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Sources, bioaccumulation, health risks and remediation of potentially toxic metal(loid)s (As, Cd, Cr, Pb and Hg): an epitomised review

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Abstract The release of potentially toxic metal(loid)s (PTMs) such as As, Cd, Cr, Pb and Hg has become a serious threat to the environment. The anthropogenic contribution of these PTMs, especially Hg, is increasing continuously, and coal combustion in thermal power plants (TPPs) is considered to be the highest contributor of PTMs. Once entered into the environment, PTMs get deposited on the soil, which is the most important sink of these PTMs. This review centred on the sources of PTMs from coal and flyash and their enrichment in soil, chemical behaviour in soil and plant, bioaccumulation in trees and vegetables, health risk and remediation. Several remediation techniques (physical and chemical) have been used to minimise the PTMs level in soil and water, but the phytoremediation technique is the most commonly used technique for the effective removal of PTMs from contaminated soil and water. Several plant species like *Brassica juncea*, *Pteris vittata* and *Helianthus annuus* are proved to be the most potential candidate for the PTMs removal. Among all the PTMs, the occurrence of Hg in coal is a global concern due to the significant release of Hg into the atmosphere from coal-fired thermal power plants. Therefore, the Hg removal from pre-combustion (coal washing and demercuration techniques) coal is very essential to reduce the possibility of Hg release to the atmosphere.

Keywords Potentially toxic metal(loid)s · Mercury · Coal and flyash · Plants and vegetables · Phytoremediation

Introduction

The increasing level of pollution is a serious threat to the environment and mankind (Fayiga et al. 2018). Fundamentally, the natural and anthropogenic sources are two sources of pollution in the natural environment. Among the two, the anthropogenic sources play the major role in elevating the pollution level. Coal mining and thermal power plants (TPPs) are the major anthropogenic contributors of pollutant to the environment (Li et al. 2018). These anthropogenic sources release potentially toxic metal(loid)s (PTMs) into the environment. The five PTMs, namely arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg) and lead (Pb), have been recognised as the most hazardous and persistent element (Lee et al. 2006; Ozden et al. 2018). These PTMs have the bioaccumulation capacity in the food chain and may cause serious risk to human health (Modabberi et al. 2018; Raj and Maiti 2019a). Direct inhalation, dermal contact and consumption of PTMs-contaminated water and soil are the main exposure routes of PTMs in humans.

The reported global anthropogenic release of As was 82,000 metric tonnes/year (Jang et al. 2016). In a case

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study on anthropogenic emission of Cd, it was reported that the total emissions of Cd in China for the year 2009 was 743.77 metric tonnes (Cheng et al. 2015). In another case study, Cheng et al. (2015) reported that the emission of Cr in China during the year 1990 to 2009 was 13,400 metric tonnes, whereas the total Pb emission from the year 1930 to 2010 was 173.8 metric tonnes (Liang and Mao 2015). Streets et al. (2018) delineated the global anthropogenic release of Hg in the order of 2000 metric tonnes/year.

Several remediation technologies have been reported to remediate toxic metal(loid)s. Physical (soil washing, selective catalytic reduction and wet flue gas desulphurisation, thermal treatment), chemical (stabilisation, electro-remediation and adsorption) and biological methods (microbial treatment, phytoremediation) (Yu et al. 2016; Raj and Maiti 2019b) have been used by several researchers to remediate PTMs from contaminated soil and water. Among all the remediation technologies, the phytoremediation technique is considered to be the best and effective approach for the remediation of PTMs from soil and water (Wang et al. 2012).

The aim of this study is to review the previous and current knowledge on the availability of major PTMs in coal, flyash (FA) and soil, and their bio-accumulation in tree and vegetable species. The study also explored the potential health risks caused due to the exposure of PTMs. In addition, the various techniques of PTMs remediation from soil and water have also been anatomised. Moreover, particular emphasis has been given to the coal Hg content and its removal techniques.

Methods to analyse PTMs in coal, flyash and soil

Single extraction The PTMs concentration in coal, FA and soil can be determined through acid digestion methods. In several studies, different acid compositions were used for the determination of total concentration of PTMs in the coal, FA and soil samples. According to Pantuzzo et al. (2009), the total concentrations of As, Cd, Cr and Pb in coal and soil can be extracted using the acid mixture of HNO_3, HCl and HF (5:15:10, *v*/*v*); acid mixture of HNO_3 and $HClO_4$ (1:4, *v*/*v*) is used for total PTMs content in FA (Jambhulkar and Juwarkar 2009). The total Hg content in coal and FA samples is determined by digesting in nitric acid (HNO_3; 1:10; *w*/*v*) on a hot plate at 70 °C for 90 min, whereas 50% aqua regia (HCl and HNO_3, 3:1) is used for total Hg determination in soil samples (USEPA 1996; ASTM 2006; USEPA 2007; Issaro et al. 2009; Park et al. 2013).

Sequential extraction method It has been used by several researchers to determine the various fractions bound with metal(loid)s in the coal, FA and soil samples. According to Tessier et al. (1979), the solid materials can be partitioned into specific fractions, and these fractions can be extracted by using specific regents. It involves five fractions: (1) exchangeable fraction, extracted with 1 M $MgCl_2$; (2) fraction bound to carbonates, extracted with 1 M CH_3COONa; (3) fraction bound to iron and manganese oxide, extracted with 0.04 M $NH_2OH{\cdot}HCl$; (4) fraction bound to organic matter, extracted with HNO_3 and H_2O_2; (5) residual fraction, extracted with aqua regia (HCl/HNO_3, 3:1, *v*/*v*) (Li et al. 2009; Subirés-Muñoz et al. 2011; Kahkha et al. 2017).

Arsenic (As)

Arsenic is the 20th most abundant element in the earth's crust. It is a metalloid having the atomic number of 33 and atomic mass of 74.9216 g/mol. The outer electronic configuration of As is $4s^2$ $4p^3$. It belongs to the fifth group of the periodic table, and resides with nitrogen, phosphorus, antimony and bismuth. In some cases like biological (uptake of As in plant and microorganisms) and chemical (behaviour of As in soils) processes, it acts as an analogue of phosphorus due to the chemical similarity (Alloway 2013). The bond formation of As with sulphur and carbon is more easy than that of phosphorus. It gets volatilised from the soil due to the biological transformation (Sadiq 1997).

Weathering from the bedrock (parent materials) is the main natural source of As. Generally, the elevated concentration of As is found in clays and shales (14.5 mg/kg), while the concentration is comparatively lower in igneous rocks (1.5–3.0 mg/kg) and limestones (1.7 mg/kg) than the world average for uncontaminated soils (7.2 mg/kg) (Jenkins 1980; Adriano 2001; Loska et al. 2003). Its concentration in contaminated soils may rises to the level of 27,000 mg/kg (Alloway 2013). According to USEPA, the permissible limit of As in soil is 24 mg/kg (Singh et al. 2015). The reported As content in the plant grown on uncontaminated soil was in the range of 0.009 to 1.5 mg/kg (Alloway 2013). Since the elevated concentration of As puts negative impacts on the environment, it is very essential to locate its origin source. Among all the sources, coal is one of the key sources, which has been focussed by several researchers (Yudovich and Ketris 2005; Wang et al. 2012). The average As content in most of the coal types has been reported in the range of 0.5–80 mg/kg, depending on the geological origin (Xu et al. 2004). The high concentration of As in coal may pose a serious threat to the soil and vegetation because the flue gas released from the burning of As-containing coal may get deposited on the nearby soil and vegetation, which may damage the soil quality of nearby areas. In the vicinity of coal mine and TPP areas, the deposition of As on to the top surface of soil occurs through atmospheric deposition via wet deposition. In coal, As is present in the form of pyrite and arsenate. The As is also associated with inorganic elements in coal (Alloway 2013). The inorganic form of As are found in various forms in the environment and is commonly found in water as pentavalent arsenate [As(V)] or trivalent arsenite [As(III)].

Chemical behaviour of As in soil and plant

In soil, the As is associated primarily with its minerals, which are derived from parent materials. Major concentration of As is present in mineral forms, including arsenates, sulphides, sulfosalts, arsenites, arsenides, native elements and metal alloys. Out of these, sulphide (e.g. arsenopyrite, pyrite, loellingite, realgar) and arsenate minerals (e.g. scorodite, beudantite, yukonite) are the most common soil-bound mineral forms, while other mineral forms are generated during weathering process (Moreno-Jiménez et al. 2012). In forest soil and peat, the As is present in organic form. Generally, the organic matter content is higher in the soil, where plant residues are deposited through litter fall (Alloway 2013). So, in such types of soil, As is present in the organic bound form (monomethylarsonic acid and dimethylarsinic acid) (Moreno-Jiménez et al. 2012). The bioavailability, volatility, toxicity and solubility of As in soils are mainly dependent upon the biogeochemical processes and chemical reactions occurring in the soil. These reactions and biogeochemical processes are usually controlled by change in the environmental conditions (seasonal variations in soil moisture and organic matter content). The change in soil temperature is also an important factor to be considered for the solubility and bioavailability of As in the soil. According to Ahmann et al. (1997), soil microbial metabolism plays a crucial role in the redox transformations of As in the soils.

As speciation

The speciation and transformation of As in the soil is directly affected by activities of the plant's root (Fitz and Wenzel 2002). Microorganisms in soil are responsible for detoxification of toxic materials like As through chemical reactions such as, oxidation and reduction processes (Rensing and Rosen 2009). For example, the reduction of As(V) to As(III) in soil occurs through microorganisms like *Pseudomonas* and *Bacillus* species, which lead to the detoxification of soil (Macur et al. 2004). Generally, bacteria which have oxidising capabilities of As(III) coexists with reducers of As(V) in soil. So, these bacteria are considered as the main regulators of inorganic speciation of As in soil pore waters. The plants have the capabilities to uptake arsenate and arsenous acid from soils, directly. Ma et al. (2008) reported that As enters into the plant from soil in the form of arsenous acid through aquaporins. Once As has been taken up by the plant's root, the arsenate is reduced to arsenite, which is released back into the external medium (As-III efflux) or gets transferred to the shoot of the plant (Fig. 1).

As concentration in coal, flyash and soil

In a study by Bai et al. (2007), the average As concentration in the coal samples was 4.09 mg/kg (Table 1). The world average As concentration of 8.3 mg/kg in coal was reported by Ketris and Yudovich (2009). In France, the reported As concentration in FA generated from power plant was found to be 43.1 mg/kg (Bidar et al. 2016), while the As contents in FA generated from three different power plants (Sual, Mauban and Masinloc coal power plants) in the Philippines were 8.4, 41.8 and 10.4 mg/kg, respectively (Brigden and Santillo 2002). It is observed from the previous reported data that the burning of higher As-containing coal in power plants may be the main reason of elevated As content in FA (Alloway 2013). The reported concentration of As in 27 samples of mine soil was 9.8 mg/kg (Zhai et al. 2009), whereas Maya et al. (2015) reported that As content in 693 samples of mine-impacted soil of Emalahleni region of South Africa was 0.5 mg/kg. The reported As content by Maya et al. (2015) was 20 times lesser than the reported As concentration in mine soil of Palapye region of Botswana. In a similar study, Bhuiyan

