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Review

Heavy metals pollution from smelting activities: A threat to soil and groundwater

Muhammad Adnan [a,b], Baohua Xiao [a,*], Muhammad Ubaid Ali [c], Peiwen Xiao [a,b], Peng Zhao [a,b], Haiyan Wang [a,b], Shaheen Bibi [d,e]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou 550081, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] Department of Soil Sciences, Southern Federal University, Rostov-on-Don, Russia
[d] Lanzhou Veterinary Research Institute, Chinese Academy of Agricultural Sciences, Lanzhou 730046, PR China
[e] Graduate School, Chinese Academy of Agricultural Sciences, Beijing 100081, PR China

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ABSTRACT

Throughout the literature, the word "heavy metal" (HM) has been utilized to describe soil contamination; in this context, we characterize it as those elements with a density greater than 5 g per cubic centimeter. Contamination is one of the major global health concerns, especially in China. China's rapid urbanization over the past decades has caused widespread urban water, air, and soil degradation. This study provides a complete assessment of the soil contamination caused by heavy metals in China's mining and smelting regions. The study of heavy metals (HMs) includes an examination of their potential adverse impacts, their origins, and strategies for the remediation of soil contaminated by heavy metals. The presence of heavy metals in soil can be linked to both natural and anthropogenic processes. Studies have demonstrated that soils contaminated with heavy metals present potential health risks to individuals. Children are more vulnerable to the effects of heavy metal pollution than adults. The results highlight the significance of heavy metal pollution caused by mining and smelting operations in China. Soil contaminated with heavy metals poses significant health concerns, both carcinogenic and non-carcinogenic, particularly to children and individuals living in heavily polluted mining and smelting areas. Implementing physical, chemical, and biological remediation techniques is the most productive approach for addressing heavy metal-contaminated soil. Among these methods, phytoremediation has emerged as a particularly advantageous option due to its cost-effectiveness and environmentally favorable characteristics. Monitoring heavy metals in soils is of utmost importance to facilitate the implementation of improved management and remediation techniques for contaminated soils.

1. Introduction

The environment has a significant impact on the living situations of human beings. The biosphere is widely acknowledged as a crucial element of the natural environment, primarily due to its pivotal function in offering a habitat for diverse living species. Environmental contamination refers to changes in the atmosphere, hydrosphere, and lithosphere's physical, chemical, and biological properties that present a potential risk to the survival of many organisms, including both fauna and flora (Masindi and Muedi, 2018). The anthropogenic influence on climate change is increasingly emerging as a significant threat to the long-term sustainability of life on our planet (Wang et al., 2023a, 2023b). Particulate matter (PM) (Chen et al., 2019), Perfluoroalkyl substances (PFASs) (Zhou et al., 2021), and Persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs) (Lian et al., 2021), a significant global environmental concern, serve a crucial function in the deterioration of ambient air quality and the occurrence of severe harm to human health (Chen et al., 2019). Governmental organizations and the general public are concerned about air PM due to its potential health consequences and pollution events (Li, Qian, and Wang, 2013). Soil pollution from organic and inorganic contaminants, such as HMs, is a worldwide problem (Li et al., 2024; Vamerali et al., 2010). "Heavy metals" is a term commonly associated with pollution and potential toxicity or ecotoxicity and refers to a specific group of substances that

* Corresponding author.
E-mail address: xiaobaohua@mail.gyig.ac.cn (B. Xiao).

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possess metallic properties, including both metals and semimetals; however, metal(loids) of environmental significance include asbestos, cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), molybdenum (Mo), zinc (Zn), thallium (Tl), antimony (Sb), and various others (Li et al., 2019a,2019b; Vamerali et al., 2010). Heavy metals are "those whose density exceeds 5 g per cubic centimeter" (Adnan et al., 2022a,2022b; Ali and Khan, 2018; Chen et al., 2021; Feng and Wu, 2023). Due to its similar environmental reactivity and common chemical features, the metalloid arsenic (As) is frequently categorized as an HM (Ayyanar and Thatikonda, 2020; Blasi et al., 2012; Chen et al., 2015).

The rapid modernization process in China has resulted in a notable concern regarding the poisoning of agricultural land by HMs. In China, a significant proportion of agriculturally polluted soils, estimated at around 82%, contain toxic inorganic pollutants such as Pb, Cd, Cr, and As (Adnan et al., 2022a,2022b; Chen et al., 2014). The values obtained were significantly higher than those reported in prior investigations conducted outside China. The issue of trace metal pollution in aquatic environments is a global concern (Poteat and Buchwalter, 2014). One of the biggest threats to environmental sustainability is soil and water contamination with HMs due to human activities (Gupta et al., 2013). The most significant threats to water security are related to groundwater, and groundwater levels are a source of worry due to challenges like drought, reduced river flows, lost wetland ecosystems, saltwater intrusion, and soil salinization (Kinzelbach et al., 2022). Elemental risks in soil are highly challenging to break down, and their presence can threaten plant and human health via the food chain and drinking water in various ways (Burges et al., 2015; Zhang et al., 2018). The global prevalence of HM pollution has resulted in significant ecological and health-related challenges (Spurgeon et al., 2011). Regarding nutrition, essential elements like Cu and Zn have lower toxicity to people and freshwater species than unnecessary metals like Pb, Cd, and Hg (Fu et al., 2017). Lead is an element that possesses hazardous properties and offers no discernible benefits for sustaining life (Le Roux et al., 2019). Mercury is an element known for its hazardous properties (Jiang et al., 2006).

Polluted land remediation is one of the most significant problems in today's world (Hou, 2021). Environmental factors, such as climate, soil properties, abiotic stress, or multipollutant combinations (PAHs, solvents, explosives, pesticides, heavy metals), are often cited as barriers to the transfer of plant-driven soil depollution (phytoremediation) methods from controlled environments (in vitro, growth chambers, greenhouses) to complicated settings in the real world (Sulmon et al., 2014). Soil remediation strategies, contaminant removal strategies, polluted medium concentrations, and end-use decisions are all influenced by site specifics (Mulligan et al., 2001). The mitigation of HM contamination in soils is of utmost importance in managing pollution sources and developing remediation techniques for contaminated soils (Yao et al., 2012). Acquiring knowledge about the attributes of soil contamination caused by HMs and assessing the possible hazards associated with environmental exposure are essential prerequisites for successfully preventing and managing soil pollution. The provided information is pivotal in informing decision-making procedures for the cleanup of contaminated soils (Chen et al., 2015).

This research comprehensively examines soil contamination in China's mining and smelting areas, specifically caused by the accumulation of HMs. It also encompasses investigating the potential adverse effects linked to HMs, the origins and concentrations of HM presence, and the use of remedial actions for soil polluted with HMs within a particular geographic region.

2. Morphological characteristics of heavy metals

Humanity lives in an era with significant levels of heavy metal contamination, as seen by the substantial rise in global heavy metal pollution. The inadequate management of abandonment smelting sites has resulted in significant environmental contamination. Environmental research has to prioritize understanding the effects of heavy metal contamination in smelting sites. One notable characteristic of these pollutants is their inherent toxicity and chemical components, differentiating HMs from the bulk of chemical contaminants in the environment.

