Heavy Metal Accumulation in Rice and Aquatic Plants

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Aquatic ecosystems are contaminated with heavy metals by natural and anthropogenic sources. Among heavy metals, cadmium (Cd), arsenic (As), chromium (Cr), lead (Pb), and mercury (Hg) cause significant damage to aquatic ecosystems and can invariably affect human health. These metals can enter the human body through food chains, and the presence of heavy metals in food can lead to numerous human health consequences. Heavy metals in aquatic plants can affect plant physicochemical functions, growth, and crop yield.

heavy metals | aquatic plants | food chain | health risks | ecological challenge

1. Introduction

Heavy metals generally refer to elements that are metals and metalloids which have an atomic weight between 63.5 and 200.6, specific gravity greater than 5.0, and atomic density greater than 4 g cm^{-1} [1]. In addition to natural sources of heavy metals that originate from weathering of metal-bearing rocks, volcanic eruptions, and atmospheric depositions, anthropogenic activities including mining, leakage and emissions from industries, use of agrochemicals including fertilizers, and application of sewage sludge to crop lands are the key sources of heavy metal accumulation in soil and water ecosystems [2]. Heavy metal accumulation can further be defined as an amalgamation of heavy metal elements to the ecosystem, particularly to the aquatic ecosystem [3].

Rice and an array of aquatic plants such as water chestnut (*Trapa* spp.), water spinach (*Ipomoea aquatica*), watercress (*Nasturtium officinale*), taro (*Colocasia esculenta*), and lotus (*Nelumbo nucifera*) are important sources of food, particularly in many Asian countries as well as in West and Central African regions [4]. These plants accumulate heavy metals causing various issues to human health, the environment, and ecosystems [5][6].

2. Heavy Metals Present/Accumulated in Rice and Aquatic Plants

Aquatic macrophytes play a pivotal role in the nutrient recycling and aerobic or anaerobic conditions of the water bodies they are present in [7]. They have the remarkable capability of absorbing nutrients and pollutants, accumulating them in their tissues, and growing in unfavourable conditions [8]. Heavy metals are one of the most serious offenders of polluting aquatic systems, mainly due to their toxicity, persistence in the environment, and incorporation into food chains [9].

Some aquatic food sources have shown to be reliable sources of treating contaminated land. For example, *Eleocharis dulcis* (Chinese water chestnut) is used to treat uranium mine runoff in Australia [10], and *Neptunia oleracea* (water mimosa) has been identified as a feasible phytoremediator to clean aquatic systems contaminated with arsenic (As) [11]. Despite the advantages of being able to use aquatic plants to remove heavy metals, the disadvantage stands in the high probability of it being harmful to humans by entering food chains or direct consumption.

As the most abundantly prevalent aquatic food source, the accumulation of heavy metals on rice plants can have widespread repercussions. Due to their ability to adapt to waterlogged or submerged conditions by forming special air channels called aerenchyma which allow O_2 transport to submerged tissues, contamination of irrigation water can lead to accumulation of heavy metal in rice plants. Sharma et al. [12] summarises some recent studies from various locations worldwide on the contaminations of rice grains with potentially toxic elements and exemplifies a range of elements including lead (Pb), cadmium (Cd), chromium (Cr), iron (Fe), zinc (Zn), arsenic (As), uranium (U), thorium (Th), copper (Cu), nickel (Ni), molybdenum (Mo), manganese (Mn), barium (Ba), and antimony (Sb).

In most nations, rapid economic development and urbanisation can lead to attempts by people to combine traditional cultivation methods with urbanised practices, often using unsuitable urban environments for cultivating crops. Cultivation of aquatic plants for human consumption in water bodies that are contaminated with pollutants and heavy metals can lead to accumulation of metals to various degrees within the plants.

Some aquatic plants tend to bioaccumulate metals depending on their initial concentration in waters. In such instances, the types of metals accumulated may vary depending on the plant species, as seen in *Nasturtium officinale* (watercress) which tend to accumulate Cd, Cr, and Co in different concentrations [13].

