

Accumulation and health risk from heavy metals in agricultural crops in the Mantaro Valley in the central Andes of Peru

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ABSTRACT

Cultivation of food crops in soils contaminated with heavy metals (HMs) can pose serious risks to human health. In this study, we evaluated HMs accumulation in soils and agricultural products (corn, broad beans, artichoke and alfalfa), the degree of soil contamination, and the associated health risks from three food crops using the Monte Carlo simulation model. The results revealed elevated concentrations of As, Cd, Cu, Pb and Zn in the soils, exceeding the maximum permissible limits established by both national and international standards. Soil contamination levels were particularly high for Cd, Pb and Zn. Ecological risk was also found to be very high for Cd, with artichoke-cultivated soils contributing most significantly to ecological risk. Alfalfa and artichoke tissues showed higher concentrations of As, Cd and Pb, whilst broad beans accumulated more Zn and Cu. Artichoke and alfalfa samples exceeded food safety limits for Pb. Artichoke, broad beans and corn are not HMs accumulators, as their accumulation factors were below 1. Non-carcinogenic health risks from broad beans consumption were close to the threshold hazard index of 1, suggesting a probability of adverse health effects due to HMs exposure. Broad beans and corn posed the highest carcinogenic risks, with unacceptable risk probabilities exceeding 55% in both children and adults. Arsenic and nickel showed the greatest contribution rates to carcinogenic risk in both groups. These findings suggest that food crops cultivated in HMs-contaminated soils present significant health risks for consumers. Therefore, it is necessary to adequately inform the population about these risks and to promote monitoring and management strategies that ensure food safety.

1. Introduction

Soil is a fundamental natural resource that underpins food security, the quality of agricultural products, and human health, thereby ensuring human survival and social development (Chai et al., 2021; Liu et al., 2016; Zhao et al., 2022). It represents the largest sink for heavy metals, which derive from diverse pollutants generated by human activities (Gong et al., 2024). Industrial activity, transport emissions, and the application of agricultural fertilizers and pesticides are the principal contributors to soil contamination, leading to the accumulation of heavy

metals (HMs) such as As, Cu, Zn, Fe and Pb (Ma et al., 2023; Xu et al., 2024). Wastewater (Alamer and Galal, 2022; Cao et al., 2022), atmospheric deposition (Liu et al., 2016), smelting activities (Xiao et al., 2019), and vehicular traffic (Yang et al., 2022) are also important sources of contamination.

The term “heavy metals” is widely used in the environmental science literature, particularly in studies on environmental contamination (Pourret and Hursthouse, 2019). However, no authoritative definition has been issued by any organization or regulatory body (Duffus, 2002; Roveta et al., 2021). Consequently, operational definitions typically rely

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on periodic table criteria, encompassing transition elements, rare earth elements, metalloids, and certain non-metals with similar properties (Duffus, 2002; Roveta et al., 2021).

Soil contamination by HMs is a major environmental problem that has received considerable global attention due to their toxicity and persistence (Aradhi et al., 2023; Wan et al., 2022), as they cannot be degraded by microorganisms (Yang et al., 2022). Heavy metals can alter soil properties and interfere with nutrient uptake in plants (Chai et al., 2021; Wan et al., 2022). Most HMs are not essential elements for plants and may accumulate along the food chain, posing a serious threat to soil ecosystems and human health (Zang et al., 2017). Excessive intake of HMs can lead to severe health problems; their toxicity affects the neurological, skeletal, reproductive, cardiovascular and endocrine systems, as well as causing hepatic and renal damage (Abd Elnabi et al., 2023; Briffa et al., 2020; Fulke et al., 2024). To evaluate the degree of contamination and ecological risk, contamination indices and potential ecological risk indices are commonly applied in soils with agricultural crops (Chai et al., 2021; Kang et al., 2020; Sheng et al., 2023). Ecological risk assessment is a widely used tool to evaluate the impact of HMs on ecosystems (Kuerban et al., 2020). It incorporates both the toxicity response coefficient and the background value of each metal to provide a comprehensive assessment of the ecological risk posed by HMs (Gan et al., 2022).