Mineralogy plays a significant role in the environmental distribution of HMs (Xu and Fu, 2022). One must have a solid understanding of HMs or soil mineralogy to evaluate polluted regions' historical and current state. Heavy metal knowledge, including stats, particulate matter, dissolved forms, and different types, is shown in Fig. 1. The geochemistry of main elements indicates the mineralogy, while trace elements exhibit distinct patterns among the various minerals (Hower et al., 2022). It is an essential constituent within diverse minerals commonly encountered in sedimentary, igneous, and hydrothermal rock formations (Ansari et al., 2023). Previous research observation implies that the leachability of trace metals in the samples is influenced by bulk chemistry and mineralogy (Piatak et al., 2004). Thus, even in complicated circumstances with multiple industries located nearby, the mineralogy of the particulate inputs can be utilized directly to uncover the origin of detected HM inputs at any given area (Gregurek et al., 1998). Significant variations in Cd, Pb, and Zn bioaccessibility were observed throughout multiple studies, and in addition to pH, the bioaccessibility of soil is also influenced by its mineralogy (Wang et al., 2023a,2023b).

The majority (67) of the 114 known elements—90 of which occur naturally on Earth—form metals, and all but one of them (Hg) are solids; atomic or molecular gases consist of eleven elements, whereas solid or liquid nonmetals comprise twelve additional elements (Smith and Nordberg, 2015). Rare earth elements are vital in many fields, including manufacturing, petroleum and textile production, and farming (Hedrich and Schippers, 2021). The concentrations of platinum-group elements, namely Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Osmium (Os), Iridium (Ir), and Platinum (Pt), exhibit extremely low levels ranging from 0.000022 to 0.00052 parts per million (ppm) in the upper continental crust; however, these concentrations are within the range of 1–15 ppm in ore deposits (Hedrich et al., 2020). Metals are typically classified based on their shared physical characteristics in the solid state, and these characteristics include high electrical and thermal conductivity, metallic brilliance resulting from their high reflectivity, and mechanical properties such as strength and ductility (Smith and Nordberg, 2015). Spinel group minerals have been identified as a common host for metal-bearing pollutants in mineral analyses of contaminated soils influenced by smelter emissions and dust from mining activities; although most studies have focused on the high-temperature processes that give rise to spinel group minerals, recent research has shown that spinel group minerals that include metals can also form in surficial soils at room temperature (Schindler et al., 2019).

Metals present in geogenic soil particles, specifically minerals, generally exhibit greater stability than metals bound inside slag particles or particles formed during the cooling process of smelting flue gas (Baieta et al., 2023). Here, researchers describe the results of a theoretical investigation on the interactions between substituted thioureas and three common HM ions: Cd^{2+}, Hg^{2+}, and Pb^{2+} (Barzaga et al., 2021). The Sudbury soil investigation reached comparable findings regarding the perceived greater mobility of Cu^{2+} than Ni^{2+} and also observed that the enhanced mobility of Cu^{2+} in the Sudbury soils is atypical, as Cu^{2+} typically exhibits reduced mobility compared to Ni^{2+} due to the development of more potent complexes with organic matter, Fe-Mn-oxides, and clay minerals (Lanteigne et al., 2012). There is a consensus among individuals that some naturally occurring minerals, mainly manganese oxides, can facilitate the conversion of Cr(III) to Cr (VI) (Li et al., 2023a,2023b). Cobalt (Co), which appears on numerous international lists of strategic and critical minerals, is one example of a critical metal found in high amounts in Cu slags (Ettler et al., 2022). Metallurgical slags are the most significant mineral waste produced during the pyrometallurgical extraction of metals from ores (Vítková

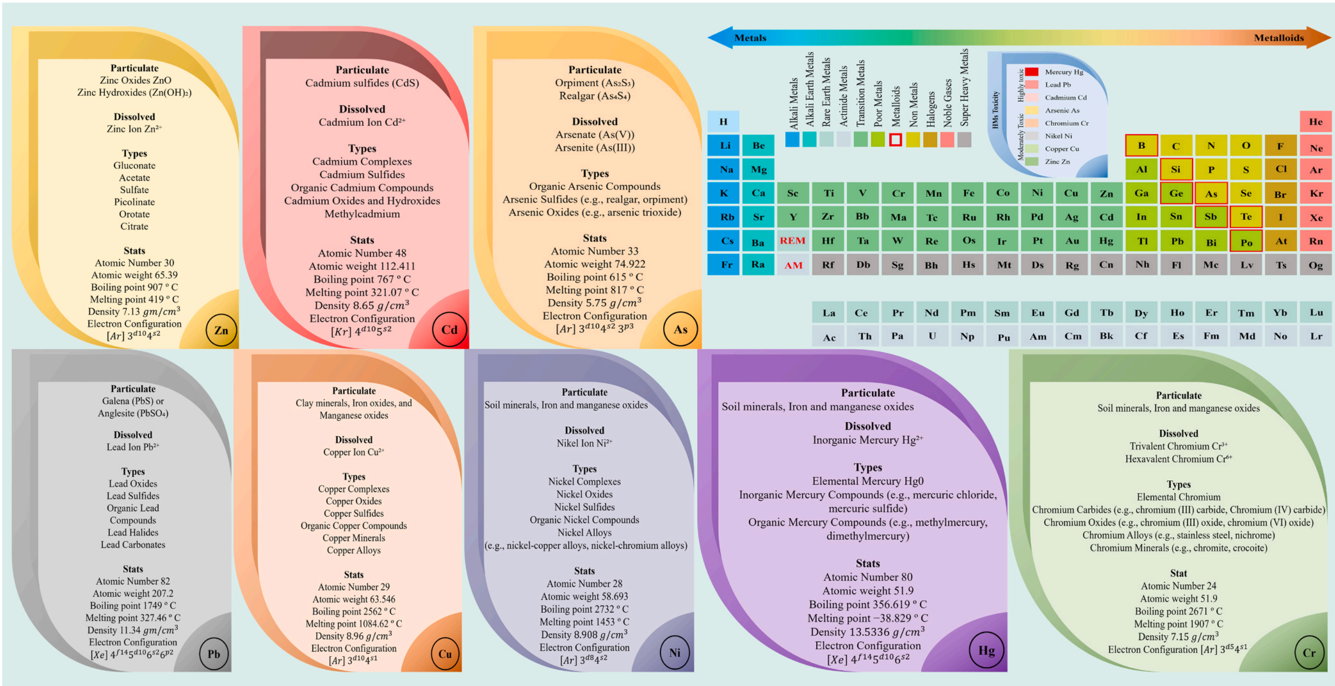

Fig. 1. A comprehensive overview of heavy metals.

et al., 2010).

Anthropogenic pollutants are being released into the environment at an ever-increasing rate due to recent rapid population growth, urbanization, and life expectancy (Lari et al., 2022). Environmental and toxicological concerns have been brought to the forefront by the growing consumption of compound metals (Egorova and Ananikov, 2017). One of the primary adverse consequences of inactive mines typically relates to the abandonment of substantial quantities of waste; in particular, the accumulation of tailings, which are byproducts generated during the mineral ore extraction process, often occurs in steep stockpiles, and these stockpiles are susceptible to erosion, thereby posing a potential risk of environmental contamination in the surrounding area (Bori et al., 2016). Urban and peri-urban environments and areas surrounding extraction sites bear the brunt of the detrimental effects on human health and the environment caused by the worldwide rise in the production, usage, and generation of chemicals and waste (Ataria et al., 2023).

