Agriculture Association of Textile Chemical and Critical Reviews Journal (2022) 59-76

AATCC Review

14 August 2022: Received
19 September 2022: Revised
30 September 2022: Accepted
22 October 2022: Available Online

http://aatcc.peerjournals.net/

Review Article

Open Access

Heavy Metals: Soil Contamination and Its Remediation

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Abstract

Heavy metals are the most important soil contaminants in the environment. Heavy metals are the integrated components of the biosphere and thus occur naturally in soils and plants. Heavy metals (Cd, Cr, Cu, Hg, Pb, and Zn) have occurred widely as a result of human, agricultural and industrial activities which is responsible for the contamination of soils. Some of these metals are micro-nutrients that are necessary for plant growth, such as Zn, Cu, Mn, Ni, and Co, while others have unknown biological functions, such as Cd and Pb. Agricultural activities involve the addition of inorganic fertilizers, insecticides, pesticides, and amendments to the soil for increasing productivity are responsible for soil contamination/pollution. Water used for irrigation and the release of industrial effluents in water resources pollute the soil with solid wastes, heavy metals, and several other organic and inorganic substances. Reclamation of such contaminated soils through the phytoremediation method was found to be the cheapest and an effective method for extraction or removal of pollutants from contaminated soils.

Keywords: *Heavy Metals, Soil Pollution, Sink, Phytoremediation, and bioremediation.*

Introduction

Heavy metals are conventionally defined as elements with metallic properties and an atomic number is more than 20 [49] [27]. Soil pollution by heavy metals has a harmful impact on biological activities in soil because heavy metals are not biodegraded easily. Some toxic heavy metals i.e.Pb, Co, Cd cannot be biodegraded but it can be accumulated in living organisms, which causes various diseases and disorders even in relatively lower concentrations [71]. They are also known to have an effect on plant growth, and ground cover and have a negative impact on soil microflora [77]. The development of industry, intensive agricultural practices, the transport sector, and other developmental activities in cities in the last 150 years have been so rapid and extensive that has resulted in soil alteration especially changes in the soil constituents. The application of agricultural inputs resulted in a change in the natural ecosystem. The wild flora has been replaced by agricultural activities. Productive soils are regularly being dumped with chemicals and industrial materials. This has deteriorated the soil, which has resulted in a decline in soil productivity in several parts of the country. When a trace of toxic elements from soil or rock enters the environment, follows normal biogeochemical cycles, being governed by air, water, and gravity until it reaches a geochemical sink. Soil is a universal sink for many substances, particularly the metals that accumulate in soil and move under the process of leaching, plant uptake, and erosion, which temporarily form sink and on decay, the elements are released into the soil. Accumulation of heavy metals and metalloids through the disposal of high metal wastes, mine tailings, leaded gasoline and paints, application of fertilizers in the soil, animal dung manures, sewage sludge, pesticides/herbicide, coal combustion residues, toxic gases emission for the industrial areas, wastewater irrigation, spillage of petrochemicals, and atmospheric deposition are responsible for the contamination of soil. The most common heavy metals that constitute an ill-defined group of inorganic chemical hazards found at contaminated sites are lead, chromium, arsenic,

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DOI: https://doi.org/10.58321/AATCCReview.2022.10.02.59

cadmium, mercury, and nickel [113] [43] .

The different agricultural inputs like inorganic fertilizers and micronutrients are manufactured products containing certified amounts of plant nutrients to facilitate crop growth when applied to cultivated lands. In addition to the active ingredients, however, fertilizers and micronutrients may contain trace elements such as cadmium and lead that are potentially harmful to consumers of the harvested products. When the phosphatic fertilizers and micro-nutrients were applied in the soil, the amounts applied invariably exceeded the amounts taken up by plants. In addition, parts of plant biomass would be reincorporated into the soil after the crop harvests, thus recycling part of the nutrients and contaminants [78]. Therefore, active ingredients of phosphatic fertilizers, along with micro-nutrient ingredients namely phosphorus, zinc, iron, and manganese are expected to accumulate in soil receiving routine applications. The phosphorus contents of the cultivated soils would invariably increase in proportion to the amount of fertilizers used in cultivated lands. Fe and Mn are abundant in soils and increases in their concentrations could not easily be distinguished from the already high background levels. However, the concentration of Zn in the soil would be sensitive to the inputs and may be used as an indicator of micro-nutrient inputs. The content of lead and cadmium which are present in soil are either geogenic or added through applications of phosphatic fertilizers. The cadmium content of phosphatic fertilizers in Indonesia is 35-255 g mt^{-1} [2]. Single super phosphate was used in India, and contains Cd in the range of 2-200 mg kg^{-1} (Foy et al., 1978). Heavy metals and other elements are more toxic soil contaminants that came from sewage sludge. Thus, the soils treated with the repeatedly or large amount of sewage sludge it may accumulate heavy metals and consequently become unable to even support plant life [60] .

Agricultural soils in many parts of the world are contaminated by heavy metal toxicity such as Cd, Cu, Zn, Ni, Co, Cr, Pb, and As. This could be due to the continuous application of phosphatic fertilizers, sewage sludge application, dust from smelters, industrial waste, and bad irrigation practices in agricultural lands [9] [82] [68] .

Materials and Methods

The present study is based on different forms of review literature, which is collected from the published in various national and international journals, books and book chapters, conferences/seminars proceedings, searched online documents from Research Gate, CeRA, and Google Scholar, etc. The keywords i.e. heavy metals in soil, heavy metals in plants, the toxic effect of heavy metals, phytoremediation, phytotoxicity, rhizofiltration used for the completion of the information to the formulation of this manuscript.

Sources of heavy metals in soil

Heavy metals occur naturally in the soil environment through the weathering process of the parent material. It can be found in the form of hydroxides, oxides, sulphides, sulphates, phosphates, silicates, and organic compounds. The most common heavy metals are Pb, Ni, Cr, Cd, As, Hg, etc. [32]. The different man-made activities disturb and accelerate the geochemical cycles of metals in the soils of rural and urban environments, which may accumulate various toxic heavy metals to cause risks to plant health and the ecosystem [18] . Different sources of heavy metals are presented in Table 1 and illustrated in figure 1.