The transfer of HMs from soils to the edible parts of plants constitutes the principal pathway by which HMs enter the food chain, with implications for human health (Sharma et al., 2018). Consequently, health risk assessment is another effective tool for estimating the potential effects of HMs on both children and adults, and for preventing threats to human health (Chen et al., 2021). This assessment includes deterministic methods, which may yield less reliable results due to the inability to account for uncertainty, and probabilistic methods such as Monte Carlo simulation, which incorporates uncertainty and the sensitivity of exposure pathways, thereby providing a more reliable risk evaluation (Kong et al., 2025; Wang et al., 2025; Zhao et al., 2022).

In the Mantaro Valley, located in the Junín region of Peru, there are 25 districts where farmers have irrigated their crops (corn, broad beans, artichoke) and pastures with water from the Mantaro River for more than 80 years (MINAGRI, 2011). However, several tributaries of the river receive wastewater discharges from mining and industrial activities, as well as from urban centers. For example, Pb concentrations in Mantaro River water have shown high contamination levels in the area adjacent to the slag deposit, and soils in the city of La Oroya Antigua have accumulated elevated Pb levels (Arce and Calderón, 2017). The same authors reported that the University of Saint Louis Missouri detected high blood Pb levels in children in 2005, along with other metals in La Oroya and in Concepción (control site), indicating that the problem of environmental contamination is not restricted to La Oroya but extends throughout the Mantaro basin.

Heavy metals are present in the agricultural soils of the Mantaro Valley primarily due to continuous irrigation with Mantaro River water, which receives discharges from upstream mining and metallurgical operations (Custodio et al., 2020). In addition, the long-term use of phosphate- and nitrogen-based fertilizers and pesticides—commonly applied to enhance agricultural productivity—may further contribute to metal accumulation in soils. Despite the agricultural importance of the valley and its role as the main food production area for central Peru, the extent of HMs contamination in cultivated soils and the degree of potential consumer exposure remain largely unknown. This situation represents a regional concern, as the presence of HMs in crops may compromise food safety and public health.

Although previous studies, such as those by Custodio et al. (2020, 2021), have quantified concentrations of Cu, Fe, Zn, Pb, and As in corn, barley, and artichoke grown in the province of Concepción, our study substantially expands the geographic scope to include the provinces of Huancayo, Concepción, and Jauja on both margins of the Mantaro River. It also incorporates and compares HMs contamination (As, Cd, Cr, Cu,

Fe, Ni, Pb, and Zn) in soils and in multiple representative crops of the Mantaro Valley (corn, broad beans, artichoke, and alfalfa). Furthermore, it contrasts deterministic and probabilistic human health risk assessments, providing a more comprehensive and representative understanding of contamination patterns and potential oral exposure risks in this important agricultural region of the central Andes. Therefore, the results of this study will provide essential baseline information to support the implementation of policies and monitoring strategies for HMs in agricultural soils and crops in the area, and to protect these agroecosystems.

Throughout the entire valley, during the dry season, farmers use water from the Mantaro River to irrigate extensive agricultural fields. They grow crops such as corn, broad beans and artichoke for local consumption and for supplying regional and national markets. These foods of plant origin provide nearly all essential human nutrients, thereby playing a crucial role in nutrition and promoting health. However, the level of contamination in these agricultural soils remains unknown, which is a regional concern given that heavy metals can compromise food security and consumer health. Therefore, we established the following objectives: (1) to evaluate the heavy metal content in agricultural soils and crops, (2) to assess the level of contamination and the ecological risk index associated with heavy metals in agricultural soils and (3) to evaluate the non-carcinogenic and carcinogenic human health risks associated with the consumption of agricultural products irrigated with water from the Mantaro River.

