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# Heavy Metal Toxicities in Soils and Their Remediation

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## Abstract

Pollution of soils with heavy metals from various sources has become a common feature across the globe due to increase in anthropogenic activities and industrial development and has attracted the attention of all stakeholders. In spite of the differential tolerance of plants to heavy metal toxicities, impairment in the productivity of most of the agricultural crops is steadfast throughout the globe. Bio-transfer of these metals remains unabated from polluted sites and even through animal milk and dung. The remediation methods are broadly grouped into engineering, electrokinetics, and bioremediation. These have their own merits and demerits, but the bioremediation is quite effective and the current results are encouraging. Therefore, the sources of heavy metals to soils (including pathways), their effect on soils and plants, and few of the proven phytoremediation methods have been elaborated here.

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## 7.1 Introduction

With rapid industrialization and urbanization, several environmental issues including soil pollution are attracting global attention. Industries do generate enormous quantities of wastes containing heavy metals, hydrocarbons, pesticides, and other toxic chemicals; those are usually dumped in the nearby open area/soil/water. Metallic element with relatively high density which is toxic even at suboptimal concentration is commonly referred to as “heavy metals” (Lenntech Water Treatment and Air Purification 2004), comprises a group of metals and metalloids with atomic

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density greater than water or more than  $4 \text{ g cm}^{-3}$ , or more (Hawkes 1997). Heavy metals enter the soil through soil-applied agrochemicals, food processing waste, detergents, cosmetics and construction waste, etc. These can accumulate in soil and groundwater above toxic levels, thereby posing grave risk to human health. Heavy metals threatening the ecosystem are mainly lead (Pb), mercury (Hg), chromium (Cr), nickel (Ni), arsenic (As), cadmium (Cd), copper (Cu), and zinc (Zn). Soil contamination occurs due to addition of heavy metals through industrialization, urbanization and agricultural intensification to a limited extent (Zhou 1995; Gowd et al. 2010; Luo et al. 2011). Extensive damage to soils and crops with these metals has been reported from several countries, viz., Australia (Markus and Mcbratney 1996), Hong Kong (Chen et al. 1997), Saudi Arabia (Al-Shayeb and Seaward 2001), Croatian capital of Zagreb (Romic and Romic 2003), Turkey (Aydinalp and Marinova 2003), Bolivia (Miller et al. 2004), Thailand (Zarcinas et al. 2004), Jordan (Al-Khashman 2007), India (Sharma et al. 2007; Chopra et al. 2009), Iran (Shakeri et al. 2009), Greece (Christoforidis and Stamatis 2009), Algeria (Mass et al. 2010), Nigeria (Ololade 2014), Nanxun County, Southeast China (Zhao et al. 2015), etc.

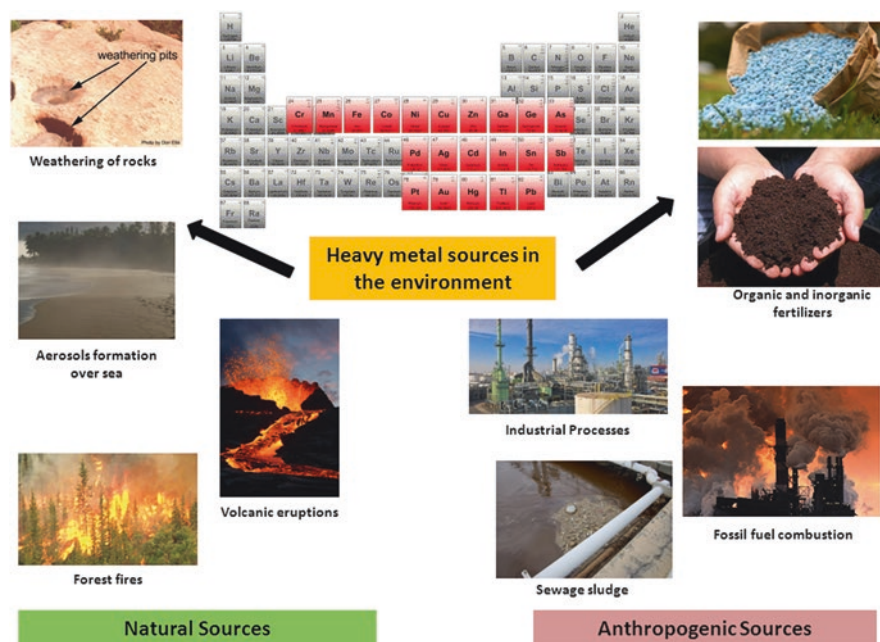
Soil acts as the sink for several heavy metals, and most of them do undergo neither microbial nor chemical degradation (Kirpichtchikova et al. 2006) unlike organic contaminants, and their concentrations persist in soils for long periods (Adriano 2003). Heavy metal-contaminated soil may pose risks to humans as well as the ecosystem through direct contact or transport through the food chain, drinking water (safety and marketability), phytotoxicity and/or decline in land usability for agricultural production, etc. (McLaughlin et al. 2000a, b; Ling et al. 2007).

Noticing heavy metal contamination in the soil is rather difficult since these are neither rich in color nor have odor. The impact of the pollution is a creeping poison as its damage to the soil environment could not be explicitly quantified in temporal means. Whenever the limit of the pollutants exceeds the maximum allowable limit for either crop/animal/soil biota, the repercussions become eminent. Therefore, Wood (1974) termed heavy metal contamination as chemical time bombs.

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## 7.2 Sources and Forms of Heavy Metals

There are several sources for heavy metal contamination in soils (Fig. 7.1). The origin of heavy metal pollution can either be natural and/or anthropogenic sources besides other means. Though considered to be associated with industrialization, roadways and automobiles too ingest heavy metals to the soils. Zinc, copper, and lead released from road travel account for majority of the total metals in road runoff (Mishra and Shukla 2014). On the other hand, the loading could be due to excessive fertilizer, chemical usage, irrigation, atmospheric deposition, and pollution by waste materials. Organic manures also play role in their availability, e.g., the chelation of free metal ions regulates their availability and mobility in soils and/or water through the formation of metal-humate complexes with varying degrees of stability (Sanyal 2001; Sinha and Bhattacharya 2011). Heavy metals are present in the soil ecosystem as i) easily available to plants in dissolved form (in soil solution) and



**Fig. 7.1** Sources of heavy metals in soils

exchangeable form (in organic and inorganic components) and ii) long-term availability to plants and present in soil as lattices of soil minerals and as insoluble precipitates, e.g., Cd, a toxic nonessential metal, has become an environmental hazard to various forms of life on the earth. Generally, soil contamination occurs through either point source or diffuse pollution.