The improper and continuous use of herbicides, pesticides, and fungicides to protect the crops from pests, fungi, etc. but alters the basic composition of the soils and makes the soil toxic for plant growth. Organic insecticides like DDT, aldrin, benzene hexachloride, etc. are used against soil-borne pests and they accumulate in the soil because they do not degrade or are slowly degraded by the microorganisms (bacteria) in soil. Consequently, they have a very deleterious effect on plant growth, stunting their growth and reducing the yield and size of fruit [60]. Therefore, intensification of agricultural production by practices of irrigation (causes salination), excessive fertilizers, pesticides, insecticides etc. have created the problems of soil pollution.

The use of different inorganic fertilizers is required for the adequate supply of essential nutrients i.e. NPK for crop growth under intensive farming systems and it content a trace amount of heavy metals (Cd and Pb) as impurities particularly phosphatic fertilizers. The continuous application of inorganic fertilizers in excess amounts may increases significantly the heavy metals concentration in the soil [40].It can be adversely affected plant growth, because these metals interfere with metabolic functions in plants, including physiological and biochemical processes, inhibition of photosynthesis and respiration, and degeneration of cell organelles and leading to plant death [26] [80] [81]. Contamination of soils by heavy metals may also change the composition of microbial activities in the soil and adversely affect soil characteristics [46] [48].

Table 1: Sources of heavy metals

Heavy metals	Sources	References
Cadmium	Geogenic sources, anthropogenic activities, metal smelting and refining, fossil fuel burning, application of phosphate fertilizers, sewage sludge.	[66] [2] [41]
Chromium	Electroplating industry, sludge, solid waste, tanneries.	[45]
Lead	Mining and smelting of metalliferous ores, burning of leaded gasoline, municipal sewage, industrial wastes enriched in Pb, paints.	[29]
Nickel	Volcanic eruptions, land fill, forest fire, bubble bursting and gas exchange in ocean, weathering of soils and geological materials.	[45]

Figure 1: Natural and anthropogenic sources of heavy metals

Anthropogenic source of heavy metals

The different industrial activities, agriculture activities, wastewater (sewage sludge), mining, manufacturing, and the use of synthetic products can result in heavy metal contamination of urban and agricultural soils. Thus, anthropogenic sources of heavy metals are toxic beyond the natural fluxes for some metals. Some important anthropogenic sources which significantly contribute to the heavy metal contamination in the environment include automobile exhaust which releases lead; smelting which releases arsenic, copper, and zinc; insecticides which release arsenic and burning of fossil fuels which release nickel, vanadium, mercury, selenium, etc. Potentially contaminated soils may also occur at the past application of wastewater or municipal sludge, areas in or around mining waste piles and tailings, industrial areas where chemicals may have been dumped on the ground, or in areas downwind from industrial sites.

Further, the incorrect way of chemical waste disposal from different types of industries can cause contamination of soil. Human activities like disposal of industrial waste, heavy metals, toxic chemicals, oil, and fuel, etc. have also been found to contribute more environmental pollution due to the everyday manufacturing of goods to meet the demands of the large population [31] . The concentration of heavy metals in any soil depends initially on the nature of the parent materials. The findings of [24] observed that the heavy metals concentration was maximum in basaltic rocks and minimum in granite rocks and similarly, [104] also reported that the heavy metal composition in coal ash (Table 2).

Table 2: Heavy metals in some typical igneous rocks and coal ash.

S. No.	Trace elements (mg kg^{-1})	Rock types		Coal ash	
		Granite	Basalt	Mean coal ash content	Crustal abundance
1.	Cr	9.0	16.03	246	100
2.	Cd	0.010	0.067	11	0.2
3.	Cu	10.7	22.4	217	55
4.	Ni	6.4	18.0	171	75
5.	Pb	28.7	18.0	287	13
6.	Zn	74.9	132.0	572	70

Fertilizers and soil amendments

The excess use of nitrogenous fertilizers leads to the acidification of soil and contaminates the agricultural

Table 3: Concentration of heavy metal in different inorganic fertilizers and soil amendments.

Fertilizers	Heavy Metals (mg kg^{-1})										
	Zn	Cu	Fe	Mn	B	Mo	Pb	Cr	Cd	As	Ni
Urea (1)	4.0	0.6	36	0.5	1.0	5.3	4.0	6.0	1.0		
Ammonium Nitrate (2)	-	<0.60	-	-	-	-	<0.40	-	<0.20	<0.40[1]	<0.20[1]
Calcium Ammonium Nitrate (1)	7.6	2.8	407	24.8	9.0	56	116	9.0	6.0	-	-
Ammonium Sulphate Nitrate (1)	54.7	1.9	409	53.8	6.5	5	-	-	-	-	-
Ammonium Sulphate (1)	11.3	0.8	23	3.5	6.0	6	-	-	-	-	-
Triple Super Phosphate (1)	418	49.8	3483	75.0	21.5	270	11.1-13.2	88.9	5.0-6.2	15.3-16.2	15.6-25.2
Single Super Phosphate (1)	165	15.5	4050	8900	133	335	487	88	187	-	-
Rock Phosphate (1)	187	32.0	19917	975	71.5	555	962	184	303	16.5-20.5	16.8-50.4
Potassium Chloride (1)	10.0	3.12	110	3.5	16.3	26	-	-	-	-	-
Potassium Sulphate (1)	2.0	7-10	-	2.2-13	4.0	0.2	-	-	-	-	-
Nitro Phosphate 15-15-15 (1)	40	14.0	36	532	144	133	285	54	89	-	-
Nitro Phosphate 10-10-10 (1)	45.5	5.4	4507	120	134	140	-	-	-	-	-
Amm. Phos. Sulp. 10-10-10 (1)	164	9.4	2425	52	242	249	-	-	-	-	-
NPK 12-32-16 (1)	114	16.4	9358	230	207	91.5	-	-	-	-	-
NPK 10-26-26 (1)	38.0	13.3	7750	116.5	176	88	0	0	-	-	-
Diammonium Phosphate (1)	112	7.2	11275	307	396	75.3	195	81	109	-	-
Dairy manure (mean) (2)	-	18	-	-	-	-	7.5	-	0.7	6.8	9.6
Poultry manure (3)	330-456	48-78	-	-	-	-	6.0-8.4	<1.0-7.7	0.20-0.30	-	7.1-9.0
Swine manure (3)	540-1200	250-600	-	-	-	-	7.0-11	2.2-1.3	0.50-0.82	-	11.33

