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Heavy metals and its impact in vegetable crops

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Abstract
Environmental pollution is rapidly booming worldwide. The soil contaminated with heavy metals like lead Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb and Hg has serious environmental problems since these metals are non-essential and toxic to plants and animals and have significant toxic effect on human being health. Recently due to various anthropogenic activities such as mining, industrialization and agricultural activities like application of pesticides, fungicides and fertilizers, heavy metals are released in to the soil, water and atmosphere. These released heavy metals enter into the plant system through various physiological process and it affects the plant growth and development. The concentration of heavy metals in the environment varies due to various activities and it becomes toxic when it reaches above the permissible limits. The possible introduction of these elements has contributed to the increasing occurrence of heavy metals in the ecosystem through their direct ingestion from contaminated soils, consumption of vegetables grown on the contaminated soils or drinking wastewater that has percolated through such soils. Vegetables are grown all over the world for human needs and relished as nutritional supplement. Accumulation of heavy metals occurs only when the vegetable crops are cultivated in heavy metal contaminated environment, as a result these heavy metals enters into the food chain. When heavy metals contaminated vegetables are consumed by human beings it causes various severe health ailments. These heavy metals not only affect the plants and human beings, it also affects the nutrient status of soil, soil health, water source and also other aquatic living organisms. There are various remediation processes to reduce the level of heavy metals from these sources. This paper aims to review the different heavy metal accumulation and its impact in vegetable crops.

Keywords: Heavy metals, vegetables, toxicity, anthropogenic, contamination

Introduction
Heavy metals include some metalloids, transition metals, basic metals, lanthanides and actinides. The main elements that are considered as heavy metal are chromium (Cr), manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), molybdenum (Mo), mercury (Hg), nickel (Ni), tin (Sn), lead (Pb), cadmium (Cd), antimony (Sb), etc.

Three kinds of heavy metals are of concern, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides such as U, Th, Ra, Am, etc. *Lead, mercury, cadmium* and chromium are at the top on the toxicity list among various metal ions, the first three, called "the big three", are in the limelight due to their major impact on the environment.

Heavy metals are very toxic to the plants and humans when they are consumed beyond the permissible limits. These heavy metals are released into the environment through various anthropogenic activities in large quantities. Main source of these heavy metals and trace elements are in sewage sludge from industrial water-water outlets and surface runoff water (Babel, S *et al.*, 2006) [21]. Even-though the sewage sludge is a carrier of nutrients for the plant growth and development, continued use of sewage sludge for long time will cause negative impact on the environment and plants due to polluted organics like hormones, antibiotics, endocrine disruptors and persistent organic pollutants (POP's) as well as toxic low-molecular weight compounds as polychlorinated biphenyls (PCB), polynuclear aromatic hydrocarbons (PAHs) (Nrgholi, B. 2007) [32]. Many studies have reported negative or toxicity effects of the heavy metals. They are poisonous for macro and microorganisms through their direct influence on the biochemical and physiological processes, reducing growth, deteriorating cell organelles and preventing photosynthesis and in crop plants; they are of great concern due to the probability of food contamination with heavy metals through the soil-root interface. The heavy metals are not essential for plant growth, they are absorbed and accumulated by plants in higher levels causing toxic damage to cells and tissues as a result of the complex interaction of major toxic ions with other essential or non-essential ions (Ahmadpour, P *et al.*, 2012) [4]. When these toxic heavy metals and trace elements contaminates the soil and water, plant system absorbs and accumulates these toxic elements. On consumption of these contaminated vegetables for prolonged period by human beings cause major harmful ailments as a result of bio-magnification.

Essential and Non-essential Heavy metals

Based on the effect of heavy metals in the plants they are categorized as essential and non-essential heavy metals. All these heavy metals become toxic to living organisms when reached its permissible limit. Some of the heavy metals like (Fe, Cu and Zn) are essential for plants and animals (Wintz *et al.*, 2002) [46]. The availability of heavy metals in medium varies, and metals such as Cu, Zn, Fe, Mn, Mo, Ni and Co are essential micronutrients (Reeves and Baker 2000) [7], whose uptake in excess to the plant requirements result in toxic effects (Monni *et al.*, 2000; Blaylock and Huang 2000) [27, 14]. They are also called as trace elements due to their presence in trace (10 mg kg-1, or mg L -1) or in ultra-trace (1 lg kg^{-1}, or lgL^{-1}) quantities in the environmental matrices.