The rate of application of the contributors and its concentration are the chief factors for enhancing heavy metal contamination of agricultural soil besides the soil characteristics itself. Applications of soil amendments such as compost refuse as well as nitrate fertilizers too contribute to the heavy metal pollution, limiting itself. Notwithstanding to this fact, sewage sludge has more pronounced effect than the above (Table 7.1).

Wastewater irrigation-based heavy metal contamination is a serious concern as it contaminates the agricultural produce. The inadvertent ingestion of contaminated water is also a potential pathway (Shukla and Tiwari 2013). As assessment made at Jabalpur, MP showed the extent of pollution due to use of sewage water in soil and plants from Jabalpur, Morena, Gwalior, Katni, Sagar, Dhar, Indore, and Dewas districts of Madhya Pradesh. The sludge samples were neutral to alkaline in reaction and rich in Zn, Cu, N, and K, with a tendency to accumulate more in the surface layer. The pollutant content was relatively higher in Gwalior as compared to Morena. Plants irrigated with the sewage either in Khan Nalla near Indore or Dewas factory area had higher content of heavy metal. Further, average contents of heavy metals in Katni were relatively higher in cauliflower as compared to brinjal. Although the

**Table 7.1** Range of heavy metal concentrations ( $\mu\text{g g}^{-1}$ ) in agricultural amendments

Agricultural amendments	Range of metals ( $\mu\text{g g}^{-1}$ )					
	Cr	Ni	Cu	Zn	Cd	Pb
Sewage sludge	8.40–600	6–5300	50–8000	91–49,000	<1–3410	2–7000
Compost refuse	1.8–410	0.9–279	13–3580	82–5894	0.01–100	1.3–2240
Farmyard manure	1.1–55	2.1–30	2–172	15–556	0.1–0.8	0.4–27
Phosphate fertilizers	66–245	7–38	1–300	50–1450	0.1–190	4–1000
Nitrate fertilizers	3.2–19	7–34	–	1–42	0.05–8.5	2–120
Lime	10–15	10–20	2–125	10–450	0.04–0.1	20–1250
Pesticides	–	–	–	–	–	11–26

Modified from Ross (1994)

**Table 7.2** DTP-extractable heavy metal contents ( $\text{mg kg}^{-1}$ ) in sewage-polluted soils

Location	Cr	Cd	Ni	Pb
Uthamapalayam	0.04	0.15	0.09	2.27
Vedapatti	0.06	0.11	0.09	1.61
Palapatti	–	0.12	0.17	1.84
Vachinampalayam	–	0.11	0.04	3.21

Source: Stalin (2011)

contents of Zn and Pb were decreased, distribution of pollutant elements was irregular. By contrast, sewage-irrigated soil samples in the state of Tamil Nadu have shown insignificant buildup of heavy metals except Pb (Table 7.2) which was still below the toxic limit (Stalin 2011). The pathways for the entry of heavy metals to soils can broadly be divided into “solid wastes to soil pathway” and “agricultural supplies to soil pathway” which are discussed as under.

### 7.2.1 Solid Wastes to Soils Pathway

Heavy metals with varied complex composition arising from a variety of solid wastes are known to pollute the agroecosystem. Among all, mining for various purposes and industrial solid waste contamination are considered as the major culprits. Mining activities, particularly for extraction and manufacturing of metal products, result in pollutant generation released into the nearby agricultural soils (Parth et al. 2011). When the industrial wastes are piled, facilitation of sunlight, rain, and washing helps easy movement of heavy metals which later spread to the surrounding water and soils. Cr as metal pollutant exists as  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  in minerals in soils of chromite mining area of Kaliapani, Sukinda, Odisha, while the latter is highly mobile in soil and causes phytotoxicity in plants. More than 90% of soil samples collected from villages within 1 to 10 km radius from the chromite mines were polluted with Cr at an above toxic limit considering 0.05 ppm  $\text{Cr}^{6+}$  (Shukla and Tiwari 2013).



**Fig. 7.2** Industrial effluents and soils irrigated with sewage water

**Table 7.3** DTPA-extractable metal status in the soils ( $\text{mg kg}^{-1}$ ) of industrial effluent irrigated areas

Nature of contaminated site	DTPA metal status ( $\text{mg kg}^{-1}$ )			
	Cd	Ni	Fe	Pb
Dye	0.53	2.16	250	3.98
Gold processing	2.34	2.17	238	5.28
Sewage	1.90	6.69	216	15.01
Foundry	0.43	19.83	270	2.87
Electroplating	0.37	2.93	221	3.61
Textile	0.48	2.57	56	2.29
Painting	0.11	31.35	216	4.98
Casting	0.46	1.28	207	2.68

Source: Shukla and Behera (2012)

The soil irrigated with industrial effluents (Fig. 7.2), viz., casting, painting, and sewage effluents, had the highest metal status (Shukla and Behera 2012) and the content varied widely with the industry (Table 7.3). The highest DTPA-Ni was obtained in painting industrial effluent irrigated areas ( $31.35 \text{ mg kg}^{-1}$ ), Cd in gold processing effluent irrigated areas ( $2.34 \text{ mg kg}^{-1}$ ), and Pb in sewage effluent

**Table 7.4** Regulatory guidelines for some heavy metals ( $\mu\text{g g}^{-1}$ ) in agricultural soils

Standards	Cd	Cu	Pb	Zn	Mn	Ni	Cr
Indian standard (Awashthi 2000)	3–6	135–270	250–500	300–600	--	75–150	--
European union standards (EU 2002)	3	140	300	300	--	75	150

irrigated soils ( $15.01 \text{ mg kg}^{-1}$ ). Among the metals, the order of availability was  $\text{Ni} > \text{Pb} > \text{Cd}$ . Similarly the highest total Pb was obtained from gold processing and sewage effluent irrigated area ( $354$  and  $344 \text{ mg kg}^{-1}$ ), Cd in painting ( $11 \text{ mg kg}^{-1}$ ) and sewage-irrigated areas ( $9.81 \text{ mg kg}^{-1}$ ), and Ni in electroplating ( $317 \text{ mg kg}^{-1}$ ) which reflected in plant content too. Higher Ni in foundries ( $512 \text{ mg kg}^{-1}$ ) and electroplating ( $475 \text{ mg kg}^{-1}$ ), Pb in dye ( $498 \text{ mg kg}^{-1}$ ), textile ( $500 \text{ mg kg}^{-1}$ ), Cd in sewage irrigation ( $35.6 \text{ mg kg}^{-1}$ ), and sewage effluent irrigated areas ( $469 \text{ mg kg}^{-1}$ ) were also observed. The sewage-irrigated soils of Amritsar and Jalandhar were analyzed to contain  $0.318$  and  $3.34 \text{ mg kg}^{-1}$  DTPA-Cd and Pb, respectively (Shukla and Tiwari 2014) (Table 7.4).

