Chapter

Introductory Chapter: How to Assess Metal Contamination in Soils?

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1. Introduction

The average concentrations of metal or metalloid referred as metal(loid) hereafter, except those of radioisotopes or daughter nuclides and inert gases, have remained virtually unchanged in the earth's crust despite the ups and downs in the overall distribution [1]. The total element content in the earth's crust is dominated by O, Si, Al, Fe, Ca, Na, K, Mg, P, and Ti representing ≥99%, while the other elements in the periodic table comprised the remaining 1% and are termed as "trace elements" [2]. The abundances of naturally occurring metal(loid)s in the earth's crust, also known as *Clarke values*, have been estimated by several researchers [3–5]. The *Clarke values* in different reports slightly varied because these are hypothetical concentrations as computed using assumed proportions of various crustal rock types [6]. The ore minerals, which contain significant contents of several metal(loid)s in their crystal structure, are listed in **Table 1**.

The changes in both distribution and abundances of metal(loid)s in the ecosphere have become catastrophically high in recent decades presumably attributable to a wide range of anthropogenic inputs [2]. The anthropogenic emission of the toxic metal(loid)s into the atmosphere is estimated to be the one-to-three order of magnitude higher than the natural fluxes [7]. Soil, an ecosphere compartment, is the primary sink for metal(loid)s released into the environment by anthropogenic activities, which often persist for an indefinite period as most metal(loid)s resist the microbial or chemical degradation [8, 9]. Metal(loid)s are usually adsorbed by the organic, inorganic, or colloidal constituents of soil, e.g., humus, hydrous oxides, and hydroxides of Al, Fe, or Mn and Al, phyllosilicates, and some sparingly soluble calcium salts [10]. However, the anthropogenic contaminants such as ash, mine waste, demolition rubble, and so forth can serve as the parent material of a nonnatural soil type, namely, Anthrosols [2], which should have different metal accumulation characteristics than the natural pedogenic soils. The anthropogenic metal(loid)s in soils might have increased mobility than those from pedogenic or genic origins [11]. The metal(loid) contamination of soil is colorless, odorless, and barely noticeable as the environmental impact is not expeditious. The ecological damage due to the metal(loid)s triggered when the corresponding bioavailability is above the threshold or there is a change of environmental conditions [12, 13]. Moreover, the impact of contamination is enhanced when multiple metal(loid)s are involved rather than a single species [14]. The magnitude of metal(loid)s concentration in soils depends on the type of exposure and may be varied on different sites. The physicochemical characteristics and the distribution of metal(loid)s diversified based on the interaction with the soils and local transport mechanisms [15, 16]. The adverse effects on soils due to the accumulation of metal(loid)s are summarized in **Table 2**.

The environmental and geochemical changes of soils as a result of the intrusion of metal(loid)s not only affect the safety of living beings but also hamper the sustainable development due to the impact on the economic or political considerations

Ore minerals	Associated metalloids
Argentite (Ag_2S), PbS	Ag, Au, Cu, Sb, Zn, Pb, Se, Te
Arsenopyrite (FeAsS), AsS	As, Au, Ag, Sb, Hg, U, Bi, Mo, Sn, Cu
Barite ($BaSO_4$)	Ba, Pb, Zn
Sphalerite (ZnS)	Cd, Zn, Pb, Cu
Cobaltite ((Co, Fe) AsS)	Co, Fe, As, Sb, Cu, Ni, Ag, U
Chromite (Fe, Cr_2O_4)	Cr, Ni, Co
Bornite (Cu_5FeS_4), chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$)	Cu, Zn, Pb, Cd, As, Se, Sb, Ni, Pt, Mo, Au, Te
Cinnabar (HgS)	Hg, Sb, Se, Te, Ag, Zn, Pb, Mn
Pyrolusite (MnO_2)	Mn, Co, Ni, Zn, Pb
Molybdenite (MoS_2)	Mo, Cu, Re, W, Sn
Galena (PbS)	Pb, Ag, Zn, Cu, Cd, Sb, Tl, Se, Te
Stibnite (Sb_2S_3)	Sb, Ag, Au, Hg, As
Cassiterite (SnO_2)	Sn, Nb, Ta, W, Rb
Uraninite (UO_2)	U, V, As, Mo, Se, Pb, Cu, Co,
Vanadinite ($Pb_5(VO_4)_3Cl$)	V, U, Pb
Wolframite ((Fe, Mn) WO_4)	W, Mo, Sn, Nb
Sphalerite (ZnS), smithsonite ($ZnCO_3$)	Zn, Cd, Cu, Pb, As, Se, Sb, Ag, In

†*Source: Alloway [2].*

Table 1.
Common source of ore minerals of the metal(loid)s.†

Agricultural effect	Reduction of soil fertility Reduction of nitrogen fixation Increased erosion factor Increasing soil loss Increase nutrient deficiency Reduction of crop yields Imbalance in the soil biota (flora, fauna, microorganism) Decrease of soil biodiversity
Industrial effect	Transfer of dangerous chemicals Ecological imbalance Release of pollutant gases Increased salinity
Urban effect	Clogging of the drains Soil deposits Flooding areas Health problems Contamination of drinking water sources Problems of waste management

†*Source: Weissmannová and Pavlovský [50].*

Table 2.
Summary of adverse effects on soils due to the accumulation of metal(loid)s.†

[17]. Moreover, natural attenuation is often ineffective to eliminate the excess metal(loid)s from the soil, while the remediation process requires high cost and long duration in most instances [13]. Hence, it is necessary to estimate the variation in metal(loid) abundances of soils, which are susceptible to anthropogenic exposure, continuously or even periodically to avoid foreseeable mandatory soil cleanup requirements. The protocols for the assessment of metal(loid) contamination of soils will be discussed in the current chapter, preceded with a brief overview of the sources and toxicity impacts of metal(loid)s in soils.