China has emerged as the world's largest producer of raw and refined Pb and its largest consumer (Shi et al., 2019). Over the past few decades, the southern part of China has experienced significant growth, emerging as one of China's most rapidly developing areas. China is well recognized as the leading producer of Cr slag, boasting roughly 25 companies producing Cr salts, and the combined firms have a joint annual production capacity of 329,000 tons, leading to a yearly emission of Cr slag of up to 450,000 tons (Gao and Xia, 2011). The amounts of lead resulting from human activities, known as anthropogenic lead concentrations, have experienced a global increase since the emergence of metallurgy over 5000 years ago (Le Roux et al., 2019). Mercury's hazardous constant and bioaccumulative qualities make it a significant public health and ecosystem issue in both its inorganic and organic forms (Cheng and Hu, 2012a, 2012b). China possesses enormous Hg reserves, positioning it as the third-largest holder globally (Jiang et al., 2006).

The Yuguang Gold and Lead Co. Ltd. smelter in Jiyuan, Henan Province, China, is internationally acknowledged as a leading Pb and Zn smelting enterprise (Wu et al., 2020). Currently, China is the leading worldwide producer of Pb. The soil in select provinces, specifically Guangdong, Henan, Hunan, Pb, and Cd, has experienced the deposition of diverse constituents due to the mining and smelting operations associated with lead. The cumulative global land area utilized for surface mining operations from 1976 to 2000 was approximately 3700, 000 ha, accounting for roughly 0.2% of the Earth's total land surface; however, in the last twenty years, there has been notable growth in worldwide mining extents, as evidenced by a recently obtained data revealed a significant expansion of mining areas, reaching 5727,700 hectares (Anda et al., 2022). According to several studies, the worldwide mining sectors generated 4140,000 metric tons of lead and 12,000,000 metric tons of zinc in 2010 (Yin et al., 2016).

Asia, particularly China, has been widely recognized as the primary global contributor of atmospheric mercury (Hg) emissions (Jiang et al., 2006). Elemental mercury (Hg^0, boiling point: 356.7 °C), monovalent mercury ($Hg_2{}^{2+}$), and divalent mercury (Hg^{2+}) all appear in nature, with divalent mercury being the most stable and abundant variety (Cheng and Hu, 2012a). As the most populous developing nation, China exhibits rapid industrial expansion and is responsible for consuming almost half of the worldwide mercury supply; additionally, China contributes to roughly 25% of anthropogenic mercury emissions (Cheng and Hu, 2012b). Accurately determining historical atmospheric Hg concentrations is challenging due to the limited availability of direct monitoring data, which commenced approximately four decades ago (Gačnik and Gustin, 2023). Most mercury ores are found in China's southwestern and central regions, specifically in the provinces of Guizhou, Shanxi, Henan, and Sichuan, and approximately 70% of the element Hg is concentrated inside Guizhou Province, a region that has been actively mining this particular metal for over >600 years (Jiang et al., 2006).

Due to their inherent complexity, environmental and chemical systems frequently require extensive data collection, processing, and analysis to reveal previously unknown patterns, correlations, and basic insights (Ren et al., 2022). U.S. National Academies report on environmental engineering for the 21st Century identifies five grand challenges: ensuring a steady supply of food, water, energy; and controlling climate change and adapting to its effects; designing a future free of pollution and waste and remediating contaminated groundwater is crucial for protecting water quality, but it necessitates foresight into the movement of new anthropogenic and geogenic pollutants and contaminants (Deng et al., 2023). The potential extraction of metals from diverse waste deposits is a viable approach for meeting societal metal demands and mitigating the environmental impacts of waste disposal (Kinnunen and Hedrich, 2023). Recently, it has become clear that chemical extractions of metals from multi-contaminated soils do not provide enough information about the bioavailable fractions of the metals, nor accurately reflect the toxicity of all substances in soil, their synergic and antagonistic effects, and their interactions with the soil matrix and organisms (Bori et al., 2016). Determining HM chemical speciation in a solid environmental sample often involves a sequential extraction process, wherein the various species are extracted in a particular order, and these species include the adsorbed-exchangeable carbonate phase, the reducible phase, the oxidizable phase, and the residual fraction (Li et al., 2013). Soil metal content can be quickly and reliably determined by X-ray fluorescence (XRF) spectrometry; a declining pattern indicates potential instability (Shen et al., 2019). The mineralogy research utilized X-ray diffraction analysis (Martina Vítková et al., 2011). Sequential extraction and magnetic separation were carried out to comprehend nanomineral assemblages (Hower et al., 2022).

3. Heavy metals distribution

On a global scale, climate change's depletion, contamination, and impact significantly strain groundwater supplies (Ravenscroft and Lytton, 2022). Water is a fundamental and indispensable resource for life's maintenance and survival (Herojeet et al., 2015; Mishra et al., 2023; Pan et al., 2018; Parvin et al., 2022). The Xiangjiang River, a significant tributary of the Yangtze River, serves as the principal water source for agricultural, household, and industrial purposes (Zhong et al., 2012). The Xiangjiang Valley is a significant region in Hunan that plays a crucial role in extracting, processing, and refining non-ferrous and rare metals, and it is a vital hub for many activities, such as agriculture, water supply for domestic and irrigation purposes, transportation, and fishing (Chai et al., 2010). Moreover, the water near the smelter exhibited notable contamination, characterized by elevated levels of HMs. Additionally, the well water in the affected region may have been contaminated with As and Cd due to smelting operations (Cai et al., 2019). Stormwater transports toxins from various land operations, depositing them into the river (Jiang et al., 2019). In contemporary times, substantial efforts have been made to tackle the water contamination problem. There has been an overall enhancement in the sustainability of the aquatic ecosystem in central China (Li et al., 2019a, 2019b). Nevertheless, it is crucial to strengthen one's understanding of managing water contamination in this area. Waste management is central to more than half of the Sustainable Development Goals (SDGs); however, in 2015, China's industrial activity generated 39.76 million tons of hazardous waste, accounting for nearly 10% of the global aggregate (Li et al., 2023a,2023b). The distribution of China's water resources is also extremely disparate, and northern river basins are home to 44% of the population and 65% of the country's arable land, although they receive just 13% of the country's total water supply, or 757,000 L per head per year (Zhang et al., 2010).

Various factors can influence soil contamination, including land-use patterns, the intensity of human activities, the duration of soil contamination, and the proximity to discharge sources (Chen et al., 2015). Heavy metals are released into the environment, resulting in contamination, mostly attributed to anthropogenic activity, including industrial and agricultural practices. The soil horizon is particularly susceptible to disruption by HMs in an ecosystem, and the soil profile has a significant role in transporting HMs. Soil contamination by HMs can arise from multiple sources, encompassing air deposition, waste disposal practices, combustion of waste materials, discharge of municipal effluents, emissions from vehicular traffic, application of pesticides, and prolonged utilization of wastewater in agricultural activities (Bakshi et al., 2018). The various sectors contributing to the growth of HM pollution are classified into sections, as illustrated in Fig. 2. Special health subsidies are required for mining and smelting sites due to the prolonged prevalence of serious health concerns among the local population in this region.