3. Mechanisms of Heavy Metal Accumulation

The mechanism of uptake of heavy metals by aquatic plants can differ based on the type of plant and the level of metal-polluted water. The ability of plants to carry out elemental accumulation from the substrate is referred to as the bioconcentration factor (BCF), which is a deciding factor in judging their bioaccumulation capabilities. As such, those with high BCF are referred to as hyperaccumulators. The BCF value of As, Cd, and Pb in brown rice have been in the range of 0.001–0.224, 0.001–2.434, and 0.001–0.048, respectively [14]. The bioaccumulation coefficient is the ratio between the metal concentration in dried tissue of the plant and that in the surrounding medium. This coefficient can vary between different metals and range from several hundred for species such as As and up to 10,000 for cationic species such as Cu and Pb [15]. Metals which are taken up by plant tissues may leak back into the surrounding medium, and hence the net uptake of metals by a plant—which in turn is influenced by external and internal factor—depends both on the uptake as well as the leakage. The metal uptake in aquatic plants is also influenced by a range of biotic and abiotic factors which include temperature, pH, and ionic populations of the aqueous systems [16].

Metals present in the contaminated water—mainly as positive ions—bind to negatively charged binding sites on the plant cell wall [16]. Depending on the affinity of metals to these sites, there may be a hard and non-exchangeable bond or a looser and more exchangeable bond [16]. This binding creates a gradient across the membrane, promoting metal transport into the cell [17]. This uptake increases with external metal concentration but not necessarily with a linear correlation [16]. With time, as the metal concentration in tissues increase, leading to a saturation, a subsequent decrease in effective uptake is seen. This may also occur due to the toxic effects caused by metals, such as oxidative stress, which can be caused by Cu, Cd, and Zn [18].

Upon entering the plant roots, metal ions may be stored in the root or transported to the shoot—most probably through the xylem, with some suggestions that the phloem could contribute to this as well [19]. The transport of metals within the xylem or phloem can be facilitated by binding to organic acids, phytochelatins, or metallothioneines [19]. The heavy metals thus accumulated through the roots within the polluted water may deposit in various parts of the aquatic plant, posing detrimental consequences when the plant is used as a food source. **Figure 1** depicts a schematic representation of the uptake and distribution of heavy metals in aquatic plants as well as some images of some common aquatic plant foods.