Source: [8] [74] [110]

soils. Excess and imbalance use of fertilizers are regularly to soils in intensive farming systems to provide adequate N, P, and K for crop growth. The compounds used to supply these elements contain trace amounts of heavy metals (e.g., Cd and Pb) as impurities and continuous application of fertilizers in soils may significantly increase the heavy metals content in the soil [40] . Further, for the proper development and complete the life cycle, plants must acquire not only macronutrients (N, P, K, S, Ca, and Mg), but also micronutrients or heavy metals (i.e. Co, Cu, Fe, Mn, Mo, Ni, and Zn) that are essential for healthy plant growth [49] , and crops may be supplied with these as an addition to the soil or as a foliar spray. The concentration of heavy metals in fertilizers and soil amendments is presented in table 3.

Pesticides / Herbicides

Pesticides (DDT, Aldrin, and Dieldrin) are synthetic toxic chemicals that kill different types of pests and insects causing damage to agriculture, but it has many ecological repercussions. For example copper-containing fungicidal sprays such as Bordeaux mixture (copper sulphate) and copper oxychloride [40] . Lead arsenate was used in fruit orchards for many years to control some parasitic insects. Compared with fertilizers, the use of such materials has been more localized, being restricted to particular sites or crops [57] . They are generally insoluble in water and non-biodegradable and these chemicals will be accumulated in the soil. Thus, it will affect human health through many physiological and metabolic disorders. However, the herbicides like sodium arsenite (Na_3AsO_3), sodium chlorate ($NaClO_3$), etc. can decompose in few months. Also, they affect the environment and are not environmentally friendly. Further, different findings suggested that spraying herbicides cause more insect attack and diseases of plants in comparison to manual weeding.

Bio-solids and Manures

The use of different bio-solids (e.g., composts, livestock manures, and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Zn, and so forth, in the soil [7]. Certain animal wastes such as poultry, cattle, and pig manures produced in agriculture are commonly applied to crops and pastures either as solids or slurries [92]. Pig and poultry manures have also contaminated the soils by the addition of heavy metals i.e. Cu and Zn because these metals added as diets and growth promoters for pig/poultry health products [92]. The manures produced from animals on such diets contain high concentrations of As, Cu, and Zn and, if repeatedly applied to restricted areas of land, can cause the considerable buildup of these metals in the soil in the long run. The different heavy metal contents in municipal solid waste and its standards are presented in table 4. Bio-solids (sewage sludge) are primarily organic solid products, produced by wastewater treatment processes that can be beneficially recycled [100]. The bio-solid materials applied in soil are a common practice in many countries that allow the reuse of bio-solids produced by urban populations [109]. The bio-solids term is more common in place sewage sludge because it is thought to reflect more accurately the beneficial characteristics inherent to sewage sludge [90]. Bio-solids content various heavy metals (Pb, Ni, Cd, Cr, Cu& Zn), and these metals concentrations are governed by the nature and industrial activity, as well as the type of process employed during the bio-solids treatment [55]. Under certain conditions, metals added to soils through bio-solids can be leached downwards through the soil profile and can have the potential to contaminate groundwater [56].

Table 4: Heavy metals content in municipal solid waste (MSW) and its standards.

Heavy Metals	Municipal Solid Waste	German Standards
	(mg ka^{-1})	
Lead (Pb)	420	150
Chromium (Cr)	107	150
Nickel (Ni)	84	50
Cadmium (Cd)	2.8	3.0
Mercury (Hg)	1.9	3.0
Copper (Cu)	222	150
Zinc (Zn)	919	500

Waste Disposal

The application of industrial and wastewater-related effluents to land are a common practice in many parts of the world [75]. Worldwide, it is estimated that 20 million hectares of arable land are irrigated with waste water. The findings of the various studies suggested that agriculture based on wastewater irrigation accounts for 50 percent of the vegetable supply to urban areas [12]. In general, farmers are not bothered about harmful effects of these contaminants and they are only interested in getting more yields and profits from intensive agricultural practices. Further, the long-term or continuous irrigation of lands through wastewater effluents can accumulate the concentration of heavy metals in the soil.

Basic Chemistry of Heavy Metals

In order of abundance of heavy metals i.e. Pb, Cr, As, Zn, Cd, Cu are found at contaminated soils [101] and they are capable of reducing crop production due to the risk of bioaccumulation in the food chain. Basic chemistry is necessary for understanding the bioavailability and remedial options of these heavy metals in the soil because the fate and chemistry in soil depend significantly on the chemical form of the heavy metals (Table 5). Once, heavy metals are adsorbed on soil colloids it is redistributed into various chemical forms with varying bioavailability, mobility, and toxicity [14]. However, the distribution is believed to be governed by reactions of heavy metals in soils such as mineral precipitation and dissolution, ion exchange, adsorption, and desorption, aqueous complexation, biological immobilization and mobilization, and uptake by the plants [50].

Table 5: Basic chemistry of the heavy metals.

