



REVIEW

Heavy Metal/Metalloid Indexing and Balances in Agricultural Soils: Methodological Approach for Research

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ABSTRACT

Heavy metal(loid) accumulation in agricultural soils is a threat to the soil capacity, quality, and productivity. It also increases human exposure to heavy metal(loid)s via consumption of contaminated plant-based foods. The detrimental effects of soil contamination also deteriorate the environment of plants and animals. For sustainable agriculture, therefore, the soil must be protected from toxic levels of heavy metal(loid)s. Studies on heavy metal(loid) balances in agricultural soils are important in predicting future risks to sustainable production from agro-ecological zones and human exposure to heavy metal(loid)s. The latest and continuous indexing of the problem seems a prerequisite for sustainable agriculture. This review provides some background information and then summarizes key methodological approaches for studies on indexing and balance of heavy metal(loid)s in agricultural soils. In the end, important soil and health indices are explained that may be useful in understanding the extent of the problem. The provided information would contribute to sustainable heavy metal(loid) management in the agricultural soils, high crop production, better soil protection, and ultimately to human health.

KEYWORDS

Food crops; health risks; soil contamination; sustainable agriculture

1 Introduction

Contamination of soil resources with heavy metal(loid)s poses a serious threat to the usefulness of the soils for humans and other living organisms. Plant and human toxic levels of heavy metal(loid)s are building in soils along with widespread industrialization, an increasing number of automobiles, extensive mining activities, and chemical-based agriculture [1,2]. Soil heavy metal(loid) contamination is the problem of both industrialized developed countries and over-populated developing countries [3]. Heavy metal(loid)s persist in the environment without degradation and, thus, present a continuous health risk for a longer period. From the soil, these contaminants may be taken up by the growing plant roots and stored in edible plant parts [2,4–6]. The contamination of soils with heavy metal(loid)s has been reported to cause several fatal diseases in humans, including malignancy [1]. Other life-threatening diseases that may be linked with heavy metal(loid) exposure include gastrointestinal and kidney dysfunction, nervous system disorders, skin lesions, vascular damage, immune system dysfunction, and birth defects. Similar to their ill effects on animals and humans, the toxicity of heavy metal(loid)s in plants induces oxidative stress,



disrupts the photosynthetic machinery, and blocks many vital metabolic processes [7]. Therefore, the soils contaminated with heavy metal(loid)s are largely unfit for cultivation, residence, or recreation.

Once the soil is contaminated with heavy metal(loid)s, soil remediation is the only option for restoring such soils for human use [8,9]. Various physical, chemical, and biological remediation strategies have been suggested to date. Because of the complex nature of soils and the contaminants, there is no universally valid technology for soil remediation. The *ex-situ* methods of soil remediation are impractical for large-scale agricultural soils. Soil replacement, thermal desorption, soil washing, and chemical immobilization are also unfeasible in resource-poor conditions in developing countries. Although the addition of organic amendments for immobilization of heavy metal(loid)s have shown considerable success, bioremediation, especially phytoremediation, is probably the most economic strategy of soil remediation [10]. However, the remediation of soils having toxic levels of several heavy metal(loid)s is extremely complex [11]. Cost considerations, the expected period for soil remediation, hazards to adjacent locations, depth of the aquifer, the topography of the land, and acceptance of remediation strategies by the inhabitants are some other significant issues that render soil remediation impractical in most cases. Therefore, especially in agricultural soils, the best approach is to monitor and check heavy metal(loid) load in the environment.

The fundamental research to recommend the right fertilizer rates of plant nutrients [12] and to monitor the risk of heavy metal(loid) in agricultural soils are element balance studies [13,14]. Based on such studies, several European countries have made policy decisions about the use of agricultural inputs, especially wastewater irrigation [15]. Such studies may permit us to predict the time frame under which a specific input may contaminate the soils to the levels not suited for sustainable agriculture [16–19]. However, the latest investigations on the topic are lacking in most developing countries [20]. Soil surveys, which lack in several aspects from heavy metal(loid) balance studies, reported toxic levels of heavy metal(loid)s in potentially contaminated peri-urban areas in developing countries [21–23]. These pollutants may gradually accumulate in agricultural soils in rural and urban areas of developing countries. In these countries, therefore, there is an interesting need for studies on heavy metal(loid) status and balance. The heavy metal(loid)s with potentially higher contamination levels (e.g., arsenic As, cadmium Cd, chromium Cr, copper Cu, mercury Hg, lead Pb, and zinc Zn) should focus on such studies.

