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BIOACCUMULATION OF HEAVY METALS IN EDIBLE MACROPHYTES:

A REVIEW

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Abstract: The ever-increasing rate of urbanization and industrialization has led to a rise in various forms of pollution in the ecosystem. Heavy metal is one such pollutant that has been widely spread and can affect the environment in different forms. They can accumulate readily in living systems including plants. Food crops or edible plants contaminated with heavy metals can be consumed by humans and result in various health issues. Food crops are a necessity in the human diet and contamination of them can be harmful. In this review, we focus on heavy metals accumulation in different crops, their source, effects on nutrient contents on the plants, and their health risk. From the various reports, we can understand that the type of plants, and the ecosystem in which they are grown plays a major role in the accumulation of heavy metals. They can be classified as excluders, accumulators, and hyperaccumulators according to their affinity to accumulate metals. Heavy metal accumulation can also influence the nutrient content of the plants, which can be a reason for nutrient deficiency in the human population.

Keywords: Heavy metals, health risks, food crop, nutrient, toxicity

Introduction

Heavy metal pollution has been a concerning environmental risk, especially in developing countries. Metallic elements having a specific density greater than 5.0 with atomic density >4g/cm^3 are classified as heavy metals (Hawkes, 1997; Weast 1984; Saxena et al., 2013). With high densities, zinc (Zn), mercury (Hg), lead (Pb), and cadmium (Cd) are classified as heavy metals (Oves et al., 2012) and arsenic (As) is considered one due to their properties (Chen et al., 1999). They are toxic above the threshold limit and are persistent, and can be accumulated easily in nature. Because of these properties, they can lead to unfavorable consequences on the living system once they enter the food chain (Sharma R.K. et al., 2005; Nagajyoti P.C. et al., 2010).

Macrophytes are one of the important sources of nutrients in our diet. However, they may act as a way to introduce various toxic metals into our bodies (Waq as et al., 2015; Yang et al., 2011). Heavy metals can enter our bodies through vegetables as plants act as perfect bioaccumulators of heavy metals. When the maximum limits are exceeded for the non-essential and essential elements it may result in different physiological, genetic, and morphological abnormalities which include mutagenic consequences, reduced growth, and a high death rate (Luo et al., 2011; Li et al., 2010; Khan et al., 2010a). 90% of heavy metal consumption in humans is through vegetables (Martorell et al., 2011; Khan et al., 2014; Kim et al., 2009; Ferré-Huguet et al., 2008).

Here, we will try we summarize the consequences of heavy metal pollution in different ecosystems on varieties of edible plants, their source, toxicity on the plants, and human health. We will also further review some results of metal contamination on the nutrient contents of the macrophytes which may have an adverse problem on human food security.

Sources of heavy metals

Contamination of waterways has been a major concern in recent years with the increasing pace of urbanization, industrialization, and change in land-use patterns. This can be a threat the biodiversity and will affect those components that are dependent on the waterways. Among many others, heavy metals are considered to be a key pollutant of aquatic ecosystems due to their non-biodegradability, environmental persistence, and toxicity.

Heavy metals can derive from both lithogenic and anthropogenic sources in the environment. Lithogenic origins may consist of forest wildfires, sea salt, windblown aerosols, weathering of rock minerals, and volcanic particles. On the other hand, heavy metals can also be introduced into the ecosystem due to human activities including pesticides, organic matter, composts, fertilizers, and sewage sludge (Singh and Agarwal, 2007; Lopez Alonso et al., 2000). It can also be from metallurgic industries, smelting, mining, and industrial waste (Singh, 2001), and untreated municipal and industrial effluents (Singh et al., 2004; Singh and Kumar, 2006; Mapanda et al., 2005; Barman et al., 2000; Sharma et al., 2006, 2007). Another source is atmospheric depositions (Temmerman and Hoeing, 2004).

Plants grown in those areas with metal-contaminated soil or wetlands are exposed to heavy metals, which can lead to uptake in plant systems, thus entering the human system.

