



QUANTITATIVE ANALYSIS OF HAZARDS OF HEAVY METALS ON HUMAN HEALTH AND AGRICULTURAL PRODUCTION

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Abstract

Using inductively coupled plasma-optical emission spectrometry, the current study intends to explore the risks that heavy metals pose to human health and agricultural productivity (legumes, wheat, and potatoes) collected in Bangladesh. To determine Bangladesh's risk of soil pollution, a field investigation was conducted. The overall concentration of heavy metals (Cd, Cr, Cu, Pb, and Zn) as well as their bioavailable and water-soluble fractions were measured in the soil samples. All of the samples had levels of arsenic (As) and cadmium (Cd) below the limit of detection (LOD), whereas the potato samples had levels of Cd below the European Commission's (EC) maximum permissible level (MPL). The United States Environmental Protection Agency (USEPA) technique was used to compute the risk assessment associated with direct intake of agricultural goods. Lead (Pb) had the greatest mean concentration of harmful elements in the samples of legumes. All samples had levels of mercury (Hg) and lead (Pb) greater than LOD, whereas wheat samples had

lower Pb levels than EC. There was a reasonable range for the risk index. The calculated high hazard index values for mercury in wheat indicate a significant risk to human health. The findings indicate that the quantities of heavy metals were below the benchmarks used to evaluate the soil. There is controversy regarding the appropriate application of standard values classified by land utilisation to assess a potential danger relative to metal bioavailability, since only the soluble, exchangeable, and chelated metal species in the soils reflect the labile fractions available to plants. Standardising a trustworthy approach for determining the risk of heavy metals is advised.

Keywords: heavy metals, hazards, human health, agricultural products, productions

INTRODUCTION

Metals are lustrous, electrically conductive, extremely malleable substances that voluntarily give up their electrons to become cations. Metals are found naturally in the earth's crust, and the concentrations around them vary spatially due to the metals' varying compositions. The characteristics of the specific metal as well as certain environmental factors are utilised to monitor the atmospheric dispersion of metals [1]. In general, metals that negatively affect the environment and living organisms and have a density higher than 5 g/cm³ are referred to as heavy metals [2].

These metals are necessary for the functioning of many physiological and biochemical processes in living beings when they are present in incredibly low quantities; but, when these amounts are exceeded, they become hazardous. Heavy metal exposure is continuously happening and is becoming worse in many parts of the world, even though it is recognised to have several detrimental long-term health effects. Heavy metal toxicity is a major source of environmental contamination and a developing concern for ecological, evolutionary, nutritional, and environmental reasons [3, 4].

In contaminated agricultural soils, the heavy metals lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) are commonly found [5]. Because these inorganic chemical hazards are not biodegradable like organic toxins are, they have the potential to accumulate to hazardous amounts in the soil [6]. Given how commonly consumed rice is worldwide, it has emerged as a major dietary source of heavy metals, especially in Asia, where more than 90% of the world's rice is produced and consumed [7–10].

These pollutants may potentially pose a health risk to humans when taken through food. The accumulation of heavy metals is directly related to a number of diseases, such as diabetes, Alzheimer's disease, and various malignancies [11]. In addition to specific metals exhibiting specific signs of toxicity, the following general symptoms have been linked to poisoning with copper, lead, aluminium, zinc, mercury, cadmium, and arsenic: gastrointestinal (GI) dysfunctions, diarrhoea, stomatitis, shivering, hemoglobinuria causing a rust-red depression, and pneumonia (when volatile vapours and fumes are inhaled) (Figure 1) [12].

Long-term exposure may decrease the progression of muscular dystrophy, Parkinson's disease, and multiple sclerosis. Common side effects include allergies, and long-term exposure to any metal or any of its constituents can even cause cancer [13–15]. Cancer is known to be caused by lead. Increased levels of lead absorption have the potential to permanently damage the brain, kidneys, and central nervous system (CNS) [16]. Arsenic is a dangerous substance for human health because it weakens muscles, affects the neurological system, and coagulates protein [17]. Numerous earlier studies have demonstrated that inorganic mercury has the potential to be both teratogenic and embryotoxic. There have also been reports of gastrointestinal and cardiovascular effects from mercury consumption [18–20]. Cadmium is the reason for the increased risk of lung cancer [21]. There is a discernible drop in body weight when nickel consumption is high [22].

