showing the higher or extraordinary potential ability to absorb heavy metals from the contaminated soil or aquatic systems and accumulated in various part of the plant (Ma et al. 2001; Yang et al. 2002). The metal uptake by a plant and total metal present in soil does not have a true correlation in the heavy metal dynamics. Knight et al. (1994) reported that no significant correlation was observed between Zn accumulated by the *Thlaspi caerulescens* and total Zn metal in the soil. However, the close relation was also observed between metal concentration in plant shoot and metal concentration in soil solution. The bioavailability of metals is the part of total metal concentration, and these fractions are truly represented of plant uptake. Plant roots and microbial population and their interaction much determine the availability of a metal and also the form of metal in soil. Plants secrete various types of low-molecular organic acids through root exudates and act as a chelating agent or supply the food materials to soil microorganism (Dotaniya et al. 2013c, d). The interaction of microorganisms and plant roots can enhance the metal bioavailability in rhizosphere due to secretion of protons, amino acids, enzymes, and phytochelatins. A part of proton extrusion of the roots is

**Table 6.2** Genes of transportation isolated from plants involved in heavy metal uptake

Genes	Plant	Elements	References
<b>OsNramp1</b>	Rice	Mn	Belouchi et al. (1997)
<b>OsNramp2</b>			
<b>Cpx-type heavy metal ATPases</b>	<i>Arabidopsis</i> rice	Cu, Zn, Cd, Pb	Tabata et al. (1997), Williams et al. (2000), Belouchi et al. (1997), and Hirayama et al. (1999)
<b>Nramp</b>	<i>Arabidopsis</i>	Cd, divalent metals	Belouchi et al. (1997), Alonso et al. (1999), and Thomine et al. (2000)
<b>CDF family proteins</b>	<i>Arabidopsis</i>	Cd, Co, Cd	Maser et al. (2001)
<b>ZIP family (ZAT1, ZAT2, ZAT3)</b>	<i>Arabidopsis</i>	Cd, Zn, Mn	Van der Zaal et al. (1999)
	<i>T. caerulescens</i>		Lombi et al. (2002), Pence et al. (2000), and Assuncao et al. (2001)

mediated by the plasma membrane H<sup>+</sup>-ATPase and H<sup>+</sup> pump. The molecular bases and various effects of these mechanisms are a matter of research regarding heavy metal removal by plant systems. *Arabidopsis thaliana* is an AtHMA4 P-1B-ATPase which is responsible for the transportation of Zn and Cd. Verret et al. (2004) described that AtHMA4 is located in the plasma membrane and expressed its effect on tissue surrounding the root vascular vessels. Yang et al. (2005) mentioned that the ectopic overexpression of AtHMA4 positively influenced the root growth in the presence of toxic metals like Zn, Cd, and Co, whereas a null mutant exhibited a lower translocation response in the plant root-shoot system with regard to Zn and Cd metals. In plant nutrient-deficient conditions, plant which secreted the phytosiderophores can reduce the plant-available metal form, *i.e.* Fe<sup>3+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup> (Dotaniya et al. 2013c). The metal transportation from contaminated sites to plant root membrane and further in various plant parts is mediated by a particular gene in a specific plant species. A broader understanding about the metal transportation process in plant is required for the better understanding for the formulation of the effective strategies to develop genetically engineered plant species that can accumulate higher amount of metal from toxicant. A range of gene is responsible for a particular metal or metal accumulations mentioned in Table 6.2.

## 6.8 Remediation Techniques

The polluted environment can be remedied with the help of physical, chemical, and biological techniques. Various types of remediation techniques are also categorized in various heads as per the mode of action listed in Table 6.3. In classical method of heavy metal remediation from soil and water bodies with the help of chemical and physical technologies are mentioned from ancient periods. With these techniques addition of chemical (chemical remediation's), which mobilize or immobilize the heavy metal contents from contaminated sites; and in physical remediation

**Table 6.3** Technologies for remediation of heavy metal-contaminated soils (Wuana and Okieimen 2011)

Category	Remediation technologies
<b>Isolation</b>	i. Capping
	ii. Subsurface barriers
<b>Immobilization</b>	i. Solidification/stabilization
	ii. Vitrification
<b>Toxicity and/or mobility reduction</b>	i. Chemical treatment
	ii. Permeable treatment walls
	iii. Biological treatment bioaccumulation, phytoremediation (phytoextraction, phytostabilization, and rhizofiltration), bioleaching, biochemical processes
<b>Physical separation/extraction</b>	i. Soil washing, pyrometallurgical extraction, in situ soil flushing, and electrokinetic treatment

excavations, capping, soil mixing, soil washing and solidification, mixing of contaminated soil with uncontaminated soil are included (Dotaniya et al. 2012b; Dotaniya and Lata 2012; Velazquez et al. 2016). In bioremediation techniques, use of biological means for reducing the heavy metal toxicity in environment. These techniques have advantages and disadvantages as per the potential of remediation and cost.

### 6.8.1 Physical Remediation

This type of technique is applicable on particular form of metals. It consists of mechanical screening, floatation, electric and magnetic separation, and floatation (Gunatilake 2015). The potential efficiency of these techniques depends on soil properties and type and extension of pollution. Sometimes contaminated soil is washed with good-quality water. Highly metal-polluted soils can be remediated by physical scraps in which heavy metal-contaminated upper layer of soils shifted to another place. Sometimes, uncontaminated soil is mixed with contaminated soil to reduce the heavy metal concentration in lower side to grow the forage or crops. These methods are primarily important for check and balance mode for the soil and water pollution. It is almost necessary before discharging polluted WW into soil or water bodies. In the heavy metal remediation point of view, it is crucial for organic load containing metals or solid disposal in natural systems.



## 6.8.2 Chemical Remediation

It is mostly used for the removal of heavy metal from a smaller area. In this head it consists of chemical precipitation, coagulation and flocculation, electrochemical treatments, ion exchange, membrane filtration, and electrodialysis. The chemical precipitation method is one of the widely used methods, in which use of chemical formed insoluble precipitation with metals as hydroxide, carbonate, sulfide, and phosphate ions. Fine particle coagulates into bigger particle and can be removed by physical methods. The coagulation and flocculation methods are based on zeta potential. Apart from these, electric field is also used for the remediation of pollutant from liquid medium. The opposite ions of metals are accumulated on the metal-bearing cathode plate and insoluble anode. These methods are costly in nature and require highly skilled persons.

