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Review Article

Heavy metals stress, mechanism and remediation techniques in rice (*Oryza sativa* L.): A review

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Abstract

The rapid pace of urbanization and industrialization makes soil and environment polluted, which may cause a severe issue of food chain contamination. Discharge of heavy metal(oid)s from industrial and municipal wastewater streams, and groundwater contamination causes a reduction in crop yields, degradation of soils and ruin quality. Cultivated Asian rice and heavy metal(oid)s have two ways of interaction, either heavy metal(oid)s accumulation cause harmful effects on rice crop or rice plants possess their resistance mechanism to protect against the toxic effects of heavy metal(oid)s, their uptake, and translocation also detoxify the heavy metal(oids) contamination. Besides, several inorganic (liming and silicon) and organic (compost and biochar) amendments have been applied in the soils to reduce/immobilize heavy metal(oid)s stress in rice. Selection/development of rice varieties resistant to heavy metals stress and bioaccumulation, crop rotation, water management and exogenous application of microbes could be a reasonable approach to alleviate heavy metal(oid)s toxicity in rice. This article review that heavy metals, such as aluminum, arsenic, cadmium, chromium, copper, mercury, and lead are the major environmental pollutants, mainly in the places having more significant anthropogenic pressure. In agricultural areas, accumulation of heavy metals is of primary concern because of their adverse effects. This review article also briefly discusses the impact of the heavy metals on human health, soil, plants, and their metabolic mechanisms induced by the biological and geological redistribution of heavy metals by soil and water pollution.

Keywords: Accumulation; Dynamics; Heavy Metal(oids); Rice; Soil; Uptake

Introduction

Although there is plenty of food in the world produced to feed everybody, yet until now, 815 million people are hungry or living in extreme poverty. As presented in SDG 2 (Sustainable Development Goal 2), the world population is increasing, and it is expected to rise 10 billion in 2050. Hence the biggest challenge is to ensure the provision of enough food according to the nutritional needs. There is a need to increase food production approximately up to 50% globally because these increased 2 billion people have to feed by 2050. Therefore, food security is a serious issue which needs a holistic approach to overcome all types of malnutrition, the sensible use of genetic resources and biodiversity, the income and productivity of minute level food producers and flexible change in food production patterns [1]. In 2016, the number of malnourished people worldwide was approximately 815 million, which is up from around 777 million in 2015 but significantly less from 900 million in the year 2000. This latest boost is the reason for immense concern and poses a serious challenge for global commitments to end the huger until 2030 [2]. The significant decline in rice production is due to various factors, including biotic, urbanization, and environmental. According to an estimate, there would be a drastic increase up to 9 billion in the world population by 2050. This situation warns us to perk up the production of rice by using conventional techniques as well as the modern approaches of biotechnology so that we can compete with the needs of the population [3]. The influence of heavy metals on the development and growth of rice varies according to the specific heavy metal for that mechanism. Essential heavy metals such as Cu, Fe, and Zn play a useful role in the growth and development of rice. These heavy metals improve several essential mechanisms for the plant growth and enhanced yield and also the nutritional level of rice at their optimum level. Heavy metals such as As, Cd, Hg and Pb which do not play any valuable role in the growth of plant, severe impacts have been observed at very less concentrations of these heavy metals in growth medium. The review of published research work indicated that the presence of heavy metal(oid)s caused adverse effects in living organisms. Therefore, clean soil is needed to grow healthy rice plants which can be achieved by using low cost and less time taking techniques such as dilution and turnover of surface contaminated soil and addition of minerals, fertilizers or biochar. This review specifically concentrates on the nature, sources, properties with possible remediation strategies of heavy metals which can affect the nutritional value of rice and can ultimately disturb the food chain.

Rice crop in the world

Rice is one of the significant crops of the world because of its role as food content for humans and animals and also as raw material for different industries [4]. It is estimated that about fifty percent population of the world consume rice daily as dietary intake. Several industries also use various by-products of rice crop as raw material. Among other uses, rice straw is also used as animal feed and as organic manure in the soil [5]. Rice is ranked as the second most consumed food by humans. Humans take cereal food in their daily intake, and wheat bread and other derived meals are at the topmost priority. In 2016, rice was produced globally, about 483.1 million tons and consumed by over fifty percent of the population [6].

In the world, the demand for the food is increasing constantly, but the resources are decreasing simultaneously [7]. Rice is the foremost food crop yielded and consumed globally, accounting for almost 20% in cereals trade and approximately 26% in cereal yield [8]. The rice cultivated in Asia can be divided into different groups based on ecology, genetics, and different culinary properties. Different rice genetics (Indica Kato, Jaonica Kato, and aus) differ with the temperate and tropical regions. Aromatic rice with definite flavors are popular in Pakistan (Basmati), Iran (Sadri) and India. Rice of this region is known as drought tolerant and consists of early maturing type [9].

Rice crop in Pakistan

Currently, the main production of rice is produced in India, Vietnam, Japan, Pakistan, China, Bangladesh, Thailand, Philippines, Myanmar, and Indonesia. From the total production of rice, 92% is produced in Asian countries. Pakistan produces a significant amount of rice crop and is designated as the fourth largest country after China, India, and

Indonesia [10]. In Pakistan, Punjab province is the largest rice-producing region of the country. In 2015-16, rice crop covered 4.45 million acres of the total land and 3.502 million tones was the total production of rice. Sindh province contributes 38% of the national production of rice crop while KPK and Balochistan provinces contribute 2% and 8%, respectively.

On the other hand, Punjab province contributes up to 52% of the national rice production [11]. After wheat, rice is the second staple food and foremost resource of foreign exchange income after cotton and accounts for 0.6% of Pakistani GDP and 3% in value-added for agriculture zone. Rice was cultivated on 2.724 million hectares during 2016 in Pakistan, which was 0.6% less than the previous year's cultivation area of 2.792 million hectares. However, there was an increase in the production of rice up to 0.7%. The reasons for the decrease in cultivation area were shifting of rice crop to maize and sugarcane crop by farmers and less domestic prices of the crop in the market [11].

In Punjab, rice was being cultivated on an area of 1.736 million hectares with 2.5% decrease over the previous year, mainly due to the low market prices. While 3.475 million tons of production with a 10.8% increase in Basmati production was achieved that accounts for 51% of the total national production of rice in Pakistan. The yield remained better due to adequate supply/availability of inputs at subsidized electricity rates and intermittent rains at appropriate intervals [12]. Three types of rice varieties are cultivated in Pakistan, i.e., Basmati types (aromatic), medium-long grain, and bold grain. Basmati rice is popular throughout the world for its excellent cooking and eating qualities combined with a very pleasant aroma. Super Basmati, an aromatic rice variety, was released in 1996 about2 decades ago and is still the most popular among consumers, traders and farmers. In 2001 and 2011, two different varieties of Basmati rice, named "Basmati 2000" and "Basmati 515", respectively, were introduced in Pakistan but none of them completely substituted or competed in the field against "Super Basmati" variety [13].