## 7.2.2 Agricultural Supplies to Soil Pathway

Pollutants from agrochemical sources include fertilizers (Aydinalp and Marinova 2003), manures (Mullins et al. 1982), herbicides (Shrotriya et al. 1984), etc. which are directly applied on the soils for optimum crop productivity. Also the fertilizers and manures accidentally add arsenic, uranium, and vanadium through some phosphatic fertilizers to the soil. Besides, chromium, lead, mercury, and nickel are also added to the soil inadvertently. Small amounts of heavy metals are found in rock phosphate (Mortvedt 1995; Dissanayake and Chandrajith 2009; Lema et al. 2014). Animal manure is the main organic fertilizer that may entertain heavy metals. Heavy metals in biosolids exist in either inorganic form or organic complex form and could affect their chemical reactions in the soil. Repeated applications of these fertilizer sources aggravate their accumulation. Some countries have set tolerance limits on heavy metal in soils, and most of the fertilizer regulations relate Cd limits to P concentrations.

## 7.3 Basic Soil Chemistry and Risk of few Important Heavy Metals

The abundance of heavy metals at contaminated sites in the ascending order of Hg, Cu, Cd, Zn, As, Cr, and Pb (USEPA, 1996) is responsible for impairment in the crop production either due to their bioaccumulation or biomagnification when these enter the food chain from soil to higher animals besides groundwater contamination too. Notwithstanding to this fact, the fate and its transport to soil depend on its chemical form and speciation. After reaching the soil, these are adsorbed and redistributed

into various forms with degree of toxicity (Shiowatana et al. 2001; Buekers 2007). The distribution of heavy metal in soil is controlled by (i) mineral dissolution and precipitation; (ii) adsorption, desorption, and ion exchange (iii); aqueous complexation; (iv) biological mobilization and immobilization; and (v) plant uptake (Levy et al. 1992).

### 7.3.1 Lead

The major forms of Pb are lead oxides, ionic lead, Pb(II), hydroxides, and lead-metal oxyanion complexes that are released into the soil environment. Under reduced soil conditions, sulfide and lead sulfide (PbS) are considered as the most stable solid forms. In general, the lead accumulation is confined to leafy vegetables and on the surface of root crops. Plants grown in lead contaminated soils do not accumulate excess amount of lead. However, direct eating of contaminated soil may lead to Pb poisoning. Lead content in farm produce less than 300 ppm is generally considered as safe. The risk of lead poisoning through the food chain increases as the lead level rises above this concentration (Wuana and Okieimen 2011).

### 7.3.2 Chromium

Chromium (VI) is the chief form commonly distributed at contaminated sites, although Cr (III) oxidation state is not uncommon, depending on pH and redox conditions. Cr (VI) is more toxic and mobile than Cr (III). Under anaerobic conditions in presence of organic matter, sulfide and ferrous ions, Cr (III) gets reduced to Cr (VI). The mobility of Cr is determined by the sorption characteristics of the soil. The leachability of Cr (VI) is proportional to soil pH. Cr is highly toxic for plants and causes various deleterious impacts on its growth and metabolism.

### 7.3.3 Arsenic

Arsenic could be seen in several oxidation states, viz., -III, 0, and III to V (Smith et al. 1995). Under aerobic conditions, As (V) dominates and under reducing conditions As (III) dominates. Under extreme reducing conditions, elemental arsenic and arsine and AsH<sub>3</sub> may be present. A nonessential and generally toxic to plants, arsenic, intercepts the root through inhibition of root extension and proliferation. Upon translocation to the aerial parts, it inhibits plant growth by arresting biomass accumulation and loss in fertility (Garg and Singla 2011).

### 7.3.4 Cadmium

Zn has the chemical similarity with Cd as a divalent Cd (II), and their intersubstitution may cause the malfunctioning of metabolic processes (Campbell 2006).

### 7.3.5 Mercury

Hg (highly toxic for plants) usually exists in mercuric ( $\text{Hg}^{2+}$ ), mercurous ( $\text{Hg}_2^{2+}$ ), elemental ( $\text{Hg}^0$ ), or alkylated form (methyl/ethyl mercury). Stability of Hg depends upon the redox potential and pH. Under oxidizing conditions, the mercurous and mercuric mercury are more stable, while organic and/or inorganic Hg may be reduced to elemental form under mild reducing conditions. This may then be converted to most toxic alkylated forms by biotic or abiotic processes. Sorption to sediments, soils, and humic materials is the important mechanism for the removal of Hg from solution (Wuana and Okieimen 2011).

## 7.4 Impact of Heavy Metals on Soils

### 7.4.1 Soil Microbial Activity

The environmental risk of heavy metal pollution on the functioning of soil microorganisms adjacent to large industrial complexes is an absolute necessity in the current industrial scenario. Generally poisoning and inactivation of enzyme systems in soil is considered as the heavy metal toxicity (Rai et al. 1981). For example, Cd concentration of  $0.16 \mu\text{g g}^{-1}$  protects 95% of soil invertebrates and 85% at  $0.8 \mu\text{g g}^{-1}$  (van Straalen and Denneman 1989). A decrease in the population of actinomycetes and bacteria was noticed by Hiroki (1992) in a heavy metal-contaminated (Cd, Zn, and Cu, 1.1–2.7, 234–571, and 310–751  $\text{mg kg}^{-1}$  soil, respectively) paddy field. However, fungi remained unaffected. The degree of intolerance to heavy metals appears to be: fungi > bacteria > actinomycetes.