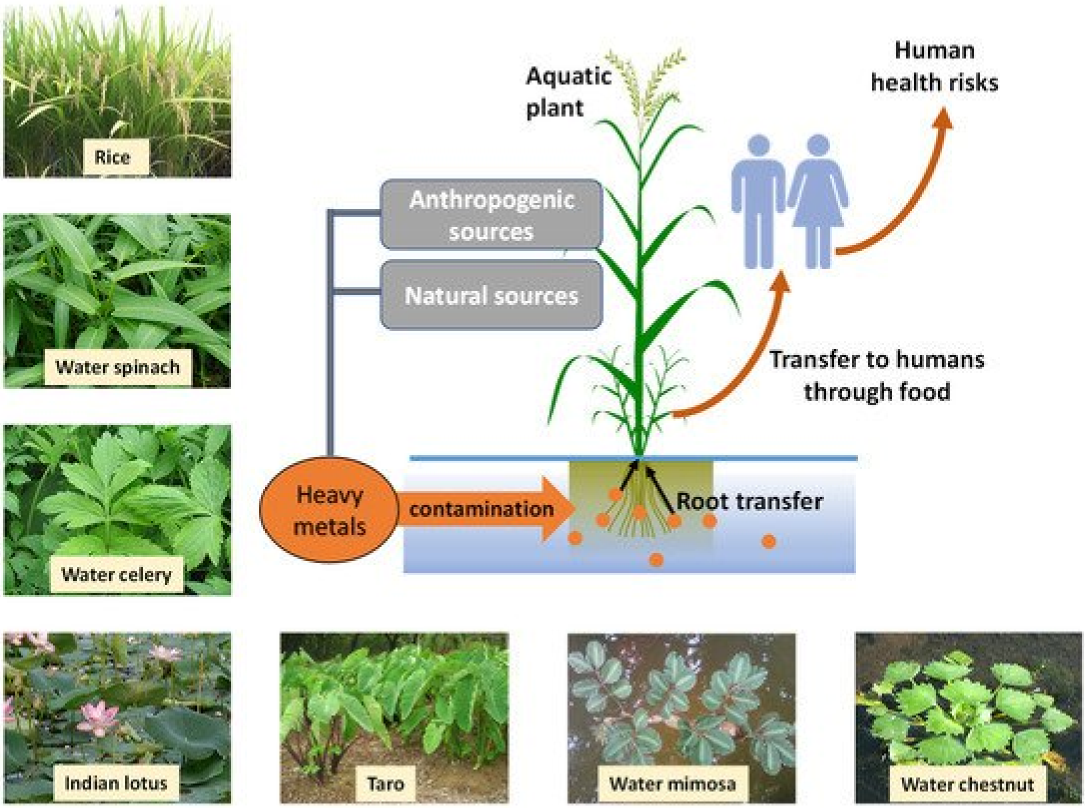

Figure 1. Pathway of heavy metal transfer from original sources to humans. Some common aquatic plants used for human food is inset in the image.

4. Sources of Heavy Metals for Bioaccumulation

Sources of entry of heavy metals to the environment may be categorised into two broad groups as *lithogenic sources* and *anthropogenic sources*. Lithogenic sources include weathering of soil minerals, volcanogenic particles, windblown dust, sea salt, and forest wildfires. The large range of anthropogenic sources include, but are not limited to, industrial activities and the waste they generate (battery production, metal products, metal smelting, cable coating industries, etc.), sewage sludge, brick kilns, agrochemicals (pesticides and fertilizers), wastewater irrigation, fossil fuel emission, power plants (coal combustion), etc. Furthermore, mining and industrial processing for extraction of mineral resources and their subsequent applications for industrial, agricultural, and economic development has led to an increase in the mobilization of these elements in the environment and disturbance of their biogeochemical cycles. In the recent past, electronic waste dumps, which are a consequence of manufacturing high numbers of electronic equipment, have been a source of much concern to human and ecological risks due to the presence of excessive amounts of toxic heavy metals [20].

Upon entry to plants through these various sources, the effects that heavy metals have on plants can be multitude, especially since heavy metals can be divided into two groups based on their interactions with plants: (i) elements which are essential for plant growth such as Fe, Mo, Ni, and Zn, which can become toxic when their concentrations exceed specific threshold levels and (ii) elements which are non-essential to plants such as Cd, Hg, Pb, and As. As such the greatest hidden risks may be posed by those heavy metals which are toxic to plants at very low concentrations and yet may accumulate in plant tissues in higher concentrations whilst showing few changes in reduction yield or visible symptoms [21][22].

5. Heavy Metals in Food Chain from Rice and Aquatic Plants to Humans

Plants can be divided into three main categories, depending on their ability to cope with heavy metals in the medium they grow in [23].

- Indicator plants—plants which are usually sensitive to heavy metals. These can be used as indicators as for the presence of metal in the substrate they have grown in.
- Excluders—these plants can tolerate heavy metals in the substrate up to a threshold concentration. This is achieved by preventing the accumulation of the heavy metal in the cell by either blocking the uptake in roots or by energy dependent efflux pumps. Most metal (hyper) tolerant plants are categorised into this group.
- Hyperaccumulators—in addition to the ability to tolerate high concentrations of specific elements, these plants can actively take them up and accumulate them in their aerial parts. Often these plants have specific mechanisms to avoid poisoning themselves by the accumulated metals.

The quantity of heavy metals accumulated in aquatic plants also depends on various physicochemical factors, such as the bioavailability in water, absorption rate through the plant membrane, stability of the metal in the biotic and abiotic environment, distribution in the various plant tissues, and the ability to form deposits in tissues [24]. The concentration of the heavy metal is comparatively greater in higher links of a food chain than their respective concentration in the lower links [25]. Thus, the heavy metals which may have bioaccumulated in aquatic plant foods make their way to humans along the food chain [25]; this may be through direct ingestion of plant product such as rice, or via consumption of animals who may have consumed the polluted aquatic plant. Once in humans, heavy metal accumulation often takes place in some target organs which serve as deposits of these metal elements. These are however not seen to be subsequently excreted in mothers' milk, unlike the other group of persistence chemicals such as aromatic organochlorine compounds, including dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyl (PCB), and dioxins [26].

Certain heavy metals found in wastewater are non-threshold toxins which may render toxic effects even at low concentrations. These include As, Cd, Cr, Pb, and Hg, all of which cause risks for human health upon direct ingestion or build up through food chains [27]. These can be found in different forms in the environment, as outlined in **Table 1** [27].