The wastewater from cities in developing countries, which may also have effluent from some industries, is discharged into water canals with no prior treatment [24]. Such water may be a source of heavy metal(loid)s in agricultural soils, and it reaches even the agricultural soils in remote rural areas in developing countries. In industrialized countries, the atmospheric deposition might have these containments from mining, industries, automobiles, and other sources [25,26]. Given this continuous addition of heavy metal(loid)s in agricultural soils, the sustainable productivity of the agro-ecosystems is at risk. It is also probable that the soil buffer capacity may already be near saturation and urgent steps may be needed to protect the soil by adopting sustainable heavy metal(loid) management. Soil contamination by heavy metal(loid)s is already one of the major issues worldwide [27,28]. However, research on the rate and extent of soil degradation by heavy metal(loid) contamination is limited, especially in populated developing countries. To devise a sustainable soil use policy, long-term research data are needed regarding the contamination rates of soil resources around the world. One of the major reasons of limited research in this area in the developing countries might be the complicate nature of research on trace elements in complex soil environments. The next sections of this review provide an analytical background of the studies that are prerequisites to monitor and manage soil contamination by heavy metal(loid)s.

2 Monitoring of Soils, Waters, and Plants

Continuous monitoring of soil, water, and plant samples is fundamental in determining the present levels and forecasting any emerging contamination threats to soil resources. Therefore, the samples of agricultural origins should be routinely tested for the concentration of heavy metal(loid)s. Such analysis should be made

along with routine soil analysis for fertility estimation, plant analysis for diagnosing nutrient deficiencies, and water analysis for irrigation water quality.

2.1 Monitoring of Soils

Repeated and continuous sampling of agricultural soils is necessary to study the trends of potential soil contamination. The sampling period may be the harvesting period of each major crop. From each sampling location, composite (from 2 to 5) soil samples should be randomly collected from a crop field separately from 0 to 30 cm and 30 to 60 cm depths [29]. Deeper soil samples are required only if there are chances of leaching, such as for sandy soils and areas with high rainfall. Soil samples of each depth should be thoroughly mixed, packed in polyethylene-zip bags, and accurately labeled. The standard methods for the collection, transport, and storage of the samples are detailed elsewhere [30].

In the laboratory, soil samples are air-dried and crushed with mortar and pestle. Soil samples are then sieved through 2 mm nylon sieves. Sub-samples from the homogenized samples are processed for physical and chemical analysis. Soil samples should be analyzed for total, plant-available, and other chemical pools of relevant heavy metal(loid)s (e.g., As, Cd, Cr, Cu, Hg, Pb, and Zn) [31,32]. To accurately detect low levels of heavy metal(loid)s in the samples, inductively coupled plasma (ICP) fitted with a mass spectrometer is the best choice. In resource-limited conditions, atomic absorption spectrophotometer (AAS) is a low-cost alternative. Soil physical (such as texture and bulk density), chemical [such as pH, electric conductivity (EC), exchangeable sodium percentage (ESP), cation exchange capacity (CEC), basic cation saturation percentage (BCSP), soil organic matter, calcium carbonate] and fertility (e.g., availability of macro-and micro-nutrients) properties [33,34] may further aid in interpretations of the potential effects of heavy metal(loid) contaminations in soils. Hence, such soil properties should also be measured.

2.2 Monitoring of Plants

In the proximity (maximum of within 1 m radius) of each sampling point of the soil sample, plant samples may also be collected alongside soil samples. Heads (spikes from wheat and panicles from rice), cobs (from maize), cotton seeds (from cotton), or any other edible plant part should be separately sampled from the rest of the plant materials. As per standard protocols, the plant samples should also be composited, mixed, stored (in paper bags), and labeled.

In the laboratory, grains (from wheat, rice, and maize) and other edible plant parts (from vegetables and fruits) are separated and dried in hot-air ovens at 60°C–70°C until constant weights. The rest of the plant materials from each crop are first chopped into small pieces and then dried. The dried samples are ground and homogenized. Sub-samples are then digested in acids (such as in 2:1 mixture of nitric and perchloric acids) [30]. After wet digestion, plant samples are analyzed on ICP or AAS for the total contents of the relevant heavy metal(loid)s.