Major constraints in rice production

The hindrances are generally categorized into socio-economic issues, technological, biophysical, soil fertility, agricultural equipment, and institutional management. Some major constraints faced by the farmers in the production of rice crop were disease and pest's incidence (80%), lack of market or crop price (75%), shortage of labor (65%) and heavy metal(oid)s stress and salinity (36%) problems. Good management practices of diseases, pests, and soil salinity issues will help to enhance the production quantity in all rice cultivated areas [14].

Nature of heavy metal(oid)s

Heavy metal(oid)s are the natural substances that cannot be destroyed or degraded biologically. Life cannot survive and develop without the metallic ions as the life is as much organic as inorganic. A heavy metal(oid) is poisonous when comparatively it is dense metalloid or metal which is well-known for its possible toxicity, especially in the context of the soil environment. Excess of necessary concentration of heavy metals or unwanted quantity on earth crust is termed as the toxicity of heavy metals (Figure 1). These heavy metals increase by anthropogenic activities and enter in the human, animal and plant tissues through inhalation, manual handling, and diet, and can also bind to, and interrupt the working of essential cellular mechanisms. Heavy metal(oid)s can be major environmental pollutants; their potential toxicity is a problem of rising significance for nutritional, environmental, evolutionary, and ecological reasons. The heavy metal(oid)s in the soil are not biodegradable and therefore, are enormously persistent in the environment [15].

Essential heavy metal(oid)s

Several heavy metal(oid)s (Zn, Fe, and Cu) are essential for animals and plants [16]. The availability in a specific amount, metal(oid)s such as Co, Ni, Zn, Mn, Fe, Mo, and Cu are some essential micronutrients [17]. The uptake of these essential micronutrients in excess to plant needs can show toxic outcomes [18].

Source of heavy metal(oid)s

In the environment, there are various sources of heavy metal(oid)s such as domestic sewage, agricultural sources, industrial sources, atmospheric sources, and natural sources (Figure 2) [8, 19]. In the developing world, the terrestrial environment is being contaminated by a variety of sources including smelting and mining processes, electroplating, excess fertilization, wastewater irrigation, and sewage sludge [20], and all of these activities may result in agricultural loam pollution by heavy metal(oid)s [21, 22] (Figures 1& 2). In the plant systems, different metal(oid)s have wide ranges of sources as described in (Table 1).

Effects of heavy metal(oid)s on plants

Heavy metal(oid)s have negative effects on the biochemical and physiological function of plants. The majority of these apparent effects are chlorosis, leaf rolling altered metabolism, efflux of cations, necrosis, inhibition in growth rate, altered stomatal actions, alteration in membrane mechanisms, decreased potential of water, change in various essential enzymes, inhibition of photosynthesis and inhibition of respiration process [23]. All of the plant species and human beings are affected by the heavy metal(oid)s stress. A short comparison of heavy metal(oid)s stress on the rice growth, and human beings are described in (Table 2 & 3).

Remediation potential of heavy metal(oid)s

It is widely accepted that metal toxicity depends on the metal's bioavailability in soil and the relative concentrations of other compounds, which usually moderate the toxicity responses [24]. Some heavy metal(oids) their concentration in soil at different sites are mentioned in (Table 4). Various remediation techniques are used to reduce potentially toxic metal(oid)s bioavailability for plant uptake some of them are: liming with different compounds such as slag ($CaSiO_3$), slaked lime ($Ca(OH)_2$), burnt lime (CaO), limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Use of some organic amendments, water management, Zn fertilization, and crop rotation have also been found to be effective in the reduction of metal uptake by the plants (Figure 3) [25].

Dynamics of various heavy metal(oid)s in the soil-plant systems

Arsenic (As)

Nature of Arsenic

Arsenic (As) is highly toxic and class I carcinogen as classified by U.S. EPA, Environmental Protection Agency of the United States, and can cause serious risk to the human health [26]. Arsenic occurs in nature in the form of major constituents as arsenate, arsenides, elemental As, oxides, sulfides, and other almost 200 minerals [27, 28]. Arsenic is the main component of naturally occurring sulfur-rich minerals in the geological environment such as orpiment (A_s2S_3), arsenopyrite (FeAsS) and realgar (As_4S_4).

Sources of arsenic

Many natural processes like alluvial deposits and weathering of rocks can release As into paddy environment and contribute to increasing the amount of As. On the other hand, various anthropogenic activities such as the use of As rich water in the irrigation system and mining activities enhance the deposition of As in the paddy ecosystems. Arsenic containing wood preservatives, herbicides, and insecticides are some other anthropogenic sources which affect rice ecosystem [29].

Uptake and translocation mechanism of arsenic

In paddy ecosystem, arsM gene coded process can convert inorganic As into organic As such as MMA(III), MMA(V), DMA(III) and DMA(V) which are mono-methyl-arsonous and dimethylarsinous respectively [30]. Organic As species that are MMA (V) and DMA (V)in rice crop can enter from rhizosphere where microorganisms act and mediate methylation process because rice plants cannot methylate inorganic As*in-vivo* [26]. There is not any specific mechanism which can show the uptake of As in rice crop. But it is known that a gene, aquaporin Lsi1, can mediate the uptake of organic As in the rice crop [31].