Since the outbreak of the Industrial Revolution and the growth of technology, the degradation of the biosphere by toxic metals has grown

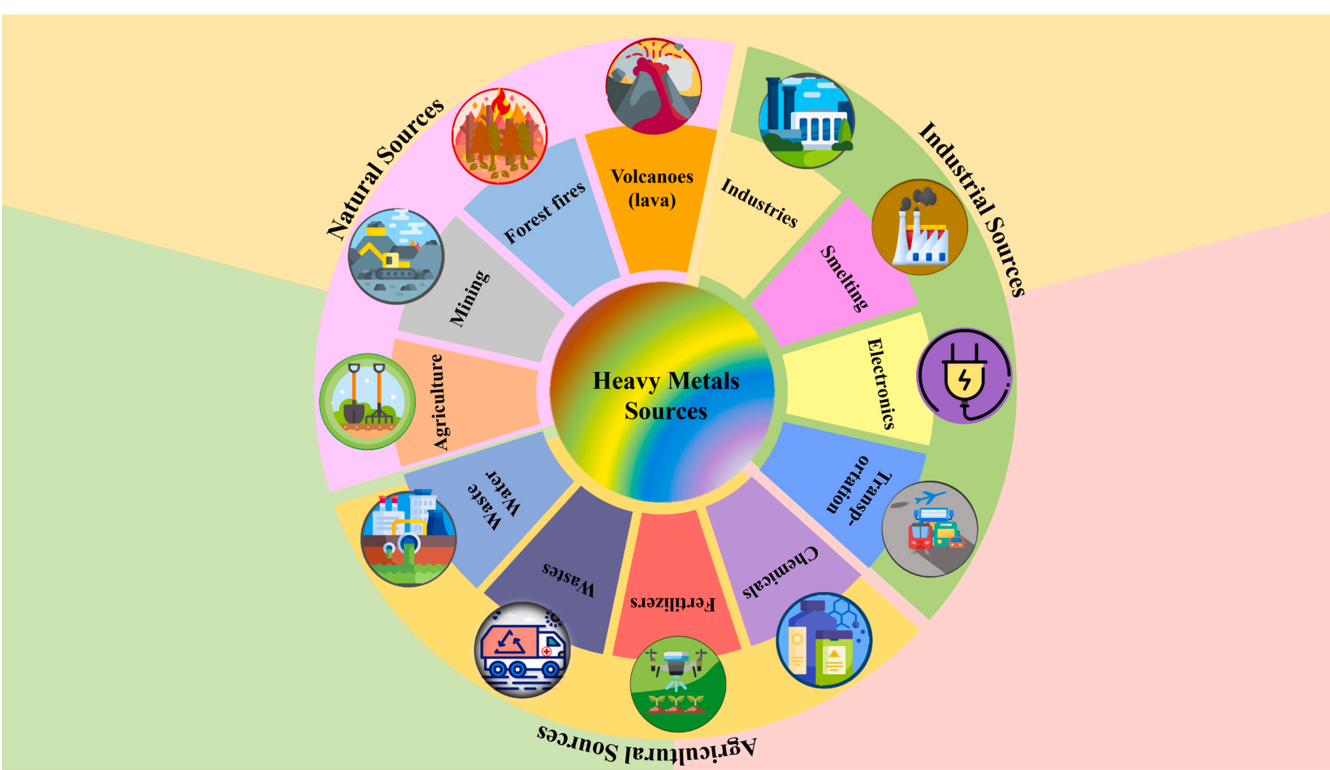

Fig. 2. Illustrates the various sources of heavy metal pollution.

significantly (Abdu and Abdullahi, 2017). In the urban environment, the main origins of HMs can be due to industrial activities such as mining, smelting, and fossil fuel burning; additionally, traffic emissions, including vehicle exhausts and the byproducts of tire wear, brake linings, and bearings, contribute to the presence of HMs; also natural sources such as minerals, forest fires, and oceans play a role in introducing HMs into the urban atmosphere (Li et al., 2013). A diverse range of anthropogenic sources contributes to the abundance of inorganic substances in the environment (Masindi and Muedi, 2018). Anthropogenic activities, mainly releasing industrial waste from mining, have been recognized as the leading cause of HM contamination in China (He et al., 2023a,2023b; Zhang et al., 2015). Significant contamination issues in this region can be attributed to the interconnection of community development and the extensive utilization of chemicals (Wang et al., 2013). Non-ferrous metal mining and smelting are the main processes leading to soil contamination with HMs (Xing et al., 2020), and farmlands near these processes are also impacted (Li et al., 2020). Many trace elements, including As, Cd, Pb, and others, have been released into soil, water, and river sediments due to the historical Pb and Zn mining and smelting operations in some areas of southern China (Williams et al., 2009; Xie et al., 2014; Zhao et al., 2015). A study was conducted to examine the occurrence of HMs in soils across many cities in China, which indicated that a considerable fraction of these soils exhibited contamination from diverse HM species (Bi et al., 2020). Despite the considerable body of study in the existing literature regarding soil pollution caused by HMs in the vicinity of China's lead/zinc mining and smelting sites, there is a lack of comprehensive data on atmospheric deposition, specifically within smelting facilities (Qiu et al., 2016).

The geological history of HMs in China exhibits a comparatively diminished concentration. Anthropogenic inputs have a greater impact than natural sources in modifying the biogeochemical cycles of natural flow (Izah et al., 2016). Throughout different historical periods, the predominant sources of atmospheric Pb emissions were coal burning, leaded gasoline, and non-ferrous smelting (Shi et al., 2019). The transportation sector, including auto transportation, contributes to atmospheric and soil pollution by emitting HMs such as Cr, Cu, Pb, Cd, Zn, and others (Su, 2014). Certain farming regions near mining and smelting operations have been contaminated (Li et al., 2020). Based on a prior investigation, the principal origins of Zn, antimony (Sb), Pb, and As within the paddy soils of this region predominantly contributed from mining operations, smelting processes, and agricultural practices (Zhang et al., 2020). Previous research has indicated that agricultural activities were the predominant contributors of Cd and Cu in paddy soils (Zhang et al., 2020). Elevated levels of HM deposits were observed in the soil surrounding multiple smelting facilities in the Henan province (Qiu et al., 2016). Elevated concentrations of HMs in rivers can be ascribed to the release of industrial and urban waste, resulting in the buildup of HMs in sedimentary reservoirs (Buchauer, 1973).

A combination of natural parent materials and several anthropogenic emission sources determines the accumulation of HMs in urban soils. Researchers undertook a study to examine the risk factors related to urban topsoil, during which they detected both naturally occurring and anthropogenic toxins (Guo et al., 2020). Because of the geological origin of this karst Devonian limestone bedrock, there are significant amounts of HMs in the soil (Huang et al., 2020). The elevated concentrations of Cr and Ni in soils can be attributed to the weathering of ultramafic rocks. Black shales contain abundant HMs, including Pb, Zn, Cu, Cd, and As (Abou El-Anwar, 2019). The four major industrial zones in China are the Beijing Tianjin-Tangshan zone, Central and South Liaoning zones, Yangtze River Delta, and Pearl River Delta zones (Yang et al., 2018). The main sources of Zn and Pb production are derived from the minerals sphalerite (ZnS) and galena (PbS), in which Zn and Pb are the predominant components of the ores (Yin et al., 2016). Heavy metals such as As, Cd, Cu, Pb, and Zn have been enriched in soils due to Pb/Zn smelting activities, and Pb/Zn mineral resources are extensively distributed in China (Xu and Fu, 2022). The primary contributors of HMs in the atmosphere are the emissions of gas and dust resulting from energy production, transportation activities, metallurgical processes, and construction materials. Besides mercury, HMs predominantly penetrate the atmosphere in the form of aerosols and subsequently settle in the soil through natural processes such as sedimentation and rainfall.

The soil ecosystem near a prominent mining site undergoes considerable contamination due to human activities, leading to a substantial accumulation of HMs across most areas (Chen et al., 2018). The discharge of HM wastewater, particularly in developing nations, into the environment is rising due to the rapid expansion of sectors such as metal plating, mining activities, fertilizer production, tannery operations, battery manufacturing, paper production, and pesticide manufacturing (Fu and Wang, 2011). The extensive fusion process over an extended period has resulted in significantly elevated levels of Pb and Cd within the soil near and adjacent wheat grains (Wu et al., 2020).

