

Heavy Metals and Metalloids

Subjects: Environmental Sciences | Soil Science

Contributor: Fulvia Chiampo

The contamination of soil by heavy metals and metalloids is a worldwide problem due to the accumulation of these compounds in the environment, endangering human health, plants, and animals. Heavy metals and metalloids are normally present in nature, but the rise of industrialization has led to concentrations higher than the admissible ones. They are non-biodegradable and toxic, even at very low concentrations. Several techniques have been developed over the years:

- physical remediation (e.g., washing, thermal desorption, solidification),
- chemical remediation (e.g., adsorption, catalysis, precipitation/solubilization, electrokinetic methods),
- biological remediation (e.g., biodegradation, phytoremediation, bioventing), and combined remediation (e.g., electrokinetic–microbial remediation; washing–microbial degradation).

Keywords: heavy metals and metalloids ; contaminated soil ; removal techniques

1. Introduction

Soil contamination by heavy metals and metalloids is a problem that all countries in the world are facing. In recent years, the attention to heavy metal pollution has increased since they are non-biodegradable; they accumulate in soil causing damage to the environment, animals, and humans for a long time ^[1]. Multiple health effects are associated with exposure to heavy metals and metalloids: kidney and bone problems, neurobehavioral and developmental disorders, blood pressure problems, and tumor formation.

The problem becomes relevant when the concentration of heavy metals in the soil is high. Around the world, it is estimated that the number of sites with soil contaminated by heavy metals and metalloids is around five million ^[2], and anthropological activities are usually the origin of this pollution. Most of these heavy-metal-contaminated sites are in developed countries, such as the United States of America, Australia, the European Union State Members, and China. For example, in the USA, around 6000 km² have been contaminated by heavy metals/metalloids; 250,000 sites are polluted in the European Union; and 810,000 km² of farmland in China have been contaminated by heavy metals/metalloids ^[3]. The study of Cheng et al. ^[4] reports that more than 30,000 tons of chromium and 800,000 tons of lead have been released into the environment globally in the past half-century. Different studies have focused on determining the concentrations of heavy metals and metalloids in the European Union ^[5], China ^{[6][7][8]}, and Brazil ^{[9][10]}. The amounts of these pollutants in soils are different and worldwide average concentrations depend on the type of soil, environmental conditions, and the distance from the contamination source.

Heavy metals and metalloids are non-biodegradable and toxic, even at very low concentrations. For their removal from soil, several techniques have been developed over the years. They are based on physical, chemical, and biological processes, and they can be classified as:

- physical methods (landfilling and leaching, excavation, soil washing, calcination) that permit high removal efficiency and the treatment of large quantities of soil, but are expensive;
- chemical methods (soil washing, electrochemical remediation, adsorption) that are very effective, but can be a source of new chemical contaminants introduced into soils, for example, in soil washing;
- physical–chemical processes (ion-exchange, precipitation, reverse osmosis, evaporation, and chemical reduction) which are simple and easy to apply, but have a high-cost burden;

- bioremediation processes (bioventing, biosparging, bioaugmentation, biostimulation) which are environmentally friendly and cost-effective, but the degradation time is slower than in other treatments.

2. Origin, Characteristics, and Properties of Heavy Metals and Metalloids

The term “heavy metals” is used to refer to metals and metalloids present in the environment and having a density higher than $5000 \text{ kg}\cdot\text{m}^{-3}$ and an atomic mass higher than 20. Based on this definition, 51 elements of the periodic table are considered heavy metals/metalloids [11].

Their mobility and bioavailability in soil are due to their chemical characteristics and those of soil. The pH, surface properties of the adsorbents, presence of cations, and anions affect the interactions between soil components and metals/metalloids [12].

The most common heavy metals and metalloids in the environment are chromium, manganese, nickel, copper, zinc, cadmium, lead, and arsenic. Chromium, copper, zinc, cadmium, lead, mercury, and arsenic are the most toxic [13].

Usually, they found in the weathering of underlying bedrock, and they are present as ores (sulfides of Pb, Co, Fe, As, Pb, Zn, Ag and Ni, and oxides of Se, Al, Mn, and Sb). In soils, normally, sulfides of arsenic, mercury, lead, cadmium naturally occur together with sulfides of copper (chalcopyrite, CuFeS_2) and iron (pyrite, FeS_2) [3].