Accumulation of the heavy metal in edible macrophytes

Macrophytes are an essential source of nutrients. Contamination of the food crops may result in serious health hazards (Liu et al. 2005a; Khan et al. 2008a; Radwan and Salama 2006). Studies on plants' bio-accumulation of heavy metals, whether it is for remediation study or to study the effects of accumulation. These studies have shown that leafy plants such as lettuce are classified as hyperaccumulators due to their strong affinity to accumulate high levels of metals (Ramos et al. 2002; Cobb et al., 2000). Green leafy vegetables can accumulate relatively heavy metals in high concentrations without showing toxicity (Dean and Intawongse, 2006). Higher concentrations of Cr and Cu can be observed in vegetables such as cabbage, spinach, etc compared to their concentrations in non-leafy vegetables such as tomato and brinjal (Sharma et al. 2006). Heavy metal accumulation is reported to be highest in the leaf followed by root or stem (Xu et al. 2013a; Vanassche and Clijsters 1990).

Heavy metals can negatively impact the physiology and growth of tomatoes resulting in necrotic symptoms on leaves and chlorosis (López-Millán et al. 2009; Anwarzeb Khan et al. 2015). Cd contamination has been noted in various parts of tomatoes (Donma and Donma 2005). Tomatoes are prevalent all around the world for their high economic and nutritional values (FAOSTAT 2007). Tomatoes are rich in vitamins, minerals, and other nutrients (Paradise and Giovanelli 2002).

Rice is considered a staple food in most parts of the world, especially in Asian countries. Mohammad M.U. et al. in 2021 reported that heavy metals can accumulate in rice plants due to irrigation with contaminated water. Sharma et al. (2021) summarized some studies showing contamination of rice grains with toxic heavy metals contamination of copper(Cu), nickel(Ni), arsenic(As), chromium(Cr), lead(Pb), etc.

Aquatic plants grown in metal-contaminated water bodies may result in the accumulation of metals in the plants. In most Asian countries, aquatic edible plants such as *Ipomoea aquatica* (water spinach), *Nelumbo nucifera* (wild lotus), and *Nesturtium officinale* (watercress) are widely popular and provide many nutrients. In Thailand, sampling of *I. aquatica* at nine sites revealed heavy metals accumulation of Hg, Pb, and Cd, and Hg concentrations as high as 1.440 $\mu g\ kg^{-1}$ dry weight were reported (Göthberg A. et al. 2002). Wild lotus (*Nelumbo nucifera*) is a widely popular aquatic plant in Asian Countries for its varied useful purposes. As and Cd concentration was found to be 1.3-9.0 times higher on the tuber's peel than in the inner flesh in a study of wild lotus plants in China (Mohammed M.U. et al., 2021; Luo Y. et al. 2017). Metal accumulation may vary with the plant species as some plants have more affinity for certain metals. For example, watercress tends to accumulate Cr, Cd, and Co (Duman F. et al. 2009).

Table 1: Heavy metals concentration (mg kg^{-1}) on edible macrophytes (adapted from Mohammad M.U. 2021)

Plants	As	Hg	Cd	Cr	Cu	Ni	Pb	References
Lettuce	-	-	0.9	7.5	14.6	14	5.5	Khan et al. (2008b)
	-	-	4.22±0.51	-	23.2±2.5	-	8.59±0.9	Luo et al.(2011)
	-	-	2.0-47.3	3.0-13.4	16.3-23.0	4.0-78.9	9.2-20.6	Smilde (1992)
	-	-	0.27±0.02	-	0.98±0.10	-	0.13±0.01	Zhuang et al. (2009)
	-	-	14.98±0.53	-	8.15±0.18	-	3.64±0.55	Waterlot et al. (2013)
Rice	-	-	0.013	-	2.4	-	-	Batista et al. (2010)
	-	-	0.43	-	42.3	-	13.6	Luo et al. (2011)
	-	-	0.003-0.06	0.12-0.37	2.6-5.3	0.25	0.01-0.53	Liu W.X. et al., 2007 Mao C. et al., 2019
Tomato	-	-	0.41	-	32.60	3.10	9.70	Demirezen & Aksoy (2006)
	-	-	0.01	-	39.99	0.03	1.94	Bigdeli & Seilsepour (2008)
	-	-	0.38±0.02	0.60±0.06	2.43±0.15	0.73±0.06	2.50±0.24	Gebrekidan et al. (2013)
	-	-	7.20	-	8.70	-	29.00	Sharma et al. (2006)
	-	-	0.03±0.02	-	0.91±0.15	-	0.02±0.02	Hu et al. (2013)
	-	-	-	6.1	10.5	1.6	4.45	Noor-ul-Amin et al. (2013)
	0.46	0.13	0.11	0.34	201.75	-	5.23	Liu et al. (2006)
Potato	-	-	0.02	-	0.83	-	0.01	Radwan and Salama (2006)
	-	-	0.84	-	0.88	10.74	2.81	Mohamed et al. (2003)
	-	-	0.7	-	15.0	-	6.9	Gichner et al. (2006)
	-	-	6.3	-	24.4	-	51.2	Gichner et al. (2006)
	-	-	0.18±0.04	0.39±0.06	2.52±0.13	0.25±0.06	2.58±0.36	Gebrekidan et al. (2013)
	-	-	0.09±0.01	0.11±0.06	0.06±0.04	0.06±0.05	-	Khan et al. (2013a, b)
Spinach	-	-	2.100.75	-	111.1	75.7	18.10	Khan et al. (2010a)
	-	-	12.970.88	95.791.21	32.112.08	68.661.36	47.693.44	Gupta et al. (2012)