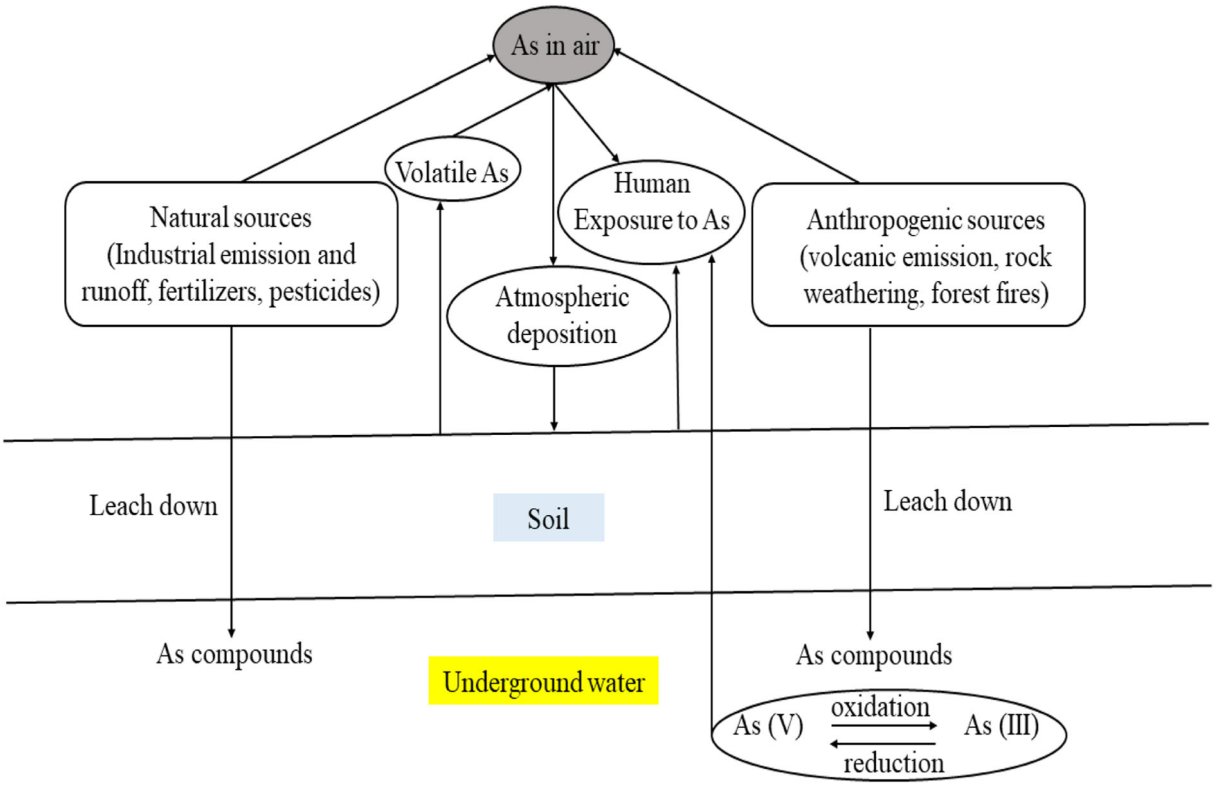

Fig. 1 Arsenic in underground water, soil and air (Alloway 2013)

et al. (2010) reported that As content in acid mine drainage-contaminated soil (Barapukuria, Bangladesh) was 17.5 mg/kg.

Accumulation of As in tree and vegetable species

Plant and vegetable species growing on the As-contaminated soil are able to uptake As from soil according to their uptake efficiencies. Therefore, high As content in soil may leads to higher accumulation in various tissues of plants and vegetables. A study was conducted by Patel et al. (2015) on tree species growing on the soil of Korba coal basin, Chhattisgarh, India, and it was found that As concentrations in leaf samples of *Mangifera indica* (mango), *Butea monosperma* (flame of forest), *Tectona grandis* (teak) and *Azadirachta indica* (margosa tree) were 3.9, 3.0, 6.4 and 43.1 mg/kg, respectively.

The qualities of vegetables are severely affected by the accumulation of metalloids in different parts, and their consumptions are the key source of accumulation in the body parts of human beings. The As accumulation in various vegetable species was also reported by several researchers. For example, the vegetable species of *Solanum tuberosum* (potato), *Raphanus sativus* (radish) and *Allium cepa* (onion) growing on the soil of Smaland, Sweden, accumulated 0.0036, 0.0055 and 0.0033 mg/kg of As, respectively (Augustsson et al. 2018). Basha et al. (2014) studied on 72 vegetable samples of three species consisting of *S. tuberosum* (potato), *Capsicum annum* (chilli) and *Momordica charantia* (bitter gourd) growing in the vicinity of Tummalapalle Uranium mines, India. However, in their study, no As accumulation was reported.

Health risks associated with the As exposure

Elevated level of As in coal, FA, soil, plant and vegetable are hazardous to people. The PTMs are exposed through ingestion, inhalation and absorption by skin as well as consumption of contaminated vegetable (Loska et al. 2003). It is well known that inorganic form of As is more harmful than its organic form. The symptoms of short-term exposure of As poisoning through food and drinking water include muscle cramp, stomach pain, vomiting and diarrhoea, while the symptoms of long-

Table 1 Concentration (mg/kg) of potentially toxic metal(loid)s in coal

Country	As	Cd	Cr	Pb	References
China	4.09	0.81	16.94	16.64	Bai et al. 2007
	3.79	0.25	15.4	15.1	Dai et al. 2007
	5	0.3	16	14	Tang and Huang 2004
	3.8	0.24	15.25	15.55	Ren et al. 2006
USA	24	0.47	15	11	Finkelman 1993
India	0.07	0.75	14.90	5.44	Verma et al. 2015
World coal	8.3	0.22	16	7.8	Ketris and Yudovich 2009

term exposure are generally observed in skin (change in pigmentation, hard patches on palms, skin lesions). Usually, these symptoms occur after a minimum exposure of 5 years, which may further lead to skin cancer. The long-term exposure of As can cause lung and bladder cancer. Other adverse effects of As on human health include diabetes and neurological complications (Abdul et al. 2015). Arsenic poisoning is also associated with infant mortality and adverse pregnancy outcomes. The symptoms of As poisoning may differ between groups of population, individuals and geographical areas.

Remediation of As from soil and water

The As-contaminated soil can be treated through ex situ method, which includes physical treatment like soil excavation and landfills. Chemical treatment (coagulation, flocculation, acid treatment) to the soil is also used for As removal (Choong et al. 2007). In water, As can be removed by oxidation techniques (photochemical oxidation, photocatalytic oxidation, biological oxidation). The oxidation process converts soluble As(III) to As(V) followed by the precipitation of As(V) (Singh et al. 2015). But the physical and chemical techniques of As removal may lead to the change in soil properties and cause destruction of soil fertility. Thus, phytoremediation technique is used for As removal from contaminated soil and water (Dickinson et al. 2009). In a study, *Vallisneria natans* (submerged macrophyte species) was used to minimise the As content from water. The study observed that the total As content in water dropped rapidly within 3 days. During the remediation process, the chlorophyll content was decreased and an increase in the antioxidant enzymatic activities was observed. The results concluded that the species of *V. natans* may be used as the potential candidate to remove As from As-contaminated water (Li et al. 2018). *Pteris vittata* (commonly known as Chinese brake fern) is also used for the removal of As from groundwater and can remove As from drinking water up to the level of 10 μg/L. The study also reported that young fern plants had more potential to remove As than old plants of similar size (Tu et al. 2004). The same plant had also been used to remove As from soil (Yan et al. 2019). Ye et al. (2011) had also worked on phytoremediation of As through *P. vittata* in a pot experiment and found that the plant removed 3.5% to 11.4% of the total As from the soil.

Cadmium (Cd)

Cadmium is a silvery-white heavy metal, which is chemically very similar to the metal like Hg in group 12 of the chemical periodic table, and also has a lower melting point. It is a non-metabolic and non-essential element. It exists as a divalent cation (Cd^{2+}) in the soil. In soil, the typical concentration of Cd ranges from 0.1 to 1 mg/kg. In non-contaminated soils, the Cd content generally increases with the decrease in sand percentage due to the association of Cd with finer particles. The high organic content in soil is also responsible for exceeding Cd level (> 1 mg/kg) in soil (Alloway 2013). Cd is enriched in soil through human activities like application of phosphate fertilisers and atmospheric deposition. The major consumption (80%) of Cd occurs through the production of rechargeable batteries, and therefore the rechargeable batteries are the major source of Cd in the soil (Raj et al. 2017). Microbial activities are also responsible for Cd binding and its release from the soil (Alloway 2013). Other sources of Cd to the environment are automobiles, agricultural implements, industrial tools, fungicides, luminescent dials, etc. (Kirkham 2006).

Chemical behaviour of Cd in soil and plant

The compounds of Cd are isotypic with other corresponding compounds like Zn^{2+}, Co^{2+}, Fe^{2+}, Mg^{2+} and Ni^{2+}. Cd may form organic chelates and complex ions ($CdOH^+$, $CdCl^+$). It forms minerals like CdO (cadmium oxide) and $CdCO_3$ (cadmium carbonate) under the strong oxidation condition, and gets accumulated in phosphate during the weathering process. In acidic soils (pH 4.5 to 5.5), the mobility of Cd is very high, while it is immobile in alkaline soils. The soil has very high affinity for Cd at pH 6. The physiological role of Cd in higher plants is not known very clearly, but it is understood that Cd is taken up from the soil and is translocated to the different parts of the plant (Alloway 2013). Cd is accumulated in high proportion in the plant's root, and the accumulation is even higher when Cd enters the plant system through foliar deposition (by atmospheric Cd deposition) (Kabata-Pendias and Pendias 2001). One of the most significant biochemical characteristics of Cd is its strong affinity for sulphhydryl (–SH) groups of various compounds. The formation of complexes with metallothionein-like protein is another important characteristic of Cd. Moreover, it also shows an affinity for phosphate groups and for other side chains of protein. It is considered that Cd is very toxic to the plants because Cd has the strong characteristics to disturb the enzymatic activities of plants. Studies also reported that Cd leads to the inhibition of chlorophyll and anthocyanin formation in the plants (Alloway 2013). In plants, the chlorophyll content acts as the indicator of upper critical limit of Cd, which means that the low chlorophyll concentration indicates high Cd accumulation (Kabata-Pendias and Pendias 2001). The reported phytotoxic level of Cd in plant ranged from 5 to 10 mg/kg, whereas the critical level of Cd was reported to be 10 to 20 mg/kg (DW) (Alloway 2013). Yan et al. (2013) found that the soil urease activity and nitrification process were inhibited with the increase in Cd^{2+} ions in the soil.

Cd concentration in coal, flyash and soil

The occurrence of Cd in coal may be due its geogenic origin. In China, Cd content was reported and found in the range of 0.81 to 0.24 mg/kg (Tang and Huang 2004; Ren et al. 2006; Bai et al. 2007; Dai and Ren 2007). Ketris and Yudovich 2009 reported the world average concentration of Cd (0.22 mg/kg) in coal, which was lower than the reported concentration in Indian coal (0.75 mg/kg) (Verma et al. 2015). The coal burning in TPP may lead to the transfer of Cd from coal to FA. Bidar et al. (2016) found 0.98 and 0.61 mg Cd/kg in two types of silico-aluminous and sulfo-calcic FA samples (TPP, France), respectively. Cd content was relatively high in FA of one of the TPPs of Finland (Pöykiö et al. 2016) (Table 2).

Accumulation of Cd in tree and vegetable species

The leaves of various tree species growing in the nearby areas of pollutes sites (TPP, roadside and industrial areas) accumulate Cd through foliar deposition. For example, Mansour (2014) gave an account of Cd concentrations in the leaves of three tree species, namely *Cupressus sempervirens* L. (Cupressaceae, Mediterranean cypress), *Ligustrum ovalifolium* Hassk. (Oleaceae, Korean privet) and *Euonymus japonicas* Thunb. (Celastraceae, Japanese spindle), and found the concentrations of 0.061, 0.333 and 0.166 mg/kg, respectively. In Nigeria, the reported Cd content in *Capsicum annuum* L. (Solanaceae, capsicum) was 0.19 mg/kg (Sobukola et al. 2010).

Health risks associated with the Cd exposure

Cd is a potential threat to humans and the environment due to its specialities of higher mobility and bioavailability than other toxic elements. It exhibits adverse effects on biological activities in humans. The intake of Cd-contaminated vegetable or food is the major source of Cd introduction in the human body (Kirkham 2006). Besides this, the occupational exposure and smoking are also the important sources of Cd (Lugon-Moulin et al. 2004). Kidney and bone tissues are the target organs and are most sensitive to the Cd exposure in humans (Fig. 2). In severe cases, high Cd contamination may lead to kidney failure. The well-known notorious disease, known as Itai-Itai ('ouch-ouch') disease, is caused due to Cd exposure. The disease results in osteoporosis (loss of calcium in bone) because of the replacement of calcium with excess of Cd in bones of the human body (Yeung and Hsu 2005). A study reported that more than 100 people lost their lives due to the Cd

Table 2 Concentration (mg/kg) of potentially toxic metal(loid)s in flyash generated from thermal power plants

Country	As	Cd	Cr	Pb	References
Czech Republic	29	nr	115	168	Bartonova et al. 2007
Spain	23.2	nr	47.7	nr	Font et al. 2012
France	43.1	0.98	nr	132	Bidar et al. 2016
South Africa	nr	nr	139	70	Koukouzas et al. 2011
Greece	20.7	nr	4.8	nr	Megalovasilis et al. 2013
Finland	13.0	2.9	66.9	28.7	Poykio et al. 2016
India	5.88	11.15	71.72	59.23	Raj and Maiti 2019a

nr not reported

poisoning during the year 1922 to 1965 (Yeung and Hsu 2005).