Table 1. Forms of arsenic, cadmium, chromium, lead, and mercury found in the environment, leading to build-up in food chains (adapted from [27]).

Element	Main Oxidising States	Natural and Lithogenic Sources	Anthropogenic Sources	Effects on Humans
Arsenic	As(III), As(V)	Weathering of rocks, volcanic eruptions, microbial colonization, As bearing minerals in the lithosphere (e.g., FeAsS, CoAsS, NiAs, AsS, As_2S, As_2O_3)	Fossil fuel combustion, mining, smelting, fertilisers, glass production, chemotherapeutic drug production	Carcinogenic and neurotoxic
Cadmium	Cd(II)	Volcanic activities, weathering, erosion, wildfire, sea salt spray, dust storm, Cd bearing compounds in the lithosphere (e.g., CdS, $CdCO_3$, $Cu_4Cd(SO_4)_2(OH)_6.4H_2O$, CdSe)	Ni–Cd batteries, fossil fuel combustions, mining, cement production, plastic stabilisers, coatings industry, phosphate fertiliser	Carcinogenic
Chromium	Cr(III), Cr(VI)	Tectonic and hydrothermal events, in the lithosphere as $FeCr_2O_4$ and $PbCrO_4$	Aircraft industry, electroplating, wood preservation, tanning, mining, textile dyes manufacturing, metal corrosion inhibition, and cleaning of glassware	Carcinogenic and Mutagenic
Lead	Pb(II), Pb(IV)	Natural fires, natural deposits, sea salt spray, and volcanic eruptions and over 100 Pb-containing minerals in the lithosphere (e.g., PbS, $PbCrO_4$, $PbSO_4$, $Pb_5(PO_4)_3Cl$, $PbMn_8O_{16}$, $PbCO_3$)	Pb–acid battery recycling (PABC), Pb-containing gasoline in petrol, pipes, pesticides, ammunition, electronic wastes, mining, ore processing, pigment in	Neurotoxic

Element	Main Oxidising States	Natural and Lithogenic Sources	Anthropogenic Sources	Effects on Humans
			paints, dyes, and ceramic glazes	
Mercury	Hg, Hg(I), Hg(II)	Weathering of rock, volcanic eruptions, degassing and wildfire. In the lithosphere as metallic form (Hg)(0) (rare) or as HgS, $Hg_3S_2Cl_2$, $HgSb_4S_8$	Coal combustion, production of non-ferrous and ferrous metals, artisanal and small-scale gold mining (ASGM), cement production, pesticides, and fertilisers production	Neurotoxic

6. Human Health Risk Associated with Heavy Metal Accumulation in Food

The accumulation of heavy metals in the human body has been demonstrated to have adverse effects on human health. Heavy metals that possibly cause adverse effects include As, Al, Fe, Cd, and Hg [28]. These metals can enter the body through various ways, such as skin or inhalation routes or intake of heavy metals through contaminated drinking water and food. Heavy metals can also react with certain compounds in the body, such as oxygen and chloride, exerting their own toxic effects [29]. Persistent exposure to heavy metals can lead to an imbalance in the body when heavy metals accumulate in the body and are used as substitutes for essential elements. Examples of heavy metals replacing essential elements of the human body include calcium replaced by lead, zinc by cadmium, and most trace elements by aluminum [30].

Most heavy metals are dangerous to humans due to their non-biodegradable nature and ability to accumulate in human tissues. Often even very low amounts of metals can cause disruption or damage to vital body functions due to the lack of suitable mechanisms to eliminate such metals from the body [31]. Humans exposed to heavy metal-polluted food may display a range of symptoms and diseases both in the short term as well as the long term [31][32]. These may affect various human body systems such as pulmonary; renal; gastrointestinal; skin; neurological; etc. systems and may result in conditions such as cardiovascular problems; depression; hematic, gastrointestinal, and renal failure; neurological damage; osteoporosis; tubular and glomerular disfunction; and various cancers [32][33][34][35][36]. Furthermore, a lack of immunological defences may be seen due to the depletion of essential nutrients in the body [37]. Heavy metal poisoning has been seen to have adverse effects in infants, children, and adolescents, which may result in developmental challenges and a decrease in intelligence quotients [38].

