

Review on Heavy Metal Contamination in Vegetables due to Wastewater

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Abstract

Because of the potential health effects of swallowing tainted food items, heavy metal contamination of soil and vegetative sections of plants as a result of wastewater irrigation is a severe issue. The impacts of trace elements (heavy metals) such as arsenic, cadmium, lead, chromium, nickel, and mercury, which are important environmental pollutants, are assessed in this article particularly in areas with high anthropogenic activities. In addition to these metals, copper, manganese, iron, and zinc are also important trace micronutrients. The presence of trace heavy metals in atmosphere, soil, and water can cause serious problems to living organisms, and the ever-present bioavailability of these heavy metal can result in bioaccumulation in the food chain which especially can be murderous to human health. This study reviews the heavy metal contamination in several areas of Pakistan over the past few years, especially to access heavy metal contamination in water (ground water, surface water, and waste water), soil, sediments, particulate matter, and vegetables. The contaminations affect the drinking water quality, ecological environment, and food chain. Furthermore, the toxicity caused by contaminated water, soil, and vegetables endangers human health. Increased population and high food demand result in the release of many contaminants into the environment, which eventually contaminate the food chain. Edible plants are the primary source of food for humans, and their contamination with toxic metals can have disastrous health consequences. Heavy metals affect the human health directly and/or indirectly; one of the indirect effects is the change in plant nutritional values. Previously, a

Number of review papers have been published on different aspects of heavy metal contamination. However, no related information is available about the effects of heavy metals on the nutritional status of food plants. This review study focuses on heavy metal sources, accumulation, transmission, health risks, and the impact of heavy metals on protein, amino acids, carbohydrates, lipids, and vitamins in plants. According to the research on heavy metals in food plants, both leafy and no leafy vegetables are good heavy metal accumulators. The bioaccumulation pattern in no leafy plants was leaf > root > stem > tuber. Because heavy metals have a considerable impact on nutritional values, plants produced on metal-contaminated soil were nutrient poor, and eating of such vegetables may lead to nutritional insufficiency in the population, particularly in poorer nations where malnutrition is already a problem.

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Introduction

Heavy metals have a high atomic density five times larger than water or more than 4 g/cm³ or more than 5 g/cm³

(Bahiru and Yegrem, 2021) and are primarily harmful in nature for humans, plants, and animals regardless of concentration (LWTAP 2004). The nonessential metals are a component of the earth's crust that permeates the upper atmosphere. Biogeochemical cycles affect the soil horizon and food chain (Alotaibi, et al. 2021). Heavy metals include metals and metalloids with high densities, such as cadmium (Cd), lead (Pb), mercury (Hg), and zinc (Zn) (Nkwunonwo, et al. 2020), whereas arsenic (As) is included in this list due to comparable qualities. When necessary and non-essential trace elements surpass their threshold limits, they can induce a variety of physiological, morphological, and genetic defects such as stunted development, carcinogenic consequences, and increased mortality (Alengebawy, et al. 2021). Food crops are an important element of our nutrition, and they may include a variety of necessary and hazardous metals, depending on growth conditions. Vegetables are the most common source of heavy metal exposure in humans, accounting for around 90% of total metal intake, with the remaining 10% coming via skin contact and inhalation of contaminated dust (Khan et al. 2014). Because of the growing need for food, food safety has become a major concern for human health in recent decades. This scenario motivates researchers and scientists to investigate the health risks linked with the ingestion of heavy metals, pesticides, and toxin-contaminated food (Li et al. 2021). Through the excessive use of agrochemicals, municipal wastewater, industrial effluents, and raw sewage for irrigation, vital and non-necessary materials are frequently introduced to our food chain (Hembrom et al. 2020). Heavy metals and metalloids prevalent in the environment, such as As, Pb, and Cd, have been classed as 1, 2, and 7 by the Fe, Mn, and Zn are necessary elements for animals and humans because they play vital roles in many metabolic functions, enzymatic activities, receptor sites, hormonal function, and protein transport at certain concentrations (Apostoli 2002; Antoin 2002). Other elements, such as As, Cd, and Pb, are non-essential and have no helpful effect in plants, animals, or people (Chang 2000), and have no nutritional purpose due to their extreme toxicity (Goldbold and Hutzelmann 1985). To set quality standards and identify the hazards to human health and food safety, it is required to identify the sources and amounts of heavy metals in soil (Sunet al. 2013). Heavy metal contamination in the environment is persistent, stealthy, and persistent. Metals are incapable of being degraded by biological organisms due to their non-biodegradable nature and extended half-life, and they remain in their body parts and surroundings. Heavy metals can travel from polluted soil and water to bioaccumulate in plants, posing health hazards. Soil features are critical in food production, and heavy metal pollution of this crucial resource, as well as their final absorption and bioaccumulation in food crops, poses severe environmental and health issues. Heavy metal concentrations are significantly affected by soil type and plant genotype, as well as their interaction. Mineral fertilizers have greater heavy metal concentrations than organic manure; hence, the use of mineral fertilizers causes soil heavy metal contamination (Hu et al. 2013). So far, a number of studies (in pots and in the field) have been carried out to investigate the influence of soil characteristics and other variables. Components influencing heavy metal movement and bioavailability from soil to crop system. A variety of biological processes and physiochemical parameters, such as soil pH, organic matter (OM) cation exchange capacity (CEC), soil texture, and soil micro biota, influence heavy metal mobility and bioavailability in contaminated soil. Soil pH has a considerable impact on the availability and accumulation of heavy metals in plant edible portions (Hu et al. 2013). Similarly, CEC and OM reduce the mobility and bioavailability of heavy metals such as Pb.