Remediation of Cd from soil and water

Effective measures have been taken to remove or minimise Cd level from the environment. Yeung and Hsu (2005) worked on the electrokinetic extraction of Cd-contaminated clay, and observed that the removal efficiency of Cd depends upon the acidic environment of the soil. Cd is also removed from soil and water through adsorption process by the application of different adsorbents (activated carbon, low-cost oxides or hydroxides of Al, Mg and Fe) (Sen and Sarzali 2008). Several plant species like *Oryza sativa* L. (Poaceae, Asian rice), *Chrysopogon zizanioides* (L.) Roberty (Poaceae, vetiver grass), *Lemna minor* L. (Lemnaceae, common duckweeds) and *Allium sativum* L. (Amaryllidaceae, garlic) are known to be good hyperaccumulators of Cd (Jiang et al. 2001; Lai and Chen 2004; Murakami et al. 2007; Hou et al. 2007). The removal of Cd through microorganisms like bacteria, fungi and algae have also been reported in the previously published literature (Barros Júnior et al. 2003; Arikpo et al. 2004; Yuan et al. 2017). *Thlaspi caerulescens* Presl and Presl (Brassicaceae, Alpine pennygrass) was known for its high Cd-accumulating ability, due to the greater Cd tolerance with less toxicity symptoms (Brown et al. 1994). The study also observed relatively high Cd translocation from contaminated solution to the upper part of the plant, which resulted in high accumulation of Cd in the shoot. Patel et al. (2005) used *Colocasia esculenta* (L.) Schott (Araceae, taro or elephant-ear) for phytoremediation of Cd from soil, and observed higher accumulation of Cd in root followed by stem and leaf.

Chromium (Cr)

Chromium is a lustrous and hard toxic metal. It is the first element in group VI of the periodic table. It is also known as transition element. It has anti-corrosive properties and used as an additive in stainless steel. Moreover, it is used in metallurgy, tannery, electroplating, wood preservation, pulp and paper production. The reported concentration of Cr in the Earth's crust is 100 mg/kg (Emsley 2001). It is associated with mafic and ultramafic rocks. The naturally occurring compounds of Cr are chromite and chromate, which have principal valences of 3 and 6, respectively. Cr(VI) is highly oxidised and hence very much less stable than that of Cr(III) (Alloway 2013). The Cr content in soil can be ranged from 1 to 3000 mg/kg (Kotas and Stasicka 2000). The igneous and sedimentary rocks contain less Cr (ranged from 5 to 120 mg/kg) (Alloway 2013). Weathering of the parent materials is the major source (natural source) of Cr in soils, and the reported range of total Cr content in soil is 0.5 to 250 mg/kg, while the average value varies from 40 to 70 mg/kg (Alloway 2013). Generally, the organic rich and sandy soils have low Cr content with an average value of 47 and 12 mg/kg, respectively, and a positive correlation exists between Cr content and fine granulometric fractions. The Cr-rich sludge and industrial wastes are the major anthropogenic sources of total Cr content in the soils.

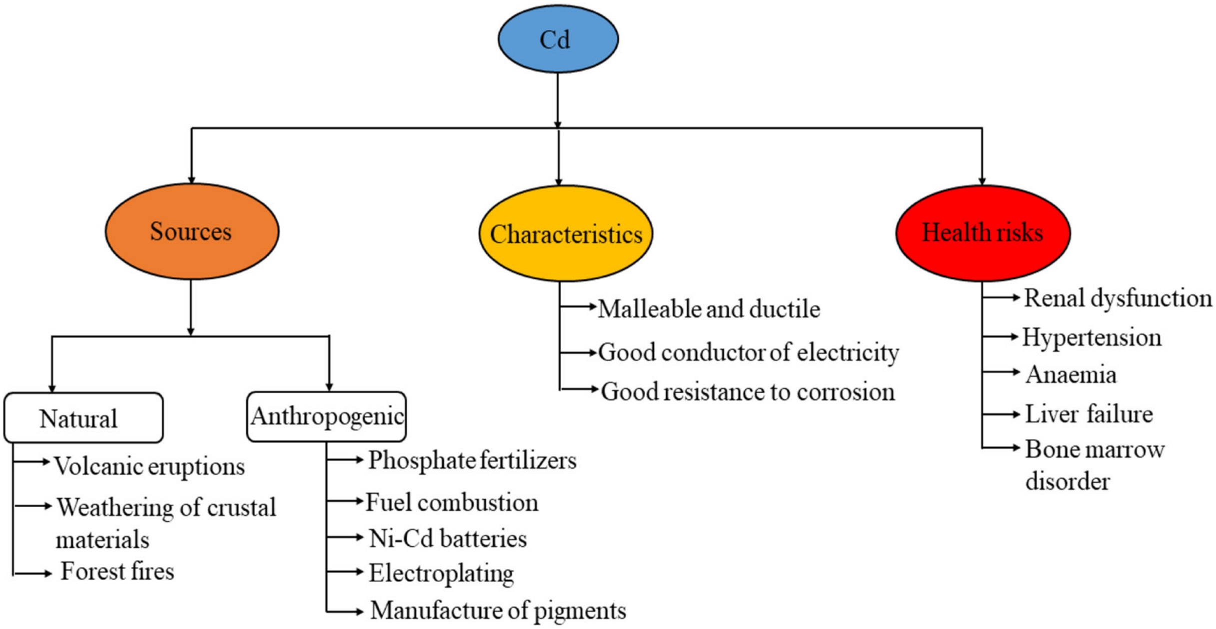

Fig. 2 Sources, characteristics and health risks of Cd

Chemical behaviour of Cr in soil and plant

In soil, Cr exists in two oxidation states as Cr(III) and Cr(VI). Cr(III) is slightly mobile in acidic condition, and it gets precipitated completely at pH 5.5. Hence, the compounds of Cr(III) are very stable in soils, whereas Cr(VI) is highly mobile in acidic and alkaline soils. So, the compounds of Cr(VI) are not stable in soils. In acidic and alkaline soil, the reduction of Cr(VI) to its lower oxidation states depends on the redox potential (Alloway 2013) (Fig. 3). The oxidising ability of Cr(VI) decreases by the consumption of H^+ ions. Cr(III) and Cr(VI) form deprotonated and hydrolysis products under neutral pH and natural Cr content. Generally, the adsorption strengths of the hydrolysis products of Cr(III) (adsorbed on the clay minerals) increases with the increase in soil pH. The high adsorption ability of Cr(III) is also based on the increase in the negative charge on the surface of clay particles (James 1996).

Plant growth is related to the positive effects of Cr(III) and influences the level of plant growth hormones (cytokinin). Generally, the Cr content in plant's shoot (growing on the non-contaminated soils) ranges from 0.02 to 0.2 mg/kg (Zayed and Terry 2003). The reasons of low Cr content in uncontaminated soil are the immobility properties of the element in plant and soil and the presence of more insoluble form of Cr(III) in the soil. The poor correlation between Cr contents in soil and plant tissues is due to the low Cr availability (0.01 to 4 mg/kg) (Zayed and Terry 2003). The plant species of Brassicaceae family is known as the potential candidate for Cr uptake (Alloway 2013). The accumulation of Cr in different plant tissues may cause severe toxic effects like leaf chlorosis, poor yield, stunted growth and less development of root systems (Kabata-Pendias and Pendias 2001). It is considered that the plant growing on the soil containing 75 to 100 mg/kg of Cr is hardly toxic to plants (Alloway 2013). Mishra et al. (1995) observed that the Cr toxicity in plant growing on sandy soil is relatively higher than that of peat soils.

Cr concentration in coal, flyash and soil

The global average Cr content in coal was reported as 16 mg/kg (Ketris and Yudovich 2009), while in India the reported concentration was 14.90 mg/kg (Verma et al. 2015). In various regions of China, the concentration ranged from 15 to 16 mg/kg (Tang and Huang 2004; Ren et al. 2006; Bai et al. 2007; Dai and Ren 2007). A study reported that the Cr content in FA released from a TPP in India was 93.33 mg/kg (Sushil and Batra 2006). In a similar study conducted in Czech Republic, it was found that Cr content in the FA of a TPP was higher (Bartoňová et al. 2007) than the previously reported Cr concentration in Indian FA. In one of the studies on mine-impacted Indian soil (Ledo mines, Tinsukia,

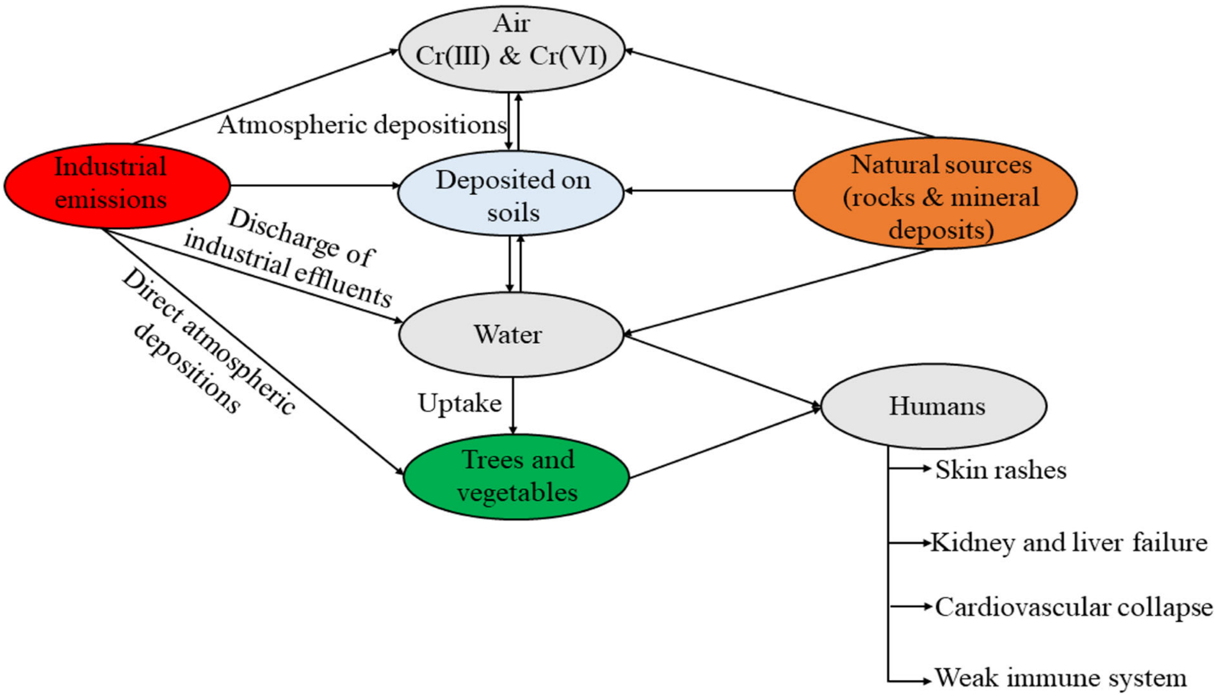

Fig. 3 Sources, cycling and health risks of Cr (Alloway 2013)

Assam), the reported Cr content was 112 mg/kg (Reza et al. 2015) (Table 3), while in a similar study by Masto et al. (2015), the Cr concentration in open cast mine-impacted soil was 98 mg/kg (Jharia coalfield, Jharkhand). A very high Cr concentration of 2652 mg/kg was observed in the soils of industrial areas of the Ganga plain in India (Gowd et al. 2010). In mine-impacted soil of South Africa, the reported Cr concentration was 419 mg/kg (mg/kg), which was higher than the Indian soil of the same type.

Accumulation of Cr in tree and vegetable species

In the leaves of *Azadirachta indica* A. Juss., (Meliaceae, margosa tree) growing on the contaminated soil of Nigeria, the concentration of Cr was found as 0.034 mg/kg (Augustine et al. 2016), whereas the measured concentration of Cr in vegetable species of *A. cepa* L. (Amaryllidaceae, onion) was 0.07 mg/kg (São Paulo, Brazil) (Guerra et al. 2012).