Despite the absence of solid waste or wastewater pollution, a nearby farm field was contaminated by air deposition from the Yuguang stack (Xing et al., 2018), and the deposition fluxes of Pb, Cd, and As demonstrate significant concentration levels (Qiu et al., 2016). Consequently, the Pb smelter was probably a source of Cd and Pb contaminants in the soil (Li et al., 2020). Numerous factors contribute to elevated levels of HMs in soil, such as air deposition, sewage drainage, etc. (Pan et al., 2018). A positive correlation has been seen between the degree of pollution and the proximity to the smelter, indicating that the distance from the smelting decreases as the pollution level increases (Wu et al., 2020).

4. Environmental effects of heavy metal contamination

Pollution is regarded as a severe threat to world health (Brooks, 2020). In recent years, urban air pollution has emerged as one of the world's most urgent environmental concerns on a global scale (Li et al., 2013). Air has a higher maximum allowable concentration of metals than either water or soil, as seen in Table S1 (Vamerali et al., 2010). Air pollution is a prominent contributor to global health issues, surpassing the prevalence of numerous widely recognized diseases (Brooks, 2020). As an illustration, the Llobregat Basin in Spain and the Yangtze River in China exhibited the most elevated levels of nonylphenol, with 37.3 and 55.4 μg/L, respectively (Xu et al., 2022). Metal pollution in marine environments can harm several physiological processes of marine organisms, specifically respiration, growth, and reproduction (Yee-Duarte et al., 2020). Toxicity can be partially categorized into two main categories, acute and chronic, depending on the duration of exposure (Egorova and Ananikov, 2017). Heavy metals are naturally occurring elements found in the Earth's crust that possess the characteristics of being non-degradable and indestructible, and these metals can accumulate within the food chain, leading to potential risks to human health and disturbances within ecological systems (Gupta et al., 2013). A common definition of toxicology is "an adverse change from normality, which may be irreversible" and emphasizes the importance of trustworthy experimental assessments of "adverse change" and "normality" (Egorova and Ananikov, 2017).

Heavy metals are extremely detrimental to the environment (Barzaga et al., 2021). Around 61 million individuals in the 49 nations surveyed are exposed to HM pollution (Landrigan et al., 2018). According to previous research, fatalities from exposure to environments contaminated with HMs exceeded nine million in 2015 (He et al., 2023a, 2023b; Landrigan et al., 2018). Furthermore, it has been observed that the number of deaths associated with indoor air pollution is significantly higher in the older population, ranging from 4.7 times greater compared to the general population (Cai et al., 2022). Throughout history, human societies have utilized HMs for various applications. The human body comprises two distinct categories of metals: essential and non-essential. High concentrations of non-essential metals, such as Cd and Pb, can have detrimental effects when ingested (Sow et al., 2019). In the context of non-carcinogenic risk assessment, the acceptable level is 1 (Wu et al., 2020). On the other hand, Zn and Pb mostly encounter exposure through ingesting. Rice is the staple diet for the vast majority of Chinese people; Hunan Province is a major rice-producing region in the middle-to-southern part of China, and there are abundant mineral resources in Hunan Province and concerns about HM accumulations in rice grains, likely, Sb, Ni, Mn, Cd, and As are some of the most prevalent pollutants found in rice grains, and eating them can be detrimental to one's health (Zhang et al., 2020).

To identify and quantify the toxicity characteristics of HM releases and their detrimental effects on the atmosphere. Mining activities have the potential to impact both human beings and the environment through the emission of pollutants. Heavy metal contamination presents a substantial risk to human well-being due to its detrimental effects on soil quality, surface and groundwater pollution, and the contamination of food webs (Bakshi et al., 2018). Human activities significantly influence ecosystems globally, resulting in a worrisome pace of decline in biodiversity and degradation of the environment (Li and Yang, 2008). The infiltration of rainwater through mine slag and tailings and the utilization of heavy metal-contaminated river water for irrigation pose a significant threat to soil quality (Fei et al., 2017). Various forms of wastewater include chemical, sanitary, industrial, and urban mining mixed sewage. HMs are fixed in the soil through several methods after being transported there via irrigation sewage. However, HMs in rice grains and their potential health implications for individuals remained unknown and also indicated that Cr found in paddy soils primarily originated from natural sources (Zhang et al., 2020). In reviewing Asian countries, it is evident that herbal treatments are commonly utilized, particularly in China; however, it's unclear whether these herbs are harmless in this polluted atmosphere.

Epidemiological research has provided evidence suggesting that extended exposure to Pb can result in adverse impacts on the blood and central nervous system, with a particular emphasis on the vulnerability of young children, even at relatively low levels of Pb exposure (Shi et al., 2019). High levels of HMs are released in Central and South China due to the large number of coal-fired power stations, the high rate of coal consumption by the manufacturing sector, and the large population. Besides that, the major smelting sites are concentrated in the central south region of China, which explains the comparatively higher levels of HM pollution in these provinces compared to other areas, as shown in Fig S1 (Jiang et al., 2021). Industrial processes generate several HMs, including Cu and Zn. Cu can cause depression or even lung cancer after being taken into the body, and these toxins mostly damage the liver, the kidneys, and the brain (Chen et al., 2018). People in drought are sometimes compelled to consume water from polluted sources, which may explain the correlation between water scarcity and health effects like esophageal cancer (Zhang et al., 2010). Furthermore, it is crucial to acknowledge that children exhibit heightened vulnerability to acute renal failure due to infections caused by diarrheal.

Insufficient evidence supports the claim that children dwelling in the local region demonstrate elevated Pb levels in their bloodstream, often known as blood lead levels (BLLs), and the observed phenomenon may be ascribed to the adverse impacts of Pb smelting on the local people (Li et al., 2020). In 2009, a report indicated the presence of increased amounts of Pb in the bloodstream of children residing close to the smelting facility, causing widespread concern among the general population (Wu et al., 2020). The children residing in Jiyuan have been exposed to soil contamination by HMs, resulting in elevated amounts of (BLLs) (Qiu et al., 2016). Hunan Province had greater BLLs than other provinces due to its significant reserves of non-ferrous metals and nonmetallic minerals, alongside severe soil pollution (Shi et al., 2019). Previous research has documented the presence of HM contamination in soil, river water, and sediment near the smelting facility (Cai et al., 2019). A noticeable correlation exists between proximity to the smelter and increased pollution levels. At the same time, the people in surrounding areas of industrial activities are exposed to HMs linked to neurotoxic effects in children and other adverse health outcomes (Zhang et al., 2010). Another case of a noteworthy, although presently uncharacterized and quantified, origin of disease associated with soil HMs contamination in industrial and mining areas (Landrigan et al., 2018). The present inquiry pertains to the correlation between diseases and exposure to HMs and an in-depth examination of the impact of HMs on various anatomical mechanisms of the human body, as shown in Fig. 3. The effects of the several forms of soil, HM, and chemical pollution on human health are not being adequately evaluated (Landrigan et al., 2018). The Three-Year Action Plan to Win the Blue-Sky Defense Battle (2018–2020) reduced premature mortality by 14,600 people between 2019 and 2020, and premature deaths decreased by 30% in south-central China, 28% in east China, and 16% in northern China, according to an estimate based on the interactions and synergies between greenhouse gases and air pollution (Cai et al., 2022). According to the International Energy Agency (IEA), the expected number of premature deaths due to air pollution from 2019 to 2030 is presented in Table S2, per the provided scenarios (IEA., 2019).