Although enzyme activity is related to soil property from biological organisms, some stimulatory effects on microbial populations were noted in a sandy soil but not in clay soil. However, irrespective of the soil, activities of urease and nitrate reductase were inhibited. As an exception, amidase activity was inhibited only at higher concentration (Hemida et al. 1997). Heavy metal stress in copper mining wasteland was exhibited in the form of microbial ecophysiological parameters, viz., ratio of microbial biomass C ( $C_{\text{mic}}$ )/organic C ( $C_{\text{org}}$ ) and metabolic quotient ( $q\text{CO}_2$ ) in red soil area, southern China (Liao et al. 2005). The microbial biomass C was negatively affected by the elevated metal levels (Wang et al. 2007). Denitrifying microbial community adapted to elevated levels of Pb by selecting for metal-resistant forms of nitrite reductases and Pb had marked impacts on the microbial community even at very low concentrations (Sobolev and Begonia 2008). However, the total bioactivity, richness, and microbial diversity decreased with concentration of heavy metal in Cd contaminated or uncontaminated soils from Hunan province of China (Xie et al. 2016).



## 7.4.2 Impact on the Plants

Anthropogenic activities are the main source of pollutants to soils, and the growth of plants growing on these soils gets impaired when the concentrations build up above the toxic limits (Chibuike and Obiora 2014). The capability of plants to accumulate essential metals equally enables them to acquire other nonessential metals (Djingova and Kuleff 2000). Plant growth is affected when the concentration exceeds optimal levels. High metal concentration had direct toxic effects, i.e., inhibition of activities of cytoplasmic enzymes and damage to cell structures through oxidative stress (Assche and Clijsters 1990; Jadia and Fulekar 2009); besides, soil microbial enzyme activities useful for plant metabolism may also be hampered. Indirectly the replacement of essential nutrients at cation exchange sites of plants may also occur (Taiz and Zeiger 2002). These toxic effects lead to a decline in plant growth and ultimately the mortality of plants occurs.

## 7.4.3 Heavy Metal Continuum in Soil-Water-Crop-Human System

Heavy metals in urban soils may enter into the human body either through skin absorption, inhalation of dust, etc. Soil, water, food, and blood samples from the Cherlapally (Uppal mandal), Patancheru and Ramachandrapuram (Ramachandrapuram mandal), and Munagala (Munagala mandal) in Ranga Reddy, Nalgonda, and Medak districts (surrounded by highly polluted industries), where farmers used industrial effluent for irrigation, were analyzed by Surendra-Babu et al. (2012) for heavy metals, viz., Pb, Cd, Cr, Co, and Ni (Table 7.5). Although irrigation water samples were within the safe limits except Co in Patancheru irrigated water, they may become toxic if they enter into food chain even at very low concentrations as they could bind certain proteins and essential elements, thereby rendering them in exhibiting normal function.

**Table 7.5** Status of heavy metal contents in soil, water, plants, and human in polluted areas

Element	Water (mg kg <sup>-1</sup> )	Soil (mg kg <sup>-1</sup> )	Rice (mg kg <sup>-1</sup> )	Human beings (%)
Pb	0.294 (Tr.)	1.24(0.44)	15.83(3.17)	79 (100)
Cd	0.010(Tr.)	0.042(0.021)	1.92(0.31)	92(100)
Co	0.080(Tr.)	0.182(0.140)	5.21(0.12)	84(100)
Ni	0.200(Tr.)	0.502(0.226)	9.28(0.89)	72(100)
Ca	39.86 (29.03)	2.64(0.57)	14.39(1.44)	24 (92)
Fe	Traces (Tr.)	3.59(7.82)	26.81(22.75)	100(100)

Figures in parenthesis are for nonpolluted areas. Source: (Surendra-Babu et al. 2012)

**Table 7.6** Heavy metal concentrations in blood serum, plasma, milk, and dung samples (n = 5)

Week	Part	Heavy metal concentration (mg kg <sup>-1</sup> )			
		Pb	Cd	Ni	Cr
Background	Serum	0.014	ND	ND	ND
	Plasma	0.0216	ND	0.138	0.141
	Milk	0.003	0.029	ND	0.125
	Dung	32.6	1.36	5.72	0.684
2nd week	Serum	0.007	ND	ND	ND
	Plasma	0.552	0.092	1.532	0.962
	Milk	ND	0.05	9.30	9.35
	Dung	34.8	2.28	6.21	8.18
4th week	Serum	ND	0.044	ND	ND
	Plasma	1.211	0.154	0.930	0.994
	Milk	ND	0.05	4.34	7.95
	Dung	44.4	1.32	48.72	13.76

ND not detectable; Source: Stalin et al. (2014)

#### 7.4.4 Soil-Animal-Milk-Human Continuum for Heavy Metals

The heavy metal contents (Cd, Pb, Cr, and Ni) were analyzed in blood, plasma, milk, and dung of Jersey cows when fed with Bajra-Napier grass grown in Ukkadam sewage farm of Coimbatore district (Stalin et al. 2014). The contents of heavy metals followed the order: dung > milk > blood (Table 7.6). In the milk samples, accumulation of heavy metals has shown an increasing trend from 10th day onward. Ni was absent up to 4th day and thereafter showed a buildup. The Cd content was nearly doubled after 10th day and remained so. The Cr content was initially low, thereafter a constant buildup with highest Cr (22.5 mg kg<sup>-1</sup>) at 22nd day. In the serum samples, Ni and Cr could not be detected initially. Cd accumulation was observed during the 3rd and 4th week. Ni and Cr accumulated in the plasma at the end of the 4th week; Ni and Cr content of the plasma were seven times more than that of initial value. Similarly, Pb also increased in the plasma from the 2nd week itself. During the 7th day, the dung sample recorded the highest content of heavy metals and remained constant.

### 7.5 Remediation Measures

Remediation measures of contaminated soils are classified into in situ and ex situ treatment (USEPA 2007). In in situ, treatment of soil is at its original place, whereas in ex situ, the soil which is contaminated is moved, excavated, and removed from the site. Yao et al. (2012) have reviewed the remediation technologies (including physical, chemical, and biological remediation). Few proven remediation methods are discussed here under.