Health risks associated with the Cr exposure

The toxicity effect of Cr(VI) is a major concern due to the poor absorbance of Cr(III) in the human body. But the reduction of Cr(VI) to Cr(III) can be highly toxic to humans, which may lead to severe health problems like lung cancer (Alloway 2013). Humans are exposed to Cr through various routes like ingestion of food and water, dermal contact with Cr compounds and inhalation of Cr-containing airborne particles (Alloway 2013). In electroplating industry, the occupational exposure of Cr(VI) may cause respiratory problems. Other health risks associated with Cr exposure are skin rashes, weakened immune systems, kidney and liver failure, alteration in genetic material etc. (Zhitkovich 2011). Ingestion of Cr(VI) may also result in cardiovascular collapse in humans.

Remediation of Cr from soil and water

Chemical precipitation is a widely accepted technique for the removal of Cr(VI) from industrial wastewater. The removal process involves Cr(VI) reduction in acidic conditions (pH 2 to 3) and further Cr(III) precipitation as hydroxyl species (Madhavi et al. 2013). The commonly used reducing agents in chemical precipitation are sodium sulphite, sulphur dioxide, sodium metabisulphite, barium sulphite and ferrous sulphate. Limestone and lime are also very frequently used as the precipitant agents in the industry for the removal of Cr(VI) due to their low cost and availability. The inorganic effluent

Table 3 Average concentrations (mg/kg) of potentially toxic metal(loid)s in soils

Country	Soil types	As	Cd	Cr	Pb	References
Bangladesh	AMD-contaminated soils	17.5	nr	nr	433	Bhuiyan et al. 2010
	Paddy soils	22.4	nr	107	188.6	Halim et al. 2015
Botswana	Mine soil	9.8	nr	125.2	22.8	Zhai et al. 2009
Brazil	Regular soils	nr	4.48	nr	nr	Galunin et al. 2014
China	Reclaimed soil	3.82	0.31	nr	44.75	Yao et al. 2010
France	Urban soil	nr	1.92	nr	230.8	Douay et al. 2007
India	Open cast mine-impacted soil	nr	0.012	98	27.3	Masto et al. 2015
Korea	AMD-contaminated soil	nr	1.1	35.8	32.9	Kim and Chon 2001
Nigeria	Mine-impacted soil	nr	0.6	nr	0.5	Sahoo et al. 2016
Poland	Reclaimed soil	nr	1.65	nr	39.9	Pietrzykowski et al. 2014
Portugal	Waste-impacted soil	38.3	0.2	92.3	30.8	Ribeiro et al. 2010
South Africa	Mine-impacted soil	0.5	nr	419	19	Maya et al. 2015
Turkey	Surface soil	8	0.2	173	33	CoŞKun et al. 2006

AMD acid mine drainage, *nr* not reported

(> 1000 mg Cr/L) can be treated effectively by the use of lime precipitation methods (Mirbagherp and Hosseini 2004). Activated carbon is also used as adsorbents to remove Cr. In biological methods, the microbes (bacteria) are used to remove Cr from contaminated water and soil. Plant species like *Jamesbrittenia fodina* (Wild) Hilliard (an endemic perennial shrub found in Zimbabwe) and *Leptospermum scoparium* Forst. & Forst. (Myrtaceae, Broom tea-tree, a native shrub of Australia and New Zealand) have been reported to accumulate Cr in their tissues (Madhavi 2013). Revathi et al. (2011) reported that *Sorghum bicolor* (L.) Moench. (Family Poaceae, commonly known as sorghum) can be used as potential hyperaccumulators of Cr. Physical processes (soil washing and in situ immobilisation) have also been suggested for Cr remediation from soils (Pagilla and Canter 1999).

Lead (Pb)

Lead is a potential toxic metal, which appears bluish-white in colour. It is a poor conductor of electricity. It turns into a dull grey colour when it comes in contact with air. It is also known as corrosion resistant. It is used in car batteries and is an important constituent of Pb-acid battery. It is also used as a colouring element in ceramic glazes. In addition, Pb is also used as an electrode during the electrolysis process. It is generally found in ores associated with Zn, Ag and Cu. Galena (PbS) is a major mineral of Pb, and generally mined in countries like Australia, Canada, China, Peru and USA. It occurs naturally (< 50 mg/kg in earth's crust) (Arias et al. 2010) in the environment, but the anthropogenic sources (gasoline, car batteries, sewage sludge and fertilisers) of Pb are found to be the most common (Grover et al. 2010; Alloway 2013). The global average Pb content in unpolluted soils was reported as 17 mg/kg (Alloway 2013).

Chemical behaviour of Pb in soil and plant

The extraction and disposal of Pb and its by-products are the possible reasons for soil contamination. Generally, there is high correlation between chemical behaviour of Pb in soil and soil organic content (Vega et al. 2010). Therefore, it gets accumulated in high organic matter-containing soil (Alloway 2013). Pb exists as a free metal ion or may also occur as organic ligands (fulvic acids, amino acids and humic acids) in soil. The free metal ions of Pb form complex with inorganic constituent (bicarbonate, sulphate) (Uzu et al. 2009). It is also believed that a small amount of Pb is soluble in soil and available for plant uptake. This is due to the strong binding of Pb with soil organic matter or colloids (Punamiya et al. 2010). Moreover, the behaviour of Pb in soil (i.e. its solubility, bioavailability and mobility) is controlled by various biochemical factors like pH, cation-exchange capacity, microbial conditions, redox reactions and mineral composition of soil (Dumat et al. 2006; Tabelin and Igarashi 2009; Lawal et al. 2010; Arias et al. 2010). These factors may affect the soil behaviour as well as the rate of Pb uptake by plants. Pb enters into the plant's root through various pathways (ionic channels—plasma membrane Ca channel). Its uptake depends upon the working of H^+/ATPase pump for the maintenance of negative membrane potential in the cells (rhizoderm) of the plant's root (Wang et al. 2007). Pourrut et al. (2008) observed that Ca^{2+}-permeable channels are the major pathways for the entry of Pb in roots. The cyclic nucleotide-gated ion channel is an alternative non-selective pathway though which Pb can be penetrated into the roots of transgenic plants (Arazi et al. 1999). Bulk of the Pb taken up by the plants remains in the roots because of binding of Pb to ion-exchangeable sites on the cell wall and extracellular precipitation deposited on cell wall (mainly in the form of $PbCO_3$). That is why the concentration of Pb in root is greater than any other parts of the plant (Sharma and Dubey 2005).

Pb concentration in coal, flyash and soil

The world average concentration of Pb in coal was reported as 7.8 mg/kg (Ketris and Yudovich 2009), whereas in China, the concentration ranged from 15 to 16 mg/kg (Tang and Huang 2004; Ren et al. 2006; Bai et al. 2007; Dai et al. 2007). The reported Pb content in Indian coal (5.44 mg/kg) by Verma et al. (2015) was found to be less than world average Pb content. In India, , the measured Pb concentration in FA was 36.66 mg/kg (Sushil and Batra 2006). Brigden and Santillo (2002) reported the Pb concentration in FA (TPPs, Philippines), which ranged from 8 to 22 mg/kg. To determine the Pb concentration in the soil, the samples were collected from industrial areas of the Ganga plain (Kanpur and Unnao), Tinsukia and Raniganj areas of India by Gowd et al. (2010), Reza et al. (2015) and Masto et al. (2015), respectively. The observed concentrations in all three regions were found as 38, 183 and 27 mg/kg, respectively. In Okaba region of Nigeria, less amount of Pb was reported in the mine-impacted soil (Sahoo et al. 2016).

Accumulation of Pb in tree and vegetable species

Knezevic et al. (2009) reported Pb concentration in tree leaves of *Paulownia elongate* S.Y.Hu (forest tree). The concentration reported in previous study varied from 0.94 to 3.16 mg/kg. In India, Patel et al. (2015) executed an experiment to determine the PTMs content in the tree leaves of *Mangifera indica*, *Eucalyptus globulus*, *Ficus religiosa*, *Butea monosperma* and *Tectona grandis*. The results showed that the Pb concentration in the leaves of six tree species ranged from 1.6 to 16.4 mg/kg (Table 4). Vegetable species growing on Pb-contaminated soil gets contaminated by the uptake of element from soil to their edible parts. To justify the concept, Basha et al. (2014) collected the vegetable samples of *Capsicum annum* (green chilli), *Solanum lycopersicum* (tomato) and *Momordica charantia* (bitter gourd) from the nearby areas of a uranium mine, India. The results of their study showed that the Pb concentration varied from 0.2 to 1.4 mg/kg. The results also demonstrated that the metal concentration in the vegetables growing in the soil of core zone area (radial distance of 10 km from mine) was comparatively higher than the buffer zone (radial distance of 10 to 25 km from mine) area of the mining region.

Health risks associated with the Pb exposure

Pb mining and smelting are the common practices in many countries, which may cause Pb exposure. It enters into the human body through ingestion, inhalation and dermal adsorption. The rate of Pb absorption in children is higher than adults (Alloway 2013). Coal mine dust and FA are major sources of Pb exposure. Pb can cause a severe threat on human health by damaging the kidney and brain (Fig. 4). It has also the capacity to cross the blood–brain barrier and can reduce the numbers of myelin sheaths of a brain cell (neuron). As a result, neuronal growth is inhibited (Markowitz and Rosner 2000). Pb is also responsible for the inhibition of heme synthesis (occurs in mitochondria and cytosol). Pb poisoning may cause abdominal pains, weakness in the fingers and ankles, anaemia and decreased heart rate (Navas-Acien et al. 2006). It disturbs the formation of synapse in cerebral cortex of a child's brain (Erickson et al. 2005), resulting in the poor growth of brain. The use of Pb in the manufacturing of water pipes is also a major source of contamination of drinking water (Assi et al. 2016).

Table 4 Global concentration of potentially toxic metal(loid)s (mg/kg) in tree and vegetable species (source—Raj and Maiti 2019a)

Country	Tree/vegetable species	As	Cd	Cr	Pb	References
Sweden	*Solanum tuberosum*	0.0036	0.018	nr	0.057	Augustsson et al. 2018
	Raphanus sativus	0.0055	0.026	nr	0.028	
	Allium cepa	0.0033	0.020	nr	0.0068	
Jamaica	*Brassica oleracea*	0.001	0.041	nr	0.003	Antoine et al. 2017
	Daucus carota	0.004	0.031	nr	0.006	
	Solanum lycopersicum	0.012	0.266	nr	0.021	
Brazil	*Allium cepa*	nr	0.02	0.07	0.49	Guerra et al. 2012
	Daucus carota	nr	0.03	0.09	0.38	
	Brassica oleracea	nr	0.08	0.48	0.93	
Nigeria	*Azadirachta indica*	nr	nr	0.034	0.120	Augustine et al. 2016
Syria	*Ligustrum ovalifolium*	nr	0.333	2.53	7.12	Mansour 2014
	Euonymus japonicus	nr	0.166	0.401	6.251	
	Cupressus sempervirens	nr	0.061	0.211	4.694	
Serbia	*Aesculus hippocastanum*	nr	0.4	nr	5.35	Tomasevic et al. 2004
	Tilia	nr	nr	nr	1.88	
India (Chhattisgarh)	*Mangifera indica*	3.9	1.65	9.5	3.3	Patel et al. 2015
	Butea monosperma	3.0	1.15	14.6	1.6	
	Tectona grandis	6.4	1.20	14.3	1.8	
	Azadirachta indica	43.1	1.12	48.6	16.4	
India (Tummalapalle Uranium mines)	*Solanum tuberosum*	nr	19.3	1.0	0.3	Basha et al. 2014
	Capsicum annum	nr	18.2	3.1	1.4	
	Momordica charantia	nr	17.6	1.3	0.6	

nr not reported

Remediation of Pb from soil and water

Stabilisation or solidification techniques are used for Pb immobilisation. Alpaslan and Yukselen (2002) reported that lime and cement are effective (88% efficiency) in the immobilisation of Pb in soil. Samani et al. (1998) used EDTA (ethylenediaminetetraacetic acid) for the removal of Pb from soil. In a study on remediation of Pb, the waste tea leaves were used for the removal of Pb from waste water, and the used material showed 92% efficiency in Pb removal (Ahluwalia and Goyal 2005).