	-	-	0.2	-	22.74	0	2.57	Bigdeli & Seilsepour 2008
Water Spinach	-	1.44	0.6-1.10	-	-	-	0.28	Ng C.C. et al. 2016 Tang L. et al. 2018 Göthberg A. et al. 2002
Indian Lotus	0.1-1.3	-	0.04-0.09	1.6-2.2	4.4-7.4	-	0.3-0.8	Luo Y. et al. 2017 Song T. et al. 2021
Typha angustata	-	-	0.02	0.62	0.34	0.15	0.50	Ramachandra, T.V., et al. 2017
Alternanthera philoxeroides	-	-	0.01	0.69	0.12	0.09	0.32	Ramachandra, T.V., et al. 2017
Ipomoea aquatic	- -	1.07 1.33	5.23 9.67	1.35 4.16	- -	- -	17.2 29.61	Joystu Dutta et al., 2008
Watercress	2.0	-	0.10	0.34	-	0.34	0.86	Robinson B. et al. 2003 Song T. et al. 2021

Mechanism of uptake of heavy metals

Essential elements such as Cu, Zn, Ni, Mo, Mn, and Fe are required in trace amounts for the growth and life cycles of plants. Even very low concentrations of Hg, Pb, Cr, Cd, and As can be toxic to plants. These metals are taken up by the plants and accumulate in the plant bodies.

The metal accumulation is highly determined by soil characteristics such as total metal contents, redox potential, organic matter content, CEC, and soil pH (Chlopecka 1996; Imai et al. 2002; Wang et al. 2012a).

Plants can be classified as accumulators, hyperaccumulators, and excluders. Accumulation of heavy metals in plants is also dependent on other physicochemical parameters including their ability to form deposits in tissues, the stability of the metal, and their bioavailability (Nazir R. et al., 2015). Different parts of the plants show variation in the bioavailability of heavy (Verma and Dubey 2003). Cd shows the highest bioavailability, while As shows the lowest (Liu et al. 2005a).

Accumulation of heavy metals increases at higher trophic levels as compared to their lower levels (Gladyshev M. et al., 2001). Thus, when a human consumes polluted plants, directly or indirectly, heavy metals enter get accumulate in the human body (Gladyshev M. et al., 2001). Once in humans, heavy metal gets distributed to the target organs and accumulates in those organs disrupting the normal body functions.