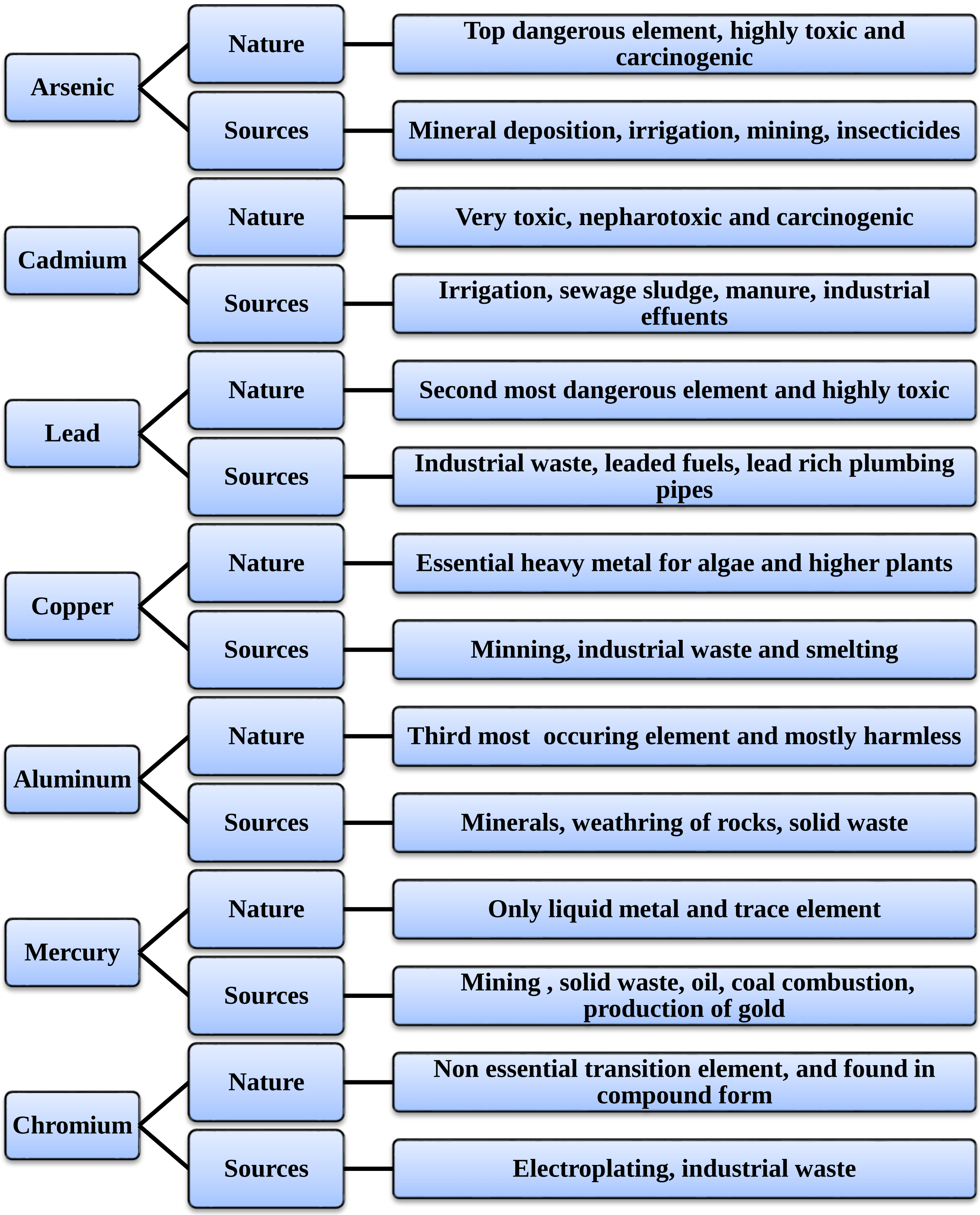

Figure 1. Nature and Sources of Heavy Metal(oids)