S. No.	Heavy Metals	Chemistry of Heavy metals				
		Atomic Number	Atomic Weight	Density (g cm^{-3})	Melting Point (°C)	Boiling Point (°C)
1.	Chromium (Cr)	24.0	52.0	7.19	1875.0	2665.0
2.	Nickel (Ni)	28.0	58.7	8.90	1455.0	2913.0
3.	Copper (Cu)	29.0	63.5	8.96	1083.0	2595.0
4.	Zinc (Zn)	30.0	65.4	7.14	419.5	906.0
5.	Arsenic (As)	33.0	75.0	5.72	817.0	613.0
6.	Mercury (Hg)	80.0	200.6	13.6	−38.8	357.0
7.	Cadmium (Cd)	48.0	112.4	8.65	320.9	765.0
8.	Lead (Pb)	82.0	207.2	11.40	327.4	1725.0

Table 6: Effect of heavy metal toxicity on plants.

Heavy metal	Plant	Toxic effect on plant	Source
As	Rice (*Oryza sativa*)	Reduction in seed germination; decrease in seedling height; reduced leaf area and dry matter production	[1]
	Tomato (*Lycopersicon esculentum*)	Reduced fruit yield; decrease in leaf fresh weight	[19]
Cd	Wheat (*Triticum*sp.)	Reduction in seed germination; decrease in plant nutrient content; reduced shoot and root length	[112]
	Garlic (*Allium sativum*)	Reduced shoot growth; Cd accumulation	[39]
	Maize (*Zea mays*)	Reduced shoot growth; inhibition of root growth	[106]
Cr	Wheat (*Triticum*sp.)	Reduced shoot and root growth	[67]
	Tomato (*Lycopersicon esculentum*)	Decrease in plant nutrient acquisition	[62]
	Onion (*Allium cepa*)	Inhibition of germination process; reduction of plant biomass	[65]
Cu	Bean (*Phaseolus vulgaris*)	Accumulation of Cu in plant roots; root malformation and reduction	[17]
	Hg Rice (*Oryza sativa*)	Decrease in plant height; reduced tiller and panicle formation; yield reduction; bioaccumulation in shoot and root of seedlings	[44]
	Tomato (*Lycopersicon esculentum*)	Reduction in germination percentage; reduced plant height; reduction in flowering and fruit weight; chlorosis	[85]
Heavy metal	**Plant**	**Toxic effect on plant**	**Reference**
Mn	Spearmint (*Mentha spicata*)	Decrease in chlorophyll a and carotenoid content; accumulation of Mn in plant roots	[4]
	Pea (*Pisumsativum*)	Reduction in chlorophylls a and b content; reduction in relative growth rate; reduced photosynthetic O_2 evolution activity and photosystem II activity	[20]
	Tomato (*Lycopersicon esculentum*)	Slower plant growth; decrease in chlorophyll concentration	[86]
Ni	Pigeon pea (*Cajanus cajan*)	Decrease in chlorophyll content and stomatal conductance; decreased enzyme activity which affected Calvin cycle and CO_2 fixation	[87]
	Wheat (*Triticum*sp.)	Reduction in plant nutrient acquisition	[6]
	Rice (*Oryza sativa*)	constraintfor root growth	[51]
Pb	Maize (*Zea mays*)	Reduction in germination percentage; suppressed growth; reduced plant biomass; decrease in plant protein content	[36]
	Oat (*Avena sativa*)	Inhibition of enzyme activity which affected CO_2 fixation	[64]
Zn	Cluster bean (*Cyamopsis tetragonoloba*)	Reduction in germination percentage; reduced plant height and biomass; decrease in chlorophyll, carotenoid, sugar, starch, and amino acid content	[54]
	Pea (*Pisumsativum*)	Reduction in chlorophyll content; alteration in structure of chloroplast; reduction in photosystem II activity; reduced plant growth	[21]

Impact of Heavy Metals Toxicity in Plants

The uptake of different heavy metals by the plant through soil solution or easily solubilized by root exudates [13]. Also plants required certain heavy metals for their development/growth and the excess quantity of these metals in soils can contaminated the soils and ultimately shows toxicity to plants. Further, the concentration of these heavy metals in plants exceeds from their optimal levels, they can adversely affect plant growth.The toxic effect of heavy metals on the plants growth varies according to the particular heavy metal involved in the process. The data presented in table 6 shows a summary of the toxic effects of specific metals on the growth, biochemistry, and physiology of various plants [16]. The growing of different plants on heavy metals contaminated soils can reduceplant growth.

Nickel

The phytotoxic effects of Ni have been known for a long time [94]. Apart from a decrease in growth, the symptoms of Ni toxicity include chlorosis, stunted root growth, and sometimes brown interval necrosis and symptoms specific to the plant species. The concentration of Ni varied from 50 to 100 mgg^{-1} (dry weight basis) is indicated by its toxicity in plants. For example, [69] reported toxicity symptoms in spring wheat at 8 mg kg^{-1} but no yield loss in oats at 90 mg kg^{-1}.parameters due to a reduction in photosynthetic activities, plant mineral nutrition, and reduced activity of some enzymes [41].

Lead

The visual non-specific symptoms of Pb toxicity are rapid inhibition of root growth, stunted growth of the plant, and chlorosis [15]. Pbphyto-toxicity leads to the inhibition of enzyme activities, disturbed mineral nutrition, and water imbalance. These disorders distress the normal physiological activities of the plant. At high concentrations Pb eventually may cause to cell death [83]. Pb toxicity inhibits the germination of seeds and retards the growth of seedlings. Lead contents in soils decreases seed germination, root/ shoot growthand dry mass of roots/shoots [59]. High Pb concentrations caused decreased rice seeds germination (14 to 30%)and reduced 13 to 45% seedling growth [103].

Arsenic

High content of arsenic in plants inhibits the metabolic process such as photosynthesis thereby it inhibiting the growth of plants [97]. The threshold value of As toxicity 40 mg kg^{-1} was established for crop plants [88]. Thus, the higher concentration of arsenic significantly reduces the biomass production and crop yields. In general, the accumulation of As in the edible parts of most plants is low, which is attributed to several reasons, including [108] (i) low bioavailability of As in soil; (ii) restricted uptake by plant roots; (iii) limited translocation of As from roots to shoots; and (iv) phytotoxicity and subsequent premature plant death at relatively low As concentrations in plant tissues. Most plants do not accumulate enough As to be toxic to animals and humans. Growth reductions and crop failure are the main consequences of soil As contamination [105] .