The environmental problem is mainly due to the anthropological activities that cause an increase in heavy metal and metalloid concentrations, especially in the refining and mining of ores, pesticide applications, fertilizer industries, and solid wastes [14]. The anthropogenic sources of metals and metalloids can be divided into five groups, as shown in Figure 1.

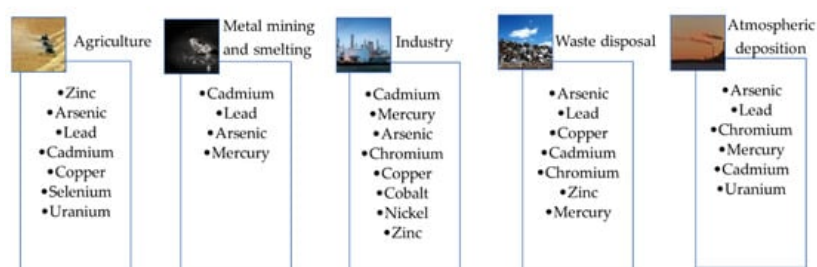


Figure 1. Anthropogenic sources of polluting metals and metalloids.

Heavy metals and metalloids are used in different sectors, increasing market demand and world production. Copper, selenium, zinc, iron, vanadium, and manganese, in trace amounts, are essential for various biological processes, such as in respiration systems, biosynthesis of complex compounds, nervous system, regulation, and functioning of enzymes. Iron, zinc, tin, lead, copper, and tungsten have an important role in electronic devices, especially in the realization of semiconductors [15]. In Table 1, the characteristics of the most toxic heavy metals and metalloids are summarized [16][17].

Table 1. Heavy metals and metalloids characteristics.

Element	Chemical and Physical Properties	Application	World Production ($\text{ton}\cdot\text{y}^{-1}$)
Chromium (Cr)	Density: $7190 \text{ kg}\cdot\text{m}^{-3}$ Atomic mass: 51.99 Heat of fusion: $21.00 \text{ kJ}\cdot\text{mol}^{-1}$	Industrial application, alloys, tanning agents, paint pigments, catalysts, photography.	15,000,000 (year: 2017)
Copper (Cu)	Density: $8960 \text{ kg}\cdot\text{m}^{-3}$ Atomic mass: 63.55 Heat of fusion: $13.26 \text{ kJ}\cdot\text{mol}^{-1}$	Electrical and electronics, transport equipment, construction, industrial machinery, pesticides.	20,000,000 (year: 2017)

Element	Chemical and Physical Properties	Application	World Production (ton·y ⁻¹)
Zinc (Zn)	Density: 7140 kg·m ⁻³ Atomic mass: 65.38 Heat of fusion: 7.32 kJ·mol ⁻¹	Paints, rubber, cosmetics, pharmaceuticals, plastics, inks, soaps, batteries, textiles, and electrical equipment	13,500,000 (year: 2019)
Cadmium (Cd)	Density: 8650 kg·m ⁻³ Atomic mass: 112.41 Heat of fusion: 6.21 kJ·mol ⁻¹	Electroplating, paint pigments, plastics, silver–cadmium batteries, coating operations, machinery and baking enamels, photography, television phosphors.	24,670 (year: 2019)
Lead (Pb)	Density: 11,340 kg·m ⁻³ Atomic mass: 207.2 Heat of fusion: 4.77 kJ·mol ⁻¹	Electrical accumulators and batteries, building construction, cable coatings ammunition.	11,600,000 (year: 2018)
Mercury (Hg)	Density: 13,530 kg·m ⁻³ Atomic mass: 200.59 Heat of fusion: 2.29 kJ·mol ⁻¹	Dental preparations, thermometers, fluorescent and ultraviolet lamps, pharmaceuticals, fungicides, industrial process waters, seed dressings.	4000 (year: 2019)
Arsenic (As)	Density: 5730 kg·m ⁻³ Atomic mass: 74.92 Heat of fusion: 24.44 kJ·mol ⁻¹	Pesticides, pharmaceuticals, alloys, semiconductors.	33,000 (year: 2019)

It is evident that these elements are used in all fields and that annual production around the world is very high, especially chromium, copper, zinc, and lead.