In these techniques various substances comprised with organic and inorganic in nature are using for the remediation of heavy metals from environment (Dotaniya et al. 2016a). These are reacting with various heavy metals and converted into non-toxic or less available to plant and microbes. Some of the substances are responsible for the immobilization of a particular metal, whereas few are used for more than one metal. The inorganic binder, *i.e.* clay (bentonite or kaolinite), fly ash, basic slag, calcium carbonate, and Fe/Mn oxides, is described in Table 6.4; and organic stabilizers such as various types of manure, organic residues, composts, and a combination of organic and inorganic substances listed in Table 6.5 may be used for the immobilization of heavy metals. Organic residues are used for the plant nutrient mobilization (Dotaniya 2014, Dotaniya et al. 2014b; Dotaniya et al. 2015b) and also use for the reduction of heavy metal in soil. The organic residues decompose with the help of soil microbial population and act as a biosorption (Dotaniya 2012; Dotaniya et al. 2012c; Meena et al. 2017). Low-molecular organic acids released during the microbial decomposition of organic material by soil biota (Dotaniya and Datta 2014; Dotaniya et al. 2014e) bind the metal or decomposed the metal and ultimately reduced the metal toxicity (Guo et al. 2006). On the other side of the decomposition, it released the plant nutrients, which also enhanced the crop plant immunity (Dotaniya et al. 2013b, 2014a). The use of biochar reduced the metal toxicity particularly Cd in spinach crop (Coumar et al. 2016a, b). The efficiency of applied organic and

**Table 6.4** Inorganic amendments for heavy metal immobilization (Guo et al. 2006)

Material	Source	Heavy metal immobilization
Lime	Lime factory	Cd, Cu, Ni, Pb, Zn
Phosphate salt	Fertilizer plant	Pb, Zn, Cu, Cd
Hydroxyapatite	Phosphorite	Zn, Pb, Cu, Cd
Fly ash	Thermal power plant	Cd, Pb, Cu, Zn, Cr
Slag	Thermal power plant	Cd, Pb, Zn, Cr
Ca-montmorillonite	Mineral	Zn, Pb
Portland cement	Cement plant	Cr, Cu, Zn, Pb
Bentonite	–	Pb

**Table 6.5** Organic amendments for heavy metal immobilization (Guo et al. 2006)

Material	Heavy metal immobilization
Bark saw dust (from timber industry)	Cd, Pb, Hg, Cu
Xylogen (from paper mill wastewater)	Zn, Pb, Hg
Chitosan (from crab meat-canning industry)	Cd, Cr, Hg
Bagasse (from sugarcane industry)	Pb
Poultry manure (from poultry farm)	Cu, Pb, Zn, Cd
Cattle manure (from cattle farm)	Cd
Rice hulls (from rice processing)	Cd, Cr, Pb
Sewage sludge	Cd
Leaves	Cr, Cd
Straw	Cd, Cr, Pb

inorganic substances is affected by climatic factors and soil parameters (Dotaniya 2013; Dotaniya et al. 2013a). The increase in the atmospheric temperature enhanced the photosynthetic rate in low-temperature regions and increased the root exudation in soil (Kushwah et al. 2014; Dotaniya et al. 2018). Soil microbes take root exudates as a food material and increased the microbial population and diversity (Dotaniya and Kushwah 2013). It helps to reduce the metal toxicity toward plants. The carbon sequestration potential of soil enhanced the plant sustainability in abiotic stress condition (Kundu et al. 2013; Meena et al. 2016), because more carbon sequestration helps in nutrient mobilization from soil (Sharma et al. 2014a, b; Dotaniya 2015; Dotaniya et al. 2016e, g). The silicon fertilization in rice crop enhanced the abiotic stress and improved the crop yield (Meena et al. 2013b).

### 6.8.3 Bioremediation

Bioremediation is the removal of heavy metal from polluted soil and WW with the help of biological techniques. The techniques are classified into (1) bioremediation by microorganism and (2) bioremediation by plants known as phytoremediation.

#### 6.8.3.1 Bioremediation by Microorganism

In this method, suitable microorganisms are used for the removal of heavy metals. In this method microorganism converted toxic metal to nontoxic or less toxic substances (Lata and Dotaniya 2013a). Technologies can be categorized into in situ or ex situ as per the place of treatment. In in situ, contaminated soil or water is treated at polluted sites; in ex situ conditions, contaminants can be displaced from polluted sites and remediated. For the removal of heavy metals from activated sludge, microorganism treatments break down the organic material with aeration and agitation and finally allow solids to settle down in the bottom of the sewage treatment plants. A particular type of microorganisms is responsible for a specific type of metal removal (Lata and Dotaniya 2013b). The part of the metals is taken by

microorganism as food materials and converted as nontoxic substances (Saha et al. 2017). These microorganisms are specific in nature and also sensitive to climatic factors. However, all the metals are not treated or remediated easily by microorganisms. For example, Cd and Pb are not readily absorbed by the microorganisms. The availability of food materials for soil biota enhanced the bioremediation rate in WW and contaminated soils (Pingoliya et al. 2014a, b; Singh et al. 2016). Increasing the N availability in contaminated soil may encourage the heavy metal biodegradation (Sims 2006). These efficient microorganisms used for the metal remediation function are known as bioremediators (Meena et al. 2013a; Singh et al. 2016). If fungi are used for the removal of heavy metals, they are known as mycoremediation. In this line, a lot of work is going on to understand the different pathways and regulatory network to remediate from various contaminated systems. Calculate the C flux from different systems for the environmental aspect for a particular compound vis-a-vis microorganisms. The genetically engineered microorganisms may be important in the process of bioremediation. The bacterium *Deinococcus radiodurans* is modified with the help of genetic engineering for remediation of toluene and ionic mercury from the radioactive reactor WW and solids (Brim et al. 2000). These techniques are specific for a particular metal and microorganisms and need specific tool and techniques for the remediation purpose (Dotaniya et al. 2016b). The higher cost for installation of modern equipment and hygienic conditions is also needed for bioremediation with microorganisms.

### 6.8.3.2 Phytoremediation

Use of various types of plants for the remediation of metals from contaminated environment is known as phytoremediation. It can be used for the removal of organic pollutant, trace metals, and radioactive materials from polluted soil and aquatic bodies. It is cost-effective, environmental, eco-friendly, and driven by the solar energy. It is used as in situ application and required less technical skill. The phytoremediation consists with two words: Greek *phyto* means plants and Latin *remediation* tends to correct or remove an evil. The green plants have immense potential to remediate pollutant and also detoxification by various mechanisms. This concept (as phytoextraction) was suggested by Chaney (1983). The phytoremediation techniques include phytoextraction, phytofiltration, phytovolatilization, phytostabilization, phytodegradation, phytotransformation, removal of aerial contaminants, etc. A list of methods, action mechanism, and medium treated is given in Table 6.6.

### 6.8.3.3 Hyperaccumulator Plants

Those plants have higher capacity of heavy metal adsorption in plant parts as compared to normal plants. These plants are not showing any adverse effect on plant growth. Such type of plants is specific with a particular metal or a group of metals. Plants that accumulated heavy metals in various parts are listed in Table 6.7.