## 7.5.1 Engineering Remediation

Physical or chemical methods to manage heavy metal contamination of soils are referred to as engineering remediation. Soil washing, phytoremediation techniques, and the principles, advantages, and disadvantages of immobilization are available in Wuana and Okieimen (2011).

## 7.5.2 Physical Remediation

### 7.5.2.1 Replacement of Contaminated Soil, Soil Removal, and Soil Isolation

Complete replacement of contaminated soil with addition of large amount of non-contaminated soil or blending with the latter is referred as soil breeding. Through soil removal the contaminated soil is renewed with the clean soil if the area is very small. But, with additional engineering measures, soil isolation of the contaminated soil from the uncontaminated soil (Zheng et al. 2002) may also prove beneficial. This method needs huge cost and manpower.

### 7.5.2.2 Thermal Desorption of Soil

The thermal desorption utilizes the pollutant's volatility character by heating the contaminated soil through steam, microwave, and infrared radiation (e.g., Hg, As). These volatile metals are collected using vacuum pressure and are subsequently removed from the soil (Li et al. 2010). The traditional thermal desorption can be separated into high-temperature desorption according to the temperature (320 ~ 560 °C) and low-temperature desorption (90 ~ 320 °C). However, being laborious and costly, this method finds limited application.

## 7.5.3 Chemical Remediation

Chemical leaching, fixation, electrokinetic remediation, vitrification, etc. are referred to as chemical remediation. The process of vitrification involves heating of the soil at very high temperature, e.g., 1400–2000 °C, for the pollutant to get volatilize or decompose. Important chemical remediation measures are as follows.

### 7.5.3.1 Soil Leaching/Chemical Leaching

Washing the contaminated soil with specific reagents to remove the heavy metal complex is the basis of soil leaching and soluble irons adsorbed on the solid phase particles. After separating from the soil, heavy metals are recycled from extracting solution. The various ionic forms of the heavy metals are transferred from soil to liquid phase and then recovered from the leachate. The leachate includes inorganic eluent, chelation agents, surfactant, etc. Chief chelating agents are ethylenediaminetetraacetic acid and citric acid in remediating the high permeability soil and tartaric acid to a little extent for average contamination (Wuana et al. 2010). Na<sub>2</sub> EDTA solutions were more effective than Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> as the former extracted lead over zinc and cadmium but to a limited extent on chromium. Cadmium and, especially, zinc

removal by a 0.01 M Na<sub>2</sub> EDTA solution were improved considerably by inclusion of 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (Abumaizar and Smith 1999).

### 7.5.3.2 Adsorption/Chemical Fixation

Addition of external reagents into the contaminated soil to form insoluble forms to decrease the migration of heavy metals to the environment is referred to as chemical fixation (Zhou et al. 2004) as their removal in polluted areas is very complex as they persist in soils for very long periods. It is based on the fact that almost all heavy metal ions can be fixed and adsorbed by clay mineral (bentonite, zeolite, etc.), a steel slag, furnace slag, etc. (Wang and Zhou 2004). For example, zeolites, the crystalline aluminosilicates (Ramesh et al. 2011), with large cation exchange capacity attract positive-charged ions and widely used for sequestration of cationic pollutants (Kumar et al. 2007). They offer absorption sites for small molecules and increase ion exchange sites in soils due to their porous structure. Zeolites can retain heavy metals in soil (Mühlbachová and Šimon 2003).

Clinoptilolite, a zeolite, is stable up to pH 2 (Ming and Mumpton 1989). Zeolite affinity to heavy metals has also been demonstrated by Tsadilas (2000). Alexander and Christos (2003) found that its sorption is up to 30 times more Pb than the soil. Based on the value of maximal sorption capacity of zeolite, addition of just 1% zeolite can retain up to 750 mg Pb kg<sup>-1</sup> soil. It has high efficiency at range of 3–5 pH too (Alexander and Christos 2003). The potential of organo-zeolitic systems to revegetate metal polluted soils was demonstrated by Leggo et al. (2006).

### 7.5.3.3 Electrokinetic Remediation

Soil electrokinetic remediation (Kim et al. 2001) is a new economically effective technology utilizing various particle and fluid interactions governing the dynamics of an electrokinetic system. These interactions are a direct result of applied electrical potential across the system and are identified as electrokinetic phenomena. The physiochemical composition of clay particles in soils is the strong basis for utilizing electrokinetic remediation in soils. Use of clay particles could be an innovative solution for efficient removal of contaminants from soils to solve groundwater and soil pollution, as they have a net negative surface charge.

The principle is that the DC voltage is applied to form the electric field gradient on both sides of the electrolytic tank which contains the contaminated soil; contaminants in the soil are taken to the processing chamber to reduce the contamination, which is located at the two polar sides of electrolytic cell, through the way of electromigration, electric seepage, or electrophoresis. This method applies to low permeable soil (Hanson et al. 1992). Removal of heavy metals from clay and sandy soils was reviewed by Virkutyte et al. (2002).

### 7.5.4 Bioremediation

This type of remediation mainly includes phytoremediation and microbial remediation for heavy metal removal from soils. While phytoremediation is a form of bioremediation wherein plants are used to either sequester the environmental

contaminants or convert them to harmless forms (Cunningham and Berti 1993; Raskin et al. 1994, 1997; Salt et al. 1995,1998), a predominant method followed widely (Alkorta and Garbisu 2001; Garbisu and Alkorta 1997; Garbisu et al. 2002; Tangahu et al. 2011; Moosavi and Seghatoleslami, 2013); bioremediation includes all methods and processes to biotransform a contaminated environment to uncontaminated status which primarily refers to use of microbes (Boopathy 2000) or microbial processes to degrade and transform environmental contaminants into harmless or less toxic forms (Garbisu and Alkorta 2003) either be ex situ or in situ. The physical removal of the contaminated material is referred to as ex situ, while treatment of the contaminated material in place is referred to as in situ. In situ bioremediation is one of the most attractive options, of which soil bioventing, the process of supplying oxygen to contaminated soil in hopes of stimulating microbial degradation of contaminants, is a promising technology (Hellekson 1999) wherein indigenous microbes are utilized to biodegrade organic constituents adsorbed to soils in the unsaturated zone.