Cadmium

Cadmium contaminations in soils are mainly from the application of bio-solids, use of phosphates fertilizer, and effluents from cadmium-using and recycling industries. The toxic effect of Cd to an induced reduction in the number of flowers and in vitro pollen germination, it stimulated tube growth, decreased the number of ovules/pistil (ovules were morphologically normal and receptive), inhibited the number of pods and seeds. Cd treatment increased protein content in physiologically matured seeds. Further, the rate of Cd- enriched sewage sludge/ city compost resulted was obtained significant yield reduction in Alfisol and Ultisol. The applied Cd remained in the top 10 cm soil (87-96%) and resulted in a lower recovery of Cd (8.3%) in the leachates [30].

Chromium

The Chromium toxicity in plants depends on its valence state, Cr (VI) which is highly toxic and mobile whereas Cr (III) is less toxic. Since plants lack a specific transport system for Cr, it is taken up by carriers of essential ions such as sulphate or iron. Effects of Cr toxicity on plant growth and development include alterations in the germination process as well as in the growth of roots, stems and leaves, which may affect total dry matter production and yield. Cr toxicity was also had deleterious effects on plant physiological processes such as photosynthesis, water relation, and minerals nutrition, and alteration of metabolic activities have also been described in plants by the direct effect on enzymes or by its ability to generate oxidative stress. The high levels of Cr in plants can inhibit seed germination and subsequent seedling growth [84].

Impact of Heavy Metals Toxicity in Soils

Heavy metals are considered one of the major soil contaminants for creating soil pollution and these metals shows the toxic effect on soil microorganism by the change of the population size,bio-diversity, and various activities of the soil microbial communities [3]. The toxicity of heavy metals in soils is a very serious issue due to their presence in the food chain, thus, it destroying the entire ecosystem. There are various ways through which heavy metals present risks to humans, animals, plants, and ecosystems as a whole. Such ways include direct ingestion, absorption by plants, food chains, consumption of contaminated water, and alteration of soil pH, porosity, colour, and its natural chemistry which in turn impact the soil quality [61] [79].

The soil properties i.e. organic matter, clay contents, and pH have major influences on the extent of the effects of metals on biological and biochemical properties [91]. Heavy metals indirectly affect soil enzymatic activities by shifting the microbial community which synthesizes enzymes [89]. Heavy metal content also exhibits toxic effects on soil biota by affecting important microbial processes and decreasing the number and activity of soil microorganisms. [42] reported that the enzyme activities are influenced in different ways by different metals due to the different chemical affinities of the enzymes in the soil system and each soil enzyme exhibits a different sensitivity to heavy metals. The order of inhibition of urease activity generally decreased according to the sequence Cr > Cd > Zn >Mn>Pb. Diversity and activity of soil microbes play significant roles in the recycling of plant nutrients, maintenance of soil structure, detoxification of noxious chemicals and the control of plant pests and plant growth communities are important indices of soil quality.

It is important to investigate the functioning of soil microorganisms in ecosystems exposed to long-term contamination by heavy metals [107]. [3] also reported that heavy metals exert toxic effects on soil microorganisms hence resulting in the change in the diversity, population size, and overall activity of the soil microbial communities and observed that the heavy metal (Cr, Zn and Cd) pollution influenced the metabolism of soil microbes in all cases. In general, the concentration of heavy metals increases in the soil it adversely affects soil microbial properties i.e.enzyme activity, and respiration rate, which appear to be very useful indicators of soil contaminants.

Impact of long-term application of inorganic fertilizers on the accumulation of heavy metals in Vertisols

The findings of the long-term fertilizer experiment with soybean-wheat cropping sequence in a Vertisolsare presented in table 7 and revealed that the hazardous heavy metals (Cd, Pb, Ni, and Cr) and essential heavy metal (Zn, Fe, Mn, and Cu) contents were found to accumulate significantly due to continuous application of different agricultural inputs (inorganic fertilizers and organic manures) to the soil. Further, the highest contents of Cd, Pb, and Ni were found in the treatment receiving super optimal dose fertilizers (150% NPK through urea, SSP, and MOP, respectively) and the lowest values were recorded in the control plot [96].

However, the essential heavy metals (Zn Cu, Fe, and Mn) are not limiting factors even after 35 years of intensive cropping with continuous applications of various inorganic fertilizers and organic manure. The highest contents of essential heavy metals were noted in 100% NPK+15 t FYM ha^{-1}treatment plots, which is obviously due to annual acceleration through farm yard manure which contributes significantly to the availability of these essential heavy metals, followed by 150% NPK treatments and the lowest values were recorded in control plot [95].

Table 7: Effect of different treatments on hazardous and essential heavy metals.

Treatments	**Hazardous heavy metals content (mg kg^{-1})**			
	Cd	**Pb**	**Ni**	**Cr**
50% NPK	0.032	1.733	0.357	0.134
100% NPK	0.034	1.809	0.388	0.156
150% NPK	0.042	1.886	0.405	0.180
100% NP	0.026	1.630	0.327	0.052
100% N	0.020	1.764	0.514	0.143
100% NPK + FYM	0.018	1.591	0.296	Trace
100% NPK – S	0.017	1.742	0.327	0.047
Control	0.018	1.425	0.195	Trace
CD (*P = 0.05*)	**0.01**	**0.15**	**0.05**	**0.01**
Treatments	**Essential heavy metals content (mg kg^{-1})**			
	Zn	**Fe**	**Mn**	**Cu**
50% NPK	0.47	20.64	17.20	1.58
100% NPK	0.48	21.81	17.91	1.40
150% NPK	0.75	26.05	16.84	1.64
100% NP	0.53	28.73	19.65	1.46
100% N	0.50	19.71	12.56	1.25
100% NPK + FYM	0.92	31.04	16.58	1.82
100% NPK – S	0.49	26.89	15.00	1.32
Control	0.42	17.04	14.19	1.18
CD (*P = 0.05*)	**0.09**	**2.32**	**1.60**	**0.18**

Permissible limits of heavy metals content in water,soil and plant

The accumulation of heavy metals in agricultural soil and plants from different sources of soil contaminates, it may deteriorate the soil quality and that can increase risks to human health. The maximum allowable limits of heavy metals in irrigation water, soil, and vegetables have been established by standard regulatory bodies such as World Health Organization (WHO), Food and Agricultural Organization (FAO), and Ewers U, Standard Guidelines in Europe as shown in table 8

Table 8: Maximum allowable limits of heavy metal in irrigation water, soils and vegetables.