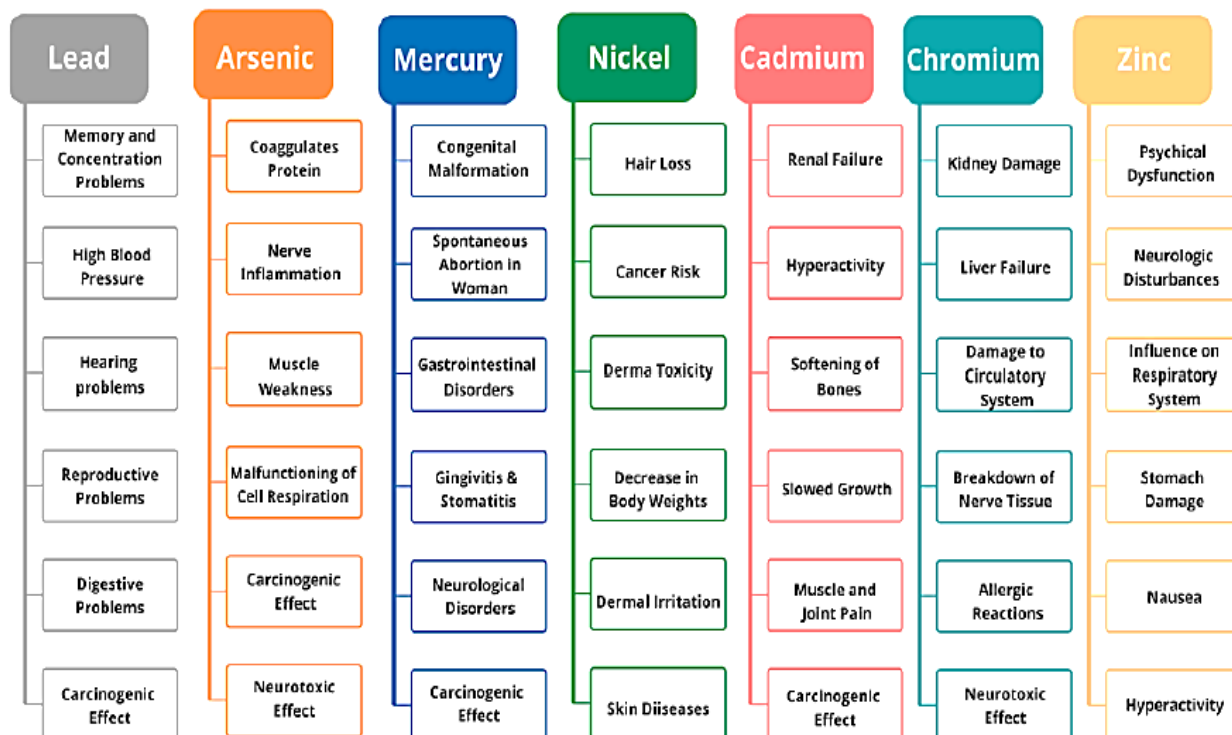


Figure 1: Effects of heavy metals on human health [12].

The most typical adverse reaction to a nickel overdose is hair loss. The most severe adverse health effects, such as chronic bronchitis, reduced lung function, and lung and nasal sinus cancer, have been associated to exposure to dust containing certain nickel compounds [23–25]. Numerous organs that show stress due to metal exposure have been found to have higher levels of glycogen when Cr and other metals coexist [26]. Zinc makes cardiovascular disease more likely. It could cause stomach injury, hypertension, and nausea. It is also accountable for the neurotoxic consequences on human health. Zinc overuse has the potential to cause psychic dysfunctions. Numerous changes in the neurological system are also brought about by the infusion of zinc into the body [27–29]. Heavy metals and metalloids (HMs) are examples of environmental pollutants. HMs are also regarded as pollutants in agricultural soil because they can negatively impact crop health and productivity when they are present in the soil at high concentrations [30]. Among the elements that are frequently found to contaminate agricultural soils and have detrimental effects on plants at elevated levels are Cd, Pb, Cr, As, Hg, Ni, Cu, and Zn [4, 31]. Among them, Cd, Pb, As, Hg, and Cr are exceedingly toxic and detrimental to plant health at almost any level of contamination [32–34]. Many materials fall under the category of essential mineral nutrients for plant growth and productivity. These elements can enhance a number of plant cellular functions at relatively low concentrations, including ion homeostasis, pigment synthesis, photosynthesis, respiration, enzyme activity, gene regulation, sugar metabolism, nitrogen fixation, etc [35]. When accumulated at concentrations above ideal, these same vital nutrients, however, can have adverse impacts on the growth, development, and reproduction of plants [36]. However, if the concentration falls below a predetermined level, they may also cause plants to show symptoms of a mineral deficit [37]. HM pollution of agricultural soil is a global issue. Aside from particular geological and climatic factors, growing industrial, municipal, agricultural, residential, medical, and technical applications, as well as rapid urbanisation, appear to be the main causes of the current environmental contamination caused by heavy metals (HM). However, the problem is more pervasive in many developing countries, perhaps due in part to the variables listed above as well as a lack of awareness regarding the detrimental effects of these elements on human and agricultural health [38–40]. The current study aims to evaluate the dangers that heavy metals pose to agricultural productivity and human health in an objective manner.