#### 7.5.4.1 Microbial Remediation

The microorganisms cannot degrade and destroy the heavy metals (Yao et al. 2012), but can affect their migration and transformation. Several mechanisms by which microbes remediate heavy metals include either individually or in combinations of electrostatic interactions, van der Waal forces, redox interactions, extracellular covalent bonding, and precipitation with their cell surfaces which have been reported in the literature. However their efficiency in remediation or the response depends on the concentration and availability of heavy metals (Goblenz et al. 1994). Ex and in situ bioremediation of refractory pollutants by specific microbes is possible (Iranzo et al. 2001), and is an efficient strategy due to its low cost and high efficiency (Rajendran et al. 2003). Sulfate-reducing bacteria were found to modify the form of Cd in sewage-irrigated soils (Jiang and Fan 2008). They can reduce the mobility and bioavailability of contaminants through various ways (Gang et al. 2010). However, acceptable solutions are not guaranteed. Microorganisms that use metals as terminal electron acceptors or reduce metals as a detoxification mechanism could aid in the removal of metals from contaminated environments (Garbisu and Alkorta 2003). *Bacillus pumilus* and *Pseudomonas aeruginosa* were identified as Pb-resistant bacteria (Chen et al. 2011). Highest efficiency of decabromodiphenyl ether removal and metal phytoextraction was obtained by using co-planting of *Sedum alfredii* with tall fescue inoculated with *Bacillus cereus* JP12 in co-contaminated soil at China. Bacterial inoculation increased plant biomass and decabromodiphenyl ether degradation. Soil microbial activity was promoted by planting tall fescue which enhanced degradation and mineralization of BDE-209. Soil microbial activity and community structure were altered during the remediation (Lu and Zhang 2014).

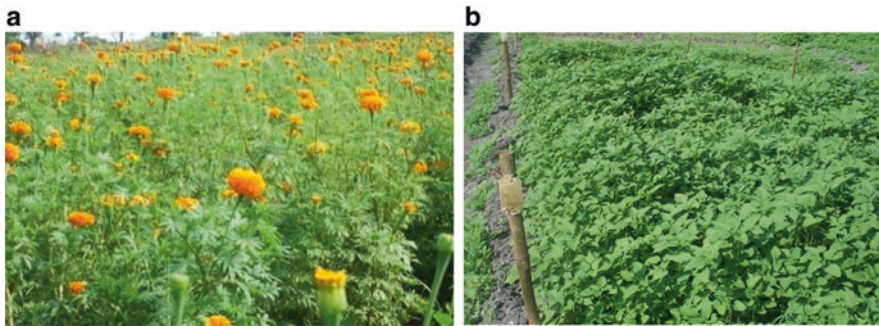
#### 7.5.4.2 Rhizoremediation

Rhizoremediation, an emerging technology for large recalcitrant compounds, is a phytoremediation method involving plants and their rhizosphere microbes, either naturally or through introduction (Gerhardt et al. 2009). In this method, plant

exudates stimulate the survival of bacteria, for an efficient degradation of pollutants involving root, their exudates, rhizospheric soil, and microbes. The spreading of the bacteria and its penetration to soil layers are facilitated by the plant root system. In order to improve the efficiency of phytoremediation or bioaugmentation, inoculation of pollutant-degrading bacteria on plant seed is suggested (Kuiper et al. 2004). Khan (2005) reviewed the role of rhizoremediation of heavy metals in soils. Generally, plant growth-promoting rhizobacteria, P-solubilizing bacteria, and arbuscular mycorrhizal fungi maintain soil fertility in conventional agriculture wherever agrochemicals are used very minimum. The insoluble glycoprotein, glomalin, produced by AM fungi could sequester trace elements and be considered for biostabilization. These phytoextraction strategies need more studies. They can be contaminant degraders (Gerhardt et al. 2009), besides promoting plant growth under stress conditions. The rhizoremediation process can be enhanced with the proper control of factors influencing plant growth as well as microbial activity in the rhizosphere environment (Tang et al. 2010). Plant- and microbe-mediated biotransformation of heavy metals into nontoxic forms and plants and their mechanisms are well known (Dixit et al. 2015). Some of the microorganisms useful in bioremediation of heavy metals are *Flavobacterium* spp., *Rhodococcus* spp., *Pseudomonas* spp., *Alcaligenes* spp., *Arthrobacter* and *Bacillus* spp., *Corynebacterium* spp., *Azotobacter* spp., *Nocardia* spp., *Mycobacterium* spp., *Methosinus* spp., etc. (Girma 2015).

#### 7.5.4.3 Animal Remediation

Animal remediation is in accordance with the characterization of some lower animals by adsorbing, degrading, and migrating the heavy metals and thus minimizing their toxicity. For example, earthworm's activities can increase the availability of soil nutrients in soils which is a well-known fact. Hopkin (1989) has indicated that these earthworms have specificity and capacity to regulate metals in their bodies, but it could be species specific and can even reproduce in metal-contaminated soil (Spurgeon et al. 1994). *Aporrectodea caliginosa* and *Lumbricus rubellus* were found accumulating Zn, Cd, Pb, and Cu in their tissues (Dai et al. 2004). The earthworm species specific to a particular soil types and forms of metal have been reviewed by Nahmani et al. (2007) for specific metal uptake and accumulation. But very little attention has been paid to the impact of earthworms on soil metals either for metal mobility or availability (Sizmur and Hodson 2009). Recent developments in science have demonstrated the presence of metal-tolerant earthworms and change the fractional distribution of heavy metals in contaminated soil too, besides enhancement in the metal availability (Dandan et al. 2007). As they have the potential for bioaccumulation of metals in their chloragogenous tissues, they can serve as soil contamination indicator (Usmani and Kumar 2015). Dabke (2013) has found that earthworms *Eisenia fetida* (Annelida: Oligochaeta) removed heavy metals like chromium via bioaccumulation and also stimulate microbial remediation by increasing bacteria and improving soil aeration. Although *Eisenia fetida* can remove the chromium and cadmium metals, their effectiveness in removing cadmium is more



**Fig. 7.3** Phytoremediation through growing marigold (a) and amaranthus (b)

than chromium (Aseman-Bashiz et al. 2014). In addition, Ni (Kaur and Hundal 2015) and lead (Kaur and Hundal 2015; Prashanth and Prabha 2016) were also taken up by earthworm. Sahu and Sharma (2016) could even find mercury uptake by earthworms *Eudrilus eugeniae* and *Hyperiodrilus africanus* (Ekperusi et al. 2016). The same could remediate diesel-contaminated soils also (Ekperusi and Aigbodion 2015).