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

Table 1: Uses of essential heavy metals in plant system

Metals	Functions
Copper	Photosynthesis - Electron donor in photosystem I
Zinc	Many enzymes contain Zn - carbonic anhydrase, RNA polymerase – also to maintain the integrity of ribosome
Manganese	Acts as catalyst – involves in oxidation of carbohydrate
Molybdenum	Metabolism of N and S – Nitrate reduction and Biological N fixation
Nickel	Component of urease enzyme
Cobalt	Useful in expansion of leaf disc, Constituent of Vitamin B12 and Propionate

(Mahmood and Islam, 2006) [9]

Some of these heavy metals like As, Cd, Hg, Pb and Se do not have any use in the plant system. Even in low concentration it causes toxic effect to plants and it becomes hazardous to all living organisms.

Source of Heavy Metals

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

Heavy metal pollution can originate from both natural and anthropogenic sources. Activities such as mining and smelting operations and agriculture have contaminated extensive areas of world such as Japan, Indonesia and China mostly by heavy metals such as Cd, Cu and Zn (Herawati *et al.*, 2000) [6], Cu, Cd and Pb in North Greece (Zanthopolous *et al.*, 1999), in Albania (Shallari *et al.*,, 1998) [38] and Cr, Pb, Cu, Ni, Zn and Cd in Australia (Smith 1996) [37]. Heavy metals originate within the Earth's crust; hence their natural occurrence in soil is simply a product of weathering process.

Natural sources of heavy metals

The most important source of heavy metals is geologic parent material or rock outcroppings. The composition and concentration of heavy metals depend on the rock type and environmental conditions, activating the weathering process.

The geologic plant materials generally have high concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb. However, class-wise the heavy metal concentrations vary within the rocks. Soil formation takes place mostly from sedimentary rock but is only a small source of heavy metals, since it is not generally or easily weathered. However, many igneous rocks such as olivine, augite and hornblende contribute considerable amounts of Mn, Co, Ni, Cu and Zn to the soils. Within the class of sedimentary rocks, shale has highest concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb followed by limestone and sand stone. Volcanoes have been reported to emit high levels of Al, Zn, Mn, Pb, Ni, Cu and Hg along with toxic and harmful gases (Seaward and Richardson, 1990).

Table 2: Range of heavy metals in igneous and sedimentary rocks

Metals	Basaltic igneous	Granite igneous	Shales and Clays	Black shales	Sand stone
As	0.2-10	0.2-13.8	-	-	0.6-9.7
Cd	0.006-0.6	0.003-0.18	0.0-11	<0.3-8.4	-
Cr	40-600	2-90	30-590	26-1,000	-
Co	24-90	1-15	5-25	7-100	-
Cu	30-160	4-30	18-120	20-200	-
Pb	2-18	6-30	16-50	7-150	<1-31
Mo	09-7	1-6	-	1-300	-
Ni	45-410	2-20	20-250	10-500	-
Zn	48-240	5-140	18-180	34-1,500	2-41

(Cannon *et al.*, 1978) [9]

Agricultural sources of heavy metals

The inorganic and organic fertilizers (Fertilizer is a substance added to soil to improve plants growth and yield.) are the most important sources of heavy metals to agricultural soil include liming, sewage sludge, irrigation waters and pesticides, sources of heavy metals in the agricultural soils (Table 3).

Others, particularly fungicides, inorganic fertilizers and phosphate fertilizers have variable levels of Cd, Cr, Ni, Pb and Zn depending on their sources. Cadmium is of particular concern in plants since it accumulates in leaves at very high levels, which may be consumed by animals or human being. Cadmium enrichment also occurs due to the application of sewage sludge, manure and limes (Nriagu 1988; Yanqun *et al*., 2005) [31, 48]. Although the levels of heavy metals in agricultural soil are very small, but repeated use of phosphate fertilizer and the long persistence, time for metals, there may be dangerously high accumulation of some metals (Verkleji 1993) [45].

Animal manure enriches the soil by the addition of Mn, Zn, Cu and Co and sewage sludge by Zn, Cr, Pb, Ni, Cd and Cu (Verkleji, 1993) [45]. Liming increases the heavy metal levels in the soil more than the nitrate fertilizers and compost refuse. Sewage sludge is one of the most important sources of heavy metal contamination to the soil (Ross, 1994) [34] (Table 4). Several heavy metal–based pesticides (Pesticides kill unwanted pests) are used to control the diseases of grain and fruit crops and vegetables and are sources of heavy metal pollution to the soil (Verkleji, 993; Ross, 1994) [45, 34].

Table 3: Guideline for safe limit of heavy metals

Sample	Standards	Cd	Cu	Pb	Zn	Mn Ni		Cr
Agricultural soil (pg C^I)	Indian standard (Awashthi 2000) WHO/FAO (2007)	3-6	135-270	250-500	300-600	—	75-150	—
	European union standards (EU 2002)	3	140	300	300		75	150

Table 4: Heavy metal concentration (μ/g) in agricultural amendments

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

(Ross, 1994) [34]

Industrial sources of Heavy Metals

Industrial sources of heavy metals include mining, refinement (spoil heaps and tailings, transport of ores, smelting and metal finishing and recycling of metals). Mining operation emits different heavy metals depending on the type of mining.