2. Potentially toxic metal(loid)s

Metal(loid)s, which are ubiquitous in natural soil, and described to have influence on the physiological functions of living beings, e.g., plants, and other organisms, can be classified as nutritionally essential, nonessential with a possible beneficial effect, or nonessential with no beneficial effects [18] as listed in **Table 3**. The nonessential elements are potentially toxic even at deficient concentrations, while the essential ones can exert harmful impacts at elevated levels [19]. Metal(loid)s, those evoke health concerns, when accumulated in soils, exert chronic toxic effects on humans and other living beings usually via food-chain transfer. However, acute metal(loid) poisoning, even though rare, might also occur through ingestion, inhalation, or dermal contact. The toxicokinetics and toxicodynamics of metal(loid)s depend on several factors, e.g., route of exposure, dose, chemical speciation, solubility, and biotransformation, including the age, gender, and nutritional status of the exposed individuals [20]. Moreover, co-exposure to metal(loid)s mixtures may produce additive, antagonistic, or synergistic toxic effects, which could be more severe at both relatively high-dose and low-dose levels [21, 22].

An analysis of published data indicates that As, Cd, Cr, Pb, and Hg are systemic toxicants among the metal(loid)s [20], which are known to induce adverse health effects in humans ranging from dermatological, gastrointestinal, neurologic, hematologic, immunologic, metabolic, nephrotic, developmental, and behavioral disorders to cancers [23–25]. The As, Cd, Cr, Pb, or Hg might also interfere

Nutritionally essential metal(loid)s	Metal(loid)s with possible beneficial effects	Metal(loid)s with no known beneficial effects
Cobalt	Boron	Aluminum
Chromium(III)	Nickel	Antimony
Copper	Silicon	Arsenic
Iron	Vanadium	Barium
Manganese		Beryllium
Molybdenum		Cadmium
Selenium		Lead
Zinc		Mercury
		Silver
		Strontium
		Thallium

[†] *Source: Goyer et al. [18].*

Table 3.
Classification of metal(loid)s based on the health impact characteristics.[†]

metabolically with the nutritionally essential metal(loid)s, such as Fe, Ca, Cu, and Zn [26, 27]. The ecotoxicological considerations expanded the list of hazardous elements including a total of 11 metal(loid)s (As, Ba, Cd, Cr, Cu, Hg, Ni, Sb, Se, Tl, and V) [28]. The US-EPA priority pollutant list [29], however, included Ag, Be, Pb, and Zn in the list of toxic metal(loid)s and excluded Ba and V.

3. Assessment of soil contamination by metal(loid)s

A soil system is "contaminated" if any or more than a few of the toxic metal(loid) are present where it should not be or above the designated "background" concentrations [30, 31]. However, the definition of the term "background" is yet to be defined universally [6], and a selective list of definitions used to define the "background" conditions are listed in **Table 4**. A critical evaluation of "background" definitions [32] revealed that a precise global background value for an individual metal(loid) could not be proposed because there have been ups and downs in the overall natural distribution metal(loid)s in the ecosphere. Hence, it should be limited to specific geographic locations or regions and should be considered as a range instead of an absolute value to deal with the unavoidable environmental heterogenicity [32–34]. The regional "background" values of metal(loid)s represent either off-site or on-site reference locations. The off-site "background" values, as derived from real sample measurements [35, 36], often do not have sufficient metadata to validate the data accuracy [37] and also do not include the impact of transboundary atmospheric transport of metal(loid)s [38, 39]. The on-site "background" values usually represent buried fossil topsoils [40], dated peat bog samples [41], or deep soil layer from the same soil profile [42, 43]. However, the buried topsoils might subsequently be depleted by pedogenetic processes [44], and the properties of deep soil layers, e.g., organic matter content, bulk density, and so forth, are different from those of top soils [39, 45]. *Clarke values* are used as the representative "background" when regional off-site or on-site reference data is not available or cannot be obtained [6, 36]. *Clarke values*, even though used as an arbitrary off-site reference, does not sufficiently represent variations in element distributions in a regional or local context because of the lithologic discontinuities or pedogenic processes [34, 46]. The critical point is to select the correct "baseline" value to avoid mistaken identification of soil contamination that would create negative economic and social impacts. The strategies to avoid data bias in environmental monitoring of soil contamination are discussed by Desaules [37]. The distribution of geochemical data and related issues are focused in the works of Reimann and Filzmoser [47] and Reimann and de Caritat [45].

The methods used for soil contamination assessment include both statistical and geochemical methods, which are critically evaluated by several researchers, e.g., Desaules [39], Morrow et al. [48], D'Amore et al. [49], Weissmannová and Pavlovský [50], Cai et al. [51], Mizutani et al. [52], and so forth.

Definition	Reference
The concentration of a metal(loid) reflecting natural processes uninfluenced by human activities	[32]
The normal abundance of a metal(loid) in barren earth material	[6, 53]
Geogeneous or pedogeneous average concentration of a metal(loid) in an examined soil	[6, 54]

Table 4.
A selective list of definitions used to define "background" metal(loid) concentration in soils.

4. Conclusion

Metals in soil induce long-term risks to the ecosystems. Dynamics of metals in ecosphere can be assessed precisely using the information on the interactions of metals with environmental compartments. Evaluation of total metal content in soil and comparison with the "background" concentrations are the basic idea to deduce the anthropogenic inputs. However, there are differences in opinion regarding the test methods, definitions of "background," or approaches in data interpretation for the assessment of soil contamination. Hence, it might require more time to unify the understanding of soil contamination with metals.

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