5. Heavy metal concentration and associated risk

Previous findings showed extremely high Pb, Cd, Zn, and Cu accumulations in the substrates with forest ecosystems in the five Pb/Zn mining sites in south China. The investigation conducted on the six tailings dams situated in northwest Guangxi, which are predominantly linked to tin (Sn) and antimony (Sb) mining operations, unveiled significantly elevated levels of Sn, Cd, Sb, Cu, As, Pb, and Zn within the tailings substrate. The soil of the Xiangtan Manganese (Mn) mine, situated in the neighboring Hunan Province, was discovered to be contaminated with elevated levels of Mn (7990.2 mg/kg), Pb (401.15 mg/kg), Zn (640.32 mg/kg), Cd (13.15 mg/kg), and Ni (91.33 mg/kg), significantly, the concentrations of Cd and Mn were notably higher (Li and Yang, 2008). According to previous research, the total concentrations of metals exhibited significant variability across different smelting regions, as depicted in Fig S2 (Xu et al., 2021).

The proximity of smelting plants is associated with elevated levels of HM contamination, mainly Pb and Cd, in crop grains, posing a significant health hazard to the local population (Xing et al., 2018). Between 2005 and 2013, an extensive soil survey conducted throughout China revealed that 19.40 percent of the soil samples analyzed from agriculture exhibited contamination by HMs (Wu et al., 2020). The presence of elevated Pb concentrations has been identified in southern China's industrial and agricultural regions, particularly within the provinces of Guangdong and Guangxi (Shi et al., 2019).

During the 1960 s, individuals residing in Minamata, Japan, experienced the onset of severe neuropathies due to their eating of seafood tainted with methylmercury (MeHg), and the condition is presently referred to as Minamata sickness, with 2217 cases officially acknowledged inside the city by 1989 (Jiang et al., 2006). Fish have varying mercury concentrations, predominantly in the poisonous and bioaccumulative form known as methylmercury, ranging from 72% to 100% (Cheng and Hu, 2012b). New research suggests that Cu and Zn in sediments and water can be more harmful to freshwater creatures than Cr, Pb, or Cd in typical Chinese lakes (Fig S3), and in this case, the environmental concern assessment of several metals in water in Tai Lake, southern China, was: Cu > Zn > Cr ≥ Ni > Pb > Cd > As > Hg^2 (Fu et al., 2017). Even though monitoring is compulsory in seafood due to the increased water pollution, more research on chemical and HM concentrations in commonly consumed fish species is still needed, especially in the Pacific Ocean region. The atmospheric mercury concentrations in China are significantly elevated compared to the worldwide background level of 1.5–2.0 ng/m^3; additionally, the rate of atmospheric mercury accumulation in China is roughly three times higher than the global average of 23–25 $\mu g/m^2$/year (Cheng and Hu, 2012b).

China's "12th five-year plan for systematic mitigation and elimination of HM pollution" from 2009 identified Pb, Cd, As, and Hg as its top

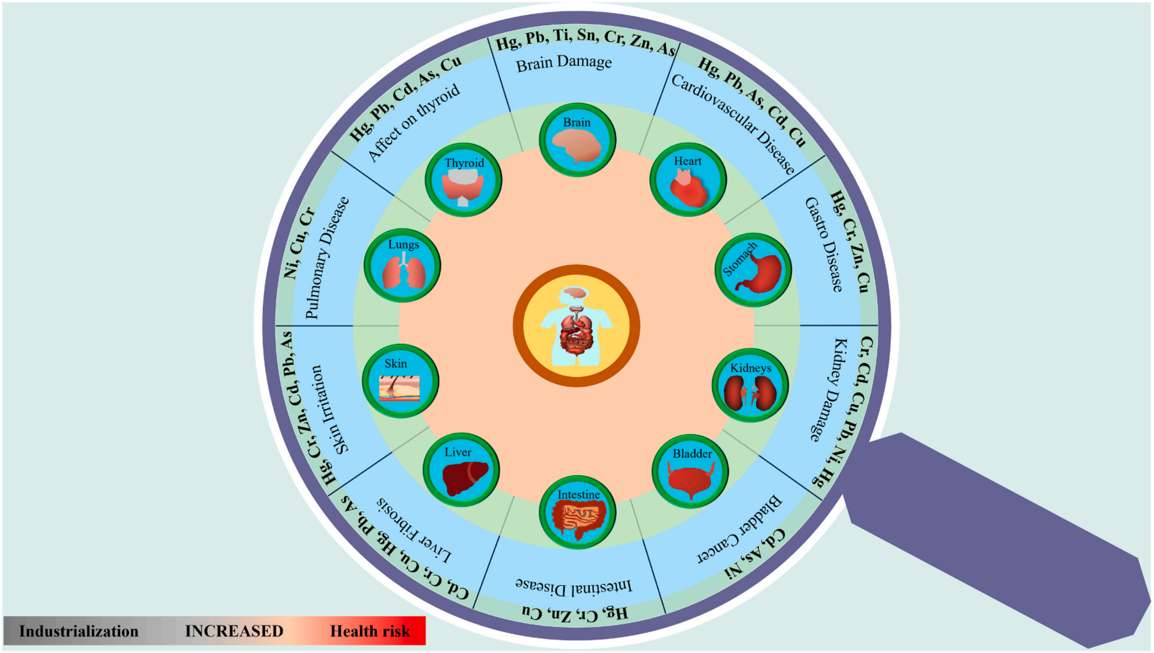

Fig. 3. An in-depth analysis of heavy metals' effects on various human organs.

four metal pollution targets, and in the conclusion of 2015, there was a notable reduction of 27.7% in the cumulative emissions of the five metals deemed of utmost importance compared to the emissions recorded in 2007 (Fu et al., 2017). According to a soil quality assessment conducted in China between 2005 and 2013, it was found that 16.1% of the soil samples analyzed did not meet the relevant soil quality requirements, and the primary contributors to these exceedances were high levels of Cd, Ni, As, Cu, Hg, Pb, DDT, and PAH contents (Hou, 2021). Even though China and India are the world's two largest PAH suppliers, Asia appears to be the most minor producer of PAHs in the Arctic, accounting for less than 50% of total PAH emissions (Lian et al., 2021). In 2014, the residential energy consumption in rural China was responsible for a mere 7% of the overall energy usage; however, it significantly contributed to over 60% of the overall exposure to PM2.5, which refers to particulate matter with an aerodynamic diameter smaller than 2.5 μm (Meng et al., 2023). Fine particle matter (PM2.5) has been a leading cause of death in China over the past two decades (Liu et al., 2023). The average concentration of PM2.5 in 74 megacities in China in 2017 was recorded at 47 g/m^3, about four times greater than the recommended guideline of the World Health Organization (Zhang et al., 2019).

6. Ways of monitoring and remediation

6.1. Remediation

Climate change and human activity are causing more severe environmental problems in many places of the world. Soil contamination by HMs due to these activities seriously threatens the natural environment. It's also important to stress the importance of adopting and refining regulations to lessen the impact of human activities on soil HM contamination. In March 2014, the Ministry of Environmental Protection (MEP) initiated a comprehensive "Action Plan for the Prevention and Restoration of Soil Contamination," this plan aimed to achieve several objectives, including enhancing the safety of arable land, maintaining control over contamination sources, improving the management of polluted sites, identifying trial locations for soil remediation, and implementing monitoring and management strategies for the soil environment (Brombal et al., 2015).