For example, coalmines are sources of As, Cd, Fe, etc., which enrich the soil around the coalfield directly or indirectly. The utilization of Hg in gold mining and the mobilization of significantly high amounts of Hg from old mines have become a significant source of this pollutant to the environment (Lacerda, 1997) [25]. High temperature processing of metals such as smelting and castings emit metals in particulate and vapor forms. Vapor form of heavy metals such as As, Cd, Cu, Pb, Sn and Zn combine with water in the atmosphere to form aerosols. These may be either dispersed by wind (dry deposition) or precipitated in rainfall (wet deposition) causing contamination of soil or water bodies.

Contamination of soil and water bodies can also occur through runoff from erosion of mine wastes, dusts produced during the transport of crude ores, corrosion of metals and leaching of heavy metals to soil and ground water. Soil contamination of heavy metals occurs due to different types of processing in refineries. Other industrial sources include processing of plastics, textiles, microelectronics, wood preservation and paper processing. Contamination of plants growing beneath the power line with high concentration of Cu is reported to be toxic to the grazing animals

Domestic Effluents

These waste waters probably constitute the largest single source of elevated metal values in rivers and lakes. Domestic effluents may consists of (a) untreated or solely mechanically treated waste waters (b) substances which have passed through the filters of biological treatment plants (c) waste substances passed over sewage outfalls and discharged to receiving water bodies often end up into the sea from coastal residential areas. The use of detergents creates a possible pollution hazard, since common house hold detergent products can affect the water quality. Angino *et al*., (1970) [1] found that most enzyme detergents contained trace amounts of the elements Fe, Mn, Cr, Co, Zn, Sr and B.

Other Sources

Other sources of heavy metals include refuse incineration, landfills and transportation (automobiles, diesel-powered vehicles and aircraft). Two main anthropogenic sources that contaminate the soil are fly ash produced due to coal burning and the corrosion of commercial waste products, which add Cr, Cu, Pb and galvanized metals (primarily Zn) into the environment (Al-Hiyaly *et al*., 1988) [2]. Coal burning adds heavy metals such as Cd, Hg, Mn, Ni, Al, Fe and Ti into the soils (Verkleji,1993) [45]. Oil burning contributes V, Fe, Pb and Ni to the environment.

How Heavy Metals are transported into the plants from soil

In soil, metals exist as a variety of chemical species in a dynamic equilibrium governed by soil physical, chemical, and biological properties (Chaney 1988). But, only a fraction of soil metal is readily available for plant uptake because of the insoluble nature of the compounds, thus unavailable for transport into roots. Metal availability and mobility in the rhizosphere is influenced by root exudates and microorganisms. It is transported by mass flow in plants.

Transport of metal ions across root cellular membrane permits the access of metals into plant tissues. Metals are first taken into apoplast, a free intercellular space directed towards the xylem, of the roots. Heavy metals are translocated apo-plastically into plant tissue due to continuum of root epidermis and cortex. The metals in root cells have to cross the endodermis and casparian strip to reach the xylem. The cell walls of the endodermis and casparian strip act as a barrier for apoplastic diffusion into the vascular system.