The phytoremediation technique is the most environmentally friendly and economically feasible approach to remove Pb from soil and water (Cheng et al. 2015). Yang et al. (2016) used biochar-supported nano-hydroxyapatite material for the remediation of Pb from soil. The results of their study showed that the application of materials to the contaminated soil enhanced the immobilisation of Pb. Several plant species like *Funaria hygrometrica* Hedw. (Bryophyta, common moss), *Vigna unguiculata* (L.) Walp. (Fabaceae, Cowpeas), *Festuca rubra* L. (Poaceae, creeping red fescue) and *Lactuca sativa* L. (Asteraceae, lettuce) have been reported as a Pb hyperaccumulator (Kopittke et al. 2007; Ginn et al. 2008; Krzesłowska et al. 2010; Uzu et al. 2009). These plants can translocate Pb from roots to their aerial parts. According to Maestri et al. (2010), the specific Pb hyperaccumulator plant species can accumulate 1000 mg/kg of Pb. Aransiola et al. (2013) designed a pot experiment to assess the remediation potential of a plant species, namely *Glycine max* (L.) Merr. (Fabaceae, soya bean). The results of their study showed that the soil remediated through *G. max* decreases the organic carbon content of soil. In addition, their results also suggested that the plant has good potential for the removal of Pb from soil. A study on Pb removal from water by using biochar was conducted by Liu and Zhang (2009). In their study, rice husk and pinewood were used for the preparation of two biochars, and the results demonstrated that pH of the solution was the influencing factor of the adsorption of Pb onto the biochars. The results also concluded that the biochar prepared from pinewood showed higher Pb adsorption capacity than that of biochar of rice husk.

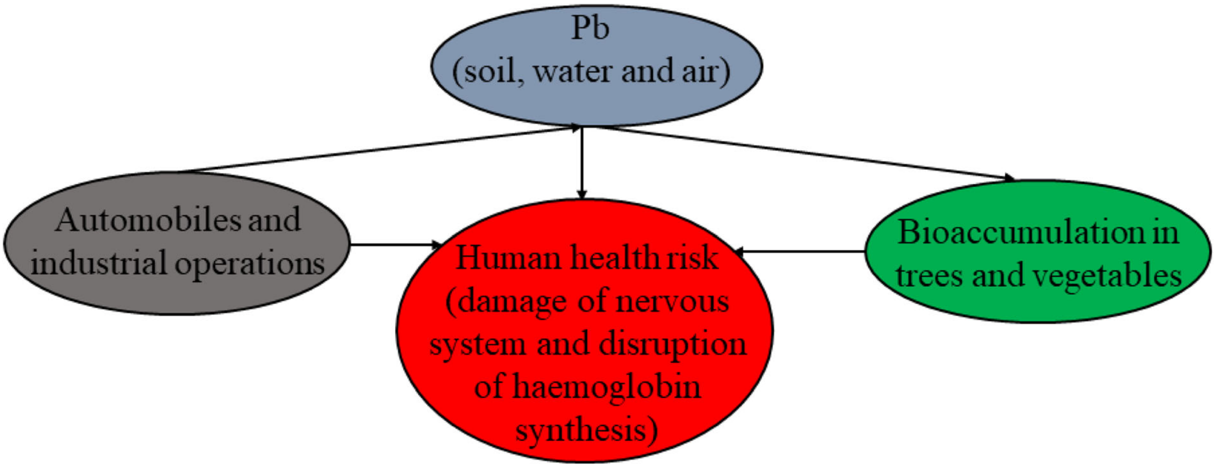

Fig. 4 Sources and health risks of Pb

Mercury (Hg)

It is highly toxic in nature and accounts for only about 0.08 ppm in the Earth's crust. The recommended guidelines for chronic exposure of total Hg in agricultural soil and drinking water are 6.6 mg/kg (EA 2009) and 1 mg/L (WHO 1993), respectively. Hg is mostly found in the deposits of cinnabar ore and contributes in the atmosphere both naturally and anthropologically. India and China are the largest Hg emitters due to the burning of Hg-containing coal in the TPPs for energy generation (Pacyna et al. 2006). Forest fires, fossil fuels (coal and petroleum), cinnabar (ore) and volcanoes are the natural sources of Hg. On the other hand, the establishment of new industries such as pulp, paper and mining are among the major anthropogenic sources which contribute to the rising levels of Hg in the atmosphere. Due to high toxicity and bioaccumulation tendency in the food chain, the Hg is considered as the most likely element to be studied in recent years.

Chemical behaviour of Hg

Hg has three different forms: (1) elemental Hg (Hg^0), present in gaseous phase; (2) particulate Hg (Hg^P), binds with particles; (3) oxidised gas phase Hg (Hg^{2+}) (Galbreath and Zygarlicke 2000). The coal combustion led to the release of 30–75% of total Hg into the atmosphere. It gets vaporised and converted into the Hg^0 (Iwashita et al. 2004). As, flue gas cools down under suitable conditions, Hg^0 gets oxidised and a little amount of Hg gets absorbed on the FA. The separation of particulate bound Hg (Hg^P) is feasible by using air pollution control devices (ACPDs) (electrostatic precipitators and fabric filters). Hg^{+2} is soluble in water, so it can be easily arrested using wet scrubbers (Ito et al. 2006). During precipitation, Hg gets deposited on the soil which is further circulated into the water ecosystem. The highly toxic and organic form of Hg (methylmercury) is formed from the conversion of elemental Hg by the anaerobic microorganisms present in the water.

Health risks associated with the Hg exposure

Hg is considered as the most hazardous element. Infants and young children are very sensitive to Hg. In pregnant women, it can pass from the mother to the developing foetus, and can be transferred through the breast milk to the infants. Its acute health effects are headache, chest pain, low vision, cough, eye irritation, nausea, sore throat, vomiting, high blood pressure and increased heart rate. The chronic health effects of Hg are anxiety, fatigue, tremors, irritability, low remembering power, loss of appetite and sleeping problems. It has negative impacts on the immune system, digestive system and nervous system due to its severe toxic effects. It also shows the toxic effects on eyes, kidneys, lungs and skin. In the year 1950, a serious Hg pollution had occurred in Japan due to the discharge of a significant volume of Hg-containing waste to the sea from a chemical company. The discharged methyl-Hg gets bioaccumulated and biomagnified in fish at the Minamata Bay, and the consumption of these Hg-contaminated fish led to the outbreak of Hg-poisoning, which is known as Minamata disease (Wang et al. 2012).

Removal of Hg from coal

Coal burning liberates a lot of harmful gases such as carbon dioxide, carbon monoxide and sulphur dioxide, which are present in flue gas emitting from the stacks. Many technologies for the cleaning of flue gas have been practised; even some coal cleaning pre-combustion technologies have also been started. Several countries have started using coal cleaning techniques for the removal of Hg, and cleaning also enhances the quality and heating value. A variety of technologies have been implemented for controlling the emission of Hg^0. One of the techniques for Hg emission control is the injection of strong oxidising agents in the flue gas such as Cl_2, Br_2 and O_3. Hg solidification may be another approach to arrest and solidify the Hg, but this technique is quite expensive (Luo et al. 2013). Kolker et al. (2017) observed that iron-sulphides contain Hg in bituminous coal, and in low rank coal there is a large quantity of organic bound Hg present. It is assumed that the decrease in sulphur concentration in the bituminous coal led to the increase in Hg concentration. More than 60% Hg can be arrested using desulphurisation system and fabric filters from the flue gas. Technologies such as coal washing and demercuration techniques are also often used for Hg removal from coal (Kumar and Kumar 2018).

Coal washing: Coal is crushed and mixed with the liquid, which allows the impurities to separate out and settle down. There are some devices which can mechanically remove the impurities using the air currents by large pulsating waves physically, which usually occurs in various coal washeries. Using the combination of water and air currents, the generated centrifugal force sometimes is more effective to remove impurities from coal. Dense media is also an efficient technique, which basically consists of magnetite. The small size coal is treated with froth flotation technique, which mainly focuses on the chemical separation. Barrel washing technique is also used in some cases. The simple coal cleaning processes easily remove Hg with pyrite (Dziok and Strugała 2017).

Demercuration technique: The design of process development unit (PDU) is a much feasible technology for removal of Hg from the low rank coal before its combustion by a simple thermal advancement. Along with the Hg removal, it also removes the moisture from coal. This technique is expected to remove approximately 80–90% of Hg (Li et al. 2013).

Remediation of Hg from soil and water

Several methods of Hg remediation such as stabilisation, immobilisation, thermal desorption, electro-remediation, adsorption, selective catalytic reduction, wet flue gas desulphurisation and phytoremediation have been reported by various researchers (USEPA 2007; Bower et al. 2008; Wang et al. 2012; Raj and Maiti 2019b). Out of all the reported remediation techniques, phytoremediation technology has been proven as the most efficient technology for the removal of Hg from soil and water (Wang et al. 2012). Some plant species are considered as the best accumulator of Hg and hence effectively used to remove Hg from contaminated soil and water: (1) plant species used for removal of Hg from soil: *Brassica juncea* (Indian mustard), *Jatropha curcas*, *Polypogon monspeliensis* (beard grass), *Pteris vittata* (Chinese brake fern), *Helianthus annuus* (sunflower), *Achillea millefolium* (herbaceous perennial plant); (2) plant species used for removal of Hg from water: *Typha domingensis* (used in a constructed wetland), *Ulva lactuca* (Chlorophyta), *Gracilaria gracilis* (Rhodophyta), *Fucus vesiculosus* (Phaeophyta), *Vallisneria neotropicalis* (submerged aquatic plant), *Lemna minor* (duckweeds), *Pistia stratiotes* (water lettuce) and *Azolla pinnata* (aquatic fern) (Su et al. 2008; Mishra et al. 2009; Wang et al. 2012; Marrugo-Negrete et al. 2015; Raj and Maiti 2019b) (Table 5).

Conclusions

The anthropogenic sources of PTMs are the major concern for the environment. PTMs like As and Hg are highly hazardous, and the availability of Cr in the drinking water also causes severe health risks among humans. Moreover, the uptake of Cd and Pb from the contaminated soil to the plant is a serious threat for the plant system. Generally, the most common natural sources of PTMs emission are volcanic eruptions and weathering of crustal materials, while the anthropogenic sources are coal combustion in coal-fired TPPs, use of phosphate fertilisers and Ni-Cd batteries. The exposure of these PTMs to humans led to severe consequences like kidney and liver failure, damage of the nervous and immune system, and disruption of haemoglobin synthesis. As these PTMs get accumulated in soil and further in plant system, their removal from soil and water is the most

Table 5 List of plant species used for phytoremediation of potentially toxic metal(loid)s (PTMs) (Visoottiviseth et al. 2002; Salido et al. 2003; Sampanpanish et al. 2006; Alvarado et al. 2008; Zhang et al. 2009; Srivastava et al. 2011; Xue et al. 2012; Nahar et al. 2017; Niazi et al. 2017; Souri et al. 2018; Saravanan et al. 2019; Shukla and Srivastava 2019)

PTMs	Plant species
As	*Vallisneria natans*, *Pteris vittata*, *Pityrogramma calomelanos*, *Hydrilla verticillata*, *Ceratophyllum demersum*, *Elodea canadensis*, *Myriophyllum propinaquum*, *Lemna gibba*, *Eichhornia crassipes*, *Wolffia globosa*, *Eleocharis acicularis*, *Brassica juncea*, *Isatis cappadocica*, *Arabidopsis thaliana*
Cd	*Oryza sativa*, *Chrysopogon zizanioides*, *Lemna minor*, *Allium sativum*, *Thlaspi caerulescens*, *Colocasia esculenta*
Cr	*Leptospermum scoparium*, *Jamesbrittenia fodina*, *Sorghum bicolor*, *Vigna mungo*, *Cynodon dactylon*, *Pluchea indica*
Pb	*Funaria hygrometrica*, *Vigna unguiculata*, *Festuca rubra*, *Lactuca sativa*, *Glycine max*, *Brassica juncea*, *Pteris vittata*
Hg	*Brassica juncea*, *Jatropha curcas*, *Polypogon monspeliensis*, *Pteris vittata*, *Helianthus annuus*, *Achillea millefolium*, *Typha domingensis*, *Ulva lactuca*, *Gracilaria gracilis*, *Fucus vesiculosus*, *Vallisneria neotropicalis*, *Lemna minor*, *Pistia stratiotes*, *Azolla pinnata*

concerning issue for researchers. Some remediation techniques used for PTMs removal are soil washing, stabilisation, electro-remediation, adsorption and thermal desorption. But the most common, cost-effective and environment-friendly remediation technique is phytoremediation, in which certain hyperaccumulator plant species are used to remove PTMs from soil and water. The removal of Hg from coal in the pre-combustion stage is also an important approach (coal washing and demercuration) to prevent the onset of Hg to the environment (air, soil and water). In the near future, there is a need to overcome the complications of PTMs remediation techniques, and to find out more efficient and environment-friendly techniques.