Cd toxicity to soil is well recognized; it is a hazardous heavy metal that produces toxicity even at low concentrations. When compared to other elements, the bioaccumulation rate of Cd in field crops is greater (Arao and Ae 2003). Various agricultural solutions, such as bio fortification and correct fertilizer usage, have been proposed to increase the nutritional composition of soil. Most research in recent years have focused on. As contamination of the food chain (as well as other heavy metals and metalloids reported to be beyond the acceptable limits. Food crops irrigated with industrial effluents and wastewater are the primary cause of soil and water contamination.

Heavy metal and metalloid pollution of crops

The health risks associated with toxic metals are determined by the concentrations of these metals in certain media and the extent of exposure. The present moment even at low quantities of hazardous metal, long-term and chronic exposure can cause health problems (Mahalakshmi. 2012; et al.). Among the abiotic stresses to plants, heavy metal toxicity is one of the major stresses and the toxicity is based on physiochemical properties of heavy metals (Saxena and Shekhawat 2013). The aims of this paper are to summarize the literature about the heavy metals as a major environmental issue and critically discuss the information about heavy metal (As, Cd, Cr, Cu, Ni, and Pb) contamination in soil and the grown food plants, metal bioaccumulation, soil-to-plant transfer, nutritional effects, and health risk.

Heavy Metal in soil

Heavy metal pollution of soil is a severe worldwide environmental concern causing dangers to humans, animals, microorganisms, and plants as well as polluting surface and groundwater. Heavy metals and other pollutants enter the soil ecosystem via natural and anthropogenic processes. Trace element concentrations in soil environments are primarily determined by geology (Carral et al. 1995), but anthropogenic activities such as solid waste disposal, wastewater irrigation, sludge application, automobile exhaust, mining and smelting processes, urbanization, agricultural activities, and industrialization also play a role to add heavy metals into the soil environment. Similarly, the physiochemical properties of soil have a significant impact on heavy metal content and availability to plants. The organic component of the soil has a significant impact on heavy metal concentrations (Khan et al. 2015). Soils with high organic waste concentrations have heavy metal concentrations of less than 1000 mg kg⁻¹ soil, but industrial waste-contaminated soil has concentrations of more than 10,000 mg kg⁻¹ soil. Increasing concentrations and variations in heavy metal distribution in metal-amended soil often increase heavy metal concentrations in plants (Castro et al. 2009). Because soil is a key instrument for waste management and trash dumping, it is the primary source of heavy metal contamination in the food chain (Zhuanget al. 2009). The principal route of heavy metal intake into the human body is through the soil–crop system in the agricultural region (Liu et al. 2007), where anthropogenic activities are the principal causes of pollution. The primary route of exposure to heavy metals in urban environments is through ingestion, absorption through skin, and inhalation of dust particles (Sindern et al. 2007), whereas the primary source of pollution in urban soil is anthropogenic, which includes vehicular emissions, power plants, tyre weavers, and other sources. The intricate structure and variety of soil microbes make ecotoxicological evaluation of polluted soil extremely challenging. However, these test techniques are regarded as a useful tool for determining the bioavailability of pollutants to certain species. For representing metal-contaminated sites, the ecological risk assessment approach is generally applicable for this purpose, soil quality values, also known as guideline values, are used. These recommendations are based on the dose–response relationship data derived from laboratory tests on ecological processor single plant or animal species.