MATERIALS AND METHODS

Study was conducted in Bangladesh in 2023. Following methodologies were used.

Quantitative Methodology of Hazards of Heavy Metals and Risk Assessment

In the investigation, all chemicals (pH 65%, H₂O 70%, H₂O + Sulfuric Acid 70%) and standard stock solutions of hazardous metals with analytical grade (purity >99%) were utilised. For every dilution, double-distilled water was utilised. The agricultural lands served as the basis for the sample size. Regarding this, samples from Bangladeshi agriculture production were gathered in March 2023. Eighty samples in all were gathered: forty-two samples of legumes (chickpeas, lentils, and beans; n = 14), nineteen samples of potatoes, and nineteen samples of wheat. Following collection, each sample was given a label, kept in sterile polythene bags categorised by kind, and then sent to the lab for examination. To remove any potential surface contamination, distilled water was used to wash the obtained samples. Subsequently, the potato samples were diced using a knife, and all of the samples were dried at 100 °C in an oven. After that, the samples were placed in polyethylene bags to await examination after being ground into a fine powder in a commercial blender. In order to reduce the impact of the organic matrix and avoid the potential for sample contamination and analyte loss, the study's samples underwent acid decomposition in a closed vessel microwave oven system (Milestone Ethos D, with a maximum power of 1400 W and a maximum pressure of 100 bar in Teflon vessels). Samples of agricultural products were dried for 48 hours at 105°C after being cleaned with distilled water. Using an agate pestle, the dry samples were mashed, homogenised, and then separated into glass bottles pending analysis. After cleaning and soaking in a 10% nitric acid solution for the whole night, all of the glass containers were rinsed with deionized water. In the microwave digestion system, triplicate agricultural product samples (0.25 g) were processed for 30 minutes at a maximum temperature of 300 °C using 9 mL of nitric acid (65%) and 1 mL of hydrogen peroxide (70%). Next, the residue was put in a 10 mL volumetric flask and diluted with deionized water to a volume of 10 mL. The same procedure was used for a blank digest. Three duplicate analyses of each prepared sample were performed using an ICP-OES equipped with a flared end EOP Torch 2.5 mm type of torch. The radio-frequency (RF) generator (1400 W) was the ideal operating parameter; grade 6 argon gas was utilised for the nebulizer, plasma, and auxiliary gas. There was also no delay time between the replicate analysis and the delay time. The RF generator's frequency (resonance frequency) was 26.12 MHz, and the analysis was a three-time replicate. The solid state, detector, and spray chamber types were modified Lichte, cyclonic, and Charge Coupled Device (CCD), in that order. The sample delivery pump used was a four-channel, software-controlled peristaltic pump, which allows for precise sample flows. The prewash pump ran at 60 rpm for 15 seconds, 30 rpm for 30 seconds, and 45 seconds total. The sample injection pump ran at 30 rpm at the end.

Quantitative Methodology of Hazards of Heavy Metals on agricultural productions

Using a stainless-steel trowel, samples were obtained from the top 3 cm of the soil bank. Every sample is a composite made up of multiple subsamples that were gathered over a stretch of one metre in length. The sampling sites and the underlying geology and land use features (sample identification numbers 5, 11, 14, and 21). After being gathered, the samples were placed in plastic bags and brought to a lab. Every soil sample was allowed to dry at ambient temperature before being passed through a 2 mm grid sieve. Each sample weighed around 1 g when it was fixed with polymer resin. After that, a cross section polisher (JEOR, IB-09020CP) was used to clean and polish the surface of the fixed sample. Using a combination of energy dispersive X-ray spectroscopy (EDS) (JEOR, JSM-6010LA) and scanning electron microscopy (SEM), high-resolution pictures of the particle morphologies were observed, and spot elementary analyses were carried out. To ascertain the total quantity [28], the water-soluble amount (i.e., leaching by rainfall and/or land water) [29], and the bioavailable amount [30], three distinct heavy metal extraction techniques were used. In a beaker, 10 ml of concentrated HNO₃ (1+1) was combined with a 2.0 g sample, and the beaker was sealed with a watch glass. After being heated to 95°C, the mixture