2.3 Monitoring of Water

Irrigation water samples from tube-wells and canals should be collected from field inlets. This allows accounting for all contamination coming from the point and non-point sources. Irrigation water samples from running canals should be collected from the upper, central, and lower depths, and composited. Extensive sampling is often required to encounter diurnal and seasonal variations in water contamination. Tube-well samples should be collected after running it for 10 min. Water samples may be stored in labeled polyethylene bottles (of about 2 L capacity) and transported to laboratory on the same day.

In the laboratory, canal water samples are filtered, and the filtrate is analyzed for the total contents of metal(loid)s. For that, about 1 L of filtered canal water or tube-well water is boiled to near-dryness and then digested in nitric acid for determination of soluble contents of heavy metal(loid)s on ICP or AAS.

Analysis of the filtrate allows the quantification of only the soluble fraction of heavy metal(loid)s in irrigation water. However, irrigation water often contains suspended materials. This is specifically true for canal water that has sediments from the mountains and wastewaters that have suspended material from industries or municipal usage. In such cases, the suspended material is first separated by filtration. After that, the solid material is dried and processed for metal(loid) analysis as for soil samples.

3 Balance of Heavy Metal/Metalloids in Soils

To allow a better understanding of the effects of agricultural interventions, heavy metal(loid) balance studies are suggested [13,14]. In such studies, all the inflows and outflows of heavy metal(loid)s should be considered (Fig. 1). For this, volunteer farmers may be selected for their consent to allow sampling from their fields to access the input and yield data. Several crops, including cereals, forages, fiber crops, vegetables, and fruits should be selected from the region. The selection of the fields should be from low (remote areas with tube-well or canal irrigation, or rain-fed areas) and high potential of soil pollution (near roads, mining areas, industries, cities, or irrigated by wastewater) with heavy metal(loid)s. Farmers should be allowed to practice their routine crop rotation, cultivar selection, input management, and crop husbandry. All such data, however, should be recorded in quantitative terms.

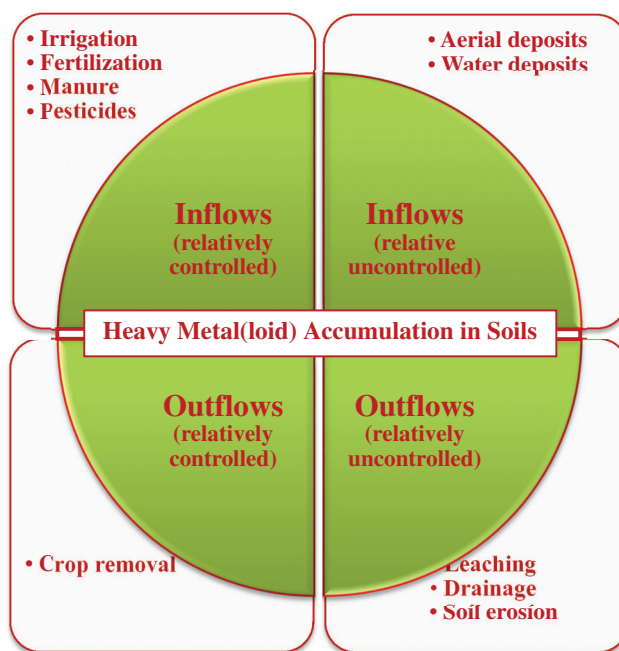


Figure 1: Inflows and outflows of Heavy metal(loid)s that are important for soil Heavy metal(loid) balance studies

3.1 Inflows and Outflows

In multiyear field experiments, soil samples should be collected from the fields for the analysis of initial levels of heavy metal(loid)s. Thereafter, during 2 or more consecutive years, soil, irrigation water, plant (root, shoot, and grain), and crop inputs samples should repeatedly be collected from fields at full maturity or during harvesting periods of all current and succeeding crops [35,36]. If weeds are removed manually by farmers, weed samples should also be collected for heavy metal(loid) outflows. Samples of irrigation water, pesticides, and soil amendments (fertilizers, organic manures, chemical amendments, etc.) should

be directly collected by the farmers. Soil, water, and amendment samples should be collected and analyzed as detailed above.

For atmospheric deposition, collection setups may be designed that collect wet and dry depositions in separate chambers [26,37]. The collector should include a funnel, insect check, collector tube, filter paper, and collection bottle. At specific intervals, samples should be collected from the collector and transported to the laboratory. In the laboratory, dry deposits should be processed and analyzed as per soil analysis, and wet deposits may be analyzed as per water analysis.