**Table 6.6** List of phytoremediation strategies (Yang et al. 2005; Dotaniya and Lata 2012)

Phytoremediation techniques	Action mechanism	Medium treated
Phytoextraction	Direct accumulation of contaminants into plant shoots with subsequent removal of the plant shoots	Soil
Rhizofiltration (phytofiltration)	Absorb and adsorb pollutants in plant roots	Surface water and water pumped through roots
Phytostabilization	Root exudates cause metals to precipitate, and biomass becomes less bioavailable	Groundwater, soil, mine tailings
Phytovolatilization	Plant evaporates certain metal ions and volatile organics	Soil, groundwater
Phytodegradation (plant-assisted bioremediation)	Microbial degradation in the rhizosphere region	Groundwater within the rhizosphere and soil
Phytotransformation	Plant uptake of organic contaminants and degradation	Surface and groundwater
Removal of aerial contaminants	Uptake of various volatile organics by leaves	Air

**Table 6.7** Heavy metal distribution in hyperaccumulators at tissue/cellular level

Tissue/organ	Element	Plant species	Reference
Trichome	Zn, Cd	<i>Arabidopsis halleri</i>	Kupper et al. (1999)
	Cd	<i>Brassica juncea</i>	Salt et al. (1995)
	Ni	<i>Alyssum lesbiacum</i>	Kramer et al. (1997)
Epidermal	Zn	<i>T. caerulescens</i>	Kupper et al. (1999)
	Zn	<i>T. caerulescens</i>	Vazquez et al. (1994)
	Ni	<i>Alyssum</i>	Kramer et al. (1997)
Mesophyll	Zn	<i>Arabidopsis halleri</i>	Kupper et al. (1999)
	Cd	<i>Sedum alfredii H.</i>	Xiong et al. (2004)
Cell wall	Ni	<i>T. goesingense</i>	Kramer et al. (2000)
	Cu	<i>Elsholtzia splendens</i>	Yang (2002)
	Zn	<i>Sedum alfredii H.</i>	Kramer et al. (2000)
	Pb	<i>Sedum alfredii H.</i>	He et al. (2003)
Vacuole	Zn	<i>T. caerulescens</i>	Kupper et al. (1999)
	Zn	<i>T. caerulescens</i>	Vazquez et al. (1994)
	Cd	<i>Sedum alfredii H.</i>	Xiong et al. (2004)
	Zn	<i>Sedum alfredii H.</i>	Kramer et al. (2000)

The hyperaccumulator plant should have higher capacity to produce plant biomass and suitable for a wide range of contamination. Hyperaccumulator plants do not transfer the metal into edible parts. The capacity of phytoremediation can be enhanced through inserting various foreign genes into plants through genetic engineering or biotechnological techniques (Table 6.8).

**Table 6.8** Genes introduced into plants and the effects of their expression on heavy metal tolerance, accumulation, or volatilization (Yang et al. 2005)

Gene	Product	Source	Target	Maximum observed effect <sup>a</sup>
<i>merA</i>	Hg(II) reductase	Gram-negative bacteria	<i>Liriodendron tulipifera</i>	50 $\mu\text{mol L}^{-1}$ $\text{HgCl}_2$ ; 500 $\text{mg HgCl}_2 \text{ kg}^{-1}$
			<i>Nicotiana tabacum</i>	V: Hg-volatilization rate increase 10 fold
<i>merA</i>	Hg (II) reductase	Gram-negative bacteria	<i>Arabidopsis thaliana</i>	T: 10 $\mu\text{mol L}^{-1}$ $\text{CH}_3\text{HgCl}$ (>40-fold)
<i>merB</i>	Organomercurial lyase	Gram-negative bacteria	<i>A. thaliana</i>	V: upto 59 $\text{pg Hg(0) mg}^{-1}$ fresh biomass $\text{min}^{-1}$
<i>APSI</i>	ATP sulfurylase	<i>A. thaliana</i>	<i>B. juncea</i>	A: twofold increase in Se concentration
<i>MT-I</i>	MT	Mouse	<i>N. tabacum</i>	T: 200 $\mu\text{mol L}^{-1}$ $\text{CdCl}_2$ (20-fold)
<i>CUP1</i>	MT	<i>Saccharomyces cerevisiae</i>	<i>B. oleracea</i>	T: 400 $\mu\text{mol L}^{-1}$ $\text{CdCl}_2$ (approximately 16-fold)
<i>gsh2</i>	GSH synthase	<i>E. coli</i>	<i>B. juncea</i>	A: Cd concentration 125%
<i>gsh1</i>	$\Gamma$ -Glu-Cys synthase	<i>E. coli</i>	<i>B. juncea</i>	A: Cd concentration 190%
<i>NtCBP4</i>	Cation channel	<i>N. tabacum</i>	<i>N. tabacum</i>	T: 250 $\mu\text{mol L}^{-1}$ $\text{NiCl}_2$ (2.5-fold), Pb sensitive
				A: Pb concentrations 200%
<i>ZAT1</i>	Zn transporter	<i>A. thaliana</i>	<i>A. thaliana</i>	T: Slight increase
<i>TaPCS1</i>	PC	Wheat	<i>Nicotiana glauca R.</i>	A: Pb concentrations 200%
			Graham	

A accumulation in the shoot, *GSH* glutathione, *MT* metallothionein, *T* tolerance, *V* volatilization

<sup>a</sup>Relative values refer to control plants not expressing the transgene

Hyperaccumulation or the removal of metals from soil or water system can be calculated with various parameters, i.e., bioconcentration factors, translocation factor, and translocation efficiency and crop removal with the help of below formulas.

**Bioconcentration Factor (BCF)** It is defined as the contamination removal capacity of the plant and was calculated by Zhuang et al. (2007).

$$\text{BCF} = \frac{\text{Cr}_{\text{harvested tissue}}}{\text{Cr}_{\text{soil/water}}}$$

Here,  $\text{Cr}_{\text{harvested tissue}}$  is a concentration of Cr in harvested plant parts (root, shoot), and  $\text{Cr}_{\text{soil}}$  is total applied Cr levels of respective treatment.

**Translocation Factor (TF)** Means transfer of Cr metal ions from root to shoot part and quantified by formula proposed by Adesodun et al. (2010).

$$TF = \frac{Cr_{shoots}}{Cr_{roots}}$$

**Translocation Efficiency (TE)** TE was calculated with the help of formula described by Meers et al. (2004).

$$TE(\%) = \frac{Cr_{content\ in\ shoots\ (mg/kg)}}{Cr_{content\ in\ the\ whole\ plant}} \times 100$$

**The Cr Removal (%)** Percent Cr removal represented the Cr removal capacity of the crop with respect to contamination level; it was calculated as per given formula:

$$\begin{aligned} Cr\ removal(x) &= \frac{\text{Total Cr uptake by plant}}{\text{Total Cr applied to the soil}} \\ &= Cr\ removal(\%) = \text{Value}(x) \times 100 \end{aligned}$$

#### 6.8.3.3.1 Phytoextraction

In this technique, plant uptake contaminants from soil and water through plant roots and accumulate in aboveground parts, *i.e.* shoots. This is also known as phytoaccumulation, phytoabsorption, or phytosequestration. This process which stored metal in shoot is a crucial biochemical process; and researches are focused more on potential uptake in aboveground part, because the root biomass is generally not feasible (Tangahu et al. 2011). Phytoextraction may be classified into two types.

##### 6.8.3.3.1.1 Natural Phytoextraction

It is usually conducted through planting selected species in the contaminated soil. These plants are grown under normal farming conditions to reach the optimal size, harvested and disposed of appropriately. The plants (such as *Pteris vittata*) are highly specialized, occur naturally, and can tolerate highly elevated concentrations of metals that would be toxic to other plants. Typically, these plants are small, have a shallow root system, and grow relatively slowly.