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References

Abdul, K. S. M., Jayasinghe, S. S., Chandana, E. P., Jayasumana, C., & De Silva, P. M. C. (2015). Arsenic and human health effects: A review. *Environmental Toxicology and Pharmacology, 40*, 828–846.

Adriano, D. (2001). *Trace elements in terrestrial environments: Biogeochemistry, bioavailability and risks of metals*. New York: Springer.

Ahluwalia, S. S., & Goyal, D. (2005). Removal of heavy metals by waste tea leaves from aqueous solution. *Engineering in Life Sciences, 5*, 158–162.

Ahmann, D., Krumholz, L., Hemond, H., Lovley, D., & Morel, F. (1997). Microbial mobilization of arsenic from sediments of the Aberjona watershed. *Environmental Science and Technology, 31*, 2923–2930.

Alloway, B. J. (2013). *Heavy metals in soils: Trace metals and metalloids in soils and their bioavailability, Environmental Pollution (vol 22)*. Dordrecht, The Netherlands: Springer.

Alpaslan, B., & Yukselen, M. A. (2002). Remediation of lead contaminated soils by stabilization/solidification. *Water, Air, and Soil Pollution, 133*, 253–263.

Alvarado, S., Guédez, M., Lué-Merú, M. P., Nelson, G., Alvaro, A., Jesús, A. C., & Gyula, Z. (2008). Arsenic removal from waters by bioremediation with the aquatic plants water hyacinth (*Eichhornia crassipes*) and lesser duckweed (*Lemna minor*). *Bioresource Technology, 99*, 8436–8440.

Antoine, J. M., Fung, L. A. H., & Grant, C. N. (2017). Assessment of the potential health risks associated with the aluminium, arsenic, cadmium and lead content in selected fruits and vegetables grown in Jamaica. *Toxicology Reports, 4*, 181–18.7.

Aransiola, S.A., Ijah, U.J.J. and Abioye, O.P. (2013). Phytoremediation of lead polluted soil by *Glycine max* L. *Applied and Environmental Soil Science*. http://dx.doi.org/10.1155/2013/631619.

Arazi, T., Sunkar, R., Kaplan, B., & Fromm, H. (1999). A tobacco plasma membrane calmodulin-binding transporter confers Ni^{2+} tolerance and Pb^{2+} hypersensitivity in transgenic plants. *Plant Journal, 20*, 171–182.

Arias, J. A., Peralta-Videa, J. R., Ellzey, J. T., Ren, M., Viveros, M. N., & Gardea-Torresdey, J. L. (2010). Effects of *Glomus deserticola* inoculation on *Prosopis*: Enhancing chromium and lead uptake and translocation as confirmed by X-ray mapping, ICP-OES and TEM techniques. *Environmental and Experimental Botany, 68*, 139–148.

Arikpo, G. E., Eja, M. E., Ogbonnaya, L. O., & Opara, A. A. (2004). Cadmium uptake by the green alga Chlorella emersonii. *Global Journal of Pure and Applied Sciences, 10*, 257–262.

ASTM. (2006). ASTM D6414: Standard test methods for total mercury in coal and coal combustion residues by acid extraction or wet oxidation/cold vapour atomic absorption

Assi, M. A., Hezmee, M. N. M., Haron, A. W., Sabri, M. Y. M., & Rajion, M. A. (2016). The detrimental effects of lead on human and animal health. *Veterinary World, 9*, 660.

Augustine, A. U., Onwuka, J. C., & Albert, C. Q. (2016). Determination of heavy metal concentration in Neem (Azadirachta indica) leaves, bark and soil along some major roads in Lafia, Nasarawa state Nigeria. *Journal of Environmental Chemistry and Ecotoxicology, 8*, 38–43.

Augustsson, A., Uddh-Söderberg, T., Filipsson, M., Helmfrid, I., Berglund, M., Karlsson, H., Hogmalm, J., Karlsson, A., & Alriksson, S. (2018). Challenges in assessing the health risks of consuming vegetables in metal-contaminated environments. *Environment International, 113*, 269–280.

Bai, X., Li, W., Chen, Y., et al. (2007). The general distributions of trace elements in Chinese coals. *Coal Quality Technology, 1*, 1–4 (in Chinese with English abstract).

Barros Júnior, L. M., Macedo, G. R., Duarte, M. M. L., Silva, E. P., & Lobato, A. K. C. L. (2003). Biosorption of cadmium using the fungus *Aspergillus niger. Brazilian Journal of Chemical Engineering, 20*, 229–239.

Bartoňová, L., Klika, Z., & Spears, D. A. (2007). Characterization of unburned carbon from ash after bituminous coal and lignite combustion in CFBs. *Fuel, 86*, 455–463.

Basha, A. M., Yasovardhan, N., Satyanarayana, S. V., Reddy, G. V. S., & Kumar, A. V. (2014). Trace metals in vegetables and fruits cultivated around the surroundings of Tummalapalle uranium mining site, Andhra Pradesh, India. *Toxicology Reports, 1*, 505–512.

Bhuiyan, M. A., Parvez, L., Islam, M. A., Dampare, S. B., & Suzuki, S. (2010). Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. *Journal of Hazardous Materials, 173*, 384–392.

Bidar, G., Waterlot, C., Verdin, A., Proix, N., Courcot, D., Détriché, S., Fourrier, H., Richard, A., & Douay, F. (2016). Sustainability of an in situ aided phytostabilisation on highly contaminated soils using fly ashes: Effects on the vertical distribution of physicochemical parameters and trace elements. *Journal of Environmental Management, 171*, 204–216.

Bower, J., Savage, K. S., Weinman, B., Barnett, M. O., Hamilton, W. P., & Harper, W. F. (2008). Immobilization of mercury by pyrite (FeS_2). *Environmental Pollution, 156*, 504–514.

Brigden, K. and Santillo, D. (2002). Heavy metal and metalloid content of fly ash collected from the Sual, Mauban and Masinloc coal-fired power plants in the Philippines, 2002. *Greenpeace AraştırmaLaboratuarıTeknikNotu, 7*.

Brown, S. L., Chaney, R. L., Angle, J. S., & Baker, A. J. M. (1994). Phytoremediation potential of Thlaspicaerulescens and bladder campion for zinc- and cadmium-contaminated soil. *Journal of Environmental Quality, 23*, 1151–1157.

Cheng, S. F., Huang, C. Y., Lin, Y. C., Lin, S. C., & Chen, K. L. (2015). Phytoremediation of lead using corn in contaminated agricultural land—An in situ study and benefit assessment. *Ecotoxicology and Environmental Safety, 111*, 72–77.

Choong, T. S. Y., Chuah, T., Robiah, Y., Gregory Koay, F., & Azni, I. (2007). Arsenic toxicity, health hazards and removal techniques from water: An overview. *Desalination, 217*, 139–166.

CoŞKun, M., Steinnes, E., Frontasyeva, M. V., Sjobakk, T. E., & Demkina, S. (2006). Heavy metal pollution of surface soil in the Thrace region, Turkey. *Environmental Monitoring and Assessment, 119*, 545–556.

Dai, S., & Ren, D. (2007). Effects of magmatic intrusion on mineralogy and geochemistry of coals from the Fengfeng–Handan coalfield, Hebei, China. *Energy & Fuels, 21*, 1663–1673.

Dickinson, N. M., Baker, A. J. M., Doronila, A., Laidlaw, S., & Reeves, R. D. (2009). Phytoremediation of inorganics: Realism and synergies. *International Journal of Phytoremediation, 11*, 97–114.

Douay, F., Roussel, H., Fourrier, H., Heyman, C., & Chateau, G. (2007). Investigation of heavy metal concentrations on urban soils, dust and vegetables nearby a former smelter site in Mortagne du Nord, northern France. *Journal of Soils and Sediments, 7*, 143–146.

Dumat, C., Quenea, K., Bermond, A., Toinen, S., & Benedetti, M. F. (2006). Study of the trace metal ion influence on the turnover of soil organic matter in cultivated contaminated soils. *Environmental Pollution, 142*, 521–529.

Dziok, T. and Strugała, A. (2017). Method selection for mercury removal from hard coal. In *E3S Web of Conferences, EDP Sciences*, 14, 02007.

EA. (2009). Contaminants in soil: Updated collation of toxicological data and intake values for humans. Mercury. Science Report SC050021/SR TOX7. Bristol: Environment Agency.

Emsley, J. (2001). *Chromium. Nature's building blocks: An A–Z guide to the elements*. Oxford: Oxford University Press.

Erickson, T.B., Ahrens, W.R., Aks, S., Baum, C. and Ling, L. (2005). Pediatric toxicology: Diagnosis and management of the poisoned child. McGraw Hill Professional.

Fayiga, A. O., Ipinmoroti, M. O., & Chirenje, T. (2018). Environmental pollution in Africa. *Environment, Development and Sustainability, 20*, 41–73.

Finkelman, R. B. (1993). Trace and minor elements in coal. In *Organic geochemistry* (pp. 593–607). New York: Springer.

Fitz, W., & Wenzel, W. (2002). Arsenic transformations in the soil–rhizosphere–plant system: Fundamentals and potential application to phytoremediation. *Journal of Biotechnology, 99*, 259–278.

Font, O., Córdoba, P., Leiva, C., Romeo, L. M., Bolea, I., Guedea, I., Moreno, N., Querol, X., Fernandez, C., & Díez, L. I. (2012). Fate and abatement of mercury and other trace elements in a coal fluidised bed oxy combustion pilot plant. *Fuel, 95*, 272–281.

Galbreath, K. C., & Zygarlicke, C. J. (2000). Mercury transformations in coal combustion flue gas. *Fuel Processing Technology, 65*, 289–310.

Galunin, E., Ferreti, J., Zapelini, I., Vieira, I., Tarley, C. R. T., Abrão, T., & Santos, M. J. (2014). Cadmium mobility in sediments and soils from a coal mining area on Tibagi River watershed: Environmental risk assessment. *Journal of Hazardous Materials, 265*, 280–287.

Ginn, B. R., Szymanowski, J. S., & Fein, J. B. (2008). Metal and proton binding onto the roots of *Fescue rubra*. *Chemical Geology, 253*, 130–135.

Gowd, S. S., Reddy, M. R., & Govil, P. K. (2010). Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India. *Journal of Hazardous Materials, 174*, 113–121.

Grover, P., Rekhadevi, P. V., Danadevi, K., Vuyyuri, S. B., Mahboob, M., & Rahman, M. F. (2010). Genotoxicity evaluation in workers occupationally exposed to lead. *International Journal of Hygiene and Environmental Health, 213*, 99–106.

Guerra, F., Trevizam, A. R., Muraoka, T., Marcante, N. C., & Canniatti-Brazaca, S. G. (2012). Heavy metals in vegetables and potential risk for human health. *Scientia Agricola, 69*, 54–60.

Halim, M. A., Majumder, R. K., & Zaman, M. N. (2015). Paddy soil heavy metal contamination and uptake in rice plants from the adjacent area of Barapukuria coal mine, Northwest Bangladesh. *Arabian Journal of Geosciences, 8*, 3391–3401.

Hou, W., Chen, X., Song, G., Wang, Q., & Chang, C. C. (2007). Effects of copper and cadmium on heavy metal polluted waterbody restoration by duckweed (Lemna minor). *Plant Physiology and Biochemistry, 45*, 62–69.

Issaro, N., Abi-Ghanem, C., & Bermond, A. (2009). Fractionation studies of mercury in soils and sediments: a review of the chemical reagents used for mercury extraction. *Analytica Chimica Acta, 631*, 1–12.

Ito, S., Yokoyama, T., & Asakura, K. (2006). Emissions of mercury and other trace elements from coal-fired power plants in Japan. *Science of the Total Environment, 368*, 397–402.

Iwashita, A., Tanamachi, S., Nakajima, T., Takanashi, H., & Ohki, A. (2004). Removal of mercury from coal by mild pyrolysis and leaching behavior of mercury. *Fuel, 83*, 631–638.

Jambhulkar, H. P., & Juwarkar, A. A. (2009). Assessment of bioaccumulation of heavy metals by different plant species grown on fly ash dump. *Ecotoxicology and Environmental Safety, 72*, 1122–1128.

James, B. R. (1996). The challenge of remediating chromium-contaminated soil. *Environmental Science and Technology, 30*, 248–251.

Jang, Y.C., Somanna, Y. and Kim, H. (2016). Source, distribution, toxicity and remediation of arsenic in the environment—A review. International Journal of Applied Environmental Sciences, 11559-581.