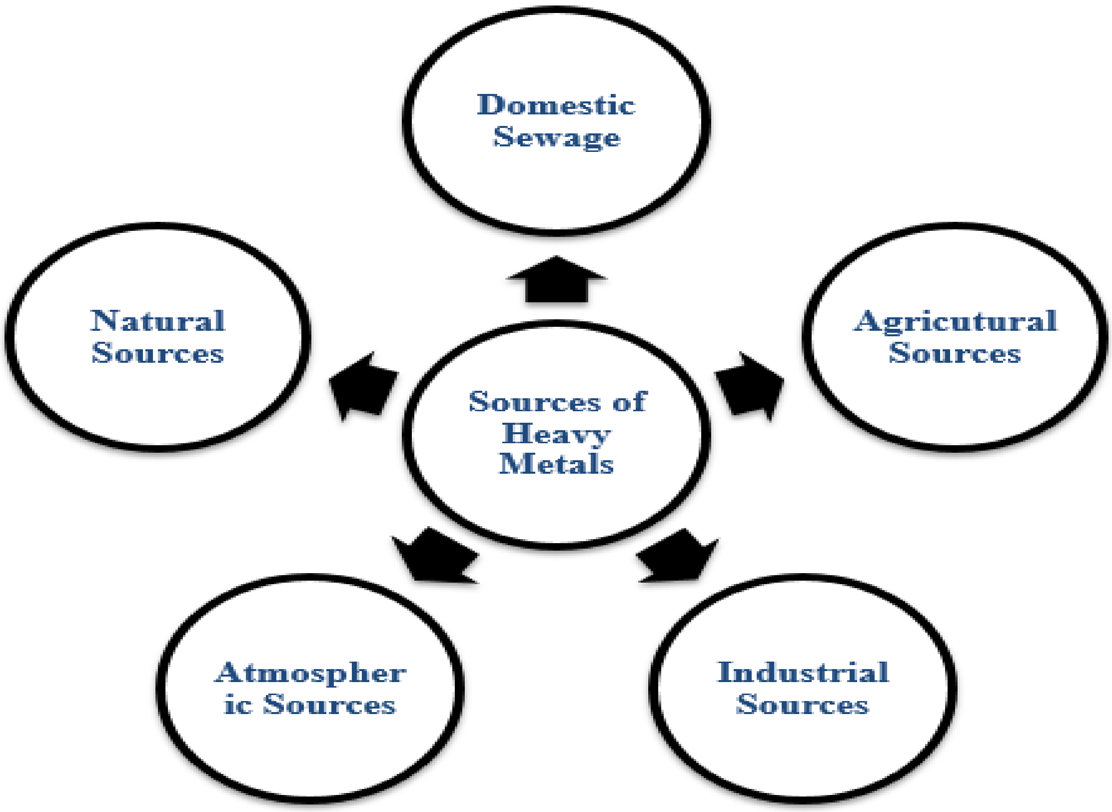

Figure 2. Sources of heavy metal(oid)s

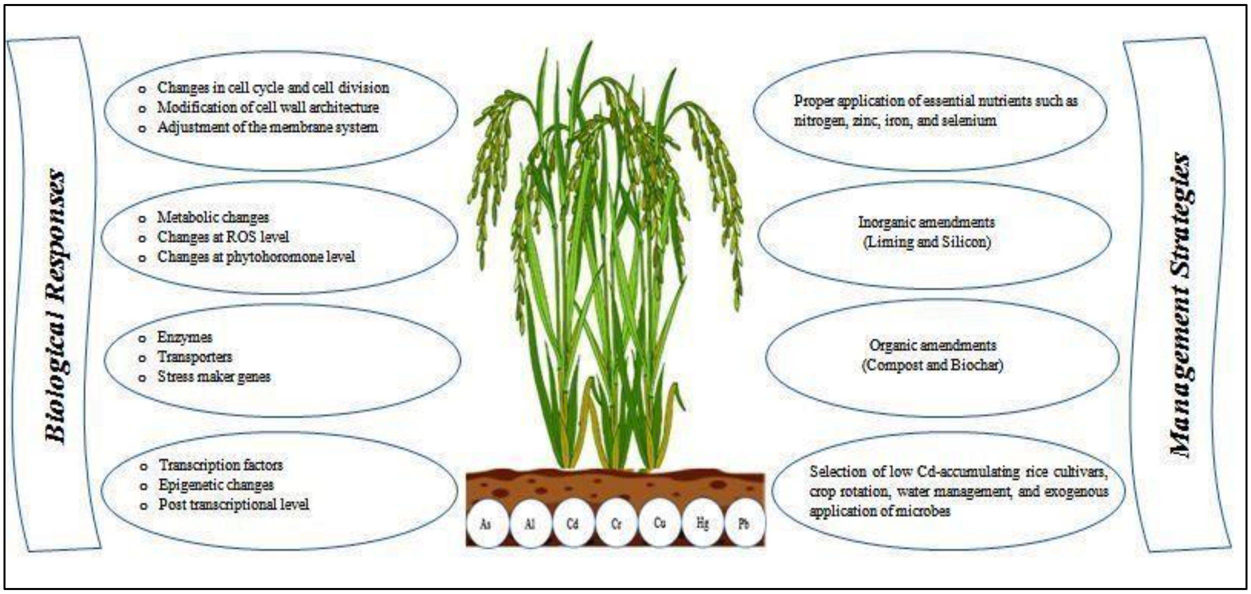

Figure 3. Remediation techniques and management strategies

Table 1. Ranges of heavy metal(oid)s in plant

Sr. No.	Heavy metal(oid)s	Range µg/g dry weight on land plants [55]
1	As	0.02-7.0
2	Cd	0.10-2.40
3	Hg	0.005-0.02
4	Pb	1-13
5	Sb	0.02-0.06
6	Co	0.05-0.5
7	Cr	0.2-1
8	Cu	4-15
9	Fe	140
10	Mn	15-100
11	Mo	1-10
12	Ni	1
13	Sr	0.30
14	Zn	8-100

Table 2. Effects of heavy metal(oid)s accumulation on rice crop

Heavy metal(oid)s	Effect on rice crop	References
As	Reduces plant height, shoot biomass, grain and straw yield reduction, straight head disease	[66, 67]
Pb	Inhibition in seed germination, fresh and dry biomass, leaf area, chlorophyll and growth	[68]
Cu	Decrease in seed germination, repressive impression in plant growth and reduction in root and shoot length	[69]
Cd	Inhibit oxidative reactions and nitrogen metabolism	[70]
Al	Reduction of root development, reduce plant vigor, inhibits shoot escalation, reduce yield	[71]
Hg	Decreases plant height, reduces tiller, reduce panicle formation, yield reduction	[55]
Cr	Reduction of root development, decrease in grain weight, decrease in yield	[57]

Table 3. Effects of heavy metals accumulation on human health

Heavy metal(oid)s	Effect on human beings	References
As	Skin Hyperkeratosis, kidney disease, heart diseases, respiratory complications, gall bladder cancer, ung cancer, bronchitis, dermatitis, poisoning	[72-75]
Pb	Developmental delay, congenital paralysis mental retardation in kids, fatal infant encephalopathy, sensor neural deafness , gastrointestinal damage, epileptics, acute and then chronic harm to CNS, Liver dysfunction and kidney failure.	[75]
Cu	Liver damage, kidney dysfunction, intestinal and stomach irritation and anemia	[75]
Cd	Lung disease, renal dysfunction, Lung cancer, bone marrow cancer, Bone defects (Osteoporosis, Osteomalacia), gastrointestinal disorder, bronchitis, increased blood pressure and kidney damage	[39]
Al	Kidney Failure	[71]
Hg	Brain damage, Kidney dysfunction and Lung damage	[76]
Cr	DNA damage, Alterations in transcription and replication of DNA	[77]

Table 4. An overview of heavy metal(oids) concentration in soil at various sites

Heavy metal(oids)	Concentration in soil mg/kg	Maximum Permissible Limit*	Fold higher than Permissible Limit	Study Area	References
As	64	20	3.2	Bolivia	[78]
	131		6.6	Korea	[79]
	354		17.7	China	[80]
	4357		217.9	Italy	[81]
	7490		374.5	Spain	[82]
Cd	14	3	4.6	China	[83]
	14		4.7	Mexico	[84]
	16		5.4	Switzerland	[85]
	19		6.4	India	[86]
	42		14.0	South Italy	[87]
Cr	224	100	2.2	Germany	[88]
	418		4.2	Greece	[89]
	590		5.9	China	[90]
	4309		43.1	Spain	[91]
Cu	235	100	2.4	Portugal	[92]
	448		4.5	China	[93]
	19581		195.8	Australia	[94]
	35582		355.8	Mexico	[84]
Ni	153	50	3.1	China	[93]
	200		4.0	Turkey	[95]
	201		4.0	Zimbabwe	[96]
	373		7.5	Spain	[91]
	2603		52.1	Mexico	[84]
Pb	302	100	3.0	Brazil	[97]
	452		4.5	Uganda	[98]
	711		7.1	UK	[99]
	1988		19.9	China	[100]
	4500		45.0	China	[101]
Zn	393	300	1.3	Portugal	[102]
	905		3.0	Portugal	[92]
	1168		3.9	Germany	[88]
	370		1.2	Nigeria	[103]
	3833		12.8	China	[100]

Effects of as on rice

Arsenic is a non-essential harmful metalloid of which the high level in rice grains is a severe problem both in terms of rice production and quality and in terms of human health.

Arsenic-rich groundwater is used extensively, mostly in the dry season, for irrigation of rice plants in India, Pakistan, and Bangladesh **[32]**. The natural concentration of As in paddy soils ranges from 4 to 8 mg kg^{-1}, which may rise by up to 83 mg kg^{-1}as reported in many parts of the world where As-contaminated groundwater is applied for irrigation of paddy soils. South Asian countries with high As in their groundwater include Nepal, various parts of India, Pakistan, Bangladesh, Myanmar, Vietnam, Cambodia, China, Taiwan, and various regions of Sumatra in Indonesia **[33, 34]**. Due to the presence of high As contents in paddy soils originating from As-contaminated irrigation water, the rice accumulates comparatively higher levels of As (20-22 times greater) than other staple crops **[35]**. Arsenic levels and its chemical species vary significantly based on the variety of rice used and the local geology of the area. Inorganic arsenicals predominate over the organic As forms in both cooked and uncooked rice and the intake of As via rice into the human body relies on the variety of rice and the process of cooking used **[36-38]**. Hua *et al.* **[3]** explained that the accumulation of As in rice have a serious human health threats and also the marketability of products. Paddy rice accumulates As from the irrigation water and soil, and the intake of this As rich rice acts as the exposure means to the humans on any stage of the life. As also has a negative impact on the quality, yield, and the growth of rice. Identification of poisoning of millions of inhabitants of India, China, West Bengal, and Bangladesh, has taken to a significant advancement in the perceptive of As exposure pathways, bioactivity, toxicity levels in the water-soil-plant system and mechanism of the bioaccumulation patterns. A comprehensive study of heavy metal(oids) stress on rice plant is presented in (Table 5).