##### 6.8.3.3.1.2 Induced Phytoextraction

In non-hyperaccumulator plants such as *Thlaspi perfoliatum*, factors limiting their potential for phytoextraction include small root uptake and little root-shoot translocation of metals. Methods that use metal-mobilizing agents have been proposed specifically to overcome these limitations. Following this approach, a high-biomass crop is grown on the contaminated soil requiring remediation. Throughout the

growth period, amendments are added to the soil to increase availability of metals to the plants. The most commonly used agents for induced phytoextraction are ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), cyclohexylenedinitrilotetraacetic acid (CDTA), citric acid, etc.

#### 6.8.3.3.2 Phytofiltration

This technique is also little bit similar to phytoextraction but is concerned with the remediation of contaminated groundwater rather than the remediation of polluted soils. The contaminants are absorbed or adsorbed, and thus their movement is less in underground water. This method is also known as rhizofiltration (by roots), blastofiltration (by seedlings), and caulofiltration (used plant shoots) (Mesjasz-Przybylowicz et al. 2004). Plants (such as *Helianthus annuus* used for rhizofiltration) are not planted directly but are acclimated to the pollutant first. Plants are hydroponically grown in clean water rather than the soil until a large root system develops. Once a large root system is in place, the water supply is substituted for a polluted water supply to acclimatize the plant. Then they are planted in the polluted area where the roots uptake the polluted water and the contaminants along with it. As the roots become saturated, they are harvested and disposed of safely.

#### 6.8.3.3.3 Phytostabilization

Phytostabilization is the process in which plants (*Festuca rubra* L, *Agrostis tenuis*) are used to immobilize soil and water contaminants. It mainly focuses on sequestering pollutants in soil near the roots rather than in the plant tissues itself. Pollutants become less bioavailable, and livestock, wildlife, and human exposure are reduced. The contaminants are absorbed and accumulated by the roots, adsorbed onto the roots, or precipitated in the rhizosphere. This reduces or even prevents the contaminants migrating into the groundwater or air as well as the bioavailability of the contaminant which prevent its spread through the food chain. This technique can also be used to reestablish a plant community on sites that have been denuded due to high levels of metal contamination. Once a community of tolerant species has been established, the potential for wind erosion (and thus spread of the pollutant) and the leaching of the soil contaminants is also reduced. Phytostabilization involves three processes which include humification, lignification, and irreversible binding.

#### 6.8.3.3.4 Phytovolatilization

It refers to the process through which plants uptake water-soluble contaminants and release them into the atmosphere as they transpire water. As the water travels along the plant's vascular system from the roots to the leaves, the contaminant may be modified whereby it evaporates or volatilizes into the air surrounding the plant.

Phytovolatilization is relevant in the remediation of soils rich in mercury, selenium, and to some extent in arsenic. The mercury ion is transformed into less toxic elemental mercury, and selenium is lost to the atmosphere in the form of dimethyl selenide (DMSe). It is also applicable for the removal of organic contaminants. For example, poplar trees have been shown to volatilize 90% of the TCE they take up.

#### 6.8.3.3.5 Phytodegradation

In this process plant secreted various types of enzymes, i.e., dehalogenase and oxygenase through root cells, which break down the organic pollutants in soil (Vishnoi and Srivastava 2008; Dotaniya and Lata 2012). Some contaminants can be absorbed by the plants and broken down by their enzymes. These smaller pollutant molecules may then be used as metabolites by the plant as it grows, thus becoming incorporated into the plant tissues. Plant enzymes that break down ammunition wastes, chlorinated solvents such as trichloroethane (TCE), have been identified.

## 6.9 Conclusions

Heavy metal pollution is emerging with time, and the functional capacities of natural resources are shrinking toward production of food materials. The increasing crop production on limited land with poor-quality resources is a challenge to researcher and policy-maker across the globe. The use of poor-quality soil and water after proper management is needed for today and tomorrow. The poor-quality water or industrial effluent is having trace metal, which is carcinogenic in nature and affects the natural biochemical mechanism in living organisms. More focus on the safe utilization of poor-quality water and contaminated soil after proper remediation or treatment. In present context, one industry is located at nearby the other industrial unit and the effluent merging at a common point and utilized for various purposes. The multi-metal toxicity should be identified, and proper strategies should be made to reduce the metal inhaled in human body. The effect of climate change on heavy metal uptake pattern in soil and in crop should be investigated. The extension of phytoremediation techniques in urban and contaminated areas also needs attention. The uses of modern biotechnological with traditional techniques are in combination to combat the heavy metal toxicity. Public awareness is also a need of today regarding heavy metal toxicity with the help of government agencies as well as nongovernment agencies (NGOs) for sustainable crop production.

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## References

- Adesodun JK, Atayese MO, Agbaje TA, Osadiaye BA, Mafe OF, Soretire AA (2010) Phytoremediation potentials of sunflowers (*Tithonia diversifolia* and *Helianthus annuus*) for metals in soils contaminated with zinc and lead nitrates. *Water Air Soil Pollut* 207:195–201
- Ahmad M, Nadeem SM, Naveed M, Zahir ZA (2016) Potassium-solubilizing bacteria and their application in agriculture. In: Meena VS, Maurya BR, Verma JP, Meena RS (eds) Potassium solubilizing microorganisms for sustainable agriculture. Springer, New Delhi, pp 293–313
- Ajay, Dotaniya ML, Meena VD (2012) Zinc-an important element for biofortification. *Agrobios News* 11(7):30–31
- Alam MGM, Snow ET, Tanaka A (2003) Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. *Sci Total Environ* 308:83–96
- Alonso JM, Hirayama T, Roman G, Nourizadeh S, Ecker JR (1999) A bifunctional transducer of ethylene and stress responses in *Arabidopsis*. *Science* 284:2148–2152
- Assuncao AGL, Martins PD, De Folter S, Vooijs R, Schat H, Aarts MGM (2001) Elevated expression of metal transporter genes in three accessions of the metal hyperaccumulator *Thlaspi caerulescens*. *Plant Cell Environ* 24(2):217–226
- Ball JW, Izbicki JA (2004) Occurrence of hexavalent chromium in groundwater in the Western Mojave Desert, California. *Appl Geochem* 19(7):1123
- Bartlett RJ, Kimble JM (1976) Behaviour of chromium in soils. II. Hexavalent forms. *J Environ Qual* 5:383–386
- Belouchi A, Kwan T, Gros P (1997) Cloning and characterization of the OsNramp family from *Oryza sativa*, a new family of membrane proteins possibly implicated in the transport of metal ions. *Plant Mol Biol* 33:1085–1092
- Bhatia M, Babu RS, Sonawane SH, Gogate PR, Girdhar A, Reddy ER, Pola M (2016) Application of nanoadsorbents for removal of lead from water. *Int J Environ Sci Technol* 14:1135–1154
- Bodek I, Lyman WJ, Reehl WF, Rosenblatt DH (1988) Environmental inorganic chemistry: properties, processes and estimation methods. Pergamon Press, Elmsford
- Bolan NS, Adriano DC, Natesan R, Bon-jun K (2003) Reduction and phytoavailability of Cr (VI) as influenced by organic manure compost. *J Environ Qual* 32:120–128
- Brim H, McFarlan SC, Fredrickson JK, Minton KW, Zhai M, Wackett LP, Daly MJ (2000) Engineering *Deinococcus radiodurans* for metal remediation in radioactive mixed waste environments. *Nat Biotechnol* 18(1):85–90
- Campbell PGC (2006) Cadmium-A priority pollutant. *Environ Chem* 3(6):387–388
- Chabukdhara M, Nema AK (2012) Assessment of heavy metal contamination in Hindon River sediments: a chemometric and geo chemical approach. *Chemotherapy* 87:945–953
- Chaney RL (1983) Plant uptake of inorganic waste constituents. In: Parr JFEA (ed) Land treatment of hazardous wastes. Noyes Data Corp, Park Ridge, pp 50–76
- Chowdhury TR, Basu GK, Mandal BK, Biswas BK, Samanta G, Chowdhury UK (1999) Arsenic poisoning in the Ganges Delta. *Nature* 401:545–546
- Coumar MV, Parihar RS, Dwivedi AK, Saha JK, Lakaria BL, Biswas AK, Rajendiran S, Dotaniya ML, Kundu S (2016a) Pigeon pea biochar as a soil amendment to repress copper mobility in soil and its uptake by spinach. *BioResources* 11(1):1585–1595
- Coumar MV, Parihar RS, Dwivedi AK, Saha JK, Rajendiran S, Dotaniya ML, Kundu S (2016b) Impact of pigeon pea biochar on cadmium mobility in soil and transfer rate to leafy vegetable spinach. *Environ Monit Assess* 188:31
- Dominguez-Nunez JA, Benito B, Berrocal-Lobo M, Albanesi A (2016) Mycorrhizal fungi: role in the solubilization of potassium. In: Meena VS, Maurya BR, Verma JP, Meena RS (eds) Potassium solubilizing microorganisms for sustainable agriculture. Springer, New Delhi, pp 77–98
- Dotaniya ML (2012) Crop residue management in rice-wheat cropping system. Lap Lambert Academic Publisher, Germany