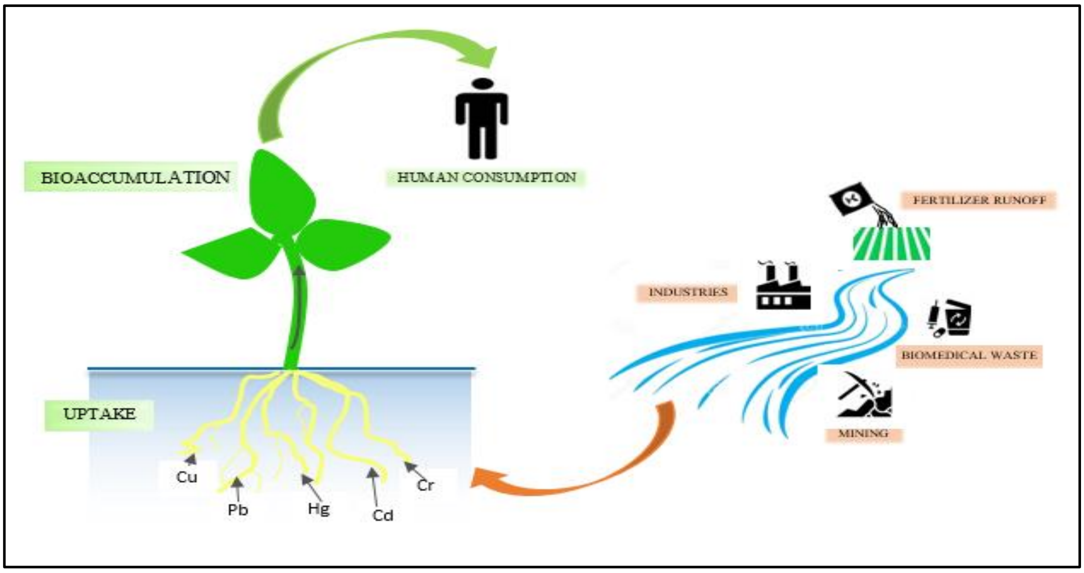

Figure 1: Mechanism of bioaccumulation in macrophytes.

Mechanism of toxicity in plants

Interaction with heavy metals can impact the absorption and transfer of essential micronutrients (Thys et al. 1991; Hernández et al. 1998), which further can affect their growth and physiological functions. (Fjällberg et al. 2005; Li et al. 2005; Di Salvatore et al. 2008). Metal-induced oxidative stress can affect photosynthesis resulting in growth reduction (Wani et al., 2006; Le Guédard et al., 2012; Bibi Hussian et al., 2005). The coordination mechanism between the essential elements can be disturbed by hindering the photosynthetic machinery (Gill et al. 2012; Astolfi et al. 2004), and eventually lead to plant death (Gabbrielli and Sanita di Toppi 1999).

It is observed that in high Cd concentrations, plants showed growth retardation. Cd can induce toxicity, disrupting growth and seed germination (Li et al. 2005a). Similarly, Munzuroglu and Geckil 2002 reported a high concentration of Cu contamination is undesired for seedling growth disrupting normal physiological functions (Upadhyay and Panda 2009; Bouazizi et al. 2010; Hansch and Mendel 2009). It can further trigger damage to the plasma membrane and root inhibition (Bouazizi et al. 2010). Heavy metal contamination greatly affects cell division, growth, and developmental processes (Soares et al. 2001).

Apart from inhibiting growth, heavy metals also affect plant structures and cell structures. Symptoms of toxicity can be observed in plant leaf structure, and root structure (Mangabeira et al. 2001; Vasquez et al. 1991). Common symptoms in such plants include changes in mitochondrial structure, leaf thickness reduction, and the absence of palisade structure (Bini et al. 2012). High concentrations of Fe may alter the cellular structure by damaging the DNA, protein, and cell membrane (de Dorlodot et al. 2005; Arora et al. 2002). Cell membrane structure can be changed due to disruption of plant cellular metabolism (Prasad 1995). It can result in photosynthesis reduction by affecting the structure of chloroplast (Li et al. 2005b; Mahmood et al. 2010; Ramos et al. 2002).

Table 2: Standards for heavy metals (mg kg−1) in plants (from Khan A. et al. 2015).

Heavy metals	**Commission Regulation EU (2006)**	**USFDA (1990)**	**Indian Standard (Awasthi 2000)**	**SEPA China (1995, 2005)**	**FAO/WHO (1984, 2001a)**
As	-	-	1.1	0.5	0.1
Cd	0.2	25	1.5	0.1-0.2	0.1
Cu	20	-	30	20	73
Cr	1	-	20	0.5	2.3
Ni	-	-	1.5	10	66.9
Pb	0.30	11.5	2.5	9	0.3

Effects on the nutrient level

Vegetables are a major source of nutrients for humans, directly or indirectly. Vegetables provide a different form of nutrients and are a daily requirement. In order to meet our nutrient requirements a balanced diet of varied nutritional contents is essential (Dellapenna and Grusak 1999). The nutrient content in vegetables can decline due to heavy metals, which in turn can lead to health problems (Arora et al. 2008; US Department of Health and Human Services 2005).