Jenkins, D. (1980). Biological monitoring of toxic trace metals. *Toxic trace metals in plants and animals of the world*. Part I (Vol. 2). Las Vegas: U.S. Environmental Protection Agency.

Jiang, W., Liu, D., & Hou, W. (2001). Hyperaccumulation of cadmium by roots, bulbs and shoots of garlic (*Allium sativum* L.). *Bioresource Technology, 76*, 9–13.

Kabata-Pendias, A., & Pendias, H. (2001). *Trace elements in soils and plants* (3rd ed.). Boca Raton: CRC Press.

Kahkha, M. R. R., Bagheri, S., Noori, R., Piri, J., & Javan, S. (2017). Examining total concentration and sequential extraction of heavy metals in agricultural soil and wheat. *Polish Journal of Environmental Studies, 26*, 2021–2028.

Ketris, M. P., & Yudovich, Y. E. (2009). Estimations of Clarkes for carbonaceous biolithes: World averages for trace element contents in black shales and coals. *International Journal of Coal Geology, 78*, 135–148.

Kim, J. Y., & Chon, H. T. (2001). Pollution of a water course impacted by acid mine drainage in the Imgok creek of the Gangreung coal field, Korea. *Applied Geochemistry, 16*, 1387–1396.

Kirkham, M. B. (2006). Cadmium in plants on polluted soils: Effects of soil factors, hyperaccumulation, and amendments. *Geoderma, 137*, 19–32.

Knezevic, M., Stankovic, D., Krstic, B., Nikolic, M. S., & Vilotic, D. (2009). Concentrations of heavy metals in soil and leaves of plant species *Paulownia elongata* SY Hu and *Paulownia fortunei* Hemsl. *African Journal of Biotechnology, 8*, 5422-5429.

Kolker, A., Senior, C., van Alphen, C., Koenig, A., & Geboy, N. (2017). Mercury and trace element distribution in density separates of a south African Highveld (# 4) coal: Implications for mercury reduction and preparation of export coal. *International Journal of Coal Geology, 170*, 7–13.

Kopittke, P. M., Asher, C. J., Kopittke, R. A., & Menzies, N. W. (2007). Toxic effects of Pb^{2+} on growth of cowpea (*Vigna unguiculata*). *Environmental Pollution, 150*, 280–287.

Kotas, J., & Stasicka, Z. (2000). Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution, 107*, 263–283.

Koukouzas, N., Ketikidis, C., & Itskos, G. (2011). Heavy metal characterization of CFB-derived coal fly ash. *Fuel Processing Technology, 92*, 441–446.

Krzesłowska, M., Lenartowska, M., Samardakiewicz, S., Bilski, H. and Woźny, A. (2010). Lead deposited in the cell wall of *Funaria hygrometrica protonemata* is not stable–a remobilization can occur. Environmental Pollution, *158*, 325-338.

Kumar, D. and Kumar, D. (2018). Fine coal washing. Sustainable management of coal preparation. *Woodhead Publishing*. 179–206. https://doi.org/10.1016/B978-0-12-812632-5.00008-2 .

Lai, H. Y., & Chen, Z. S. (2004). Effects of EDTA on solubility of cadmium, zinc, and lead and their uptake by rainbow pink and vetiver grass. *Chemosphere, 55*, 421–430.

Lawal, O. S., Sanni, A. R., Ajayi, I. A., & Rabiu, O. O. (2010). Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead (II) ions onto the seed husk of *Calophyllum inophyllum*. *Journal of Hazardous Materials, 177*, 829–835.

Lee, C. S. L., Li, X., Shi, W., Cheung, S. C. N., & Thornton, I. (2006). Metal contamination in urban, suburban, and country park soils of Hong Kong: A study based on GIS and multivariate statistics. *Science of the Total Environment, 356*, 45–61.

Li, Y., Yang, L., Ji, Y., Sun, H., & Wang, W. (2009). Quantification and fractionation of mercury in soils from the Chatian mercury mining deposit, southwestern China. *Environmental Geochemistry and Health, 31*, 617.

Li, L., Pan, S.W., Hu, J.J., Kuang, J.F., Qi, M., Ye, K. and Tang, N. (2013). Experimental research on fly ash modified adsorption of mercury removal efficiency of flue gas. *In Advanced Materials Research, Trans Tech Publications*. 800, 132–138.

Li, Y.J., Wang, Z.K., Qin, F.X., Fang, Z.Q., Li, X.L. and Li, G. (2018). Potentially toxic elements and health risk assessment in farmland systems around high-concentrated arsenic coal mining in Xingren. *China Journal of Chemistry*. https://doi.org/10.1155/2018/2198176.

Liang, J., & Mao, J. (2015). Source analysis of global anthropogenic lead emissions: Their quantities and species. *Environmental Science and Pollution Research, 22*, 7129–7138.

Liu, Z., & Zhang, F. S. (2009). Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *Journal of Hazardous Materials, 167*, 933–939.

Loska, K., Wiechula, D., Barska, B., Cebula, E., & Chojnecka, A. (2003). Assessment of arsenic enrichment of cultivated soils in southern Poland. *Polish Journal of Environmental Studies, 12*, 187–192.

Lugon-Moulin, N., Zhang, M., Gadani, F., Rossi, L., Koller, D., Krauss, M., & Wagner, G. J. (2004). Critical review of the science and options for reducing cadmium in tobacco

(*Nicotiana tabacum* L.) and other plants. *Advances in Agronomy, 83*, 111–180.

Luo, G., Ma, J., Han, J., Yao, H., Xu, M., Zhang, C., Chen, G., Gupta, R., & Xu, Z. (2013). Hg occurrence in coal and its removal before coal utilization. *Fuel, 104*, 70–76.

Ma, J., Yamaji, N., Mitani, N., Xu, X., Su, Y., McGrath, S., & Zhao, F. (2008). Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. *Proceedings of the National Academy of Sciences, USA, 105*, 9931–9935.

Macur, R., Jackson, C., Botero, L., McDermott, T., & Inskeep, W. (2004). Bacterial populations associated with the oxidation and reduction of arsenic in an unsaturated soil. *Environmental Science and Technology, 38*, 104–111.

Madhavi, V., Reddy, A. V. B., Reddy, K. G., Madhavi, G., & Prasad, T. N. K. V. (2013). An overview on research trends in remediation of chromium. *Research Journal of Recent Sciences, 2*, 71–83.

Maestri, E., Marmiroli, M., Visioli, G., & Marmiroli, N. (2010). Metal tolerance and hyperaccumulation: Costs and trade-offs between traits and environment. *Environmental and Experimental Botany, 68*, 1–13.

Mansour, R. S. (2014). The pollution of tree leaves with heavy metal in Syria. *International Journal of ChemTech Research, 6*, 2283–2290.

Markowitz, G., & Rosner, D. (2000). "Cater to the children": The role of the lead industry in a public health tragedy, 1900–1955. *American Journal of Public Health, 90*, 36.

Marrugo-Negrete, J., Durango-Hernández, J., Pinedo-Hernández, J., Olivero-Verbel, J., & Díez, S. (2015). Phytoremediation of mercury-contaminated soils by *Jatropha curcas*. *Chemosphere, 127*, 58–63.

Masto, R. E., Sheik, S., Nehru, G., Selvi, V. A., George, J., & Ram, L. C. (2015). Assessment of environmental soil quality around Sonepur Bazari mine of Raniganj coalfield, India. *Solid Earth, 6*, 811–821.

Maya, M., Musekiwa, C., Mthembi, P., & Crowley, M. (2015). Remote sensing and geochemistry techniques for the assessment of coal mining pollution, Emalahleni (Witbank), Mpumalanga. *South African Journal of Geomatics, 4*, 174–188.

Megalovasilis, P., Papastergios, G., & Filippidis, A. (2013). Behavior study of trace elements in pulverized lignite, bottom ash, and fly ash of Amyntaio power station, Greece. *Environmental Monitoring and Assessment, 185*, 6071–6076.

Mirbagherp, S. A., & Hosseini, S. N. (2004). Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse. *Desalination, 171*, 85–93.

Mishra, S., Singh, V., Srivastava, S., Srivastava, R., Srivastava, M., Dass, S., Satsang, G., & Prakash, S. (1995). Studies on uptake of trivalent and hexavalent Cr by maize (*Zea mays*). *Food and Chemical Toxicology, 33*, 393–397.

Mishra, V. K., Tripathi, B. D., & Kim, K. H. (2009). Removal and accumulation of mercury by aquatic macrophytes from an open cast coal mine effluent. *Journal of Hazardous Materials, 172*, 749–754.

Modabberi, S., Tashakor, M., Soltani, N. S., & Hursthouse, A. S. (2018). Potentially toxic elements in urban soils: Source apportionment and contamination assessment. *Environmental Monitoring and Assessment, 190*, 715.

Moreno-Jiménez, E., Esteban, E., & Peñalosa, J. M. (2012). *The fate of arsenic in soil–plant systems*, *In Reviews of environmental contamination and toxicology (pp. 1–37)*. New York, NY: Springer.

Murakami, M., Ae, N., & Ishikawa, S. (2007). Phytoextraction of cadmium by rice (*Oryza sativa* L.), soybean (*Glycine max* (L.) Merr.), and maize (*Zea mays* L.). *Environmental Pollution, 145*, 96–103.

Nahar, N., Rahman, A., Nawani, N. N., Ghosh, S., & Mandal, A. (2017). Phytoremediation of arsenic from the contaminated soil using transgenic tobacco plants expressing ACR2 gene of *Arabidopsis thaliana*. *Journal of Plant Physiology, 218*, 121–126.

Navas-Acien, A., Guallar, E., Silbergeld, E. K., & Rothenberg, S. J. (2006). Lead exposure and cardiovascular disease—A systematic review. *Environmental Health Perspectives, 115*, 472–482.

Niazi, N. K., Bibi, I., Fatimah, A., Shahid, M., Javed, M. T., Wang, H., Ok, Y. S., Bashir, S., Murtaza, B., Saqib, Z. A., & Shakoor, M. B. (2017). Phosphate-assisted phytoremediation of arsenic by *Brassica napus* and *Brassica juncea*: Morphological and physiological response. *International Journal of Phytoremediation, 19*, 670–678.

Ozden, B., Guler, E., Vaasma, T., Horvath, M., Kiisk, M., & Kovacs, T. (2018). Enrichment of naturally occurring radionuclides and trace elements in Yatagan and Yenikoy coal-fired thermal power plants, Turkey. *Journal of Environmental Radioactivity, 188*, 100–107.

Pacyna, E. G., Pacyna, J. M., Steenhuisen, F., & Wilson, S. (2006). Global anthropogenic mercury emission inventory for 2000. *Atmospheric Environment, 40*, 4048–4063.

Pagilla, K. R., & Canter, L. W. (1999). Laboratory studies on remediation of chromium-contaminated soils. *Journal of Environmental Engineering, 125*, 243–248.

Pantuzzo, F. L., Silva, J. C. J., & Ciminelli, V. S. (2009). A fast and accurate microwave-assisted digestion method for arsenic determination in complex mining residues by flame atomic absorption spectrometry. *Journal of Hazardous Materials, 168*, 1636–1638. https://doi.org/10.1016/j.jhazmat.2009.03.005.

Park, C. H., Eom, Y., Lee, L. J. E., & Lee, T. G. (2013). Simple and accessible analytical methods for the determination of mercury in soil and coal samples. *Chemosphere, 93*, 9–13.

Patel, M. J., Patel, J. N., & Subramanian, R. B. (2005). Effect of cadmium on growth and the activity of H_2O_2 scavenging enzymes in *Colocassia esculentum*. *Plant and Soil, 273*, 183–188.

Patel, K. S., Sharma, R., Dahariya, N. S., Yadav, A., Blazhev, B., Matini, L., & Hoinkis, J. (2015). Heavy metal contamination of tree leaves. *American Journal of Analytical Chemistry, 6*, 687.

Pietrzykowski, M., Socha, J., & van Doorn, N. S. (2014). Linking heavy metal bioavailability (Cd, Cu, Zn and Pb) in Scots pine needles to soil properties in reclaimed mine areas. *Science of the Total Environment, 470*, 501–510.

Pourrut, B., Perchet, G., Silvestre, J., Cecchi, M., Guiresse, M., & Pinelli, E. (2008). Potential role of NADPH-oxidase in early steps of lead-induced oxidative burst in *Vicia faba* roots. *Journal of Plant Physiology, 165*, 571–579.