All the above-highlighted challenges show the significance of monitoring systems for identifying baseline values and risk areas. The central focus of soil monitoring is evaluating traditional contaminants, such as hazardous substances or persistent organic pollutants (POPs). Nevertheless, due to the progress made in analytical tools and the growing accessibility of information concerning their harmful effects, certain emerging contaminants are anticipated to be integrated into these initiatives (Cachada et al., 2018).

A research investigation was undertaken to observe the soil fertility and HM concentration levels in significant agricultural regions to find changes in soil characteristics essential for adopting sustainable agricultural methods via integrated soil management (Jo and Koh, 2004). According to an extensive soil monitoring initiative undertaken by the Chinese government, they have experienced contamination due to industrial activities, mining operations, and farming practices (Huang et al., 2018). The monitoring campaign for soil contamination took place from 2006 to 2010 and obtained approval through collaborative work. The central authorities executed a substantial economic investment of roughly 1 billion RMB (Brombal et al., 2015). China's active participation in a range of international forums, including the International Conference on Soil Pollution and Remediation (SOILREM), the Sino-EU Panel on Land and Soils, and the International Committee on Contaminated Land (ICCL), demonstrates the commitment of both governmental authorities and professionals to establishing sustainable mechanisms for the exchange of policies and practices (Brombal et al., 2015).

The Chinese government has implemented the National Remediation Project of Heavy Metal Contaminated Soil (NRP-HMCS) to address the detrimental consequences of HM contamination. However, the mitigating effects of HM poisoning are also attributed to inadequate financial support and a lack of recognition for immediate remediation measures in certain places (Zou et al., 2017). According to statements made by government authorities in 2013, it was anticipated that the central government would apportion approximately 5 billion dollars in direct expenditure for soil treatment endeavors from 2011 to 2015 (Brombal et al., 2015). The growing attention and emphasis on sustainable remediation principles in China may result in developing and adopting more effective and ecologically conscious remediation approaches (Brombal et al., 2015).

The Chinese government has articulated its goal to close down over 500 industrial facilities responsible for soil pollution to address and alleviate this environmental issue; a proposition has been put up to allocate around 3% of Shanghai's economic production, equivalent to nearly 2220 billion RMB, to address this matter. The available research indicates that China has substantial potential for improving the rate of soil contamination remediation and cultivating strong technical skills and delivery techniques (Shi et al., 2019). The importance of waste management methods, particularly the control and minimization of waste generated by human activities, takes priority over the remediation of pollutants (Jo and Koh, 2004).

Remediation strategies, which can be based on either background HM concentrations or a site-specific risk estimate, are affected by the type, nature, distribution, and physicochemical characteristics of HMs in soil (Bakshi et al., 2018). The sequential extraction technique is employed to gain insights into metal transport and bioavailability mechanisms by extracting metals from soil or ground using a series of distinct methods. One interesting conclusion is that it is possible to reduce pollution levels significantly, which in turn can yield substantial economic advantages (Landrigan et al., 2018).

Water, groundwater, industrial effluent, soil, sediment, and sludge are just a few of the media that have undergone remediation using various techniques, such as isolation, immobilization, toxic control, physical accumulation, and removal are the five main approaches used in soil remediation. Consequently, earthworms have the potential to fulfill a crucial function in remediating HM contamination in soils (Bakshi et al., 2018). Fungi are frequently employed as biosorbents to eliminate hazardous metals due to their notable metal absorption and retrieval abilities (Dhaliwal et al., 2020). Vegetation also aids in developing microbial communities and can potentially return a sizable amount of percolating water to the atmosphere via transpiration, hence decreasing the levels of soluble HMs in waterways.

Plants can remediate harmful HMs from various sources, such as soil, silt, sewage sludge, and water. Compared to alternative remediation technologies, phytoremediation also demonstrates high cost-effectiveness. Remediating a contaminated site might involve many methods, such as excavation, extraction, segregation, or incineration of toxic soils, followed by transporting and restoring the remaining materials to the affected area. Phytoremediation is an environmentally and economically friendly technique; Fig. 4 provides more details. Most people acknowledge that phytoremediation is effective (Bradl and Xenidis, 2005). Phytoremediation uses plants to facilitate the degradation or removal of soil contaminants (Li and Yang, 2008). Table S3 provides an overview of several phytoremediation strategies (Ali et al., 2013). Phytoremediation encompasses a range of methodologies that use diverse plant species to effectively sequester, degrade, and mitigate environmental pollutants resulting from anthropogenic activities, hence facilitating the remediation of contaminated areas (Dhaliwal et al., 2020). The findings indicated a consistent distribution of eight HM elements among mangrove plants. The mangrove plants in the Maowei Gulf exhibit a notable capacity to absorb metals efficiently through their intricate root systems. The root exhibited the highest concentration of HMs, while other plant parts displayed significantly lower levels. This observation implies that the roots possess a proficient mechanism for sequestering HMs, specifically As, Cd, Pb, Ni, and Cr. Additionally, mangrove plants have developed adaptations to restrict the upward movement of HMs, thereby safeguarding their vulnerable components (Wu et al., 2015). The toxicity measurement is a significant challenge, particularly in light of the continuous escalation of industrialization and urbanization; consequently, exploring strategies for controlling toxicity and implementing corrective measures is imperative.

Food consumption is crucial in supplying essential nutrients, including vitamins and minerals, to sustain bodily functions (Pan et al., 2018). Reducing the availability of HMs in soils where crops grow is an important step toward achieving this goal, as it will lead to less HM buildup in food sources. Therefore, assessing the effect of metal immobilization in polluted soils on the concentration and accumulation of HMs in locally consumed agricultural grains is important, as this has implications for human health (Xing et al., 2018). HMs can bioaccumulate within food chains, even at low concentrations, contributing