The results of human exposure to toxic heavy metals can be multifaceted, and these complexities can affect different internal and external organs in humans in both an acute and chronic manner. The pollution of waterbodies can have a direct influence on the presence of heavy metals in aquatic plants (and their entry to humans) who consume such aquatic plants. For example, consumption of contaminated rice can cause a range of diseases such

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as cancer of the lung, bladder, and skin through arsenic-contaminated rice and neurotoxicological effects by lead- and mercury-contaminated rice [39][40][41][42][43]. Exposure to toxic heavy metals from contaminated aquatic ecosystems and aquatic plants food results to several detrimental effects to human health (**Table 2**).

Table 2. Human diseases and health conditions caused by exposure to toxic heavy metals found in aquatic plants used as human food.

Heavy Metal	Target Organ	Disease Condition/Clinical Effect	References
Arsenic	Nervous system, skin, pulmonary, gastrointestinal	Nausea, vomiting, multi-organ dysfunction syndrome, long QT syndrome, 'rice water' diarrhoea, nasal septum perforation, peripheral neuropathy, encephalopathy, respiratory cancer, skin cancer, prostate cancer, hypopigmentation,	[44][45]
Cadmium	Skeletal, renal, pulmonary	Osteomalacia, proteinuria, glucosuria, emphysema, pneumonitis, inhibition of progesterone and oestradiol, alterations in uterus, ovaries and oviduct, progesterone synthesis of ovaries, endocrine disruption, acting as estrogen in breast cancer, excess risk of cardiovascular mortality	[46][47]
Chromium	Pulmonary, gastrointestinal	Nasal septum perforation, respiratory cancer, ulcers, gastrointestinal haemorrhage, haemolysis, acute renal failure, pulmonary fibrosis, DNA damage	[48][49]
Lead	Nervous system, renal, hematopoietic system, gastrointestinal	Encephalopathy, anaemia, central nervous disorders, peripheral neuropathy, nausea, vomiting, abdominal pain, nephropathy, foot-drop/wrist-drop, damages circulatory system and cardiovascular system	[50][51]
Mercury	Nervous system, renal, gastrointestinal	Proteinuria, fever, vomiting, diarrhea, acute lung injury, nausea, metallic taste, gingivo-stomatitis, tremor, neurasthenia, nephrotic syndrome; hypersensitivity, cough, fever, tremor, malaise, motor neuropathy, gum disease, delusions and hallucinations	[52][53]

7. Mitigation of Heavy Metal Accumulation in Rice and Aquatic Plants

One of the main principles of preventing food from being contaminated by heavy metals is to ensure the lowest possible levels of contamination in food by implementing good work practices and safe agricultural and irrigation practices [54]. Establishing maximum limit guidelines and legislation and adhering to these guidelines are also greatly beneficial [55]. However, this may not always be practical and feasible in instances where rural communities rely on naturally grown aquatic plants [56][57]. Suitable management of heavy metal-contaminated ecosystems plays a pivotal role in maintaining environmental health and in ecological restoration [58].

Maximum limits set for specific contaminants in food help in protecting public health. The risk associated with exposure to heavy metals in contaminated food is calculated by the daily intake rate (DIR), calculated in μg day^{-1} using Equation (1), where C denotes the concentration of heavy metal in the specific plant food (mg kg^{-1} of fresh

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weight), *IR* is the plant food ingestion rate (g fresh weight per person per day) in the region being investigated, and *BW* is the average adult body weight (kg) [59].

$$DIR = \frac{C \times IR}{BW}$$

To reduce the impact of heavy metal pollutants in water bodies, removal of the heavy metals via bioremediation is imperative [54][60]. The various physical and chemical remediation approaches are restricted and localized and are mainly applied to wastewater and/or contaminated soils and not the plant life that may reside there [61][62]. Some phytoremediation methods are well explored but might not always be suitable for edible crops and vegetables [61][62].

To move past these issues, biotechnological and nanotechnological approaches can open a path ahead for removing the metals from contaminated vegetables and plants by successfully superseding traditional methods. Certain microorganisms, for example, can respond to heavy metal stress through transport across the cell membrane, entrapment in extracellular capsules, precipitation, biosorption to cell walls, complexation, and redox reactions. Microorganisms can also encounter heavy metal stress using diverse defensive systems, such as compartmentalization, exclusion, formation of complexes, and the synthesis of binding proteins such as metallothioneins (MTs) or phytochelatins (PCs) [63].

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