References

- Atieh, M.A.; Ji, Y.; Kochkodan, V. Metals in the Environment: Toxic Metals Removal. *Bioinorg. Chem. Appl.* 2017, 2017, 4309198.
- He, Z.; Shentu, J.; Yang, X.; Baligar, V.C.; Zhang, T.; Stoffella, P.J. Heavy Metal Contamination of Soil: Sources, Indicators, and Assessment. *J. Environ. Indic.* 2015, 9, 17–18.
- Khalid, S.; Shahid, M.; Niazi, N.K.; Murtaza, B.; Bibi, I.; Dumat, C. A comparison of technologies for remediation of heavy metal contaminated soils. *J. Geochem. Explor.* 2017, 182, 247–268.
- Cheng, S.; Chen, T.; Xu, W.; Huang, J.; Jiang, S.; Yan, B. Application Research of Biochar for the Remediation of Soil Heavy Metals Contamination: A Review. *Molecules* 2020, 25, 3167.
- Tóth, G.; Hermann, T.; Da Silva, M.R.; Montanarella, L. Heavy metals in agricultural soils of the European Union with implications for food safety. *Environ. Int.* 2016, 88, 299–309.
- Li, L.; Zhang, Y.; Ippolito, J.A.; Xing, W.; Qiu, K.; Yang, H. Lead smelting effects heavy metal concentrations in soils, wheat, and potentially humans. *Environ. Pollut.* 2020, 257, 113614.
- Yu, F.; Lin, J.; Xie, D.; Yao, Y.; Wang, X.; Huang, Y.; Xin, M.; Yang, F.; Liu, K.; Li, Y. Soil properties and heavy metal concentrations affect the composition and diversity of the diazotrophs communities associated with different land use types in a mining area. *Appl. Soil Ecol.* 2020, 155, 1030669.
- Yan, D.; Bai, Z.; Liu, X. Heavy-Metal Pollution Characteristics and Influencing Factors in Agricultural Soils: Evidence from Shuozhou City, Shanxi Province, China. *Sustainability* 2020, 12, 1907.
- Bocardi, J.M.B.; Pletsch, A.L.; Melo, V.F.; Quinaina, S.P. Quality reference values for heavy metals in soils developed from basic rocks under tropical conditions. *J. Geochem. Explor.* 2020, 217, 106591.
- Brito, A.C.C.; Boechat, C.L.; de Sena, A.F.S.; Duarte, L.d.S.L.; do Nascimento, C.W.A.; da Silva, Y.J.A.B.; Saraiva, P.C. Assessing the Distribution and Concentration of Heavy Metals in Soils of an Agricultural Frontier in the Brazilian

11. Sivakumar, D.; Kandaswamy, A.N.; Gomathi, V.; Rajeshwaran, R.; Murugan, N. Bioremediation studies on reduction of heavy metals toxicity. *Pollut. Res.* 2014, 33, 553–558.
12. Ali, H.; Khan, E. What are heavy metals? Long-standing controversy over the scientific use of the term ‘heavy metals’—Proposal of a comprehensive definition. *Toxicol. Environ. Chem.* 2018, 100, 6–19.
13. Caporale, A.G.; Violante, A. Chemical Processes Affecting the Mobility of Heavy Metals and Metalloids in Soil Environments. *Curr. Pollut. Rep.* 2016, 2, 15–27.
14. Ali, H.; Khan, E.; Ilahi, I. Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. *J. Chem.* 2019, 2019, 6730305.
15. Salomons, W.; Forstner, U.; Mader, P. *Heavy Metals Problems and Solutions*, 1st ed.; Springer: Heidelberg, Germany, 1995; ISBN 9783642793189.
16. Koller, M.; Saleh, H.M. Introductory Chapter: Introducing Heavy Metals. In *Heavy Metals*; Saleh, H.M., Aglan, R., Eds.; IntechOpen: London, UK, 2018.
17. Wang, L.K.; Chen, J.P.; Hung, Y.-T.; Shammass, N.K. *Heavy Metals in the Environment*; Taylor & Francis Group: Broken Sound Parkway, NW, USA, 2009; ISBN 9781420073164.
18. Statista. Available online: (accessed on 2 December 2020).