Heavy metal(loid) leaching from contaminated soils is a problem in humid areas where precipitation is higher than potential evapotranspiration [38]. In neutral to alkaline soils, the leaching of Zn and Cu were mainly controlled by the duration and frequency of rainfall [39]. Acid rain, as compared to normal rain, greatly increases mobility and leaching of heavy metal(loid)s [40,41]. In contrast to humid areas, potential evapotranspiration is higher than total precipitation in arid to semi-arid climates. Because of high potential evapotranspiration in those areas [42] and high metal(loid) adsorption capacities of calcareous soils [43], there may be negligible leaching of heavy metal(loid)s below the root zone. Nevertheless, there are chances of metal(loid) leaching from irrigated fields in arid to semi-arid areas, especially from flood-irrigated-coarse-textured soils. However, there is a scarcity of information on leaching and leaching rates of heavy metal(loid)s from agricultural fields in developing countries. The leaching rate (L) can be calculated by the following expression [17]:

$$L = \left(\frac{\vartheta v}{p} \right) \left(\frac{G_l}{\rho k_f} \right)^{\frac{1}{n}} \quad (1)$$

where, ϑ is net volumetric water contents [(irrigation + precipitation) – ET], v is interstitial water flow velocity (depth of percolating water attained in a unit time under a constant head), and p is the thickness of the plowing layer. Other parameters [G_l is the labile fraction of the concerned metal that includes soluble and adsorbed fractions, ρ is soil bulk density, k_f is the Freundlich constant, and $1/n$ is the empirical constant] may be computed from the Freundlich adsorption model (Eq. (3)).

3.2 Balance Computations and Predictions

Samples of inflows and outflows of 2 or more consecutive years (as detailed above) may serve as a reliable indicator of metal(loid) balances in agricultural soils. For that, data on grain, straw, and forage yields should be collected from the farmers in quantitative terms. Information on crop residue management, manual weeding, and manure application rates should be as accurate as possible. The actual applied rates of fertilizer and pesticides should be recorded (Recommended rates of the fertilizers may be misleading in such cases). The measurement of the quantity of applied irrigation water seems challenging. However, it can be calculated along with the collection of data on total precipitation. From the collected data and laboratory analysis, crop removal, and soil balance of heavy metal(loid)s may be computed as [36,44]:

$$\begin{aligned} \text{Accumulation rate (g ha}^{-1} \text{ y}^{-1}) = & \text{Inflow rates (Deposition + Irrigation + Fertilization +} \\ & \text{Pesticides + other soil amendments) - Outflow rates} \\ & \text{(Crop removal + Weed removal + Leaching + Soil erosion)} \end{aligned} \quad (2)$$

Using the measured accumulation rate over the period of two or more years, predictions may be modeled using hypothetical/expected values of inflows and outflows for future scenarios. Also, predictions may be made for the next 50 years for the accumulation of heavy metal(loid)s under extreme (low/high) possibilities of inflows and outflows.

4 Fractions and Adsorption on Soil Matrixes

Heavy metal(loid) balances in agricultural soils may provide useful information on the sustainability of conventional and new agricultural practices. The inflows and outflows may differentially influence the labile and non-labile fractions of heavy metal(lid)s in soils. Other soil properties, such as the type of minerals and the chemical pools of heavy metal(loid)s in soils, may provide complementary information on the extent and effects of soil contamination. Major soil minerals and minerals of heavy metal(loid)s can be analyzed by using an X-ray diffractometer (XRD). Soil sample preparation and standard operation protocols of XRD analysis are detailed elsewhere [45,46].

The determination of chemical fractions of heavy metal(loid)s by following the standard procedure of sequential extraction [31,43,47] is helpful in the determination of potential mobility of the heavy metal(loid)s in soils, and hence their availability to growing plants and leaching/runoff to water resources. Soluble, exchangeable, carbonate-bound, Al/Fe-oxides-bound, and organic-matter-bound fractions of heavy metal(loid)s can be separately extracted by standard extractants. Residual contents of heavy metal(loid)s in soil samples are then analyzed after digesting in HF-HClO₄ [48]. The concentration of heavy metal(loid)s in the soil extracts and digests can be analyzed on ICP or AAS.