refluxed for 15 minutes without boiling. The mixture was allowed to cool before 5 cc of concentrated HNO₃ was added and refluxed for 30 minutes without boiling. Once the mixture had cooled once again, 2 millilitres of water and 3 millilitres of 30% H₂O₂ were added, and the mixture was heated until the effervescence ceased. After the mixture cooled, 1-ml aliquots of H₂O₂ were added and heated until very little effervescence was present. By adding diluted HCl, the pH of the leachant, or deionized water, was brought to 5.6. Next, 100 ml of pH-adjusted water and 10.0 g of sample were put into a plastic bottle with a top. This bottle was shaken at 300 rpm for six hours while it was capped. To separate the metal components from the residues, the samples treated with the procedures underwent centrifugation and filtration. Then, using inductively coupled plasma-atomic emission spectrometry, the following elements were identified: Zn, Pb, Pd, Cr, and Cu.

Validation of the analytical method

The validation of the analytical procedure for quantitative analysis of elements in agricultural productions and its aqueous extracts was performed by evaluating selectivity, working and linear ranges, LOD, quantification limit (LOQ), re-peatability, and reproducibility (precision). Matrix effects were studied using standard addition method, by adding 200 µL of mixed standard solutions to the original samples. The recovery values were in the 94–105% range.

Agricultural/Health risk assessment

The Chronic Daily Intake (CDI) of detection of toxic metals due to ingestion of toxic metals via consumption of food products was calculated using the following Equation [39, 40]:

$$CDI = \frac{C \times IR_i \times ED_i \times EF_i}{BW \times AT}$$

C is the concentration of the toxic metal (mg.kg⁻¹); IR_i ingestion rate was set as (legume 19 g day⁻¹, wheat 320 g day⁻¹ and potato 58 g day⁻¹); ED_i is the exposure duration of toxic metals ingestion (24 years); EF_i, is the exposure frequency (350 days year⁻¹); BW, bodyweight average (70 Kg) and AT is the mean exposure years.

Statistical analysis

Chi-square tests and analysis of variance (ANOVA) were used in the statistical analysis, which was carried out with SPSS v.24. The mean of three separate studies (done in triplicate) is shown by the harmful metal contents. The data is displayed as the mean ± SEM value. A significance level of p < 0.05 was used.

RESULTS AND DISCUSSION

The standard solutions were used to create the calibration graphs for the hazardous metals at six different points, ranging from 0.50 to 16 µgL⁻¹. The instrumental response to all of the harmful metals showed linear connections, and the metal-containing solutions had negligible intercepts and correlation coefficients that varied from 0.9699 to 0.9991 for all samples. The ranges of perceived LOD and LOQ are, respectively, 0.05–2 and 0.16–6.60 µg/kg. It was discovered that the recoveries ranged from 93% to 106%, which is appropriate for all hazardous metals. Based on baseline signals and associated interferences at particular lines seen experimentally during the measurements, the wavelengths used to determine the elements concentration (Table 1). Table 2 lists the acceptable amounts of hazardous metals together with their contents in samples of potatoes, wheat, and legumes from the Markazi province. Table 3 presents the predicted threshold height (THQ) for exposure to heavy metals (Hg, Cd, and Pb) in food products (wheat, potatoes, and legumes) in Markazi province using a deterministic method.