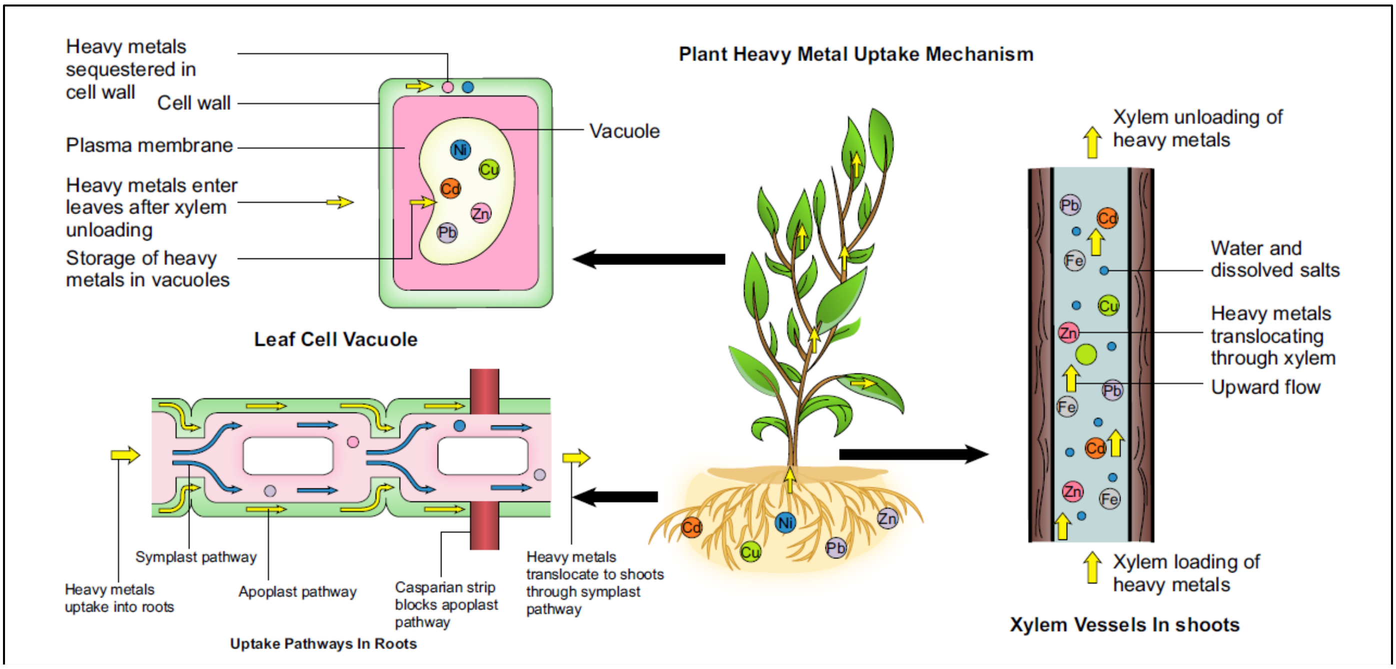

Fig 1: The three processes involved in the uptake and sequestration of heavy metals. Because of increased solubility, the heavy metals are taken up to roots from where they are translocated to shoots by means of apoplast and symplast pathway. From the shoots, the heavy metals are transported to leaves by xylem loading. In the leaves, heavy metals are stored in vacuoles. (Ghori *et al.*, 2016) [17]

For root– shoot translocation of metals, metal transporters carry metal ions from root symplast into xylem apoplast (Marschner, 1996) [26] and are probably driven by transpiration pump (Salt *et al.*, 1995) [36]. Physiological concentrations of heavy metals in the plant cell are regulated by tonoplast as well as metal transporters on the plasma membrane. Different classes of membrane proteins are known to involve in uptake of metals in plants, but still, there is a lacuna in understanding the molecular level transport of heavy metals across plant membranes. Therefore, a complete knowledge of transport processes in plants is crucial to create transgenic plants that can accumulate specific metals to improve the process of soil decontamination and remediation.

Heavy metals in soil and its accumulation

Heavy metals are very toxic and they are usually released from various industries, waste water irrigation, the application of metal-based pesticides and fertilizers and transportation and mining industries through their waste water disposal. When these waters are released continuously in the soil for prolonged period, they cause accumulation of heavy metals in these affected areas.

Waste water irrigation is the major contributor of heavy metal contents of the soil (Mapanda *et al.*, 2005) [28]. High concentrations of heavy metals were reported in vegetables from the untreated wastewater irrigated areas (Sinha *et al.*, 2005; Sharma *et al.*, 2006) [41, 43]. Use of industrial waste water for raising vegetables is very serious issue in Pakistan because these effluents are heavily loaded with harmful metals and metallic compounds (Singh *et al.*, 2004) [40]. Heavy metal pollution of agricultural land and crops in the surrounding area of mining has been considered as a primary environmental concern (Kalali *et al.*, 2011) [24]. Vegetable contamination with heavy metals is through absorption (from soil) and surface deposition (from polluted air). The plant species possess different potential to remove and accumulate different metals and results in serious health complications when such food stuff is consumed (Zurera *et al.*, 1989) [49]. According to United Nation Environment Programme, mercury is released into the environment and it reaches soil from the dental hospitals due to improper disposing of dental filling remains.

Table 5: Heavy Metals in clean water irrigation (CWI) and waste water irrigation (WWI)

Heavy metals	CWI			WWI			Safe Limits	
	Range	Mean	SE	Range	Mean	SE	Indian (Awashthi, 2000)	International (European Union, 2002)
Cr	5.65-6.45	6.07	±0.35	12.26-14.84	13.76⁴"	±1.19		150
Cd	0.81-2.38	1.41	±0.68	2.68-4.95	3.87"	±0.97	3-6	3.0
Cu	5.31-6.57	6.06	±0.57	15.23-16.52	15.95⁴"	±0.56	135-270	140
Fe	38.69-42.58	40.90	±1.66	221.58-254.26	238.59'	±13.37	75-150	
Mn	7.59-8.65	8.16	±0.47	35.81-42.38	39.19⁴"	±2.70		
Zn	7.28-9.52	8.42	±0.99	25.95-28.62	27.12⁴"	±1.16	300-600	300