For metal(loid) adsorption onto soil matrixes, single and combined metal/metalloid adsorption isotherms should be developed for many elements. The details of relevant batch experiments are given elsewhere [49,50]. Briefly, 2.5 g of air-dried soil is equilibrated in 25 mL of 0.01 M CaCl₂ solutions, having variable initial concentrations of single or combined heavy metal(loid)s. Supernatants are analyzed for a final concentration of heavy metal(loid)s on ICP or AAS. The data from the linear log equation between equilibrium element concentration (c , mg L⁻¹) and quantity of the element adsorbed on a unit mass of soil (q , mg kg⁻¹) at equilibrium with the soil solution are used in adsorption models, such as the Freundlich model:

$$q = k_f c^{1/n} \quad (3)$$

where k_f is the proportionality constant for the Freundlich equation (mg kg⁻¹), and $1/n$ is the empirical constant (L kg⁻¹).

5 Indices of Soil Pollution Level

The measured concentration of heavy metal(loid)s in soils may be directly compared with the maximum permissible limits of these contaminants in soils. The maximum permissible concentrations of heavy metal(loid)s were suggested in the soil quality standards of FAO/WHO, Russia, and the Netherland [51,52]. However, the extent of soil contamination with heavy metal(loid)s may be better computed and easily interpreted based on some soil pollution indices. Several computations have been suggested, and comprehensive information about five individual indices (for individual heavy metal(loid)) and thirteen complex indices (for more than one heavy metal(loid)s) is detailed elsewhere [53]. Geo-accumulation (I_{geo}) and single pollution (PI) indices are individual indices that are easily computable and more widely used. The I_{geo} is computed as \log_2 of the ratio of total heavy metal(loid) concentration (c_t) in the soils to 1.5 times the geochemical background (c_b) of the heavy metal(loid) [54,55]:

$$I_{geo} = \log_2 \left(\frac{c_t}{1.5 c_b} \right) \quad (4)$$

Based on I_{geo} , soils are classified into seven classes, ranging from $I_{geo} \leq 0$ (unpolluted soil) to $I_{geo} \geq 5$ (extremely high polluted soil). The other most used individual index is PI . It is the ratio of total heavy metal(loid) concentration (c_t) in the soils to the geochemical background (c_b) of heavy metal(loid):

$$PI = \frac{c_t}{c_b} \quad (5)$$

Based on PI , soil pollution by individual heavy metal(loid) is ranked in five classes ranging from $PI < 1$ (no pollution) to $PI > 5$ (very strong pollution). For multiple heavy metal(loid)s, many complex pollution indices can be computed based on PI . For example, the sum of contamination (PI_{sum}) is just a numerical sum of the single PI of all heavy metal(loid)s in the soil.

6 Indices of Human Health Risk

Measuring heavy metal(loid) levels in human blood and other tissues may provide excellent data to depict the level of exposure to humans. However, the conduction of such studies faces several challenges including the demand for a high budget and a limited number of participants. With the limited budget, the evaluation of health risk indices provides an estimation of the risk to general people. Such computations are possible with just the food composition and consumption data. The data on the consumption rate of cereals and other plant-based foods is available in the Food and Agricultural Organization (FAO) country data [56]. Food consumption rates in an area may also be taken from local household surveys. Using food consumption data and measured heavy metal(loid) concentrations in foods, average estimated daily intakes (EDI), target hazard quotient (THQ), total hazard index (THI), and cancer risk indices (CRI) may be calculated for the metal(loid)s of interest. The THQ, separately for each heavy metal(loid), may be calculated by dividing the EDI of metal(loid) by its chronic oral reference dose (RfD) [57]:

$$THQ = EDI / RfD \quad (6)$$

The RfD of various heavy metal(loid)s can be adopted from US EPA screening levels [58]. A THQ value of over 1 shows a possibility of negative health effects. The Sum of individual THQ of heavy metal(loid)s is termed as THI.

Cancer risk indices are calculated by multiplying the EDI of heavy metal(loid) by its cancer slope factor (CSF) [57]:

$$CRI = EDI \times CSF \quad (7)$$

The cancer risk is the incremental probability of an individual to develop cancer, over a lifetime, because of exposure to a potential carcinogen. The values of CSF can also be adopted from US EPA screening levels [58]. The calculated CRI values may be compared with standard permissible values to explain the risk of cancer in the population because of the consumption of the said food.

7 Conclusions

Heavy metal(loid) contamination of agricultural soils is unmonitored in several developing countries. This review highlighted the need for detailed studies on the balances of heavy metals in agricultural soils. The proposed methodological approaches of future research may be followed by soil scientists to plan and execute novel research studies on determining the current status and future trends of soil contamination by heavy metal(loid)s. Such information is a prerequisite for sustainable production of food crops with nutritious and safe food for all.

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