Heavy metals	Maximum permissible level in irrigation water (μg ml^{-1})	Maximum permissible level in soils (μg g^{-1})	Maximum permissible level in vegetables (μg g^{-1})
Cadmium (Cd)	0.01	3	0.10
Lead (Pb)	0.065	100	0.30
Nickel (Ni)	1.40	50	67
Chromium (Cr)	0.55	100	-
Zinc (Zn)	0.20	300	100
Copper (Cu)	0.017	100	73
Iron (Fe)	0.50	50000	425
Manganese (Mn)	0.20	2000	500
Cobalt (Co)	0.05	50	50
Arsenic (As)	0.10	20	-

Table 9: Values of maximum allowable limits for heavy metals in different countries (mg kg^{-1}).

Element	Austria	Canada	Poland	Japan	Great Britain	Germany
Cadmium(Cd)	5	8	3	-	3	2
Cobalt(Co)	50	25	50	50	-	-
Chromium(Cr)	100	75	100	-	50	200
Copper(Cu)	100	100	100	125	100	50
Nickel (Ni)	100	100	100	100	50	100
Lead (Pb)	100	200	100	400	100	500
Zinc (Zn)	300	400	300	250	300	300

Table 10: Heavy metals standards for compost manure solid waste.

Heavy Metals	Maximum acceptable concentration (mg kg^{-1})
Zinc (Zn)	1000
Copper (Cu)	300
Nickel (Ni)	50
Cadmium (Cd)	5
Chromium (Cr)	50
Lead (Pb)	100
Arsenic (As)	10
Mercury (Hg)	0.15

[8] and maximum allowable limits of heavy metals in different countries are presented in table 9 [73].

Standard forcompost manure solid waste

Maximum allowable limit of heavy metals and other standards for compost manure solid waste by Central Pollution Control Board (CPCB), (Management and Handling) Rules 2000, MEF [8] are presented in table 10.

Remediation of contaminated soils

Remediate means to solve a problem of soil contamination and phytoremediation means to use plants or plant parts to solve an environmental problem such as contaminated/polluted soils or contaminated groundwater. The concentration of various heavy metals in contaminated soil is strongly influenced by the selection of the appropriate remediation treatment approach. The contamination of heavy metals in the soil should be characterized by their type, amount, and distribution in the soil. Once the site is characterized, the desired level of each metal in the soil must be determined. Several technologies exist for the remediation of metal-contaminated soil [111]. The following methods are used for the remediation of heavy metals from contaminated soils.

Phytoremediation

During recent years the concept of using plants to remediate heavy metal-contaminated sites (called phytoremediation) has received greater attention [102] [38] ,. Phytoremediation may involve either phytostabilization or phytoextraction (means the use of plants to remove the contaminant from contaminated soils). The concept of using plants to accumulate metal for subsequent processing is both technically and economically attractive. The term"phytoremediation" is a Greek word *phyton*which means plants and the Latin root *remedium*(to correct or to remedy) [23] [98].It deals with the cleanup of organic pollutants and heavy metal contaminants using plants and rhizospheric microorganisms. Different definitions of phytoremediation are given by the different scientist which is presented in table 11.

Table 11: Definition of phytoremediation.

Definition of phytoremediation	Researchers
The use of plants to improve degraded environments	[63]
The use of plants, including trees and grasses, to remove, destroy or sequester hazardous contaminants from media such as air, water, and soil	[72] [25]
The use of plants to remediate toxic chemicals found in contaminated soil, sludge, sediment, groundwater, surface water, and wastewater	[76]
An emerging technology using specially selected and engineered metal accumulating plants for environmental cleanup	[52]
The use of vascular plants to remove pollutants from the environment or to render them harmless	[11]
The engineered use of green plant to remove, contain, or render harmless such environmental contaminants as heavy metals, trace elements, organic compounds, and radioactive compounds in soil or water. This definition includes all plant-influenced biological, chemical, and physical processes that aid in the uptake, sequestration, degradation, and metabolism of contaminants, either by plants or by the free-living organisms that constitute the plant rhizosphere	[33]
Phytoremediation is the name given to a set of technologies that use different plants as a containment, destruction, or extraction technique. Phytoremediation is an emerging technology that uses various plants to degrade, extract, contain, or immobilize contaminants from soil and water	[98]
Phytoremediation in general implies the use of plants (in combination with their associated microorganisms) to remove, degrade, or stabilize contaminants	[28]

The phytoremediation technology is eco-friendly and an efficient means for the restoration of polluted environments especially those of heavy metals. Nonetheless, the level of soil contamination, the quantity of metal contaminant in the soil, as well as the ability of plants to aggressively take up metals from the soil, determine the success of phytoremediation at any polluted site. Plants utilized in phytoremediation are the hyper-accumulators with very high heavy metal accumulation potential and little biomass efficiency, and non-hyper-accumulators, which possess lesser extraction capacity than hyper-accumulators, but whose total biomass yield is substantially higher and are fast-growing species (Figure 2).