Table 1: Quantitative assessment of heavy metals: Wavelength and method validation parameters

Element	Wavelength (nm)	R ² Value	Calibration range	Recovery (%)	LOD (µg/kg)	LOQ (µg/kg)
As	188.032	0.9991	0.3–1200	93	1	3.28
Cd	221.346	0.9699	0.3–1200	97	0.04	0.17
Hg	162.870	0.9899	0.3–1200	100	0.25	1.15
Pb	263.288	0.9918	1.2–1200	106	3	6.40

Table 2: Quantitative Comparison of heavy metals: Agricultural Productions

Type of food samples	Mean ± SD				P-value			
	As	Cd	Hg	Pb	As	Cd	Hg	Pb
Legume (n = 60)	---	---	35.45 ± 6.36	562.17 ± 34.39	0.000	---	0.005	0.000
Wheat (n = 30)	---	---	39.54 ± 7.26		0001	---	0.000	---
Potato (n = 30)	---	27.46 ± 2.33	17.47 ± 1.67	390 ± 12.61	0020	0.000	0.000	---

The results of the three heavy metal measurements were comparable, hence the average values are displayed as representative data without further explanation. As previously mentioned, energy-dispersive X-ray spectroscopy (EDS) in conjunction with scanning electron microscopy (SEM) was used to conduct this investigation, and the findings are shown in Fig. 2. Figure 2 indicates that each sample had significant concentrations of Si in addition to O and C. The interpretation of these high contents is as follows. As previously indicated, the majority of the soil samples were taken in sandstone. Sand-sized silicate grains make up the majority of the clastic sedimentary rock known as sandstone [31]. The silicon-oxygen (SiO₄)⁴⁻ tetrahedron is the fundamental unit of all silicate formations. The biggest known terrestrial carbon store is found in soil [38]; globally, soil carbon can store a lot more carbon than carbon found in vegetation and the atmosphere combined. As a result, it is believed that each sample naturally contains large amounts of soil carbon, silicon, and oxygen. This perspective could help explain why SEM/EDS was used to determine the large levels of Si, O, and C. It has been demonstrated that materials like alumina and silica (SiO₂) interact with heavy metal ions to increase the effectiveness of solidification [39]. Therefore, even though the soil samples do contain some heavy metals, it's probable that a plentiful Si limit the mobilities and availabilities of these elements. Adsorption and precipitation are commonly used in low-cost soil stabilisation methods to reduce heavy metal availability and mobility [39]. Much research has been done on the production and use of natural and synthetic materials such zeolite, ferrihydrite, apatite, and lime in the search for effective stabilisers [40]. Three different metal concentrations were measured for each sample: the total, the water-soluble fraction, and the bioavailable component. The main cause of lead contamination in inhabited soil is the degradation, chipping, scraping, sanding, and sandblasting of lead-based paint-bearing structures [41]. The use of lead arsenate, a pesticide, in fruit orchards and the exhaust from lead fuel, an anti-knock component, were once the main causes of lead contamination [42]. Although lead emissions from automobiles have virtually halted since leaded petrol was phased out, lead can persist in soil for hundreds of years [43]. In light of the low amounts of Cd, Cr, Cu, and Zn, it is believed that no significant sources of emissions of these metals, such as Cd-releasing mining and smelting operations or Cu-releasing mining and manufacturing activities, are located in close proximity to the studied region. All of the measured metals, with the exception of lead (Pb), had very low overall levels; however, given the relatively small amounts of water-soluble and bioavailable fractions, the majority of the metals are in non-available forms. Furthermore, it is conceivable to hypothesise that the elevated soil Si concentrations may hinder metal solubility and movement to some extent.