Finally, these guideline values are derived using statistical techniques (O'Halloran 2006). Total metal concentrations in the soil are used to calculate soil quality ratings. However, total metal concentration data is insufficient for risk assessment, and additional properties of metals such as chemical form, electric potential, and ion activity must be considered when forecasting metal toxicity. Soluble metals and free metal ions are more bioavailable and hazardous than other types of heavy metals.

Factors affecting mobility and bioavailability of heavy metals

Different soil factors have a substantial impact on heavy metal accumulation in plants.

- Soil pH,
- Organic Matter
- Redox potential,

- Total metal contents
- CEC

Soil OM

Soil OM has the capacity to bind hazardous metals, allowing it to modulate heavy metal behaviour and reduce toxicity in soil. According to Wu et al. (2014), sequential study showed that Pb availability in soil steadily reduced while Cd availability rose. Likewise, the soil OM bounded fraction of Pb grew while the percentage of Cd declined. This demonstrates that Pb has a stronger affinity and stability for OM than Cd. The differential in relative binding affinity of Pb and Cd with soil OM is due to variations in metal chemistry.

Heavy metals bound with dissolved OM are readily accessible to soil plants (Krishnamurti et al. 2004). Similarly, humic acid, which contains phenolic and carboxylic functional groups, is a key component of organic carbon that improves heavy metal mobility and availability to plant. As a result, soil with a high humic acid content is unsuitable for agricultural purposes.

pH:

Soil pH has a substantial impact on the bioavailability and toxicity of heavy metals in soil (Amini et al. 2005). Metal mobility and bioavailability are greater at low pH than at high pH.. When the pH of the soil falls below the crucial value of 4, it lowers metal absorption by plants and increases metal availability. The pH levels in soil are affected by geology, distance from the road, industry, and irrigation type. Soil pH changes as a result of wastewater irrigation (Zhuang et al. 2009). Like mobility and bioavailability of metals, the Ph plays an important role in the metal speciation in soil (Luo et al. 2011). Along with other physiochemical characteristics, pH can significantly affect the heavy metal removal from contaminated soils. Heavy metal like Cu has the tendency of making Cu–OM complexes (Li et al. 2008) which leads to affect its availability.

Cu bioaccumulations in plants are significantly affected by soil pH and negatively correlated with each other. Toxicological effects of free metal ions on ecological resources are soil with low pH should not be used for agriculture purposes due to highly availability of metals in it.

Soil texture

Soil texture along with other factor is one of the important factors that induces metal availability in soil. Clay contents cansignificantly affect the availability of heavy metals and their subsequent toxicity to living organisms. Crops grown on sandy soil are metal deficient, particularly Zn, as compared to loamy texture (Rashid and Ryan 2004); this may be due to large pore size and the low retention capacity of sandy soil to retain metals. Soil-to-plant transfer of heavy metals is strongly influenced by the soil texture. Treder and Cieslinski (2005) said that plants grown on sandy soil had greater heavy metal concentrations than those planted on clay loamy soil. The high bioaccumulation in plants is linked with higher mobility ofmetals in sandy soil as compared to clay soil.

Soil texture and soil microbiota

Heavy metals and microorganisms have a strongly unfavourable association. High heavy metal concentrations have been shown to have an impact on the structure, activity, and abundance of microbial communities (Khan et al. 2010). Similarly, there is a strong relationship between soil microbiota and soil texture; the majority of microorganisms are associated with clay concentration (Sessitsch et al. 2001). Furthermore, soil texture influences heavy metal transport from the higher to lower soil horizon. Heavy metals can flow more freely from one horizon to the next in sandy-textured soil than in clay soil. Pore size has an impact on metal mobility.