- Dotaniya ML (2013) Impact of various crop residue management practices on nutrient uptake by rice-wheat cropping system. *Curr Adv Agric Sci* 5(2):269–271
- Dotaniya ML (2014) Role of bagasse and pressmud in phosphorus dynamics. Lap Lambert Academic Publisher, Germany
- Dotaniya ML (2015) Impact of rising atmospheric CO<sub>2</sub> concentration on plant and soil process. In: Mohanty M, Sinha NK, Hati KM, Chaudhary RS, Patra AK (eds) *Crop growth simulation modelling and climate change*. Scientific Publisher, New Delhi, pp 69–86
- Dotaniya ML, Datta SC (2014) Impact of bagasse and press mud on availability and fixation capacity of phosphorus in an inceptisol of north India. *Sugar Tech* 16(1):109–112
- Dotaniya ML, Kushwah SK (2013) Nutrients uptake ability of various rainy season crops grown in a vertisol of central India. *Afr J Agric Res* 8(44):5592–5598
- Dotaniya ML, Lata M (2012) Cleaning soils with phytoremediation. *Geo You* 12(73):18–21
- Dotaniya ML, Meena VD (2013) Rhizosphere effect on nutrient availability in soil and its uptake by plants - a review. *Proc Natl Acad Sci India Sec B Biol Sci* 85(1):1–12
- Dotaniya ML, Saha JK (2017) Sewage farming: a potential threat to agriculture. *Indian Farmers Dig* 1:14–21
- Dotaniya ML, Ajay, Meena BP, Kundu S (2012a) Soil pollution: a necessary evil. *Agrobios Newsl X*(12):39–40
- Dotaniya ML, Ajay, Meena BP, Kundu S, Meena VD (2012b) Phytoremediation: a cost-effective technique. *Agrobios Newsl XI*(3):79–80
- Dotaniya ML, Meena HM, Rajendiran S, Coumar MV, Verma R (2012c) Biosorption of heavy metal with agro waste. *Agrobios Newsl XI*(7):37
- Dotaniya ML, Datta SC, Biswas DR, Meena BP (2013a) Effect of solution phosphorus concentration on the exudation of oxalate ions by wheat (*Triticum aestivum* L.) *Proc Natl Acad Sci India Sec B Biol Sci* 83(3):305–309
- Dotaniya ML, Sharma MM, Kumar K, Singh PP (2013b) Impact of crop residue management on nutrient balance in rice-wheat cropping system in an Aquic hapludoll. *J Rural Agric Res* 13(1):122–123
- Dotaniya ML, Prasad D, Meena HM, Jajoria DK, Narolia GP, Pingoliya KK, Meena OP, Kumar K, Meena BP, Ram A, Das H, Chari MS, Pal S (2013c) Influence of phytosiderophore on iron and zinc uptake and rhizospheric microbial activity. *Afr J Microbiol Res* 7(51):5781–5788
- Dotaniya ML, Meena HM, Lata M, Kumar K (2013d) Role of phytosiderophores in iron uptake by plants. *Agric Sci Dig* 33(1):73–76
- Dotaniya ML, Meena HM, Lata M (2013e) Heavy metal toxicity: pandora's box for human disease. *Read Shelf* 9(6):5–6
- Dotaniya ML, Meena HM, Lata M, Jajoria DK, Meena MD (2013f) Use of biosolids in agriculture. *Agrobios Newsl XI*(8):21–22
- Dotaniya ML, Datta SC, Biswas DR, Meena HM, Kumar K (2014a) Production of oxalic acid as influenced by the application of organic residue and its effect on phosphorus uptake by wheat (*Triticum aestivum* L.) in an inceptisol of north India. *Natl Acad Sci Lett* 37(5):401–405
- Dotaniya ML, Datta SC, Biswas DR, Kumar K (2014b) Effect of organic sources on phosphorus fractions and available phosphorus in Typic Haplustert. *J Indian Soc Soil Sci* 62(1):80–83
- Dotaniya ML, Saha JK, Meena VD, Rajendiran S, Coumar MV, Kundu S, Rao AS (2014c) Impact of tannery effluent irrigation on heavy metal build up in soil and ground water in Kanpur. *Agrotechnology* 2(4):77
- Dotaniya ML, Das H, Meena VD (2014d) Assessment of chromium efficacy on germination, root elongation, and coleoptile growth of wheat (*Triticum aestivum* L.) at different growth periods. *Environ Monit Assess* 186:2957–2963
- Dotaniya ML, Kushwah SK, Rajendiran S, Coumar MV, Kundu S, Rao AS (2014e) Rhizosphere effect of kharif crops on phosphatases and dehydrogenase activities in a Typic Haplustert. *Natl Acad Sci Lett* 37(2):103–106
- Dotaniya ML, Meena VD, Das H (2014f) Chromium toxicity on seed germination, root elongation and coleoptile growth of pigeon pea (*Cajanus cajan*). *Legum Res* 37(2):225–227