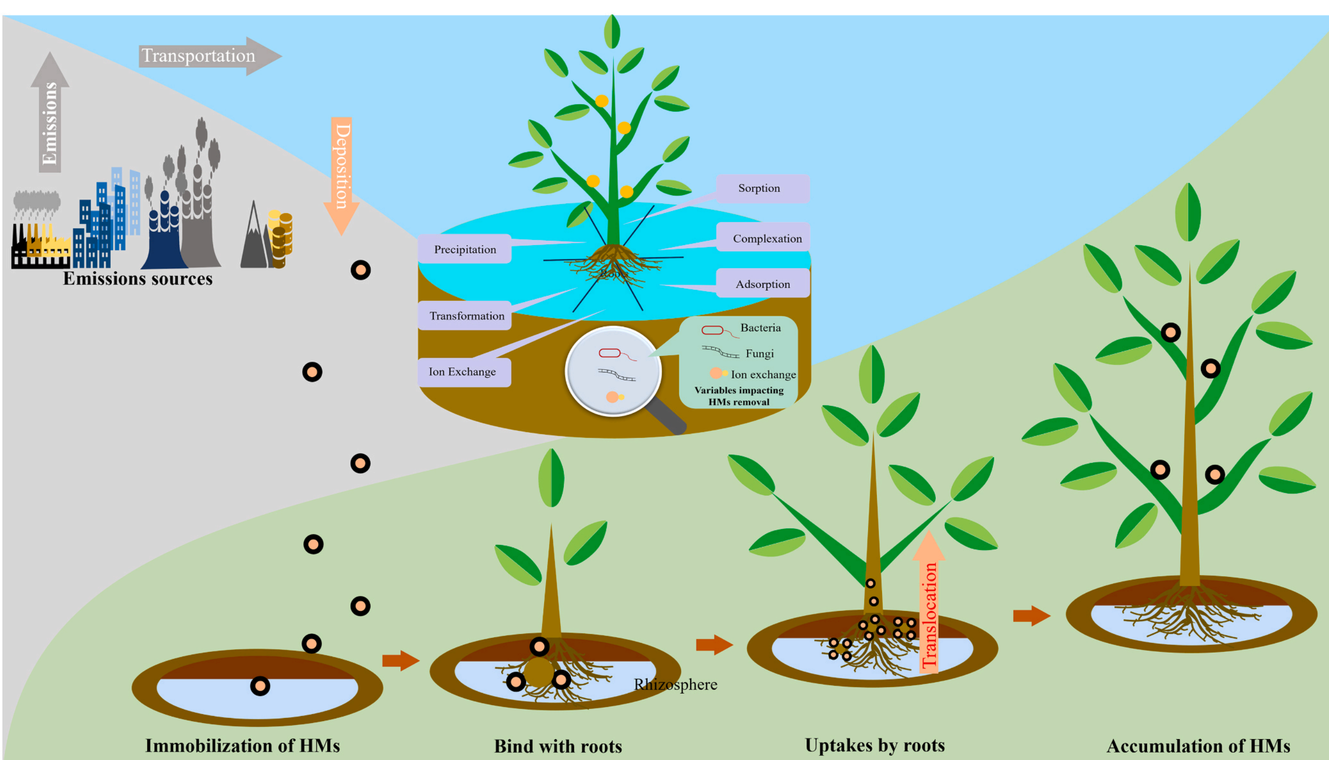

Fig. 4. The phytoremediation technique is employed to address the issue of soil contamination described in detail.

to the growing number of health hazards associated with these pollutants (Huang et al., 2020). Compared to other metallic elements, Cr and Ni exhibited greater stability in soil matrices, reducing leachability and bioavailability (Bi et al., 2020). Non-metallic components and clay minerals are also utilized to modify biochar to immobilize As (Beiyuan et al., 2023).

The recovery and recycling of these metals from water sources have been the subject of numerous proposed methods, such as coagulation, precipitation, sedimentation, adsorption, electrochemical extraction, membrane separation, and many more (Luo et al., 2022). Phytoremediation is often regarded as the best, least expensive, most environmentally friendly (Liu and Tran, 2021), and most desired technology for removing HMs from polluted sites; using edible crops for phytoremediation won't solve the issue of HM contamination, though (Gupta et al., 2013). Plants that accumulate HMs in their biomass were recently found to dramatically minimize ecological and health concerns during the rehabilitation of a significant As and Cd tailing dam in China as part of a phytoremediation project (Sulmon et al., 2014). Only a small percentage of plant species, called halophytes, can thrive in highly salty conditions; occasionally, halophytes' glandular tissues discharge HM ions onto the leaf surface in addition to Na^+ and Cl^- (Wang et al., 2014). Chemicals in hazardous wastes can be contained through solidification and stabilization (S/S) techniques, and this method was initially created in the late 1950 s for sludge management but was later adapted for soil remediation; as an example, the remediation industry in China doubled between 2017 and 2018, reaching US$2.9 billion, with S/S taking a commanding lead (48.5% market share) (Shen et al., 2019). Over the past decade, governments and industries worldwide have made substantial efforts to promote electric vehicles (EVs) to minimize the carbon footprint and environmental effects of internal combustion engine (ICE) vehicles; however, decomposing EV batteries may release various HMs and other dangerous substances; nonetheless, they are not considered hazardous waste in the United States (excluding California), the European Union, or China (Hu et al., 2017). It is noteworthy that China presently exhibits the highest production and consumption of coal compared to all other nations; based on data from the China Statistical Yearbook 2012, China's aggregate energy consumption in 2011 amounted to around 3.48 billion tons of standard coal equivalent (SCE), and coal constituted the largest share of the total energy consumption, accounting for 68.4%, while crude oil accounted for 18.6% (Li et al., 2013). An integrated management system based on the three R's of environmental protection—reduce, reuse, and recycle—should be built to prepare for the millions of batteries that will soon be retired from EVs (Hu et al., 2017). Here, for the first time, we present novel findings indicating that a comprehensive examination of the 3 R's reveals an additional component, resulting in a revised framework consisting of 4 R's: "reuse, recycle, reduce, and reverse (return);" furthermore, we propose that addressing global pollution control necessitates the adoption of 3 G's: "globally, green, growth."

Recent international initiatives, such as the Intergovernmental Panel on Climate Change, the Intergovernmental Science-Policy Panel on Biodiversity and Ecosystem Services, and the ongoing efforts to develop an Intergovernmental Science-Policy Panel on Chemicals and Waste, demonstrate the growing recognition of the global scale of anthropogenic stressors on the biosphere (Brooks, 2023). Governments have established subsidy policies to deal with the financial burden inhabitants incur at various levels throughout various areas (Meng et al., 2023). Moreover, China implemented significant legislation titled the "Soil Pollution Prevention and Control Law" (referred to as the "Soil Law"), which came into force on January 1, 2019; nevertheless, there have been notable secondary pollution occurrences after remediation efforts, for instance, the Changzhou Foreign Languages School incident 2015 involved numerous students experiencing health abnormalities after attending a school near a site undergoing remediation. This incident prompted a transition towards in situ treatments and the adoption of risk control technologies, specifically in situ immobilization techniques (Hou, 2021).

With an annual direct loss of more than 9 billion RMB yuan (about 1.3 billion USD) and an indirect loss of nearly 30 billion RMB yuan (roughly 4.4 billion USD), mining operations and the ensuing mine tailings have had a substantial economic impact (Li and Yang, 2008). Besides that, recycling lithium-ion batteries (now used in most EVs) could improve supply chain reliability and forestall shortages in the future, but the process is more expensive than mining for new metals (Hu et al., 2017).

7. Conclusion

Heavy metal contamination in soil is a matter of great concern since it can potentially negatively impact the health of animals and humans. The increasing levels of industry and urbanization further heighten this concern. The outcomes of the contamination and health risk evaluations indicate that HMs resulting from mining and smelting activities have led to significant soil pollution in the surrounding area. In addition, soil contamination by HMs presents substantial risks in terms of carcinogenic and non-carcinogenic hazards to the local population, with a particular emphasis on children and individuals residing in areas characterized by the highest contamination levels. This study highlights the necessity for more stringent regulations on mining and smelting activities to mitigate the release of HM pollutants into the environment in China, hence safeguarding its residents. Evidence suggests that children residing in the local area exhibit elevated amounts of (BLLs), and these elevated BLLs are associated with the adverse effects resulting from the process of Pb smelting on the region's residents. This study assessed the remediation techniques for removing HMs from the soil, focusing on comparing the phytoremediation strategies. Our analysis emphasized the efficacy and advantages of phytoremediation, a cost-effective and ecologically favorable technique. Identifying priority control components can aid authorities in developing more robust and efficient approaches for mitigating and managing exposure.

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CRediT authorship contribution statement

Muhammad Adnan: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Baohua Xiao:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Muhammad Ubaid Ali:** Writing – review & editing. **Peng Zhao:** Writing – review & editing. **Haiyan Wang:** Writing – review & editing. **Peiwen Xiao:** Writing – review & editing. **Shaheen Bibi:** Writing – review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest.

Data Availability

The data that has been used is confidential.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2024.116189.

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