2. Materials and methods

2.1. Study area

The study was carried out in agricultural plots located in the provinces of Jauja, Concepción and Huancayo, in the Junín region, on both the left and right banks of the Mantaro Valley (Fig. 1), between the geographical coordinates 12°2'36.18"S, 75°14'31.77"W and 11°46'19.05"S, 75°31'18.61"W. The valley is characterized by a dry, temperate climate, with minimum temperatures of −10 °C and maximum temperatures of 21 °C, and an average annual precipitation of 730 mm. The total agricultural area devoted to major food crops covers 49,507 ha. In the highlands of the Junín region, 74.9% of the agricultural area is rain-fed, while 25.1% is irrigated (MINAGRI, 2011). The predominant agricultural crops in the Mantaro Valley are corn and alfalfa, followed by broad beans and artichokes.

The study area is characterized by soils with loam textures. Sand, silt, and clay contents exhibited limited variation among plots, with sand ranging from 45.7 to 51.5%, silt from 30.9 to 34.0%, and clay from 14.5 to 23.0%. Soil electrical conductivity ranged from 18.1 to 47.2 mS/m, with lower values in corn and alfalfa plots and higher values in broad beans and artichoke plots. Soil pH varied narrowly between 7.4 and 7.6, indicating slightly alkaline conditions. Organic matter content ranged from 3.1 to 4.0%, with the highest levels occurring in alfalfa soils. The cation exchange capacity was consistently low across all agricultural plots (<5 meq/100 g) (Tabla S1).

2.2. Soil sampling and sample preparation

The sampling design was carried out considering the agricultural representativeness of the Mantaro Valley. A total of 100 soil samples were collected, providing adequate coverage of the geographic heterogeneity across the provinces of Huancayo, Concepción, and Jauja. Samples were obtained from the predominant crops irrigated with water from the Mantaro River. The number of samples assigned to each crop was intentionally unequal and based on their relative importance in terms of cultivated area and local consumption (INEI, 2023). Accordingly, corn (n = 35) and alfalfa (n = 35) were prioritized due to their extensive cultivation and frequent use, followed by broad beans (n = 20) and artichoke (n = 10). This approach ensured that analytical