- Dotaniya ML, Pingoliya KK, Lata M, Verma R, Regar KL, Deewan P, Dotaniya CK (2014g) Role of phosphorus in chickpea (*Cicer arietinum* L.) production. *Afr J Agric Res* 9(51):3736–3743
- Dotaniya ML, Thakur JK, Meena VD, Jajoria DK, Rathor G (2014h) Chromium pollution: a threat to environment. *Agric Res* 35(2):153–157
- Dotaniya ML, Saha JK, Meena VD (2015a) Sewage water irrigation boon or bane for crop production. *Indian Farm* 65(12):24–27
- Dotaniya ML, Datta SC, Biswas DR, Meena HM, Rajendiran S, Meena AL (2015b) Phosphorus dynamics mediated by bagasse, press mud and rice straw in inceptisol of North India. *Agrochimica* 59(4):358–369
- Dotaniya ML, Meena VD, Basak BB, Meena RS (2016a) Potassium uptake by crops as well as microorganisms. In: Meena VS, Maurya BR, Verma JP, Meena RS (eds) Potassium solubilizing microorganisms for sustainable agriculture. Springer, New Delhi, pp 267–280
- Dotaniya ML, Datta SC, Biswas DR, Dotaniya CK, Meena BL, Rajendiran S, Regar KL, Lata M (2016b) Use of sugarcane industrial byproducts for improving sugarcane productivity and soil health—a review. *Intl J Rec Org Waste Agric* 142:1583–1608
- Dotaniya ML, Kundu S, Saha JK (2016c) Role of biotechnology in environmental monitoring and pollution control. *Kheti* 6:26–28
- Dotaniya ML, Meena VD, Rajendiran S, Coumar MV, Saha JK, Kundu S, Patra AK (2016d) Geo-accumulation indices of heavy metals in soil and groundwater of Kanpur, India under long term irrigation of tannery effluent. *Bull Environ Contam Toxicol* 98:706–711
- Dotaniya ML, Meena VD, Srivastava A (2016e) Plastic pollution: a threat to ecosystem. *Indian Farm* 66(3):12–14
- Dotaniya ML, Rajendiran S, Meena BP, Meena AL, Meena BL, Jat RL, Saha JK (2016f) Elevated carbon dioxide (CO<sub>2</sub>) and temperature vis- a-vis carbon sequestration potential of global terrestrial ecosystem. In: Bisht JK, Meena VS, Mishra PK, Pattanayak A (eds) Conservation agriculture: an approach to combat climate change in Indian Himalaya. Springer, Singapore, pp 225–256
- Dotaniya ML, Rajendiran S, Meena VD, Saha JK, Coumar MV, Kundu S, Patra AK (2016g) Influence of chromium contamination on carbon mineralization and enzymatic activities in Vertisol. *Agric Res* 6:91–96
- Dotaniya ML, Meena VD, Kumar K, Meena BP, Jat SL, Lata M, Ram A, Dotaniya CK, Chari MS (2016h) Impact of biosolids on agriculture and biodiversity. Today and Tomorrow's Printer and Publisher, New Delhi, pp 11–20
- Dotaniya ML, Dotaniya CK, Sanwal RC, Meena HM (2018) CO sequestration and transformation potential of agricultural system. In: Martínez L, Kharissova O, Kharisov B (eds) Handbook of ecomaterials. Springer, Cham. [https://doi.org/10.1007/978-3-319-48281-1\\_87-1](https://doi.org/10.1007/978-3-319-48281-1_87-1)
- Guertin J (2005) Toxicity and health effects of chromium (all oxidation states). In: Guertin J, Jacobs JA, Avakian CP (eds) Chromium (VI) handbook. CRC Press, Boca Raton, pp 216–234
- Gunatilake SK (2015) Methods of removing heavy metals from industrial wastewater. *J Multidiscip Eng Sci Stud* 1(1):12–18
- Guo G, Zhou Q, Ma LQ (2006) Availability and assessment of fixing additives for the in situ remediation of heavy metal contaminated soils: a review. *Environ Monit Assess* 116(1–3):513–528
- GWRTAC (1997) Remediation of metals-contaminated soils and groundwater, Tech Rep TE-97-01. GWRTAC, Pittsburgh
- Halim M, Conte P, Piccolo A (2003) Potential availability of heavy metals to phytoextraction from contaminated soils induced by exogenous humic substances. *Chemosphere* 52(1):265–275
- Hassan N, Ahmed K (2000) Intra familiar distribution of food in rural Bangladesh. Institute of Nutrition and food Science, University of Dhaka, Bangladesh. Internet <http://www.unu.edu/unpress/food/8F064e/>
- He B, Yang XE, Ni WZ, Wei YZ, Ye HB (2003) Pb uptake, accumulation, subcellular distribution in a Pb-accumulating ecotype of *Sedum alfredii* (Hance). *J Zhejiang Univ Sci* 4(4):474–479
- Hirayama T, Kieber JJ, Hirayama N (1999) Responsive-to-antagonist1, a Menkes/Wilson disease-related copper transporter, is required for ethylene signaling in *Arabidopsis*. *Cell* 97(3):383–393