Student's t-test was done for mean value of heavy metal concentrations between CWI and WWI site.** Level of significance: p 5 0.01. xxx Level of significance: p s 0.001 (Vinod Kumar and Roushan K. Thakur, 2018)

Impact of heavy metals in soil

Soil contamination by heavy metals is an important problem in this modern era due to various anthropogenic activities. Heavy metal pollution not only result in adverse effects on various parameters relating to plant quality and yield but also cause changes in the size, composition and activity of the microbial community (Yao H. *et al.*, 2003) [47]. Therefore, heavy metals are considered as one of the major sources of soil pollution. Heavy metal pollution of the soil is due to various metals like Cu, Ni, Cd, Zn, Cr and Pb (Hinojosa M.B. *et al.*, 2004) [17]. The adverse effects of heavy metals on soil biological and biochemical properties are well documented. 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 (Speira T.W *et al.*, 1999) [39].

Heavy metals indirectly affect soil enzymatic activities by altering the microbial community which synthesizes enzymes (Jie., *et al.*, 2009) [20]. Heavy metals exhibit toxic effects towards soil biota by affecting key microbial processes and decrease the number and activity of soil microorganisms. Conversely, long-term heavy metal effects can increase bacterial community tolerance as well as the tolerance of fungi such as arbuscular mycorrhizal (AM) fungi, which can play an important role in the restoration of contaminated ecosystems (Mora A.P *et al.*, 2005) [13]. Chen *et al.*, (2010) [11] suggested that heavy metals caused a decrease in bacterial species richness and a relative increase in soil actinomycetes or even decreases in both the biomass and diversity of the bacterial communities in contaminated soils. Karaca *et al.*, (2010) [23] 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. Cd is more toxic to enzymes than Pb because of its greater mobility and lower affinity for soil colloids. Cu inhibits b-glucosidase activity more than cellulose activity. Pb decreases the activities of urease, catalase, invertase and acid phosphatase significantly.

Diversity and activity of soil microbes play an important role in 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 study the functioning of soil microorganisms in ecosystems exposed to long-term contamination by heavy metals. Chromium is commonly present in soils as Cr (III) and Cr (VI), which are characterized by distinct chemical properties and toxicities. Cr (VI) is a strong oxidizing agent and is highly toxic, whereas Cr (III) is a micronutrient and a non-hazardous species 10 to 100 times less toxic than Cr (VI) (Garnier J. *et al.*, 2006) [15]. Cr (VI) has been reported to cause shifts in the composition of soil microbial populations and known to cause detrimental effects on microbial cell metabolism at high concentrations (Jie. *et al.*, 2009) [20].

Heavy metal accumulation in vegetables

When vegetables are grown in these affected areas and by irrigating waste water with heavy metals, their concentration increases near the root zone and plant system absorbs the nutrients along with heavy metals, these absorbed heavy metals gets accumulated in the plant parts, usually it gets accumulated more in root part and leaves. Hence many researchers showed that accumulation of heavy metals are recorded high in leafy vegetables followed by root crops like *Amaranthus sp*., spinach, lettuce, cabbage, coriander, cauliflower and potato, onion, garlic, carrot, radish respectively

Singh and Singh (2014) [40] analysed different seasonal vegetables viz., mustard (*Brassica campestris*), cauliflower (*Brassica oleracea* var. botrytis), cabbage (*Brassica oleracea* var. capitata), and spinach (*Spinacea oleracea*) from the Kakching–Wabagai area with the help of atomic absorption spectroscopic for the quantification of Fe, Cu, Zn and Pb in these vegetables. Concentrations of Fe and Zn were more than the permissible limit; however, Cu was less with no appreciable amount of Pb. The concentration of Fe and Cu in spinach, mustard, cauliflower and cabbage was above the permissible limits and lead was not detected in the samples analyzed during 2008–09 to 2009–10.