Plant species

The bioaccumulation of heavy metal is different for different plant species reflected by their growth, reproduction, occurrence, and survival in the metal-contaminated soil. It is notable that different plant species show different toxicity to the same pollutant and in the same environmental condition, because the mechanisms of elemental uptake by plants are not the same for all plant species (Zechmeister et al. 2003). Heavy metal accumulation in food plants depends on metal

Concentrations as well as phyto-availability and phytovariety, as different plants have different uptake rates (Yang et al. 2009).

The capability of plants to absorb heavy metals varies by heavy metal, and the same heavy metal might be accumulated in various proportions in various plant species. Metal bioavailability is also influenced by the presence of organic metal compounds in plants. Organo-arsenic chemicals found in plant tissues significantly limit species bioavailability. In general, the metal absorption rates of leafy vegetables are greater and more polluted than those of nonleafy vegetables. (Yu et al. 2006).

Heavy metals in plants

Vegetables are an essential part of most people's meals, and contamination can lead to major health issues (Radwan and Salama 2006). Leafy crops, such as lettuce, are thought to be potential heavy metal hyper accumulators. One of the characteristics of green leafy vegetables is the buildup of heavy metals in their tissues without any poisoning symptoms. According to Monteiro et al. (2007), the concentrations of heavy metals in lettuce roots and shoots rose with increasing exposure length lettuce has higher capacity to accumulate heavy metal in different tissues. Heavy metal uptake is also affected by different. Heavy metals, at varying amounts, can alter tomato physiology and development, resulting in chlorosis and necrotic signs on leaves (López-Millán et al. 2009). Plants growing in wastewater-irrigated soil have significant metal concentrations in both their vegetative and nonvegetative portions. Heavy metal absorption is also influenced by different plant species and cultivars within the same species. Like other food crops, potato is important food crop grown throughout the world. It is rich with energy, dietary fibers, vitamins, carbohydrates, and essential elements such as Fe, Ca, Zn, and K (Finglas and Faulks 1984). Mineral concentrations and photosynthetic activities of plants can also be affected by toxic metals (López-Millán et al. 2009).

The soil pH substantially affects the supply of these essential nutrients to plants; low pH means more supply of nutrients. Moreover, the nutrient supply to plants is affected by a number of factors including soil type, climate, cultivation practices, and storage condition. Concentrations of heavy metals vary in different organs of the same plant. (Xu et al. 2013) reported the heavy metal accumulation in the order of leaf > root $\approx$ stem > tuber. However, other scientists conveyed that the root concentrations are higher than shoot.

In fruit plants, like tomato, the translocation rate of heavy metals to the fruit is rather low, hence characterised as low-rate translocation fruit vegetable. Accumulation and distribution of heavy metals like Cd have been found in different parts of tomato (Donma and Donma 2005). Tomato is an important food plant from economical as well as nutritional point of view. Tomato is a rich source of minerals, vitamins, and other nutrients (Giovanelli and Paradise 2002) consumed both in raw and processed form. Heavy metals are toxic to vegetables at high amounts, and large-scale irrigation with wastewater and application. The use of commercial fertilisers raises the danger of heavy metal pollution (Gil et al. 2004). Heavy metals have a significant negative impact on plant growth (López-Millán et al. 2009); other toxic effects may include root browning, mineral concentration changes, and changes in photosynthesis (López-Millán et al. 2009).

Metal moves from the plant's roots to its shoots at higher concentrations. Misra and Mani (1991) have suggested that metal concentrations in plant tissues were in the range of 0.02–7, 0.1–2.4, 0.2–1.0, 4. Heavy metals are toxic