- Hughes MF (2002) Arsenic toxicity and potential mechanisms of action. *Toxicol Lett* 133:1–16
- IRIS (2015) Integrated risk information system-database. US Environmental Protection Agency, Washington, DC
- James BR, Bartlett RJ (1983) Behaviour of chromium in soils. VIII. Adsorption and reduction of hexavalent forms. *J Environ Qual* 12:177–181
- Knight B, Zhao FJ, McGrath SP, Shen ZG (1994) Zinc and cadmium uptake by hyperaccumulator *Thlaspi caerulescens* in contaminated soils and its effects on the concentration and chemical speciation of metals in soil solution. *Plant Soil* 197:71–78
- Kong SF, Lu B, Ji YQ, Zhao XY, Chen L, Li ZY, Han B, Bai ZP (2011) Levels, risk assessment and sources of PM<sub>10</sub> fraction heavy metals in four types dust from a coal-based city. *Microchem J* 98:280–290
- Kramer U, Smith RD, Wenzel WW, Raskin I, Salt DE (1997) The role of metal transport and tolerance in nickel hyperaccumulation by *Thlaspi goesingense* Halacsy. *Physiol Plant* 115:1641–1650
- Kramer U, Pickering IJ, Prince RC, Raskin I, Salt DE (2000) Subcellular localization and speculation of nickel in hyperaccumulator and non-accumulator *Thlaspi* species. *Plant Physiol* 122:1343–1353
- Kundu S, Dotaniya ML, Lenka S (2013) Carbon sequestration in Indian agriculture. In: Lenka S, Lenka NK, Kundu S, Rao AS (eds) *Climate change and natural resources management*. New India Publishing Agency, New Delhi, pp 269–289
- Kupper H, Zhao FJ, McGrath SP (1999) Cellular compartmentation of zinc in leaves of the hyperaccumulator *Thlaspi caerulescens*. *Plant Physiol* 119:305–311
- Kushwah SK, Dotaniya ML, Upadhyay AK, Rajendiran S, Coumar MV, Kundu S, Rao AS (2014) Assessing carbon and nitrogen partition in kharif crops for their carbon sequestration potential. *Natl Acad Sci Lett* 37(3):213–217
- Lata M, Dotaniya ML (2013a) Water pollution: a global problem. *Read Shelf* 9(12):9–10
- Lata M, Dotaniya ML (2013b) Environmental pollution: a big challenge to control. *Ind Farmers' Dig* 46(8):9–11
- Lenka S, Rajendiran S, Coumar MV, Dotaniya ML, Saha JK (2016) Impacts of fertilizers use on environmental quality. In: National seminar on environmental concern for fertilizer use in future at Bidhan Chandra Krishi Viswavidyalaya, Kalyani on February 26, 2016
- Lokhande RS, Singare PU, Pimple DS (2011) Toxicity study of heavy metals pollutants in waste water effluent samples collected from Taloja industrial estate of Mumbai, India. *Res Environ* 1(1):13–19
- Lombi E, Tearall KL, Howarth JR, Zhao FJ, Hawkesford MJ, McGrath SP (2002) Influence of iron status on calcium and zinc uptake by different ecotypes of the hyperaccumulator *Thlaspi caerulescens*. *Plant Physiol* 128:1359–1367
- Losi ME, Amrhein C, Frankenberger WT (1994) Factor affecting chemical and biological reduction of Cr(VI) in soil. *Environ Toxicol Chem* 13:1727–1735
- Ma LQ, Komar KM, Tu C, Zhang W, Cai Y, Kennelly ED (2001) A fern that hyperaccumulates arsenic. *Nature* 409:579
- Manahan SE (2003) *Toxicological chemistry and biochemistry*, 3rd edn. Boca Raton CRC Press/Limited Liability Company (LLC)
- Mascagni P, Consonni D, Bregante G, Chiappino G, Toffoletto F (2003) Olfactory function in workers exposed to moderate airborne cadmium levels. *Neurotoxicology* 24:717–724
- Maser P, Thomine S, Schroeder JI, Ward JM, Hirschi K, Sze H, Talke IN, Amtmann A, Maathuis FJM, Sanders D, Harper JF, Tchieu J, Gribskov M, Persans MW, Salt DE, Kim SA, Gueriot ML (2001) Phylogenetic relationships within cation transporter families of Arabidopsis. *Plant Physiol* 126:1646–1667
- Masood S, Bano A (2016) Mechanism of potassium solubilization in the agricultural soils by the help of soil microorganisms. In: Meena VS, Maurya BR, Verma JP, Meena RS (eds) *Potassium solubilizing microorganisms for sustainable agriculture*. Springer, India, pp 137–147. [https://doi.org/10.1007/978-81-322-2776-2\\_10](https://doi.org/10.1007/978-81-322-2776-2_10)

- Meena VD, Dotaniya ML, Meena BP, Das H (2013a) Organic food safer but not healthy: truth in myth. *Ind Farmers Dig* 46(8):43–44
- Meena VD, Dotaniya ML, Rajendiran S, Coumar MV, Kundu S, Rao AS (2013b) A case for silicon fertilization to improve crop yields in tropical soils. *Proc Natl Acad Sci India Sec B Biol Sci* 84(3):505–518
- Meena VD, Dotaniya ML, Saha JK, Patra AK (2015a) Antibiotics and antibiotic resistant bacteria in wastewater: impact on environment, soil microbial activity and human health. *Afr J Microbiol Res* 9(14):965–978
- Meena RS, Meena VS, Meena SK, Verma JP (2015b) The needs of healthy soils for a healthy world. *J Clean Prod* 102:560–561
- Meena RS, Meena VS, Meena SK, Verma JP (2015c) Towards the plant stress mitigate the agricultural productivity: a book review. *J Clean Prod* 102:552–553
- Meena BP, Shirale AO, Dotaniya ML, Jha P, Meena AL, Biswas AK, Patra AK (2016) Conservation agriculture: a new paradigm for improving input use efficiency and crop productivity. In: Bisht JK, Meena VS, Mishra PK, Pattanayak A (eds) *Conservation agriculture: an approach to combat climate change in Indian Himalaya*. Springer, Singapore, pp 39–69
- Meena VS, Maurya BR, Meena SK, Meena RK, Kumar A, Verma JP, Singh NP (2017) Can *Bacillus* species enhance nutrient availability in agricultural soils? In: Islam MT, Rahman M, Pandey P, Jha CK, Aeron A (eds) *Bacilli and agrobiotechnology*. Springer International Publishing, Cham, pp 367–395
- Meers E, Hopgood M, Lesage E, Vervaeke P, Tack FMG, Verloo M (2004) Enhanced phytoextraction: in search for EDTA alternatives. *Int J Phytoremed* 6(2):95–109
- Mesjasz-Przybylowicz J, Nakonieczny M, Migula P, Augustyniak M, Tarnawska M, Reimold WU, Koeberl C, Przybylowicz W, Glowacka E (2004) Uptake of cadmium, lead, nickel and zinc from soil and water solutions by the nickel hyperaccumulator *Berkheya coddii*. *Acta Biol Cracov Ser Bot* 46:75–85
- Muller G (1969) Index of geoaccumulation in sediments of the Rhine river. *Geochem J* 2:109–118
- Parewa HP, Yadav J, Rakshit A, Meena VS, Karthikeyan N (2014) Plant growth promoting rhizobacteria enhance growth and nutrient uptake of crops. *Agric Sustain Dev* 2(2):101–116
- Pence NS, Larsen PB, Ebbs SD, Letham DLD, Lasat MM, Garvin DF, Eide D, Kochian LV (2000) The molecular physiology of heavy metal transport in the Zn/Cd hyperaccumulator *Thlaspi caerulescens*. *Proc Natl Acad Sci U S A* 97:4956–4960
- Pierzynski GM, Sims JT, Vance GF (2000) *Soils and environmental quality*. CRC Press, Boca Raton, pp 155–207
- Pingoliya KK, Dotaniya ML, Lata M (2014a) Effect of iron on yield, quality and nutrient uptake of chickpea (*Cicer arietinum* L.). *Afr J Agric Res* 9(37):2841–2845
- Pingoliya KK, Mathur AK, Dotaniya ML, Jajoria DK, Narolia GP (2014b) Effect of phosphorus and iron levels on growth and yield attributes of chickpea (*Cicer arietinum* L.) under agroclimatic zone IV A of Rajasthan, India. *Legum Res* 37(5):537–541
- Pingoliya KK, Mathur AK, Dotaniya ML, Dotaniya CK (2015) Impact of phosphorus and iron on protein and chlorophyll content in chickpea (*Cicer arietinum* L.). *Legum Res* 38(4):558–560
- Rajendiran S, Dotaniya ML, Coumar MV, Panwar NR, Saha JK (2015) Heavy metal polluted soils in India: status and countermeasures. *JNKVV Res J* 49(3):320–337
- Rana L, Dhankhar R, Chhikara S (2010) Soil characteristics affected by long term application of sewage wastewater. *Int J Environ Res* 4(3):513–518
- Reed SC, Crites RW, Middlebrooks EJ (1995) *Natural systems for waste management and treatment*. McGraw-Hill, New York
- Roberts TL (2014) Cadmium and phosphorous fertilizers: the issues and the science. *Procedia Engin* 83:52–59
- Rusan MJM, Hinnawi M, Rousan L (2007) Long term effect of wastewater irrigation of forage crops on soil and plant quality parameters. *Desalination* 215(1-3):143–152