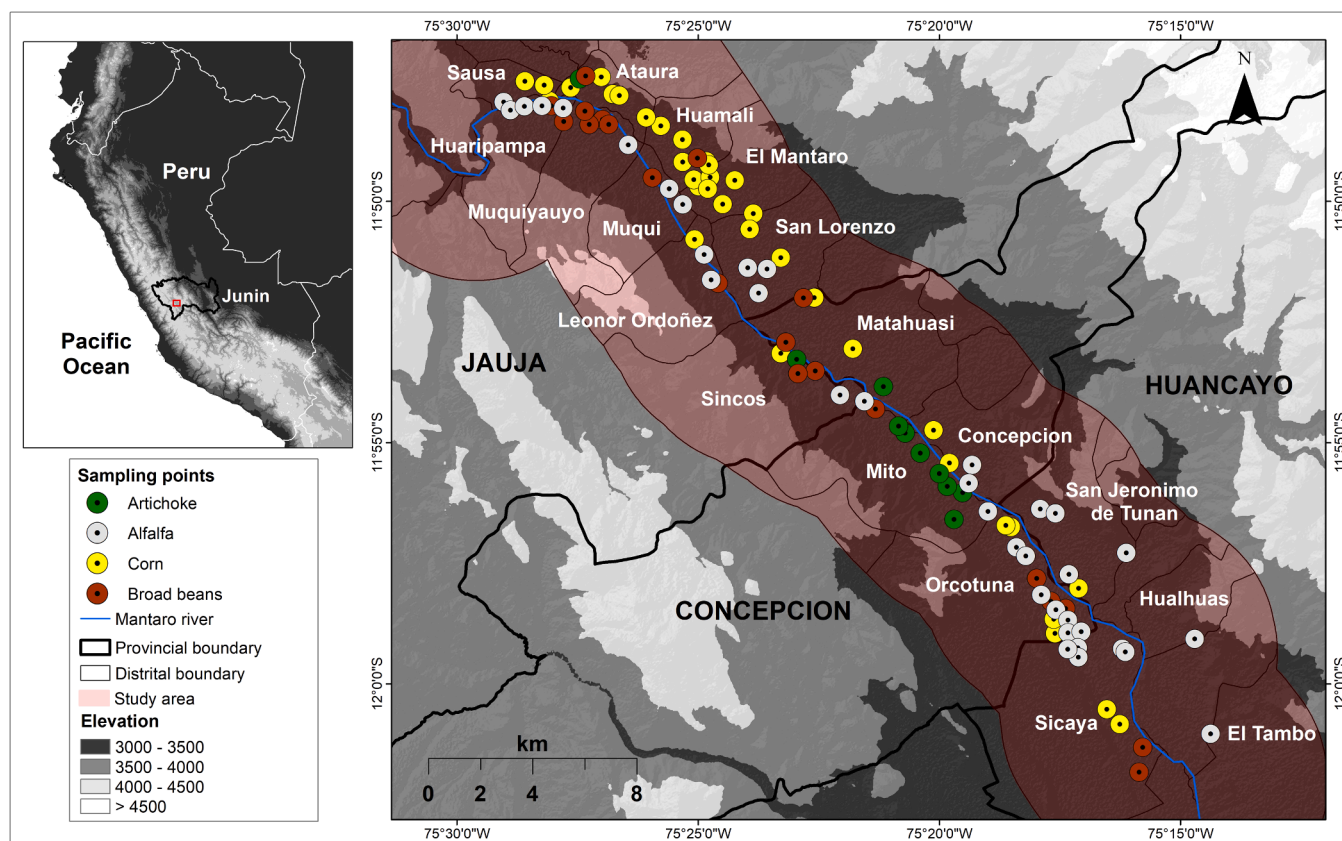


Fig. 1. Location map of soil and crop sampling sites in the provinces of Huancayo, Concepción and Jauja irrigated with Mantaro River water.

efforts were focused on the most representative agro-production systems of the Mantaro Valley.

Soil samples were collected at a depth of 20 cm. At each sampling point, eight subsamples were taken, composited, and homogenized to obtain a 2-kg soil sample following the guidelines of the Ministry of Environment (MINAM, 2014). Samples were air-dried for three days, sieved through a 2-mm stainless-steel mesh, homogenized, weighed, sealed in airtight polyethylene bags, labeled, and transported to the Soil, Water, and Plant Laboratory of the National Institute for Agricultural Research (INIA, Lima). From each composite sample, 250 g were allocated for heavy metal analysis, and 1000 g were used for the determination of soil physical and chemical properties (INIA–Ayacucho).

2.3. Collection and preparation of agricultural crop samples

Between January and March 2023, crop samples were collected from the same soil sampling points. For broad beans, 20 pod samples (3 kg each) were collected, placed in polyethylene bags, and stored in 50 L polystyrene thermal boxes with cooling gels. Then, the fresh pods were peeled and 1000 g of each sample was weighed. For corn (*cuzqueado* variety), 35 samples of 3–5 kg each were collected. The cobs were manually shelled, and 1000 g of kernels were weighed per sample. For *Creole* artichokes (inflorescences), 10 samples were collected, while for alfalfa 35 samples of 3 kg each were obtained. In the laboratory, 1000 g of artichoke (flower head, without stem or spines) and 1000 g of alfalfa (aerial part, free of weeds and plant residues) were weighed. All samples were then packaged and transported to the National Agricultural Health Service of Peru (SENASA) for chemical analysis.

2.4. Heavy metal content in soil and plant tissue samples

For soil samples, 0.5 g of each sample was weighed and digested with

10 mL of 99.99% concentrated nitric acid in a microwave oven for 30 min. The digested samples were then transferred into 50 mL centrifuge tubes, brought to volume with ultrapure water, shaken, and left to settle for 12 h. Concentrations of As, Cd, Cr, Cu, Fe, Ni, Pb and Zn were measured using inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer, NexION 2000X). Blank samples and duplicates were analyzed, along with calibration blanks (USEPA, 2014). Accuracy and precision of element determination were within 10% (relative deviation and error). For quality control of soil metal analyses, the certified reference material *Metals in Soil* (PT Round 118, Lot D118–540) was used for proficiency testing. Recovery values ranged from $98.9 \pm 5.6\%$ to $100.9 \pm 5.3\%$ for the analyzed heavy metals (Table S2). Limits of detection (mg kg^{-1}) for As, Cd, Cr, Cu, Fe, Ni, Pb and Zn in soil were 0.03, 0.02, 0.09, 0.07, 1.98, 0.04, 0.07 and 0.14, respectively.