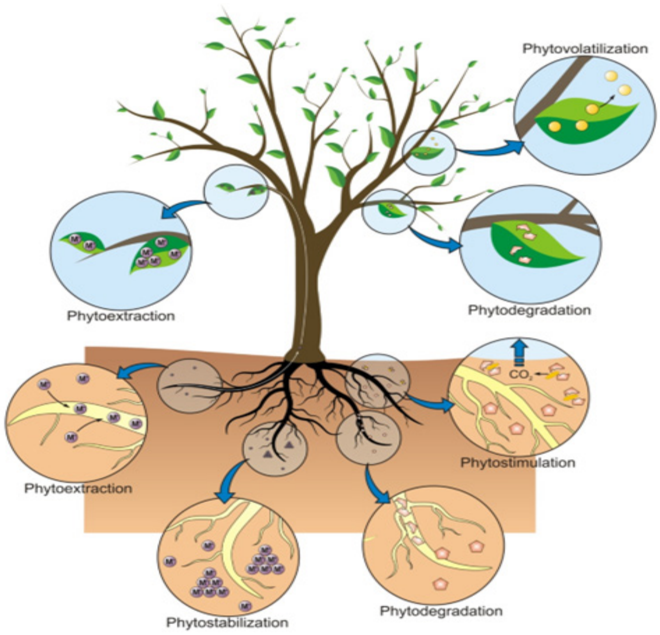

Figure 2: Phytoremediation strategies [70]

Heavy metals uptake mechanism through phytoremediation

Generally, phytoremediation is an emerging technology using selected plants to clean up the contaminated environment from hazardous contaminants to improve the environment quality.

The uptake mechanisms of both organic and inorganic contaminants through phytoremediation technology are illustrated in Figures 3 and 4. Forthe remediation of organic contaminants phytostabilization, rhizodegradation, rhizofiltration, phytodegradation, and phytovolatilization technology are used and these mechanisms are not able to be absorbed into the plant tissue. However, for the inorganic contaminants, phytostabilization, rhizofiltration, phytoaccumulation, and phytovolatilization mechanisms can be involved for the remediation of contaminated soils. Phytoremediation is currently divided into following areas [23] [99] :-

Phytoextraction: Phytoextraction is the process of removal or extraction of heavy metal into harvestable plant tissues from contaminated soils. The uptake/ absorption and translocation of heavy metal contaminants through plant roots into the plant shoots (above-ground portions of the plants) which can be harvested and burned. For example, some plant species i.e. *Suterafodina, Dicomaniccolifera,* and *Leptospermum Scoparium* have been reported to accumulate Cr content to high concentrations in their tissues.

Phytostabilisation: The use of certain plant species to immobilize the heavy metal contaminants from the soil and groundwater through absorption and accumulation in plant tissues. These contaminate are adsorbed onto roots or precipitation within the root zone that can be preventing their migration in soil, as well as their movement by erosion and deflation.

Rhizofiltration: The use of plant roots to remove heavy metal contaminants from contaminated water [22]. Rhizofiltrationis the process of adsorption or precipitation onto plant roots or absorption into and sequesterization in the roots of contaminants that are in solution surrounding the root zone by constructed wetland for cleaning up communal wastewater. A high level of Pb deposition is seen in corn root tips as revealed by histochemical and electron microscopy studies. [53] also showed that corn plants treated with 10^{-3} M Pb accumulated 138, 430 mg of Pb per kg of dry weight in root tips compared to 26,833 mg in the root basal part. Since the first 8 mm of the apical root accounts for approximately 50% of the Pb accumulated by the entire root system [53], it appears that the plant with a more branched root system will take up more Pb and other heavy metals compared to plants with longer and less branched root systems. Generally, aquatic plants are growing in contaminated water. Examples- *Scirpuslecusteris, Phragmiteskarka* and *Bacopamonnieri.*

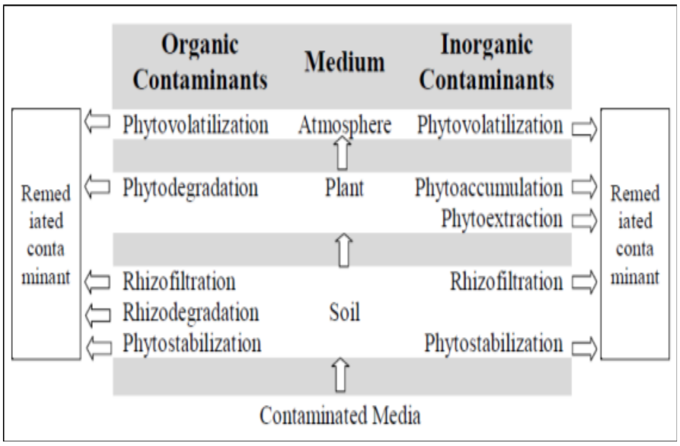

Figure 3: Uptake mechanisms on phytoremediation technology [37].

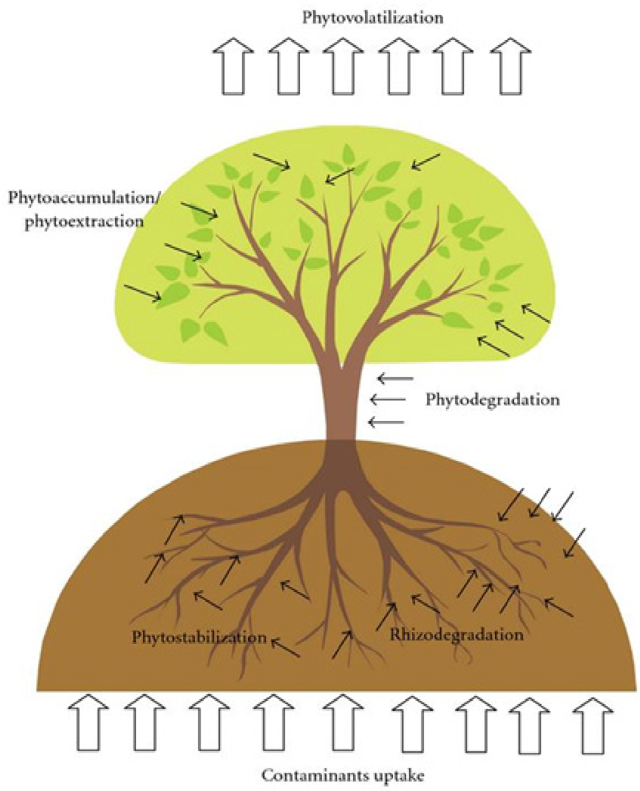

Figure 4: Phytoremediation technology foruptake ofheavy metal by the plants [93].