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Metal uptake by plants

Vegetables (both leafy and nonleafy) cultivated on polluted soil are thought to be the primary source of heavy metals. Plants are classed as accumulators, hyperaccumulators, or excluders based on their ability to absorb heavy metals. Heavy metal contamination of plants can occur via soil–plant, water–plant, and air–plant interfaces; however, the soil–plant interface is the most common cause of plant metal accumulation. According to the literature, there is a strong link between heavy metals in soil and food crops. (Khan et al. 2015). In general, heavy metal bioavailability is determined by the quantity of exchangeable metals in soil. Metals that are carbonate-bound and exchangeable are more bioavailable. The bioavailability of heavy metals in plants varies by plant organ, with roots having the highest absorption and bioaccumulation rate when compared to other sections (Verma and Dubey 2003). Similarly, metal absorption by plants is influenced by solubility and soil type. The average heavy metal absorption by plants increases as the concentration of these metals in the soil environment increases (Chaves et al. 2011). According to Liu et al. (2005), the bioavailability of Cd is the highest, while that of As is the lowest for crops grown in heavy-metal polluted soil. *Amaranthus dubius* has the potential to extract heavy metals from soil via their root system, although shoot absorption for a number of heavy metals such as As, Cr, Cu, Ni, and Pb is insignificant.

Heavy metal toxicity and plant tolerance

Heavy metals have been found to have toxicological effects on plants and animals, with varying degrees of toxicity from species to species and metal to metal. Metal toxicity is connected with their speciation in soil, according to the research; nevertheless, it is difficult to identify individual species due to their complicated nature, functioning, and distribution in soil environments (Czuprynan and Levy 1989). Heavy metal bioavailability and toxicity to living organisms are affected by soil physiochemical factors and microorganisms.

Heavy metals interact with critical micronutrients, influencing their absorption and transport by plants. hence influencing plant growth and development. Physiological processes Hernández et al. (1995) discovered the plant exhibited hazardous symptoms when exposed to high Cd concentrations. in addition, induced delay in growth. Similarly, even at low concentrations of Cd, may have a toxicological impact on seed germination Cu is also harmful to seedlings (Li et al. 2005a). Heavy metal genotoxicity to living beings is caused by heavy metals interacting with genetic material via DNA binding. A variety of transgenic and bioassay procedures, including as random-amplified polymorphic DNAs (RAPDs), micronucleus (MCN) induction, and the Comet test, have been advocated for investigating the genotoxic effects of environmental contaminants on plants (Liu et al. 2005). Depending on the soil conditions, several plant species are recommended for heavy metal toxicity testing. Because lettuce is not an acid-tolerant plant, it is employed for toxicity testing in intermediate pH environments (pH 6–8 (Chapman et al. 2012)

Among higher plants, oat is recommended for heavy metal toxicity tests under low pH conditions, whereas *Allium cepa* is Pb tolerant in acidic environments (Loureiro et al. 2006). Plants' capacity to tolerate heavy metals may be related to their chemical form (Yang and He 1995). Similarly, metal-induced reactive oxygen is a kind of reactive oxygen. The peroxidation of fatty acids is caused by reactive oxygen species (ROS). Acidic plants have many strategies to prevent the damaging effects of ROS. Antioxidant enzymes, for example, are used in defensive tactics.

Nitrogen and sulphur are two necessary nutrients for protein and glutathione production, as well as defence Heavy metal tolerance mechanisms. Likewise, metal-induced reactive According to recent research on plant tolerance mechanisms to environmental pollutants, heavy metals have a strong influence on leaf size and structure, and the first toxicity symptoms appear on leaves; thus, measuring length to width ratio can be very effective in evaluating plant tolerance to heavy metals (Zhang et al. 2014). To prevent metal toxicity, plants can evolve an advanced and sophisticated detoxification system that includes selective absorption, chelation, compartmentalization, and toxic metal secretion (Pourrut et al. 2013). Phytochelatins are important in metal detoxification (Cobbett 2000). Because of processes such as the control of phytochelatin synthesis by BjCdR15/TGA3, *Brassica juncea* (BjCdR15) and *Arabidopsis* TGA3 are good tolerants to high metal concentrations (Farinati et al. 2010). Similarly, several genes contribute to metal tolerance by regulating metal–glutathione conjugate transport. Plant protein has an active role in heavy metal homeostasis and tolerance.