For corn, broad beans, artichoke and alfalfa samples, the plant material was oven-dried at 60°C for 72 h and then ground using a mechanical pulverizer. Between 0.5 and 0.6 g of each sample was weighed and placed into digestion tubes. Digestion was performed with 6 mL ultrapure HNO_3 , 0.25 mL ultrapure HCl , and 2 mL 30% H_2O_2 in a microwave digester for 20 min. The digested solutions were brought to 50 mL with ultrapure type I water and filtered through $0.45 \mu\text{m} \times 25 \text{ mm}$ non-sterile syringe filters. Concentrations of As, Cd, Cr, Cu, Fe, Ni, Pb and Zn in food samples were determined by microwave-assisted digestion (FDA, 2015) using an inductively coupled plasma mass spectrometer (ICP-MS; Thermo, ICAP RQ, ICAPRQ01712) at the National Health Service laboratory. Certified reference materials were used to ensure the reliability of results. Blank samples and duplicates were analyzed, with accuracy and precision of element determination within 5% (relative deviation and error). The accuracy of the method was verified using the proficiency testing (PT) reference material FAPAS 07447 – *Metallic Contaminants in Berries*. Recoveries for all elements ranged from 93% to 115% (Table S3). Limits of detection (mg kg^{-1}) for

As, Cd, Cr, Cu, Fe, Ni, Pb and Zn in crop samples were 0.09, 0.03, 0.10, 0.20, 0.30, 0.06, 0.25 and 0.30, respectively.

2.5. Assessment of soil contamination and potential ecological risk from heavy metals in agricultural land

2.5.1. Contamination factor (CF)

The CF was defined as the ratio between the concentration of each metal in the soil and its concentration in uncontaminated soil (geochemical background value). It is an indicator of contamination from anthropogenic inputs associated with a single heavy metal (Hakanson, 1980), and was calculated using the following Equation (1):

$$CF = \frac{C_i}{C_b} \quad (1)$$

where C_i is the concentration of the heavy metal in the soil sample (mg kg^{-1}), and C_b is the reference value for each metal, representing its concentration in soil without anthropogenic input (mg kg^{-1}). Since background values of metals in soils are not available for Peru, the background values reported by Taylor and McLennan (1995) were used. CF was classified into four categories (Table S4).

2.5.2. Potential ecological risk

The toxicity and potential ecological risks of metals in the soil were evaluated using the method proposed by Hakanson (1980). The potential ecological risk index (RI) was calculated to assess the harmful effects of all heavy metals in the studied soils, according to Equations (2) and (3):

$$ERI = T_r^i \times \frac{C_i}{C_b} \quad (2)$$

$$RI = \sum_{i=1}^m ERI \quad (3)$$

ERI: is the potential ecological risk index of an individual metal i .

T_r^i : represents the toxic-response factor of metal i .

The toxic-response factors for As, Cd, Pb, Ni, Cr, Cu, Fe, and Zn (mg kg^{-1}) were 10, 30, 5, 5, 5, 2, 1, and 1, respectively. The classification of the ecological risk index associated with an individual metal (ERI) and the potential ecological risk index (RI) are presented in Table S4.

2.6. The accumulation factor (AF)

The AF was used to determine the potential for heavy metals to migrate from soil (C_{soil}) to plant tissues (C_{crop}) (Ahmed et al., 2022; Yang et al., 2022). The calculation equation was as follows:

$$AF = \frac{C_{\text{crop}}}{C_{\text{soil}}} \quad (4)$$

2.7. Health risk assessment

2.7.1. Non-carcinogenic and carcinogenic risk

In the assessment of human health risks, the target hazard quotient (HQ) and target cancer risk (CR), associated with heavy metals through the dietary exposure pathway, were evaluated (Su et al., 2023). HQ, HI, CR, and TCR were calculated using Equations (5–9):