In another study, 5.5 mg kg/1 of Pb in spinach (*Spinacea oleracea*) and tomato (*Solanum lycopersicum*) was reported which is more than the maximum permissible limit according to the international organization like Food and Agriculture Organization (FAO) and World Health Organization (WHO). The concentration of Cd in spinach was 0.3 mg kg/1 and it was 0.2 mg kg/1 in tomato, more than the permissible limit. The concentration of Cu and Zn in spinach was 0.03 mg kg/1 and 2.0 mg kg/1, respectively. The high level of Cd in spinach and tomato may cause different health concerns among consumers (Mohod, 2015) [30]. Bui *et al.*, (2016) [8] studied the contamination of vegetables by heavy metals near mining sites in Northern Vietnam. The average concentrations of Pb and as in fresh vegetable samples collected at the four mining sites exceeded maximum levels (MLs) set by International Food Standards for Pb (70.6% of vegetable samples) and As (44.1% of vegetable samples), while average Cd concentrations in vegetables at all sites were below the MLs of 0.2. They opined that irrigation water may be also the source of contamination in heavy metals. Green vegetable crops irrigated with waste water are highly contaminated with heavy metals and are the main source of human exposure to the contaminants. Amin *et al.*, (2013) [6] studied the accumulation of Cu, Ni, Zn, Cr, Fe, Mn, Co, and Pb in red onion (*Allium cepa*), garlic (*Allium sativum*), tomato (*Solanum lycopersicum*) and eggplant (*Solanum melongena*) irrigated with waste water. The presence of heavy metals in vegetables irrigated with waste water was significantly higher than those of tube well water. Onion (*Allium cepa*) was the heavily contaminated vegetable where the accumulation of Mn (28.05 mg kg/1) in the edible parts was 50-fold greater than *A. cepa* irrigated with tube well water irrigated soil.

Zhou *et al.*, (2016) [50] studied 22 vegetables for heavy metals accumulation and assessed the health risk factors of consuming the vegetables by Target Hazard Quotient (THQ) method. Leafy vegetables accumulated more heavy metals as compared to melon vegetables, which is an indication that cultivation of melon vegetables is suitable for soil contaminated with heavy metals. The residents are facing health risks due to vegetable consumption and that children were vulnerable to the adverse effects of heavy metal ingestion as the THQ value of children and adults was 5.41 and 4.12, respectively. Jolly. *et al.*, (2009) [21] revealed that concentration of Si, Ba, K, Ca, Mg Fe, Sc, V, Cr, Cu, Zn, As, Mn, Co, Ni, Se, Sr, Mo, and Cd in soil is higher than the world average value and Al, Ti and Pb is lower than the world average value, whereas the concentration of toxic elements like As, Co, Cu, Mn, Pb, Se, Ni, V, and Zn in vegetable samples is below the world average value. The hazard quotient (HQ) for the heavy metals showed a decreasing order of Cd>Mn>Zn>Pb>Cu>Fe>Ni>V D Co>Cr with highest HQ for Cd (2.543), which is above the safe value.

Ahada Chetan and Patel Ami, 2015 [12] reported that leafy vegetables accumulate more heavy metals when they are grown in heavy metal contaminated area. In this study leafy vegetables like *Spinacia oleracea* and *Amaranthus caudatus* were taken into study where they applied cadmium chloride and copper chloride salts to the pot culture. These plants accumulate heavy metals cadmium and copper in their plant tissue. From the growth study it was found that the heavy metal impact on growth was in the order of Cd>Cu. While heavy metal tolerance was in the range of Cu>Cd. *Amaranthus caudatus* was more sensitive towards metals than *Spinacia oleracea*. Root elongation can be selected as a simple parameter for evaluating the effect of essential and toxic metal on plant growth. Results suggest that heavy metal contents in soils have adverse impact on plant physiology and productivity. In case, if sewage water is used for irrigation purposes such plant family may accumulate a significant amount of metal and that may pose serious human health issues.

Impact of heavy metal on vegetables

Some of these heavy metals i.e. As, Cd, Hg, Pb or Se are not essential for plants growth, since they do not perform any known physiological function in plants. Others i.e. Co, Cu, Fe, Mn, Mo, Ni and Zn are essential elements required for normal growth and metabolism of plants but these elements can easily lead to poisoning when their concentration is greater than the optimal values (Rascio N. and Izzo F.N., 2011) [35]. The use of compost to improve agricultural yield without caring with possible negative effects might be a problem since the waste composts are most applied to improve soils used to grow vegetables. Considering the edible part of the plant in most vegetable species, the risk of transference of heavy metals from soil to humans should be a matter of concern.

Uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to animal and human health. The absorption by plant roots is one of the main routes of entrance of heavy metals in the food chain. Absorption and accumulation of heavy metals in plant tissue depend upon many factors which include temperature, moisture, organic matter, pH and nutrient availability. Absorption of heavy metals are more in summer than in winter due to transpiration (Sharma R.K. *et al*., 2007) [43].

Heavy metal accumulation in plants depends upon plant species and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil to plant transfer factors of the metals. Bhattacharyya P *et al*., (2008) reported that higher concentration of Pb in soils may decrease soil productivity and a very low Pb concentration may inhibit some vital plant processes, such as photosynthesis, mitosis and water absorption with toxic symptoms of dark green leaves, wilting of older leaves, stunted foliage and brown short roots. Heavy metals are potentially toxic and phytotoxicity for plants resulting in chlorosis, weak plant growth, yield depression and may even be accompanied by reduced nutrient uptake, disorders in plant metabolism and reduced ability to fix molecular nitrogen in leguminous plants (Guala S.D. *et al*., 2007) [16]. Seed germination was gradually delayed in the presence of increasing concentration of lead (Pb), it may be due to prolonged incubation of the seeds that must have resulted in the neutralization of the toxic effects of lead by some mechanisms e. g. leaching, chelation, metal binding or/and accumulation by microorganisms (Ashraf R. and Ashraf., 2007) [3].