#### 7.5.4.4 Phytoremediation

Phytoremediation is a cost-effective, environment-friendly method (Datta and Darkar 2004), an emerging green technology that uses plants to degrade; stabilize from sediment, surface, groundwater, organics, and radionuclides; and remove soil contaminants, for example, *Pteris vittata*. Microbiota from the rhizosphere could enhance phytoremediation, besides the use of genetic engineering (Marques et al. 2009). Plants with rapid biomass gain with high metal uptake are needed (Khan et al. 2000). Gramineous species and cultivars have a wide variation for Al tolerance. In cereal crops, the Al tolerance usually follows rice and rye (*Secale cereale*) > oat (*Avena sativa*) > wheat > barley (Bona et al. 1993). Plants may also be useful for metal decontamination of the polluted soils (Is et al. 2002). Phytoremediation has been grouped into phytoextraction (Lasat, 2002; Mahmood 2010; Sun et al. 2011; Pajević et al. 2016), phyto-degradation (Newman and Reynolds 2004), rhizofiltration (Yadav et al. 2011; Veselý et al. 2011), phytostabilization (China et al. 2014; Garaiyurrebaso et al. 2017), and phytovolatilization (Sakakibara et al. 2010). Among these, phytoextraction is generally most suitable for heavy metal contaminated soils like in the case of arsenic. Phytoextraction can be accomplished by using either tolerant, high-biomass plant species cottonwood (*Populus deltoides* Bartr.), cypress (*Taxodium distichum* L.), eucalyptus (*E. amplifolia* Naudin, *E. camaldulensis* Dehnh, and *E. grandis* Hill), and leucaena (*L. leucocephala* L.) or hyperaccumulator plant species. The latter (Fig. 7.3) has the advantage of producing more concentrated residue, facilitating the final disposal of the contaminant-rich biomass.

### Relative Tolerance of Plants

Plants vary in their sensitivity/tolerance toward heavy metal toxicity. A sophisticated network of defense strategies is essential either to avoid or tolerate heavy metal intoxication. A screening experiment carried out at Tamil Nadu Agricultural University, Coimbatore (Shukla and Behera 2012), to identify the poor, moderate, and hyperaccumulators for the heavy metals indicated that among the food crops, highest fresh biomass yield was recorded with *Amaranthus* species while the lowest biomass for sunflower. The dominance of extractability was in the order of  $Pb > Ni > Zn > Cu > Cd$  in sewage-irrigated soil after harvest. The highest Pb availability was recorded in the soil grown with sorghum ( $16.46 \text{ mg kg}^{-1}$ ) while the lowest in amaranthus ( $7.38 \text{ mg kg}^{-1}$ ). Similarly the Cd availability was ranged from 0.34 to  $0.706 \text{ mg kg}^{-1}$  and highest extractability in cluster bean soils. With regard to Ni, the values varied from 3.47 to  $8.71 \text{ mg kg}^{-1}$ , and the highest extractability was noticed with radish. The soils grown with mustard recorded the higher Zn extractability ( $9.55 \text{ mg kg}^{-1}$ ) followed by amaranthus ( $9.35 \text{ mg kg}^{-1}$ ). Cu availability ranged between 3.50 and  $7.70 \text{ mg kg}^{-1}$ . The highest heavy metal contents such as Pb ( $498 \text{ mg kg}^{-1}$ ), Ni ( $442 \text{ mg kg}^{-1}$ ), Zn ( $516 \text{ mg kg}^{-1}$ ), and Cu ( $193 \text{ mg kg}^{-1}$ ) were recorded in mustard crop. The lowest tissue concentration of Pb was noted with brinjal ( $124 \text{ mg kg}^{-1}$ ), Cd and Ni in tomato ( $7.9$  and  $135 \text{ mg kg}^{-1}$ , respectively), Zn in beans ( $74 \text{ mg kg}^{-1}$ ), and Cu in lablab ( $25.9 \text{ mg kg}^{-1}$ ). Shukla and Behera (2012) used the metal accumulation ratio using total soil metal status and plant tissue concentration to screen the crops for hyperaccumulation (Table 7.7). The crops having

**Table 7.7** Metal accumulation ratio of food crops

Plant sp.	Metal accumulation ratio				
	Pb	Cd	Ni	Zn	Cu
Maize	1.81	0.88	1.88	1.34	1.09
Sunflower	0.77	0.66	1.04	0.32	0.63
Tomato	0.79	0.65	0.74	0.41	0.49
Okra	0.90	0.73	0.76	0.58	0.46
Amaranthus	2.31	0.74	2.14	1.00	1.09
Mustard	2.37	0.73	2.43	1.47	1.20
Spinach	0.88	0.85	1.61	0.87	0.85
Beans	0.66	0.96	0.80	0.21	0.48
Cluster bean	1.00	1.09	0.75	0.32	0.48
Cauliflower	0.63	1.03	0.77	0.41	0.64
Radish	0.67	2.21	0.78	0.21	0.55
Brinjal	0.59	1.14	0.83	0.26	0.52
Thandu keerai	1.83	1.00	2.18	0.71	1.09
Avarai	0.74	0.94	1.00	0.26	0.16
Sorghum	0.77	1.19	0.84	0.32	0.64
Agathi	0.71	1.07	0.77	0.34	0.47
Fodder cowpea	1.10	0.91	1.04	0.23	0.35

Source: Shukla and Behera (2012)



**Table 7.8** Classification of hyperaccumulators and poor accumulators of heavy metals

Heavy metals	Hyperaccumulators	Poor accumulators
Pb	Mustard, amaranthus, maize, cluster bean, fodder cowpea	Brinjal, cauliflower, beans
Cd	Radish, cluster bean, cauliflower, Brinjal, Amaranthus, sorghum, <i>Sesbania</i>	Tomato, sunflower
Ni	Amaranthus, mustard, spinach, maize, cowpea, sunflower	Tomato, okra
Zn	Mustard, Amaranthus, maize	Radish, beans
Cu	Mustard, Amaranthus, maize	Lablab

Source: Shukla and Behera (2012)

a metal accumulation ratio of more than one were taken as hyperaccumulators and are included in Table 7.8.