$$HQ = \frac{EDI}{RfD} \quad (5)$$

The estimated daily intake (EDI) of the risk elements was calculated using the following equation (Wei et al., 2020):

$$EDI = \frac{C_{\text{crop}} \times IR_{\text{crop}} \times EF \times ED}{BW \times AT} \quad (6)$$

where C_{crop} is the concentration of metals in the crops (mg kg^{-1}); IR_{crops} represents the average daily consumption rate of vegetables (Table S5); EF is the exposure frequency (365 d year^{-1}); ED is the exposure duration (6 years for children and 30 years for adults). BW is the average body weight (18 kg for children and 70 kg for adults); AT is the average exposure time for carcinogenic risks ($365 \text{ days} \times 70 \text{ years}$).

$$HI = \sum_{i=1}^n HQ \quad (7)$$

$$CR = EDI \times SF \quad (8)$$

$$TCR = \sum_{i=1}^n CR \quad (9)$$

where EDI refers to the estimated daily intake through the ingestion pathway in $\text{mg kg}^{-1} \text{ d}^{-1}$. RfD is the reference dose of each metal in $\text{mg kg}^{-1} \text{ d}^{-1}$. The RfD values for As, Cd, Cr, Cu, Fe, Ni, Pb, and Zn are 0.0003, 0.0001, 0.003, 0.04, 0.7, 0.02, 0.004, and $0.3 \text{ mg kg}^{-1} \text{ d}^{-1}$, respectively (USEPA IRIS, 2019). HQ is the non-carcinogenic risk of individual elements; HI is the non-carcinogenic risk of multiple elements, expressed as the sum of HQ values. If $HI > 1$, it indicates an increasing non-carcinogenic risk, and vice versa for $HQ < 1$. CR refers to the carcinogenic risk of individual toxic elements; SF is the cancer slope factor for each chemical element studied. The SF values for As, Cd, Cr, Ni, and Pb are 1.5, 0.6, 0.5, 1.7, and $0.0085 \text{ mg kg}^{-1} \text{ d}^{-1}$, respectively (USEPA IRIS, 2019). TCR is the cumulative carcinogenic risk. The acceptable cancer risk range is between 10^{-6} and 10^{-4} (Jalil et al., 2022). Values exceeding 10^{-4} indicate significant effects and risks of developing cancer, whereas values below 10^{-6} are considered to have non-significant health effects.

2.8. Data analysis

One-way analysis of variance was used for the variable's concentration of metals in soils, crops, and accumulation factor according to crop type. Tukey's post hoc tests were used to assess differences between variables. The Monte Carlo simulation method was used to estimate the probability of non-carcinogenic and carcinogenic risk associated with exposure to HMs through the consumption of corn, artichokes and broad beans. To ensure the accuracy of our results, the simulation included 10,000 iterations for the parameters defined in the health risk assessment (Islam et al., 2024). All analyses and graphs were developed using the R Core Team 2015.

3. Results and discussion

3.1. Concentration of HMs in soils according to type of agricultural crops

The concentration of heavy metals (HMs) in soil varied across crop types (Table 1). Overall, the mean concentration trend in agricultural soils followed the order $\text{Fe} > \text{Zn} > \text{Pb} > \text{Cu} > \text{As} > \text{Cr} > \text{Ni} > \text{Cd}$. The concentrations of As, Cd, Cu, Pb, and Zn in the alluvial soils irrigated with water from the Mantaro River were extremely high, exceeding the maximum allowable limits established by national and international guidelines (CCME, 2021; MINAM, 2017a), with the exception of Cr and Ni. Significant differences in HMs concentrations were observed among soils under different agricultural crops. Soils under artichoke and broad beans cultivation exhibited the highest concentrations of As, Cd, Cu, Fe, Pb and Zn. These were followed by soils under alfalfa cultivation. In contrast, soils under corn cultivation showed lower concentrations of all elements studied except Ni. The content of HMs in soils according to crop type followed the trend: artichoke > broad beans > alfalfa > corn. These results may indicate that soils under artichoke and broad beans cultivation are more contaminated than those under alfalfa and corn cultivation.