Cadmium (Cd)

Nature of cadmium

Cadmium (Cd) is normally a non-essential nutrient which has nephrotoxic, carcinogenic and teratogenic effects on living beings. Cadmium is a very toxic heavy metal that may accumulate in the crops and then leads to the continuous toxicity disorders in human beings and livestock. In agricultural soil, the permissible limit of Cd is 100 mg kg^{-1} of soil **[39]**.

Sources of cadmium

Some major sources of Cd are irrigation with Cd rich water, sewage sludge, industrial effluents, excessive use of contaminated fertilizers, and manure. These sources have contaminated the agricultural soil, which becomes a significant issue **[39]**.

Uptake and translocation mechanism of Cd

Cadmium is a non-essential nutrient for the growth of the plant. Therefore, no specific transporters for Cd are expected to be found in plants. Instead, other transporters for essential metal(oid)s such as Zn, Mn and Fe may be responsible for the transport of Cd in plants. During the past few years, several transporters for Cd have been identified in rice plant **[40]**. The Nramps (Natural Resistance Associated Macrophage Proteins) compose a huge family which is conserved evolutionary throughout the organisms. These Nramps are concerned with the intercellular transport, detoxification, uptake and translocation of transition metal(oid)s. In the rice genome, there are seven *Nramp.* genes, two of which have been functionally characterized at the molecular and cellular level. OsNramp5 is identified to mediate Cd transport **[41]**. This conclusion was based on the findings that knockdown and knock out of *OsNaramp5* result in an outstanding reduction of Cd and manganese uptake, signifying that the exact expression of OsNramp5 will be critical for Cd and Manganese uptake in to the roots **[40]**.

Effects of Cd on rice

Cadmium stress reduces seed germination and rice growth. It also causes the necrosis and chlorosis. Cadmium toxicity reduces shoot and root length, root and leaf area, and the number of roots and leaves per plant. Furthermore, higher concentrations of Cd restrict gas exchange characteristics and photosynthesis in rice plants [42].

Lead (Pb)

Nature of lead

Lead is one of the major inorganic contaminants which is used since ancient times. Its occurrence in atmosphere and soil is damaging for living organisms. In soil, it constitutes complexes with the elements of soil, interferes within the soil-plant and environment associations. It is novel in its solubility in the soil, behavior form, mobility, and bioavailability to ecosystem and plants [4]. Agency for Toxic Substances and Disease Registry (ASTDR, 2003) categorized the Pb as the second most dangerous element due to exposure potential, toxicity and occurrence, only after As lead is the most toxic substance having greater transfer rate from soil to the plants, Lead has been extensively studied for the purpose of quality, bio-testing, and safety of foods [43].

Sources of Pb

Lead accumulating and added up in the agricultural soil by various anthropogenic activities. Industrial wastes, leaded fuels, and Pb rich plumbing pipes are amongst the chief sources of Pb that are contaminating the agricultural soils [44].

Uptake and translocation mechanism of Pb

Uptake, translocation and the storage mechanism of various hazardous and toxic metal(oid)s in the plants is similar as for the acquisition of micronutrients from soil to the plants. Generally, rice plants acquire micro-nutrients by roots from the soil, and this mechanism is supported by soil organic matter, chelating agents (by solubilizing micro-nutrients in rhizosphere), soil pH and redox reactions. Lead uses the same mechanism to get absorbed in the plants [45]. Lead in Pb^{+2}ionic form in soil solution is absorbed by plant roots and can disturb mineral uptake by roots. This lead content is taken up by the translocating water flow in the roots of the rice plant. The young cells located at the root apices are mainly responsible for the Pb uptake because the adsorption of Pb is higher here instead of the complete root surface. It is observed that root apices have lowest rhizodermic pH creating acidic microenvironment hence increasing the solubility of Pb in soil. Lead might be taken up by the plants through various pathways, which include ionic channels, co transporters, anti-transporters, and proton pumps [46].

Effects of Pb on rice

Lead is the toxic metal which instead of participating in rice plant growth and development, severely disturbs the morph-physiological structures, crop growth, plant metabolism and crop productivity.

Lead reduces the growth and yield of rice plants by changing biochemical and physiological properties. Lead affects the plants at all the stages of growth, starting from germination to the maturity level. Accumulation of Pb affects the root ratio, seed germination, fresh weight, dry weight, and shoot ratio in the rice plants. These effects are more adverse when leading Pb^{+2}accumulated in higher concentration. Lead inhibits the growth and viability of rice seedlings and enhances the regulation of ROS (reactive oxygen species) production rate [4].

Copper (Cu)

Nature of Copper

Copper (Cu) is the heavy metal which is essential for algae and higher plants, especially for the photosynthesis process. In photosystem -I of the plants, Cu is the main constituent of the primary electron donor. Because Cu can easily loss or gain an electron, it's the cofactor of monooxygenase, dioxygenase and oxidase (for example ammonia monoxidaze, lysyl oxidase, ceruloplasmin and amine oxidase) and other enzymes concerned with the removal of superoxide radicals, for example, ascorbate oxidase and superoxide dismutase [19].

Sources of Cu

Copper is an essential element for the metabolism and normal growth of living organisms. Copper is also an essential element for several proteins such as cytochrome oxidase of the respiratory ETC (electron transport chain) and plastocyanin of the photosynthetic system. Increased mining and industrial activities have raised the level of Cu in ecosystems. Some anthropogenic activities, including smelting and mining of Cu rich ores, add Cu to the environment. Mining activities produce a significant amount of tailings and waste rocks which are dumped at the surface **[19]**.

Effects of Cu on rice

Copper is an important metal for rice growth and development. It is recognized as a plant micronutrient and plays a major role in ATP synthesis and CO_2 assimilation. Exposure of rice to the higher concentrations of Cu significantly decreases the length of root and shoot. Rice plant that is induced with higher concentrations of Cu toxicity reduces their growth, which leads to the reduction of productivity and also impairs various important cellular processes such as electron transport and photosynthesis **[47]**.

Uptake and translocation mechanism of Cu

In soil, Cu is usually found in the bound forms to soil solids; hence, the amount of availability is very low. The Cu^{+2} ionic form is known as an available form while other species bound with the organic ligands or inorganic OH and $(CO_3)_2$ depending on soil pH. On the other hand, the speciation of Cu is not fully known. Copper chaperones and Cu dependent enzymes have the structural and functional detailed information. Copper toxicity in plants is due to the higher level of exposure, which needs to be overcome by controlling Cu uptake, its utilization, and detoxification through different means **[48]**.

Aluminum (Al)

Nature of Aluminum

After the oxygen and silicon, third-most occurring element is aluminum (Al) that constitutes almost 7% of the total inorganic solid mass of earth crust (Frankowski, 2016). Soil Al either occurs in harmless structures such as aluminosilicates and precipitate or attached with the ligands **[49]**.