- Saha JK, Panwar N, Srivastava A, Biswas AK, Kundu S, Rao AS (2010) Chemical, biochemical, and biological impact of untreated domestic sewage water use on Vertisol and its consequences on wheat (*Triticum aestivum*) productivity. *Environ Monit Assess* 161(1-4):403–412
- Saha JK, Rajendiran S, Coumar MV, Dotaniya ML, Kundu S, Patra AK (2017) Remediation and management of polluted sites. In: Saha JK, Rajendiran S, Coumar MV, Dotaniya ML, Kundu S, Patra AK (eds) *Soil pollution - an emerging threat to agriculture*. Springer, Singapore, pp 317–372
- Salt DE, Blaylock M, Kumar Nanda PBA, Dushenkov V, Ensley BD, Chet I, Raskin I (1995) Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. *Biotechnology* 13:468–474
- Sharma MM, Sharma YK, Dotaniya ML (2014a) Effect of press mud and FYM application with zinc sulphate on yield of hybrid rice. *J Environ Agric Sci* 1:1–4
- Sharma MM, Sharma YK, Dotaniya ML, Kumar P (2014b) Effect of different levels of FYM, press mud and zinc sulphate application on soil properties. *J Plant Dev Sci* 6(3):455–459
- Sims GK (2006) Nitrogen starvation promotes biodegradation of N-heterocyclic compounds in soil. *Soil Biol Biochem* 38:2478–2480
- Singh B (2002) Soil pollution and its control. In: Sekhon GS, Chhonkar PK, Das DK, Goswami NN, Narayanaswamy G, Poonia SR, Rattan RK, Sehgal J (eds) *Fundamental of soil science*. Ind Soc Soil Sci, New Delhi, pp 499–514
- Singh R, Gautam N, Mishra A, Gupta R (2011) Heavy metals and living systems: an overview. *Ind J Pharmacol* 43(3):246–253
- Singh M, Dotaniya ML, Mishra A, Dotaniya CK, Regar KL (2016) Role of biofertilizers in conservation agriculture. In: Bisht JK, Meena VS, Mishra PK, Pattanayak A (eds) *Conservation agriculture: an approach to combat climate change in Indian Himalaya*. Springer, Singapore, pp 113–134
- Smith LA, Means JL, Chen A, Alleman B, Chapman CC, Tixier JS, Brauning SE, Gavaskar AR, Royer MD (1995) Remedial options for metals-contaminated sites. Lewis Publishers, Boca Raton
- Tabata K, Kashiwagi S, Mori H, Ueguchi C, Mizuno T (1997) Cloning of a cDNA encoding a putative metal-transporting P-type ATPase from *Arabidopsis thaliana*. *Biochim Biophys Acta* 1326:1–6
- Tangahu BV, Abdullah SRS, Basri H, Idris M, Anuar N, Mukhlisin M (2011) A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. *Int J Chem Eng*. <https://doi.org/10.1155/2011/939161>
- Tchounwou PB, Patlolla AK, Centeno JA (2003) Carcinogenic and systemic health effects associated with arsenic exposure—a critical review. *Toxicol Pathol* 31(6):575–588
- Tchounwou PB, Centeno JA, Patlolla AK (2004) Arsenic toxicity, mutagenesis and carcinogenesis – a health risk assessment and management approach. *Mol Cell Biochem* 255:47–55
- Thomine S, Wang R, Ward JM, Crawford NM, Schroeder JI (2000) Cadmium and iron transport by members of a plant metal transporter family in *Arabidopsis* with homology to Nramp genes. *Proc Natl Acad Sci U S A* 97:4991–4996
- USDHHS (1999) Toxicological profile for lead. United States Department of Health and Human Services, Atlanta
- USEPA (1991) US environmental protection agency. Annual reports FY 1990, USEPA report 540/8-91/067. USEPA, Washington, DC
- Van der Zaal BJ, Neuteboom LW, Pina JE, Chardonnens AN, Schat H, Verkleij JAC, Hooykaas PJJ (1999) Overexpression of a novel *Arabidopsis* gene related to putative zinc-transporter genes from animals can lead to enhanced zinc resistance and accumulation. *Plant Physiol* 199:1047–1055
- Vazquez MD, Poschenrieder C, Barcelo J, Baker AJM, Hattton P, Cope GH (1994) Compartmentation of zinc in roots and leaves of the zinc hyperaccumulator *Thlaspi caerulescens* J & C Presl. *Bot Acta* 107:243–250

- Velazquez E, Silva LR, Ramírez-Bahena MH, Peix A (2016) Diversity of potassium-solubilizing microorganisms and their interactions with plants. In: Meena VS, Maurya BR, Verma JP, Meena RS (eds) Potassium solubilizing microorganisms for sustainable agriculture. Springer, New Delhi, pp 99–110
- Verret F, Gravot A, Auroy P, Leonhardt N, David P, Nussaume L, Vavasseur A, Richaud P (2004) Overexpression of AtHMA4 enhances root-to-shoot translocation of zinc and cadmium and plant metal tolerance. *FEBS Lett* 576:306–312
- Vishnoi SR, Srivastava PN (2008) Phytoremediation-green for environmental clean. In: The 12 world lake conference, pp 1016–1021
- Wei BG, Yang LS (2010) A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchem J* 94:99–107
- WHO (1982) World Health Organization toxicological evaluation of certain food additives. Joint FAO/WHO expert committee on food additives, WHO Food additive Series no. 683. World Health Organization, Geneva
- Williams LE, Pittman JK, Hall JL (2000) Emerging mechanisms for heavy metal transport in plants. *Biochim Biophys Acta* 1465:104–126
- Wuana RA, Okieimen FE (2011) Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecol.* <https://doi.org/10.5402/2011/402647>
- Xiong YH, Yang XE, Ye ZQ, He ZL (2004) Characteristics of cadmium uptake and accumulation by two contrasting ecotypes of *Sedum alfredii* Hance. *J Environ Sci Health* 39:2925–2940
- Yang MJ (2002) Copper hyperaccumulation in *Elsholtzia splendens* and its mechanisms. PhD dissertation, Zhejiang University
- Yang XE, Long XX, Ni WZ (2002) Physiological and molecular mechanisms of heavy metal uptake by hyperaccumulating plant species. *J Plant Nutr Fert* 8:8–15
- Yang X, Fenga Y, He Z, Stoffella PJ (2005) Molecular mechanisms of heavy metal hyperaccumulation and phytoremediation. *J Trace Elem Med Biol* 18(4):339–353
- Zhuang P, Yang QW, Wang HB, Shu WS (2007) Phytoextraction of heavy metals by eight plant species in the field. *Water Air Soil Pollut* 184:235–242