Table 1Concentration of heavy metals (mg kg⁻¹) in agricultural soils according to crop type.

Crops	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Artichoke	147.5 ± 37.87 ^b	9.24 ± 3.07 ^b	14.8 ± 2.87 ^a	479 ± 171.1 ^b	40,275 ± 4275 ^b	15.3 ± 1.234 ^b	1193 ± 487 ^b	2951 ± 1002 ^b
Alfalfa	107.5 ± 14.55 ^{ab}	6.37 ± 0.644 ^{ab}	19.2 ± 1.97 ^a	246 ± 46.3 ^{ab}	32,272 ± 1806 ^{ab}	18.7 ± 0.796 ^{ab}	583 ± 125 ^b	1925 ± 344 ^b
Corn	70.1 ± 9.62 ^a	3.3 ± 0.587 ^a	23.9 ± 2.49 ^a	130 ± 24.8 ^a	29,433 ± 1670 ^a	20.3 ± 0.873 ^a	266 ± 58 ^a	903 ± 164 ^a
Broad beans	166.4 ± 30.2 ^b	6.97 ± 1.64 ^{ab}	22.3 ± 3.07 ^a	371 ± 93.7 ^b	38,838 ± 2915 ^b	18.9 ± 1.077 ^{ab}	889 ± 257 ^b	2710 ± 651 ^b
Minimum	20.63	0.05	1.00	20.06	17,991	8.09	25.98	98.19
Maximum	764.33	34.98	120.97	1142.55	88,240	52.50	3524.59	11,263.41
CV%	125.466	136.32	65.46	129.62	41.552	29.43	151.13	133.46
EQSS	50	1.4	-	-	-	-	70	200
CSQG-CCME	12	1.4	65	63	-	45	70	200
UCC	13	0.3	35	25	35,000	50	20	71

The coefficients of variation (CV) for the analyzed metals were Pb > Cd > Zn > Cu > As > Cr > Fe > Ni. The elements Pb, Cd, Zn, Cu y As exhibited pronounced variability in their degree of enrichment, influenced by both crop type and environmental and anthropogenic factors. In contrast, Ni showed moderate variability, characterized by a narrow range and a relatively homogeneous spatial distribution. Cr and Fe displayed high spatial variability within the soil–crop system. Collectively, these findings indicate that all evaluated metals may be affected, to varying degrees, by human activities, and that crop type plays a key role in shaping soil metal enrichment patterns.

EQSS (Environmental Quality Standard for Soil) (MINAM, 2017a); CSQG-CCME (Canadian Soil Quality Guidelines) (CCME, 2021); UCC (Upper Continental Crust) (Taylor and McLennan, 1995)

Our results differ from those reported by Jalil et al. (2022) and Liu et al. (2024), who noted that heavy metals (Cu, Ni, Pb, and Zn) in cultivated soils irrigated with wastewater and freshwater did not exceed recommended standards, with the exception of Cd in soils irrigated with both wastewater and freshwater. Similarly, (Islam et al., 2024), in corn fields in the alluvial plain of the Ganges Delta in Bangladesh, reported very low concentrations of Zn, Cu, Ni, Cr, As, Pb, and Cd in soils, lower than those found in this study. In soil samples from artichoke cultivation in Concepción, Junín, (Custodio et al., 2021) reported concentrations of Pb and As above those regulated by Peruvian standards. The levels of metals in the present study were much higher than those in previous studies, and the concentrations of heavy metals could pose potential threats due to their continuous accumulation in the surrounding ecosystem.