Effects on plant growth

Heavy metals are phytotoxic and have a considerable detrimental influence on plant development, even at low doses (Di Salvatore et al. 2008). Plant development is substantially reduced in high concentrations of heavy metals (Chaves et al. 2011). Heavy metal concentrations in the soil have a significant impact on the development and metabolic processes of farmed crops (John et al. 2009). Heavy metals produce oxidative stress, interfere with photosynthetic processes, and slow development. Elevated heavy metal concentrations can cause stunted development by interfering with the photosynthetic machinery and disrupting the coordination mechanism between key components, eventually leading to plant mortality. Cu is an essential element that is necessary in many physiological activities and plant development; but, at greater concentrations, it becomes poisonous and inhibits plant development as well as normal physiological activities (Bouazizi et al. 2010). Excessive usage of heavy metals such as Cu may result in Root development is inhibited, and the plasma membrane is damaged, resulting in ion leakage from the cells. According to Soares et al. (2001), heavy metals have a significant impact on plant growth, developmental processes, and cell division dissection Plant height has been reduced by 18 to 77% when grown in metal- contaminated soil. The leaf area of plants cultivated in metal-contaminated soil decreased significantly. Changes in protein synthesis, photosynthetic activity, and respiration all contribute to this (Chaves et al. 2011). Cd concentrations beyond a certain threshold have a substantial deleterious influence on lettuce shoot development (Monteiro et al. 2007). This reduction might be the result of metal- induced chromosomal abnormality.

Metal exposure and human effects

Disruption of plant cellular metabolism Toxicological effects of metal-contaminated food on humans are determined by a variety of parameters, including chemical forms of heavy metals, dosage, exposure route, duration, frequency, age, gender, nutritional source, and biological species (Tchounwou et al. 2004). Because heavy metals are hazardous to both human health and plant tissues, the tendency of food plants to collect them in their tissues is a public health problem. Some metals are necessary by the human body, whereas others (As, Cd, Pb, and so on) are hazardous in nature even at low amounts (Gebrekidan et al. 2013) and have been linked to carcinogenic health hazards. Consumption of As-contaminated foods, on the other hand, can pose substantial health hazards. Many heavy metals are carcinogenic and can induce organ malfunction and damage. Heavy metals enter the human body through ingestion, inhalation, and dermal contact (Kim et al. 2009), causing minor to major health problems such as diarrhoea, nausea, lung diseases, anaemia, kidney disorders, stomach problems, skin diseases, neurological disorders, and cancer. Some of the illnesses are the result of acute poisoning, while others are the result of chronic exposure. Heavy metals can accumulate in many bodily areas and have a negative influence on health independent of concentration (Ikeda et al. 2000). Toxic metals' toxicological effects might differ from person to person. Higher quantities of non-essential components have an influence on live organisms' reproductive potential (Oetken et al.

2004). In order to estimate the health risks associated with heavy metal pollution of soil, a mathematical model that predicts the bioaccumulation and transformation of these harmful metals should be developed. The related health danger of some specific substances and/or phenomena in a given environment and/or environmental circumstances, dependent on exposure length and receptor availability, is referred to as health risk.

Conclusion

Food plants, particularly green leafy vegetables, are the most common food source consumed worldwide. They have a role to perform. Nutritional contribution to customers has a crucial influence. Green plants are high in critical nutrients; nonetheless, they are heavy metal accumulators that represent a significant risk to human health. Nonleafy veggies are the same way. They are also an excellent source of nutritious nutrients and a crucial part of a well-balanced diet. However, when they are exposed to environmental toxins, they collect heavy metals in their edible sections.

Heavy metals have both direct and indirect health impacts. Direct effects include direct eating of vegetables, ingestion, and skin exposure, whereas indirect effects include nutritional component loss in contaminated food crops. Vegetables, however, are substantial sources of heavy metals, posing both carcinogenic and noncarcinogenic health hazards. Our studies revealed that heavy metal concentrations in food crops are significantly greater than their background levels. Cd, Pb, and Cu concentrations were found to be over the permitted levels given by SEPA China, FAO/WHO, EU, and Indian standards, which have a substantial impact on the nutritional components of farmed crops. Furthermore, the quantities of heavy metals in plants and their nutritional content show an inverse connection. Heavy metals have a deleterious influence on the protein, lipid, and carbohydrate levels of contaminated plants. As a result, it is proposed that further comprehensive research on various aspects of heavy metal pollution on plant nutritional components be conducted, and that severely polluted land should not be used for agricultural reasons until preventive and rehabilitative measures are implemented.

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