Heavy metals can induce ROS production by autoxidation and Fenton reactions (Danjuma M.S. and Abdulkadir B. 2018). ROS production is the first form of defense during abiotic stress which in turn causes results in the damage of proteins, lipids, and nucleic acid due to oxidative stress. This can lead to metabolic, physiological, and structural disorders in the plant cells (Guédard et al. 2012; Nagajyoti et al. 2010; Bray et al. 2000; Le Upadyay and Panda 2009). Heavy metal contamination can result in damaged DNA caused by genetic instability in plants (Steinkellner et al. 1998; Liu et al. 2005b; Gichner et al. 2004). Heavy metal-contaminated food may not be able to provide enough nutrients like Fe and vitamins and may induce health disorders (Iyengar and Nair 2000). Studies have shown that consuming metal-contaminated foods can cause a deficiency of macro and micro nutrients including minerals, carbohydrates, fat, proteins, and vitamins like Zn, Fe, and Ca (Nordberg 1986; Fox 1988). The presence of trace elements from nitrogen fertilizers or chemical fertilizers can reduce the vitamin contents in plants (Price 1945). Heavy metals can also induce lipid peroxidation resulting in reduced vitamin content (Tatli Seven et al. 2012). So we can observe that there is a decrease in vitamin content when the concentration of heavy metals increases (Widowati 2012; Munzuroglu et al. 2005). Macronutrients like protein, carbohydrates, and fatty acids are also directly or indirectly affected by contamination of heavy metals.

Protein is one of the key nutrients essential for its functional, structural, and nutritional properties in the human body. Carfagna et al. 2010 stated that the lack of sulfur and nitrogen, which are required for protein synthesis may alter metabolic activities. Like other nutrients, protein content also varies for different types of species (Odhav et al. 2007; Mosha and Gaga 1999) and other biotic and abiotic components. Heavy metals can disrupt protein synthesis in plants due to physiological changes (Chaffei et al. 2004). Wang et al. in 2009 made a report that the pigment-lipoprotein complex accumulation can be altered due to high concentrations of metal. This in turn can inhibit protein synthesis. From the literature, we can observe that the protein content may decrease or increase depending on the species (Alvarez et al. 2009; Roth et al. 2006; Sarry et al. 2006; Kieffer et al. 2009).

The main energy source in the human diet comes from carbohydrates. Heavy metals can cause a reduction of carbohydrate content challenging the food security of the population. Production of ROS and the destruction of the electron transport chain due to heavy metals can inhibit the production of carbohydrates (Sandalia et al. 2001). High Pb concentration can deplete sucrose content (Gaweda 2007). Similarly, in 2010 Rodriguez-Celma et al. observed that at a high concentration of Cd, there is a decrease in carbohydrate metabolism and upregulation of the glycolytic pathway. This can alter the plant physiology (Chaffei et al. 2004). Even at low concentrations, certain activities such as carbohydrate metabolism, photosynthetic activities, enzyme activities, and assimilation of essential macronutrients are disturbed (Sanita di Toppi and Gabbrielli 1999; Vanassche and Clijsters 1990).

Not many studies have been done on the influence of heavy metals on lipids (Upchurch, 2008). Heavy metal contamination may produce ROS causing oxidative stress and ultimately leading to lipid peroxidation and chloroplast degradation (Khanna-Chopra, 2012). According to Monteiro et al., 2004 high Cd concentration can cause lipoxygenase activity resulting in lipid peroxidation. It can alter the enzymatic activities due to metal ions displacement (Wildner and Henkel 1979).