Phytovolatilization: It refers to the uptake and transpiration of contaminants, primarily organic compounds, by plants. The contaminant, present in the water taken up by the plant, passes through the plant or is modified by the plant, and is released to the atmosphere (evaporates or vaporizes).In this method growing of trees and other plants take up water along with the contaminants. Heavy metal contaminants can pass through the plants to the leaves and volatilize into the atmosphere at comparatively low concentrations.

Phytodegradation: Use of plants and associated micro-organisms to degrade organic pollutants. The contaminants can be absorbed by the root to be subsequently stored or metabolised by the plant. Degradation of contaminants in the soil by plant enzymes exuded from the roots is another phytoremediation mechanism [58]. For many contaminants, passive uptake via micro-pores in the root cell walls may be a major route into the root, where degradation can take place [33].

Hyperaccumulation: In this method different plant species is classified as hyperaccumulator when it takes heavy metals against their concentration gradient between the soil solution and cell cytoplasm, thus acquiring capacity of accumulating a very high metal concentration in tissues without much difficulty in carrying out growth and metabolic functions. Some important heavy metal hyper accumulators are given below. The data of the bioaccumulation coefficient of various brassica species are presented in table 12 which is used as indicator for hyper accumulation [10].

Table 12: Bioaccumulation coefficients of various Brassica species at maturity stage.

Species	**Heavy metals (mg kg^{-1})**			
	Zn	**Cu**	**Ni**	**Pb**
B. juncea	6.83	3.08	3.21	12.86
B. compestris	12.48	2.59	13.61	2.56
B. carinata	11.89	1.94	12.30	17.72
B. napus	9.87	1.14	8.98	9.37
B. nigra	6.56	2.04	8.66	7.94

- *Brassica juncea* (mustard)
- *Streptanthuspolygaloides* Gray (Brassicaceae)
- *Silene spp*. (Cryophyllaceae) – *S. vulganis, S. burchelli, S. cobaltica, S. nflata, S. diocia* – These varieties of *silene* produce the highest dry matter yield and also remediate > 10000 ppm Ni from the polluted soils.
- *Thlaspi spp.* (Brassicaceae) - *T. cacrulescens, T. montanum, T. ochlecum.*
- *Alyssum spp.* (Brassicaceae) -*A. argentum, A. corsicum, A. euboeum, A. heldrechii, A. murale, A. cnium, A. troodii* [5]

Advantages of phytoremediation technology

- The technology is less disruptive than current techniques
- The effectiveness in contaminant reduction
- It is low-cost technology as compared to other treatment methods.
- It is applicable to a wide range of contaminants
- It is environmentally friendly and aesthetically pleasing to the public.
- It works on a variety of organic and inorganic compounds.
- It can be either in situ / ex-situ.
- This technology is very easy to implement and maintain.
- It reduces the number of wastes to be landfilled.

Limitation of phytoremediation technology

- The time-consuming method (may take several years to remediate).
- The amount of produced biomass.
- Restricted to sites with shallow contamination with the rooting zone.
- The impacts of contaminated vegetation
- It may depend on the climatic condition.
- Possible effect on the food chain.

Chelation

Results from chelation experiments indicate that Pb concentration in the shoot can be increased dramatically when the soil Pb concentration is increased by adding a synthetic chelate to the contaminated soil. Synthetic chelate EDTA forms a soluble complex with many metals, including Pb [47], and can solubilize Pb from soil particles [102]. Application of EDTA to Pb-contaminated soils has been shown to induce the uptake of Pb by plants causing Pb to accumulate more than 1% (w/w) of the shoot dry biomass [34] [35]. Large Pb particles cannot easily cross the casparian strip due to their size and charge characteristics but once they form a complex with chelators such as EDTA, their solubility increases, the particle size decreases, and they become partially 'invisible' to those processes that would normally prevent their unrestricted movement such as precipitation with phosphates and carbonates, or binding to the cell wall through mechanisms such as cation exchange [38]. It is important to point out that the addition of chelates to the soil has to be done in a carefully controlled manner so as not to mobilize Pb into groundwater or otherwise promote its off-site migration [35].

Soil scraping

Replacement of the uppermost contaminated soil (0-15 cm depth) from the cultivated field has been possible. The maximum amount of lead was absorbed/ adsorbed by soil in clay–humus complexes. By scraping of contaminated soil highest quality heavy metals can be removed from the soil and become suitable from growing crops. One to two times further cleaning by phytoremediation or rhizofiltration leads to the remove the traces amount of heavy metals from soil and then crop produce becomes edible for animal consumption.

Conclusion

Environmental pollution through heavy metal ions is the current world growing problem. It is increasing due to the increase in urbanization and industrialization. Soil is the final sink for most of the contaminants/pollutants. The discharge of heavy metal ions as a byproduct of various human activities are accompanied with large-scale water and soil pollution. These contaminants reduce microbial activities and ultimately deteriorate the soil quality. The toxicity of heavy metals in plants shows by a reduction in growth due to changes in their physiological and biochemical activities. The remediation of heavy metals from contaminated soils is necessary to reduce the associated risks or available resources for agricultural production and human health. In this context, phytoremediation technology is frequently listed among the best available technologies for cleaning up heavy metal-contaminated soils. The phytoremediation and rhizofiltration technology is used to extract or removal of pollutants (heavy metals) from contaminated soil and water. Thus, this technology is environmental friendly and potentially cost-effective.

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