Among the nonfood crops, the highest biomass yield was recorded with cockscomb (27.9 g pot<sup>-1</sup>) followed by castor (22.9 g pot<sup>-1</sup>), balsam (22.5 g pot<sup>-1</sup>), and globe amaranth (22.1 g pot<sup>-1</sup>) out of the eight crops tested. The poor biomass yield was registered with *Zinnia* (8.08 g pot<sup>-1</sup>). The highest DTPA-extractable Pb (21.05 mg kg<sup>-1</sup>), Ni (9.02 mg kg<sup>-1</sup>), Zn (15.4 mg kg<sup>-1</sup>), Cu (6.40 mg kg<sup>-1</sup>), and Cd (0.926 mg kg<sup>-1</sup>) were recorded in soil grown with castor crop. The lowest metal extractability was noticed with aster (Pb), cockscomb (Cd), globe amaranth (Ni), balsam (Zn), and *Zinnia* (Cu). The tissue heavy metal content varied with test crops, and the order of higher absorption was Pb > Zn > Ni > Cu > Cd. The highest tissue content of Pb and Cu was observed with castor, and the values varied from 151 to 440 mg kg<sup>-1</sup> and 116 to 223 mg kg<sup>-1</sup>, respectively. The absorption of Pb and Cu was the lowest in cockscomb and balsam. With regard to Cd, Ni, and Zn, the highest content was registered with marigold, and the lowest values were noted with cockscomb and aster. The values ranged from 10.4 to 13.3 mg Cd kg<sup>-1</sup>, 141 to 300 mg Ni kg<sup>-1</sup>, and 63 to 434 mg Zn kg<sup>-1</sup>. To screen the nonfood crops for hyperaccumulation, the metal accumulation ratio was calculated by using total soil metal status and plant tissue concentration. For remediating the Pb-contaminated soils, castor and marigold were recommended by Shukla and Behera (2012). Among the 25 food and nonfood crops tested by them, mustard, amaranthus, maize in food crops and castor, and marigold under nonfood crops were found to possess higher hyperaccumulation potentials for remediating Pb-polluted soils. Since food crops cannot be used effectively, the nonfood crops were recommended to remediate the Pb-polluted soils.

### Technologies for Phytoremediation

Amaranthus and marigold when cultivated in the Pb-contaminated sites indicate that their biomass yield, Pb availability, its absorption, and removal were significantly influenced by the levels of EDTA and organic manure addition. The order of higher biomass production was marigold > castor wild > castor hybrid > fodder cowpea > cluster bean > amaranthus. Among the organics, higher biomass yield was recorded with 5 t FYM ha<sup>-1</sup> in amaranthus and cluster bean, while with fodder

**Table 7.9** Effect of EDTA (mg kg<sup>-1</sup>) and organics on the translocation coefficient of crops

EDTA	<i>Amaranthus</i>					Marigold				
	Nil	FYM	GLM	MI	Mean	Nil	FYM	GLM	MI	Mean
0	1.28	1.42	1.48	1.38	1.39	1.76	2.24	1.93	2.15	2.02
50	1.37	1.69	1.54	1.44	1.51	1.60	2.37	2.42	2.16	2.14
100	1.20	1.81	1.70	1.55	1.57	1.84	2.22	2.37	2.25	2.17
Mean	1.28	1.64	1.57	1.46		1.73	2.28	2.24	2.19	

Source: Shukla and Tiwari (2014)

cowpea, marigold, castor wild, and hybrid, addition of green leaf manure at 5 t ha<sup>-1</sup> registered the highest biomass yield. The interaction effect was found nonsignificant (Shukla and Tiwari 2014).

Shukla and Tiwari (2014) have also found that increasing levels of EDTA increased the biomass production of both crops up to 50 mg kg<sup>-1</sup> and showed a decline at 100 mg EDTA kg<sup>-1</sup> of soil. Increasing levels of EDTA addition increased the extractability of Pb, and its availability in various pools and the order of higher availability was organically bound > exchangeable + adsorbed > water soluble Pb. Addition of 5 Mg FYM with 100 mg EDTA kg<sup>-1</sup> recorded higher bioavailable fractions followed by green leaf manure (Table 7.9). Higher Pb removal and phytoextraction efficiency was noted with the addition of 5 mg FYM + 50 mg kg<sup>-1</sup> EDTA for amaranthus and 5 t GLM + 100 mg kg<sup>-1</sup> EDTA for marigold. However between the crops, marigold crop possesses higher TCF and BCF and highly efficient in removing more Pb from soil and thus can be recommended to decontaminate the Pb-polluted soils.

Application of organics/green leaf manures could remediate Pb pollution. Application of 100 mg EDTA kg<sup>-1</sup> along with either 5 t FYM or green leaf manure ha<sup>-1</sup> was found to be the best in increasing the availability of Pb and its absorption by crops. Increasing levels of EDTA addition increased the extractability of Pb, and the percent increase was marked in amaranthus (48.0%) followed by fodder cowpea (26.0%) > cluster bean (22%) and marigold (19.6%). EDTA and organics addition significantly increased the Pb content and its translocation from root to shoot.

## 7.6 Conclusions

Heavy metals refer to some significant elements of biological toxicity, including mercury (Hg), lead (Pb), chromium (Cr), cadmium (Cd), arsenic (As), etc., that enter soil as soil pollutants through various routes either knowingly or unknowingly due to increase in anthropogenic activities and industrialization. In recent years, rapid industrialization has increased the diversity of heavy metal deposition on the soil, resulting in serious environment deterioration. Crops grown in polluted soils get affected and pollutants are transported to edible plant parts gradually. Further, they migrate into the food chain by direct or indirect usage of respective crops. Heavy metals get recycled back to soil through various means like addition of crop residues and animal excreta etc. And thus the soil polluters follow the

soil-plant-animal-human-soil continuum. Although there are several tolerant plants to various heavy metals at varied degrees, plants grown on these soils show an impairment in growth. Several available remediation methods, viz., bioremediation, microbial remediation, and electrokinetic remediation, have varying degrees of merits and demerits need to be selected based on the local conditions. Although bioremediation is an effective method of treating heavy metal polluted soils, the return of heavy metal to the soil cannot be ruled out.

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