Sources of Al

In nature, Al does not occur in free form but mostly found in rocks such as in igneous rocks in the form of aluminosilicates. Aluminum is present in water and various foods. Naturally, it enters into the environment through minerals and weathering of rocks. Aluminum also released in the environment through anthropogenic activities such as wastewater effluent, solid waste of Al-based industries, and air emissions. As Al is the major element of the earth crust, the natural weathering mechanisms mostly exceed the addition of releases to land air and water associated with the activities of human **[50]**.

Effects of Al on rice

Despite numerous studies on rice high aluminum sensitivity, its exact pathways remain completely unknown. It is also unknown that how Al helps certain plants grow faster. In different areas of the world, the toxicity of Al is the growth limiting factor in acidic soil plants. Aluminum toxicity is not primarily identifiable in plants. Iron deficiency is induced in Sorghum, Wheat, and Rice when an excessive amount of aluminum is deposited. Also induce the deficiency of calcium and calcium transport problems such as the collapse of petioles or growing plants and rolling or curling of young leaves **[49]**.

Uptake and translocation mechanism of Al

In many crops, Al^{+3} is absorbed through roots located in apoplast. Cations such as highly charged $Al^{+3}$are attracted and bonded by the pectin present in cell walls and negative charges fixed on membrane surfaces. This is still unknown that which is more toxic for the plants among apoplastic $Al^{+3}$and entrance of Al^{+3} in the cytosol. Solute flow by apoplast can be restricted by binding the Al^{+3}in the cell walls to the pectin. It also rigidifies the walls **[51]**. Aluminum can directly inhibit the uptake of nutrients by blocking ion channels which are involved in K^+ and Ca^{2+} influx. Callose (1,3 beta D-glucan) production is induced in the apoplast by the accumulation of the higher amount of Al^{+3} which affects the functions of the membrane by binding with the proteins and lipids or displacing calcium from various critical locations on membranes **[51]**.

Mercury (Hg)

Nature of mercury

Mercury (Hg) is known as the only liquid metal found in many common products and processes that make use of its unique characteristics. Hg, zinc, and Cd belong to the same group of the periodic table. Hg, at the STP, is only liquid metal having atomic number80 and atomic weight 200. It's melting point is -13.6˚C, density is 13.6g/$cm^{3,}$ and the boiling point is 357˚C. Hg is normally obtained as the byproduct of various ore processing protocols **[52]**.

Sources of Hg

Mercury is naturally found element, but it is directly mobilized by the human beings for thousands of years into terrestrial and aquatic ecosystems by mining, its use in electronics devices, paints and other products, by extracting precious metal(oid)s through Hg, presence as trace element in metal ores, coals and many other materials and through industries like chlor-alkai plants (used as catalysts) **[53]**. Solid waste incinerations, as the medical and municipal waste, Oil and coal combustion, production of gold and pyro metallurgical processes are some other sources of Hg contamination **[54]**.

Effects of Hg on rice

Mercury is a non-essential element for the growth of rice. Agricultural soil is contaminated by the addition of Hg through lime, manures, sludge, and fertilizers. The dynamics are not linear between the quantity of Hg which occurs in the agricultural soil and the uptake of Hg by plants and it depend on various variables such as soil pH, plant species, cation exchange ratio, and soil aeration. When Hg accumulates in the excess in rice plants, it reduces tiller, decreases plant growth, reduces panicle formation, reduces crop yield, and enhances the bioaccumulation in seedling, root, and shoot **[55]**.

Uptake and translocation mechanism of Hg

The atmosphere is leading pathway of transporting Hg emissions, while ocean and land processes take part in the Hg redistribution in freshwater, marine and terrestrial ecosystems and manufacturing of CH_3Hg which derives the foremost route of human exposure, consumption of fish, especially marine fish. The spatial and temporal scales of Hg transport in the atmosphere and its transport to the terrestrial and aquatic ecosystems based on its physical and chemical forms. Following the emissions, the elemental Hg [Hg(0)] could be transferred to the long distances before removal by particle and oxidation and dry deposition of gas-phase or searching by precipitation. Mercury has the atmospheric residence time from months to a year **[56]**.

Chromium (Cr)

Nature of chromium

Chromium (Cr) is the *d*-block transition element in the first row of the VIB group in the periodic table. Its atomic number is 24, and atomic mass is 52. Chromium has the density of 7.19g cm^{-3}, the boiling point is 2665°C and 1875°C is the melting point. Chromium do not occur naturally in the elemental form because it is a less common element but is found in compound form. It is obtained as primary ore by mining and found in $FeCr_2O_4$ or mineral chromite form **[52]**. Chromium is a non-essential element in the plant's nutrition. Both the Cr (III) and Cr (VI) forms can be uptaken by the plants. Chromium VI is actively taken up by the plants while Cr III uptake is passive in nature. Chromium can exhibit two different oxidation states $Cr^{+3}$and Cr^{+6}. The Cr^{+6} is known to be more toxic than the Cr^{+3} form, and Cr^{+6} can be converted into $Cr^{+3}$by redox reactions **[19]**.

Sources of Cr

Some major sources of Cr contamination comprise of disposal of Cr contaminated waste and electroplating. Chromium is extensively used in industries as alloying, textile dyes, plating, minimization of water corrosion, animal hides tanning, pressure-treated lumber, refractory bricks, ceramic glazers, and pigments **[52]**.

Effects of Cr on rice crop

In plants, particularly rice, chromium at very low concentrations (0.06–1.0 mg L^{-1}) was found to support plant growth and enhance yield, but this is not categorized essential for the plants.

Chromium is the heavy metal which affects the germination process and root growth of plants. An experiment of Cr VI exhibited that 5mgL^{-1} dose raised the growth of root comparatively to control, and a dose inhibition effect was observed when a higher concentration range of 20-40 mg L^{-1} was applied. On the other hand, Cr III decreased the growth of rice in the concentration of 200 mg L^{-1}. The yield of the plant depends on leaf area, number, and growth. Chromium affects mostly the physiological and biochemical processes in pants, while yield and productivity are also affected. Chromium VI in the irrigation water considerably decreased the yield (Kg ha^{-1}) and weight of grain in paddy rice up-to eighty percent under 200 mgL^{-1} of Cr **[57]**.

Uptake and translocation mechanism of Cr

There is not a specific mechanism for Cr uptake by plants. Its uptake occurs by the movement of water and essential nutrients. Cr uptake and translocation by various parts of the plants were different concerning genus or species. In paddy varieties, accumulation of Cr is different in roots and shoots as with higher concentration in roots and lower in shoots. Amongst Cr treatments, a greater Cr content of the paddy was examined in 200mgl^{-1} of Cr concentrations while comparing with the other treatments. The shoots accumulated less Cr than the roots accumulated in all treatments. It can be due to the reason that roots have high cation exchange rate which can significantly reduce the heavy metal movement towards leaves, the limited mobility and availability of heavy metal(oid)s in the root system is the one reason for the greater amount of metal(oid)s in the root system, mostly absorbed Cr was contained in the vacuoles of roots especially in soluble form and the reason would be immobilization of Cr in root cell vacuoles, thus rendering this fewer contaminated, which can be a natural response to the toxicity by the plant **[58]**.