Impact of heavy metals on humans

Plants uptake higher concentrations of heavy metals from the soil where it is affected with heavy metals and gets accumulated in the plant tissue. These heavy metals enter into the human body through food chain, utilization of these contaminated vegetables is the only route of human exposure to heavy metals. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues (Sobha K., *et al*., 2007) [43]. Chronic level ingestion of toxic metals has undesirable impacts on humans and the associated harmful impacts become perceptible only after several years of exposure (Khan S. *et al*., 2008) [26]. The toxic effects of heavy metals and its permissible limit is listed in below table (6).

Table 6: Important Heavy Metals and their Health Implications

Heavy metal	Permissible level mg/l)	Major source	Toxic effect
Lead	0.1	Mining, paint, pigments, electroplating, manufacturing of batteries, burning of coal	Anemia, brain damage, anorexia, malaise, loss of appetite, Liver, kidney, gastrointestinal damage, mental retardation in children
Copper	0.1	Plating, copper polishing, paint, printing operations	neurotoxicity, and acute toxicity, dizziness, diarrhea
Cadmium	0.06	Plastic, welding, pesticide, fertilizer, mining, refining	Kidney damage, bronchitis, Gastrointestinal disorder, bone marrow, cancer, lung insufficiency, hypertension, Itai–Itai disease, weight loss
Zinc	15	Mining, refineries, brass manufacturing, plumping	Causes short term-metal-fume fever", gastrointestinal distress
Mercury	0.01	Batteries, paper industry, paint industries, mining	Damage to nervous system, protoplasm poisoning, corrosive to skin, eyes, muscles, dermatitis, kidney damage
Nickel	0.2	Porcelain enameling, non-ferrous metal, paint formulation, electroplating	Chronic bronchitis, reduced lung function, lung cancer,
Arsenic	0.02	Smelting, mining, rock sedimentation, pesticides,	Bronchitis, dermatitis, bone marrow depression, hemolysis, hepatomegaly,

(Muhammad umair sattar *et al.*, 2012; Ruqia nazir *et al.*, 2015) [36]

Analytical methods for testing of heavy metals

There are two basic types of analytical methods for assaying heavy metals. The classical ones are colorimetric, where the concentrations of heavy metals are measured as a group of like elements. The newer instrumental methods measure individual elements.

- Colorimeter
- flame atomic absorption spectroscopy (FAAS),
- graphite furnace atomic absorbance spectroscopy (GFAAS),
- inductively coupled plasma-atomic emission spectroscopy (ICP-AES)
- Inductively coupled plasma-mass spectroscopy (ICP-MS).
- X-Ray Fluorescence Spectrometry

International / National Standards of Permissible level of heavy metals in Food and Edible Products.

Available International / National Standards:

- Codex Alimentarius Commission (CODEX)
- Mainland
- US Food and Drug Administration (FDA)
- European Commission (EU)
- Australia

Codex Standards

CODEX STAN 193-1995 (*Amendment: 2010*)

Established Maximum of Five Heavy metals

- Arsenic
- Cadmium
- Lead
- Mercury (including methylmercury)
- Tin

Mainland

GB Standard GB 2762: Maximum levels of contaminants in food

Established maximum levels of SIX heavy metals:

- Arsenic
- Cadmium
- Chromium
- Lead
- Mercury (including methylmercury)
- Tin

USA

US Food and Drug Administration (FDA) Maximum level in selected food

- Mercury (including methylmercury)

Allowable levels in bottled water

- Arsenic
- Antimony
- Cadmium
- Chromium
- Lead
- Mercury

Recommended maximum level in Candy likely to be frequently consumed by children

- Lead

European Commission

Commission Regulation (EC) No. 1881/2006 - maximum of FOUR heavy metals in foodstuff