Effects on human health

Heavy metal accumulation above the threshold limits in human bodies can induce adverse health problems resulting in different abnormalities. Even at very low concentrations metals like Pb, Cd, As, etc. are harmful to the human body (Khan et al. 2010a; Azimi and Yargholi 2008; Mitra et al. 2009; Gebrekidan et al. 2013). Heavy metals can also further show their toxicity by reacting with other elements to form toxic oxides and chloride targeting different organs of our body (Fu Z. et al. 2020). In certain cases, essential elements in our body are replaced by heavy metals causing imbalance. There are cases of aluminum replacing most of the trace elements, zinc being replaced by cadmium, and calcium by lead (Huang Y. et al. 2019). Exposure to metal-contaminated food may result in acute and chronic diseases and symptoms (Ugulu I. et al. 2021; Engwa G.A. et al. 2019). These can affect human body systems in various ways such as gastrointestinal; pulmonary; skin; renal; neurological; etc. systems. They can lead to neurological damage; depression; cardiovascular problems; tubular and glomerular dysfunction; osteoporosis; gastrointestinal and renal failure; and different forms of cancers (Sabath E. et al. 2012; Izah S.C. et al. 2016; Vardhan K.H. et al. 2019; Ugulu I. et al. 2021) and deterioration of the immune system (Otitoju O. et al. 2014). Heavy metal poisoning can affect people of all age groups and can even limit their intelligence quotients (Dapul H and Laraque D. 2014). However, health risk assessments report children being more at risk than adults for heavy metal pollution (Zota et al., 2011; DHAenC Man et al., 2010; Qu et al., 2012).

Different countries and organizations have set standard maximum levels (MLs) of heavy metals that could be contained in a food source for human consumption. In a study conducted by Kachenko and Singh (2006), near the area of the smelting mine in Boolaroo, the level of Cd and Pb exceeded the Australian food standard for all the plants grown in the area. Therefore, we have to keep in check from excessive exposure to heavy metals. Cultivation of edible plants in metal-contaminated ecosystems should be prohibited.

Table 3: Human health problems caused by exposure to different heavy metals (Mohammad M.U. et al. 2021)

Heavy metal	Affected organ	Diseases/Clinical Impact	References
Arsenic	Skin, gastrointestinal, pulmonary, nervous system	Hypopigmentation, skin cancer, respiratory cancer, nasal septum perforation, prostate cancer, 'rice water' diarrhoea, long QT syndrome, peripheral neuropathy, multi-organ dysfunction syndrome, vomiting, encephalopathy, nausea,	Jomova K. et al. 2011; Ötles S. et al. 2010
Chromium	Gastrointestinal, pulmonary	DNA damage, pulmonary fibrosis, acute renal failure, haemolysis, gastrointestinal haemorrhage, ulcers, respiratory cancer, nasal septum perforation	Onakpa M.M. et al. 2008; Dattilo A.M. et al. 2003
Cadmium	Pulmonary, renal, skeletal	Excess risk of cardiovascular mortality, endocrine disruption, progesterone synthesis of ovaries, alterations in ovaries, oviduct and uterus, pneumonitis, emphysema, glucosuria, proteinuria, osteomalacia, inhibition of progesterone and oestradiol.	Himeno S. et al. 2019; Rahimzadeh M.R. et al. 2017
Lead	Gastrointestinal, hematopoietic system, renal, nervous system	Encephalopathy, damages cardiovascular system, foot-drop/wrist-drop, nephropathy, vomiting, nausea, peripheral neuropathy, central nervous system disorders, , abdominal pain, anaemia	Wani A. et al. 2015; PaPanikolaou N.C. et al. 2005
Nickel	Respiratory system, urinal system	cancer of the respiratory tract, kidney and cardiovascular diseases, lung fibrosis, nasal and lung cancer	Seilkop S.K. et al. 2003; McGregor D.B. et al. 2000; Giuseppe Genchi et al. 2020
Mercury	Gastrointestinal, renal, Nervous system,	gum disease, hallucinations, delusions, motor neuropathy, tremor malaise, fever, cough, hypersensitivity, tremor neurasthenia, metallic taste, nausea, acute lung injury, diarrhoea, vomiting, nephrotic syndrome, proteinuria, gingiva-stomatitis,	Mousavi A. et al. 2011; Zahir F. et al. 2005

Conclusion

Heavy metals contamination is widespread pollution affecting different ecosystems, from aquatic to terrestrial ecosystems. The living components depending on these ecosystems are also adversely affected. The edible plants supported by such ecosystems may get into the human body directly or indirectly and get accumulated. This can cause several diseases and abnormalities such as cancers, kidney damage, neurological effects, immunological problems, and hormone imbalance.

In this review, we discussed the assimilation and accumulation of heavy metals by plants in different ecosystems, the mechanism of bioaccumulation, and their health consequences. Some findings also discussed the consequences of heavy metal accumulation on nutrient content in the plants. This threatens the food security of humans and other animals that depend on these plants for their nutrients. So, further intensive studies and analysis on the relation between heavy metal accumulation and the nutrient components are required.

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