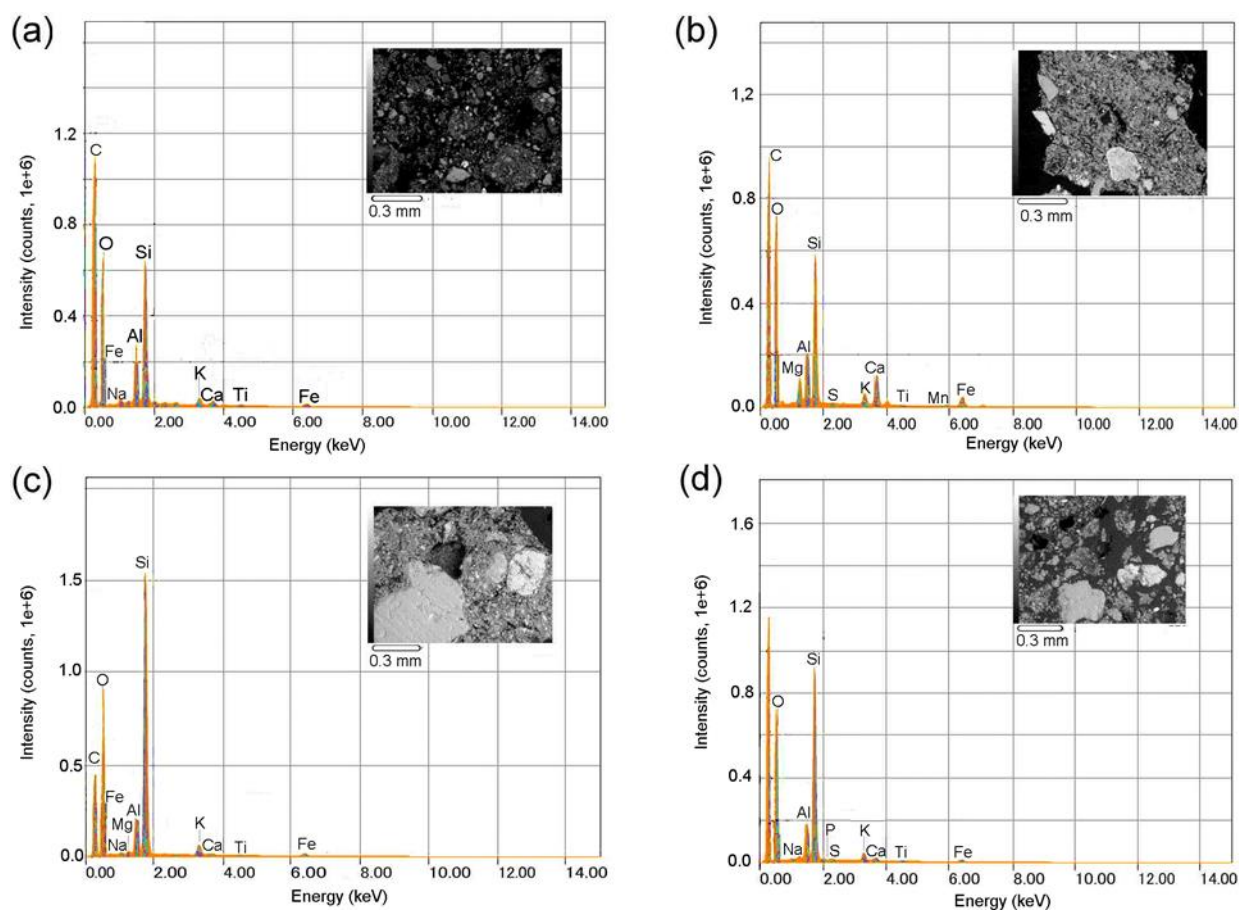


Figure 2 (a-c): EDS spectrum and SEM pictures of the soil samples

CONCLUSION

Metals classified as heavy have a very high density and can be hazardous in very little amounts. In tiny amounts, the common heavy metal contaminants are present everywhere. Aquatic habitats are contaminated by heavy metals from a variety of sources, including e-waste, home effluents, air sources, and other metal-based businesses. The raising of aquatic animals and other organisms is known as aquaculture. Aquaculture population declines due to heavy metal toxicity, which also pollutes the aquatic environment and causes morphological malformations in species. Fish illnesses are caused by these heavy metals that are poisonous. Fish eating has an indirect impact on people because of this. The introduction of heavy metals into aquatic ecosystems and water bodies has a significant effect on the food chain. Because these heavy metals remain for longer periods of time and have the ability to bioaccumulate, they have a bigger impact on the ecosystem and deteriorate the quality of water. There is little chance of heavy metal contamination in the research region, according to a comparison between these threshold values and the data that were obtained. However, in order to accurately estimate the potential risk in soils—which are typically subjected to a range of land uses—it is crucial to comprehend the distinction between the total amount and the bioavailable portion of the heavy metals. The findings demonstrated that all sample types (potatoes, wheat, and legumes) had As and Cd concentrations below LOD and that the concentration of Cd in potato samples was lower than the MPL of EC. Wheat is consumed at a higher rate than potatoes and legumes, it has been identified as the primary source of exposure to hazardous metals. Since the present values of soil quality guidelines can exaggerate the possible harm, it is recommended to establish an assessment approach based on the amount of bioavailable heavy metals. It is advised to conduct additional study to determine the probable causes of toxic metal contamination, as well as to consider control or remedial measures and ongoing agricultural product monitoring. Farmers, artisans, and other community members should also be aware of the risks associated with eating

food contaminated with toxic metals in the Markazi province. By offering guidance and taking appropriate action, these groups can lower the amount of toxic metals in food.

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