Pöykiö, R., Mäkelä, M., Watkins, G., Nurmesniemi, H., & Olli, D. A. H. L. (2016). Heavy metals leaching in bottom ash and fly ash fractions from industrial-scale BFB-boiler for environmental risks assessment. *Transactions of Nonferrous Metals Society of China, 26*, 256–264.

Punamiya, P., Datta, R., Sarkar, D., Barber, S., Patel, M., & Das, P. (2010). Symbiotic role of Glomusmosseae in phytoextraction of lead in vetiver grass [*Chrysopogon zizanioides* (L.)]. *Journal of Hazardous Materials, 177*, 465–474.

Raj, D., & Maiti, S. K. (2019a). Bioaccumulation of potentially toxic elements in tree and vegetable species with associated health and ecological risks: A case study from a thermal power plant, Chandrapura, India. *Rendiconti Lincei. Scienze Fisiche e Naturali, 30*, 649–665.

Raj, D., & Maiti, S. K. (2019b). Sources, toxicity, and remediation of mercury: An essence review. *Environmental Monitoring and Assessment, 191*, 566.

Raj, D., Chowdhury, A., & Maiti, S. K. (2017). Ecological risk assessment of mercury and other heavy metals in soils of coal mining area: A case study from the eastern part of a Jharia coal field, India. *Human and Ecological Risk Assessment: An International Journal, 23*, 767–787.

Ren, D. Y., Zhao, F. H., Dai, S. F., et al. (2006). *Geochemistry of trace elements in coals, pp 268–79*. Beijing: The Science Press.

Rensing, C., & Rosen, B. (2009). Biogeocycles for redox-active metal(loids): As, Cu, Mn and Se. In M. Schaechter (Ed.), *Encyclopedia of microbiology* (pp. 205–219). Oxford: Elsevier.

Revathi, K., Haribabu, T. E., & Sudha, P. N. (2011). Phytoremediation of chromium contaminated soil using sorghum plant. *International Journal of Environmental Sciences, 2*, 418.

Reza, S. K., Baruah, U., Singh, S. K., & Das, T. H. (2015). Geostatistical and multivariate analysis of soil heavy metal contamination near coal mining area, north eastern India. *Environmental Earth Sciences, 73*, 5425–5433.

Ribeiro, J., Da Silva, E. F., Li, Z., Ward, C., & Flores, D. (2010). Petrographic, mineralogical and geochemical characterization of the Serrinha coal waste pile (Douro coalfield, Portugal) and the potential environmental impacts on soil, sediments and surface waters. *International Journal of Coal Geology, 83*, 456–466.

Sadiq, M. (1997). Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. *Water, Air, and Soil Pollution, 93*, 117–136.

Sahoo, P. K., Equeenuddin, S. M., & Powell, M. A. (2016). Trace elements in soils around coal mines: Current scenario, impact and available techniques for management. *Current Pollution Reports, 2*, 1–14.

Salido, A. L., Hasty, K. L., Lim, J. M., & Butcher, D. J. (2003). Phytoremediation of arsenic and lead in contaminated soil using Chinese brake ferns (*Pteris vittata*) and Indian mustard (*Brassica juncea*). *International Journal of Phytoremediation, 5*, 89–103.

Samani, Z., Hu, S., Hanson, A. T., & Heil, D. M. (1998). Remediation of lead contaminated soil by column extraction with EDTA: II. Modeling. *Water, Air, and Soil Pollution, 102*, 221–238.

Sampanpanish, P., Pongsapich, W., Khaodhiar, S., & Khan, E. (2006). Chromium removal from soil by phytoremediation with weed plant species in Thailand. *Water, Air, & Soil Pollution: Focus, 6*, 191–206.

Saravanan, A., Jayasree, R., Hemavathy, R. V., Jeevanantham, S., Hamsini, S., Kumar, S., Yaashikaa, P. R., Manivasagan, V., & Yuvaraj, D. (2019). Phytoremediation of Cr (VI) ion contaminated soil using black gram (*Vigna mungo*): Assessment of removal capacity. *Journal of Environmental Chemical Engineering, 7*, 103052.

Sen, T. K., & Sarzali, M. V. (2008). Adsorption of cadmium metal ion (Cd^{2+}) from its aqueous solution by aluminium oxide and kaolin: A kinetic and equilibrium study. *Journal of Environmental Research and Development, 3*, 220–227.

Sharma, P., & Dubey, R. S. (2005). Lead toxicity in plants. *Brazilian Journal of Plant Physiology, 17*, 35–52.

Shukla, A. and Srivastava, S. (2019). A review of phytoremediation prospects for arsenic contaminated water and soil. In *Phytomanagement of polluted sites* (pp. 243-254). Elsevier.

Singh, R., Singh, S., Parihar, P., Singh, V. P., & Prasad, S. M. (2015). Arsenic contamination, consequences and remediation techniques: A review. *Ecotoxicology and Environmental Safety, 112*, 247–270.

Sobukola, O. P., Adeniran, O. M., Odedairo, A. A., & Kajihausa, O. E. (2010). Heavy metal levels of some fruits and leafy vegetables from selected markets in Lagos, Nigeria. *African Journal of Food Science, 4*, 389–393.

Souri, Z., Karimi, N., & de Oliveira, L. M. (2018). Antioxidant enzymes responses in shoots of arsenic hyperaccumulator, *Isatis cappadocica* Desv., under interaction of arsenate and phosphate. *Environmental Technology, 39*, 1316–1327.

Srivastava, S., Shrivastava, M., Suprasanna, P., & D'souza, S. F. (2011). Phytofiltration of arsenic from simulated contaminated water using *Hydrilla verticillata* in field conditions. *Ecological Engineering, 37*, 1937–1941.

Streets, D. G., Lu, Z., Levin, L., terSchure, A. F., & Sunderland, E. M. (2018). Historical releases of mercury to air, land, and water from coal combustion. *Science of the Total Environment, 615*, 131–140.

Su, Y., Han, F. X., Chen, J., Sridhar, B. M., & Monts, D. L. (2008). Phytoextraction and accumulation of mercury in three plant species: Indian mustard (*Brassica juncea*), beard grass (*Polypogon monospeliensis*), and Chinese brake fern (*Pteris vittata*). *International Journal of Phytoremediation, 10*, 547–560.

Subirés-Muñoz, J. D., García-Rubio, A., Vereda-Alonso, C., Gómez-Lahoz, C., Rodríguez-Maroto, J. M., García-Herruzo, F., & Paz-Garcia, J. M. (2011). Feasibility study of the use of different extractant agents in the remediation of a mercury contaminated soil from Almaden. *Separation and Purification Technology, 79*, 151–156.

Sushil, S., & Batra, V. S. (2006). Analysis of fly ash heavy metal content and disposal in three thermal power plants in India. *Fuel, 85*, 2676–2679.

Tang, X. Y., & Huang, W. H. (2004). *Trace elements in Chinese coal*. Beijing: The Commercial Press (In Chinese).

Tessier, A., Campbell, P. G., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry, 51*, 844–851.

Tomasevic, M., Rajsic, S., Dordevic, D., Tasic, M., Krstic, J., & Novakovic, V. (2004). Heavy metals accumulation in tree leaves from urban areas. *Environmental Chemistry Letters, 2*, 151–154.

Tu, S., Ma, L. Q., Fayiga, A. O., & Zillioux, E. J. (2004). Phytoremediation of arsenic-contaminated groundwater by the arsenic hyperaccumulating fern *Pteris vittata* L. *International Journal of Phytoremediation, 6*, 35–47.

USEPA. (1996). Method 3050B: Acid digestion of sediments. *Sludges and Soils,* Revision, p 2.

USEPA, 2007. *Treatment technologies for mercury in soil, waste and water*, EPA-542-R-07-003.

Uzu, G., Sobanska, S., Aliouane, Y., Pradere, P., & Dumat, C. (2009). Study of lead phytoavailability for atmospheric industrial micronic and sub-micronic particles in relation with lead speciation. *Environmental Pollution, 157*, 1178–1185.

Vega, F. A., Andrade, M. L., & Covelo, E. F. (2010). Influence of soil properties on the sorption and retention of cadmium, copper and lead, separately and together, by 20 soil horizons: Comparison of linear regression and tree regression analyses. *Journal of Hazardous Materials, 174*, 522–533.

Verma, S. K., Masto, R. E., Gautam, S., Choudhury, D. P., Ram, L. C., Maiti, S. K., & Maity, S. (2015). Investigations on PAHs and trace elements in coal and its combustion residues from a power plant. *Fuel, 162*, 138–147.

Visoottiviseth, P., Francesconi, K., & Sridokchan, W. (2002). The potential of Thai indigenous plant species for the phytoremediation of arsenic contaminated land. *Environmental Pollution, 118*, 453–461.

Wang, H. H., Shan, X. Q., Wen, B., Owens, G., Fang, J., & Zhang, S. Z. (2007). Effect of indole-3-acetic acid on lead accumulation in maize (*Zea mays* L.) seedlings and the relevant antioxidant response. *Environmental and Experimental Botany, 61*, 246–253.

Wang, J., Feng, X., Anderson, C. W., Xing, Y., & Shang, L. (2012). Remediation of mercury contaminated sites—a review. *Journal of Hazardous Materials, 221*, 1–18.

WHO (1993). Guidelines for drinking-water quality. Vol. 1: Recommendations. 2d ed. Geneva. Accessed 11 Feb 2019.

Xu, M., Yan, R., Zheng, C., Qiao, Y., Han, J., & Sheng, C. (2004). Status of trace element emission in a coal combustion process: A review. *Fuel Processing Technology, 85*, 215–237.

Xue, P., Yan, C., Sun, G., & Luo, Z. (2012). Arsenic accumulation and speciation in the submerged macrophyte *Ceratophyllum demersum* L. *Environmental Science and Pollution Research, 19*, 3969–3976.

Yan, J., Quan, G., & Ding, C. (2013). Effects of the combined pollution of lead and cadmium on soil urease activity and nitrification. *Procedia Environmental Sciences, 18*, 78–83.

Yan, H., Gao, Y., Wu, L., Wang, L., Zhang, T., Dai, C., Xu, W., Feng, L., Ma, M., Zhu, Y. G., & He, Z. (2019). Potential use of the *Pteris vittata* arsenic hyperaccumulation-regulation network for phytoremediation. *Journal of Hazardous Materials, 368*, 386–396.

Yang, Z., Fang, Z., Zheng, L., Cheng, W., Tsang, P. E., Fang, J., & Zhao, D. (2016). Remediation of lead contaminated soil by biochar-supported nano-hydroxyapatite. *Ecotoxicology and Environmental Safety, 132*, 224–230.

Yao, D. X., Meng, J., & Zhang, Z. G. (2010). Heavy metal pollution and potential ecological risk in reclaimed soils in Huainan mining area. *Journal of Coal Science and Engineering (China), 16*, 316–319.

Ye, W. L., Khan, M. A., McGrath, S. P., & Zhao, F. J. (2011). Phytoremediation of arsenic contaminated paddy soils with *Pteris vittata* markedly reduces arsenic uptake by rice. *Environmental Pollution, 159*, 3739–3743.

Yuan, Z., Yi, H., Wang, T., Zhang, Y., Zhu, X., & Yao, J. (2017). Application of phosphate solubilizing bacteria in immobilization of Pb and Cd in soil. *Environmental Science and Pollution Research, 24*, 21877–21884.

Yudovich, Y. E., & Ketris, M. P. (2005). Mercury in coal: a review Part 2. *Coal use and environmental problems. International Journal of Coal Geology, 62*, 135–165.

Zayed, A. M., & Terry, N. (2003). Chromium in the environment: Factors affecting biological remediation. *Plant and Soil, 249*, 139–156.

Zhai, M., Totolo, O., Modisi, M. P., Finkelman, R. B., Kelesitse, S. M., & Menyatso, M. (2009). Heavy metal distribution in soils near Palapye, Botswana: An evaluation of the environmental impact of coal mining and combustion on soils in a semi-arid region. *Environmental Geochemistry and Health, 31*, 759.

Zhang, X., Zhao, F. J., Huang, Q., Williams, P. N., Sun, G. X., & Zhu, Y. G. (2009). Arsenic uptake and speciation in the rootless duckweed Wolffia globosa. *New Phytologist, 182*, 421–428.

Zhitkovich, A. (2011). Chromium in drinking water: Sources, metabolism, and cancer risks. *Chemical Research in Toxicology, 24*, 1617–1629.