Remediation potential of different heavy metal(oid)s

Remediation potential of As

Fertilizer amendment plays a significant role in the minimization of As toxicity and better crop production. There are various positive reports on the effects of Se and Si on As accumulation. Both Si and As work as the metabolic antipodes; therefore, Si plays an effective role in the reduction of As toxicity.

The latest report depicts that the higher level of As in the soil minimizes Zn and Se level in rice plants. Silicon-based fertilizers may successfully lower the As accumulation in the rice plant, especially in the As affected soil **[6]**. Arsenic solubility, release, and retention being significantly impacted by iron oxide minerals. Nitrogen-based fertilizers also have a constructive role in the minimization of As uptake. A pot experiment was held, which revealed that addition of nitrate in rice plants reduces As uptake. Nitrates can stimulate oxidation process of nitrate dependent Fe(II), leading to adsorption of Fe(III) in soil by As co-precipitation and can stop the reduction of Fe(III) **[36]**. Rice grains contaminated with As are the main source of As in the human beings. Especially those people are effected, which consume a significant quantity of rice and other rice-based products. Therefore, development of highly developed techniques concerned with the *in-situ* measurements of As compounds, associated genes and elements at subcellular and cellular level is the need of the hour to produce As free rice to eat and stay safe **[59]**.

Remediation potential of Cd

Zheng *et al.* **[42]** experimented on the biochar that are produced from various parts of the rice plants (bran, husk, and straw) to examine how biochar may affect the mobility of Cd, Pb, As and Zn in rice (*Oryza sativa L.*) seedlings. Concentrations of rice shoot of Cd Pb and Zn lowered by up to 97%, 82%, and 73%, respectively, because of biochar amendment, although As enhanced by up to 326%. Biochar amendments considerably lowered the Cpw (Concentration of pore water) of Zn and Cd and enhanced for As. This experiment is the first one to inspect the changes in mobility of metal and formation of iron plaque in rice crop due to amending the previously polluted soil with biochar which shows that biochar has a potential to reduce Cd, Pb and Zn accumulations in the rice shoot but raise the level of As. The main reason is that biochar decreases the Cpw value of Cd and Zn and increase the Cpw value of As and biochar also increase the Cd and Pb blocking capacity of iron plaque.

Remediation potential of Pb

Scientists have already devised several approaches to combat Pb and other heavy metal(oid)s. Lead content in the soil can be remediated through biochar amendments. Biochar is a carbon-rich compound which is the product of a bio-waste synthesized through pyrolysis (limited oxygen conditions) having a potential to improve the Pb contaminated agricultural soil **[60]**. Biochar application has the potential to immobilize the Pb concentration in paddy soil and hindered in its accumulation in rice crop **[61]**. Biochar has active functional groups, porosity, high pH, and high cation exchange capacity, which help Pb to absorb and then translocate to the other parts of the plants **[62]**.

Remediation potential of Cu

Exogenous application of different oxides of nitrogen by up-regulating the compounds of some antioxidant defense system such as peroxidase, ascorbate peroxidase, superoxide dismutase and catalase activities and by stimulating P5CS enzyme (D1 pyrroline-5-carboxylate synthetase enzyme), that catalase the biosynthesis of proline, has proved that it can resist the impacts caused by Cu toxicity. Accumulation of Cu inside the cell can be prevented by the addition of $Mg^{+2}$and Ca^{+2} cations after stimulating the site-specific antagonism for metal ions. Cu toxicity can also be prevented by applying silicon by balancing nutrients and stopping the apoplast bypass stream. Copper contaminated soil can be remediated successfully by applying organic amendments and the use of soil inoculants, i.e. mychorrhizal and arbuscular fungi **[25]**.

Remediation potential of Al

Many plants have evolved different mechanisms which allow them to bear acid soils and Al toxicity better than other plants. Several ways are present that could restrict aluminum from accumulating in symplastic and apoplastic part of root tissue. Chemistry of cell wall could affect the binding of Al and the upholding of little higher pH of rhizosphere that could change the hydrolysis of Al^{+3} to $Al(OH)^{+2}$, and this can minimize the deposition in the cell wall, Pectin, the charged residue, will accumulate cations by attracting them, but this content does not constantly correlate with Al resistance and sensitivity **[51]**.

Remediation potential of Hg

There are not even single species which is Hg hyper accumulator. Therefore, the natural process of phtyoextraction of Hg from contaminated soil is limited. The immobilization is an *in-situ* technique which minimizes the solubility, mobility, and possible toxicity of Hg by the addition of stabilizing agents into the contaminated soil or water. The agents which are used to immobilize are classified into reducing agents, sulfur-containing ligands, and absorbing agents. Mercury (II) is the weak Lewis acid and form complexes with the weak Lewis bases, e.g. reduced-S-ligands **[63]**. Ruiz and Daniell **[64]** recommended that the new technologies for Hg phytoremediation depend on diverse gene combinations to increase uptake, chelation, detoxification translocation, and manipulation of plant-mediated discharge of Hg in the atmosphere.

Remediation potential of Cr

It is possible to reduce Cr VI to Cr III under acidic environment and due to higher redox value of Cr; Cr III under alkaline conditions can be oxidized to Cr VI. Investigation of potential reduction of Cr VI and oxidation of Cr III can be done by using atomic adsorption spectrometer, which measures the filtrate's total Cr concentration. There are four different mechanisms which explain the sorption of Cr VI by biosorbents. These four mechanisms include anionic and cationic adsorption, anionic adsorption, reduction, and cationic adsorption, and adsorption coupled reduction **[65]**. Table 6 gives a comparative analysis of different remediation techniques, their mechanism, applicability, and acceptance.