- Cadmium
- Lead
- Mercury
- Tin

Need for Remediation

Modern lifestyle and industrialization have led to many environmental problems because they generate different types of wastes and their dumping without proper treatment. These wastes contaminate the environment with the most crucial and fatal effects on the living entities marking their survival at stake. The most hazardous part of industrial effluents and other wastes is the release and accumulation of metals, especially heavy metals. The wastes should be treated before they are dumped into the environment to minimize their effects on the environment by converting them into less harmful forms. However, once the water or soil is contaminated by these pollutants, proper set of processes to treat them needs to be followed before they can be brought into common use. Effective treatments are quite costly. The most efficient and economical way in this aspect has been found to be bioremediation that involves the use of living organisms to treat certain pollution causing conditions by efficient uptake of the pollutants from the desired environment. Plants have been found to be quite efficient in the process, commonly termed as phytoremediation. Phytoremediation is the process of removal of heavy metals through plants. Plants have the ability to absorb the heavy metals from the soil and water. These absorbed heavy metals are accumulated in the plant tissue. Based on the accumulation of heavy metals they are classified as Hyperaccumulators and Non Hyperaccumulators

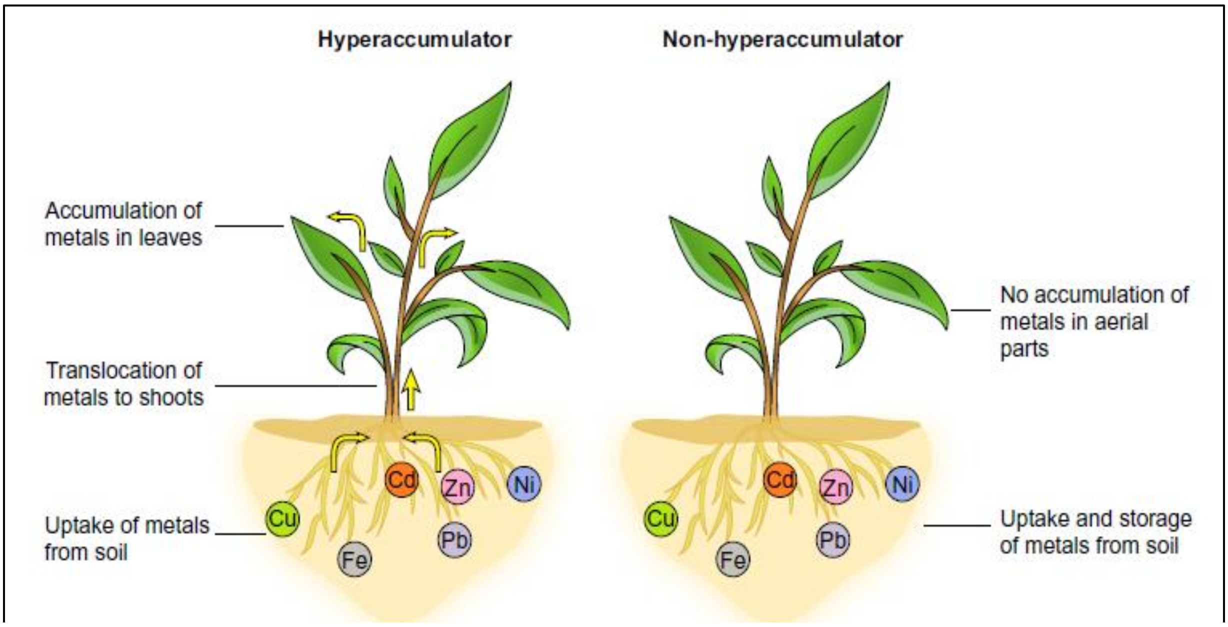

Fig 2: How hyperaccumulators are different from nonhyperaccumulators. The hyperaccumulators allow heavy metal storage in their above-ground parts, whereas nonhyperaccumulators store heavy metals in their below-ground organs. (Ghori *et al.*, 2016) [17]

Hyperaccumulators can take up heavy metals from soils through roots and translocate them to shoots and leaves. Contrastingly, non-hyperaccumulators or accumulators are those plant species that can accumulate heavy metals in their below-ground parts and cannot translocate them to shoots and leaves except some that allow limited translocation. About 450–500 plants have been identified as hyperaccumulators. There are about 45% of hyperaccumulators that belong to angiosperm families; of these, 25% of hyperaccumulators belongs to Brassicaceae family. Other families include members of Asteraceae, Caryophyllaceae, Fabaceae, Cyperaceae, Poaceae, Cunoniaceae, Lamiaceae, and many others

Conclusion

Heavy metal contamination of agricultural soils as a result of urbanization and industrialization is of great concern because of potential health hazard due to dietary intake of contaminated vegetables. Vegetables are vital to the human diet and in particular provide the nutrients to maintain normal health. The prolonged application of fertilizers, pesticides has resulted In accumulation of heavy metals especially in vegetables. Exposure to heavy metals by consumption of contaminated vegetables and its toxicity is a serious concern. However limited numbers of studies are found to assess the permissible limits of heavy metals. Also, specific study is required to assess the contamination of heavy metals in children, elderly people and women including pregnant women. Furthermore, strategy and policy are required to control the limits of accumulation in vegetables and hyper accumulators identified for specific vegetables.

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