Table 5. Comparative summary of heavy metal stress rice plants either in pot or field experiments

Sr. No	Metal(oid)s	Type of experiment	Description of Study	Results	References
1	Cd	Pot Experiment	Effect of Sulfur supply on accumulation of Cd in brown rice	Excessive S= reduction of Cd but also reduce the yield of crop	[104]
2	Cd, Pb and As	Pot Experiment	Cd, Pb and As pollution and uptake by rice grown in greenhouse	Distributions of HMs Root >> shoot > husk > whole grain. Accumulation as: 11.2–43.5% of Cd,30.1–88.1% of Asand14 –33.9% of Pb	[21]
3	Cd, Cr, Cu, Pb, Zn, As, Mn, and Hg	Field Experiment	accumulation and translocation of heavy metal(oid)s in soil and in paddy crop irrigated with lake water	Rice roots were enriched in Cd, As and Pb	[75]
4	As	Field experiment	As Accumulation in Rice Grains	As conc. depend on soil As level, water management and cultivars	[3]
5	Pb, Cd	Field Experiment	Study of correlation between mixed toxic elements and micronutrients and their effect on grain yield	Toxic elements and micronutrient elements show useful variations. Low Pb and Cd with high micronutrients produce high grain yield.	[105]
6	Cd Zn, Cu, Mn and Pb	Field experiment	Assessment of heavy metal(oid)s (Cd and Pb) and micronutrients	Elemental conc. in soil and water was as Cd>Mn>Zn>Cu>Pb	[106]
7	Hg	Pot Experiment	Identification soil Hg limit and Hg accumulation in rice grain	Hg accumulation is high from seven different soil samples to rice grain	[107]
8	Cd and As	Field experiment	Finding the water management system to lower the accumulation of HM	Conventional irrigation ensure high yield with low As and Cd uptake.	[67]
9	Cu,Pb, Zn and Cd,	Field experiment	Two combined amendments (HZ & LS) were applied at different ratios to check the bioavailability of HM	Lime stone+ Sepiolite reduced Pb 10.6-31.8%, Cd 16.7-25.5% Cu 11.5-22.1%, Hydroxyhistidine+zeolite reduced Pb 5.1-40.8%, Cd 16.7-20.0% Cu 8.1-16.2%	[108]
10	As	Field experiment	Study of As accumulation in rice grain if already present in soil and effect of iron oxide amendment on As uptake	High soil As=High As in grain, Application of iron oxide reduced As in soil	[109]
11	Cd, Cu and Pb	Field experiment	Role of iron plaque in mediating entrance of HM into food chain by roots of rice	Iron plaques could prevent Cd and Cu accumulation in rice root, but could promote Pb accumulation therein	[15]

12	Cd, Zn and Pb	Field Experiment	Effect of bioorganic amendments like steel slag and limestone on grain yield and nutrient accumulation in brown rice	Application of Steel slag decreased the bioavailability of Zn, Pb and Cd by 38.5-91.2%	[110]
13	Pb, Ni, Cr, As, Cd, Cu and Zn	Field experiment	Effects of dietary intake of HMs through rice in Cu mining areas and assessment of human health	There were strong association between soil and heavy metal(oid)s	[111]
14	Cd and Zn	Field experiment	Uptake and accumulation of Cd in rice and influence of organic amendments on it.	The treatment with amendments decreased soil Cd concentration by 1.6 and 3.3-fold	[112]
15	Cd, As and Pb	Field Experiment	HM accumulation in rice grain	There were trace amount of Cd, As and Pb in Senegal	[113]
16	Cd and Pb	Pot Experiment	Soil amendments: Peanut shell biochar& wheat straw biochar used to enhance the immobilization of HM	40.4–45.7% reduction of Cd and 68.6–79.0%, decrease in Pb	[114]

Table 6. Comparative analysis of various soil remediation techniques

Remediation Process	Techniques	Mechanism	Acceptance	Applicability	Multi Meal(oids) Sites	Required Time Period
Physical Remediation	Soil Isolation	Separating the contaminated soil from uncontaminated soil by using the sub-surface barriers	Very low and restricted to the highly contaminated soils	Small scale (short to long term)	Effective	Very less
	Soil Replacement	Digging out the contaminated soil and then replacing by clean and fertile soil	Very low and limited to the highly contaminated soils	Small scale (long term)	Effective	Very less
	Electrokinetic Remediation	Elimination of heavy metal(oids) from soil by electro-migration or electrophoresis through DC voltage application.	Very less	Small scale (long term)	Effective	Very less
	Vitrification	Decline in bioavailability of metal(oids) by producing vitreous substance using higher temperature	Very less	Small scale (long term)	Effective	Very less
Biological Remediation	Phyto-Extraction	Usage of hyperaccumulators to uptake, concentrate and translocate heavy Metal(oids) from the soil to parts of harvestable plant.	The highest public acceptability	Large scale (long term)	Usually very less except for a few plants	Very high
	Microbial Assisted	Use of microorganisms to improve plant capacity of phytoextraction.	The highest public acceptability	Large scale (long term)	Normally very less but more	Very high but also a lesser

	Phyto-Extraction				efficient than phytoextraction	amount than phytoextraction alone
	Chelated Assisted Phyto-Extraction	Use of inorganic and organic ligands to increase phytoextraction capability of plants	Higher public acceptability	Small to medium scale (long-term)	Generally Low: Effective than Phytoextraction	Very high but require less than phytoextraction
	Phyto-Stabilization	Usage of plants to reduce metal mobility and bioavailability in soils through sequestration in the roots of plant.	Medium public acceptability	Small to medium scale (short-term)	Very low	Very high
	Phyto-Volatilization	Plant uptake of heavy metal(oids) from soil and excrete into the atmosphere in vapors form.	Less to medium public acceptability	Small to medium scale (long-term)	No	Very High
Chemical Remediation	Soil Washing	Elimination of heavy metals from soil by using extractants and Forming mobile and stable complexes	Medium to high public acceptability	Small scale (long term)	Effective. But depends upon the type of, metal(oids), mobilizing Amendment and soil	A smaller amount to medium
	Immobilization	Decrease in metal bioavailability and mobility by using immobilizing amendments, and making immobile and stable complexes through adsorption	Higher public acceptability	Small to medium scale (short-term)	Effective. But depends upon the type of, metal(oids), mobilizing Amendment and soil.	Fewer to medium

Conclusions and future prospects

Natural or biogeochemical processes, anthropogenic sources such as hazardous solid waste and industrial wastewater are the major causes of heavy metal accumulation in the soil, which ultimately deteriorate the quality of life by disturbing food chain. Elevated levels of heavy metal(oid)s (Al, As, Cd, Cu, Cr, and Hg) in soil have toxic effects on animals, plants, humans, and other living beings. Heavy metal accumulation and their toxicity in agricultural soil and water can be eliminated through hyper accumulator plants by using phytoremediation or bioremediation process. To ensure the consistent parameters for health risk assessment, it is essential to identify the heavy metal bioavailability in different areas, soil, and crops. The collection of precise information on the evolutionary change of heavy metals in soils and plants is crucial, and further studies are required to determine the input of bioavailable metals to enhancing soil quality to attain food security and sustainable agriculture. Thus, there is the need to deepen the research work for better understanding of the toxicity of heavy metal(oid)s on rice or other plants and its allied areas to establish ecological equilibrium on earth.

Authors' contributions

Idea about manuscript: Q Zaman & K Sultan, Collected the data: S Javaid & S Sharif, Prepared the manuscript: S Javaid & S Sharif, Prepared the tables and figures: S Aslam, A Jamil & S Ibraheem, Technically improved the draft: U Riaz, A Aslam & N Ehsan.

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