The high levels of As, Cd, Cu, Pb, and Zn in soils under different crops could be attributed to soil characteristics and external anthropogenic inputs. The retention of As, Cd, Cu, Pb, and Zn in the Mantaro Valley soils may be influenced by the slightly alkaline pH, the moderate organic matter content, the low CEC, and the electrical conductivity. High pH and soil organic matter enhance metal adsorption and complexation, thereby reducing their mobility, whereas the low CEC limits their immobilization (Alloway, 2013; Kabata-Pendias, 2011; Zeng et al., 2011). Moreover, HMs levels in Mantaro River irrigation water did not exceed national standards (MINAM, 2017b) (Table S6), suggesting limited current contributions from irrigation. Nonetheless, past emissions from the former La Oroya Metallurgical Plant (closed in 2012) may explain historical metal inputs to soils. Previous studies reported elevated As and Pb values in Mantaro River water (Chira et al., 2022). Between 2008–2012, Pb levels exceeded national standards by 20-fold and As levels by 12-fold in the Mantaro River at La Oroya (Serrano, 2017). Emissions of Pb, Cd, and As from the La Oroya smelter during its 87 years of productive activity would have affected around 2300 km² of soils in the central region (Arce and Calderón, 2017). These findings could be attributed to the retention of HM in the soil, influenced by soil pH, the chemical speciation of the metal ion, HMs competition, soil composition, and soil aging (Bradl, 2004; K. Sharafi et al., 2024).

The variation in HMs concentration in soils according to crop type could be attributed to variations in crop management techniques such as planting intensity, crop irrigation, fertilizer application, and interactions

of soil properties with HMs (Jing et al., 2023; Pastor et al., 2024). Therefore, soils cultivated with artichokes and broad beans would be more affected than soils under alfalfa and corn cultivation. Artichoke and broad beans crops require the continuous application of chemical fertilizers and pesticides to increase the yield of their agricultural products (Qitong and Mingkui, 2017; Wei et al., 2016). Several researchers have reported that phosphate and nitrogen fertilizers commonly used not only contain essential nutrients for plant growth and development but also introduce toxic metals such as As, Cd, Pb, Cu, and Zn (Cai et al., 2019; Chen et al., 2020; Gu et al., 2014; Hu et al., 2018; Solgi et al., 2018). The presence of As, Cd, Cu, Pb, and Zn may stem from multiple agricultural and anthropogenic inputs, including manure, inorganic fertilizers, pesticides, and historically contaminated irrigation water (Bouaroudj et al., 2024; Zhao et al., 2024). Vehicular emissions also contribute notably to Pb, Cu, and Zn accumulation given the proximity of the agricultural pots to major roads (Cai et al., 2019; Gu et al., 2014; Hu et al., 2018). Additional inputs may originate from atmospheric deposition in agricultural soils (Yu et al., 2024), a process likely intensified by historical emissions from the former La Oroya smelter, a major source of Pb, Zn, As, and Cu dispersed by prevailing north–northwest winds (Álvarez-Tolentino and Suárez-Salas, 2020). These elevated HMs contents in agricultural soils could lead to the deterioration of soil functions, affect crop quality, and pose a lethal risk to animals and humans (Cao et al., 2024).

3.2. Pollution and ecological risk from HMs in soils according to crop type

The contamination and ecological risk indices for HMs in soils are presented in Table 2. Agricultural soils irrigated with Mantaro River water exhibited varying levels of contamination. Overall, contamination factors (CF) followed the order Pb > Zn > Cd > As > Cu > Fe > Cr > Ni. Lead (Pb), zinc (Zn), and cadmium (Cd) showed the highest levels of soil contamination under all four crops. As and Cu exhibited very high contamination in soils under artichoke, broad beans, and alfalfa, and considerable contamination in corn soils. Iron (Fe) showed moderate contamination in artichoke and broad beans soils and low contamination in corn and alfalfa soils. Whereas, Cr and Ni displayed low contamination across all crop types, this could indicate that their sources and mobility in the soil have less impact on agricultural practices (Chen et al., 2023). In total, 41% of sampling sites showed very high contamination for As, 58% for Cd, 35% for Cu, 49% for Pb, and 64% for Zn.

Very high soil contamination showed the same trend as HMs content in soils according to crop type (artichoke > broad beans > alfalfa > corn). Artichoke soils were the most impacted, likely due to repeated fertilizer and pesticide applications during the crop's growth cycle (Quispe Rodríguez and Quispe Medrano, 2019). Broad beans and alfalfa soils were also affected by As, Cd, Pb, Zn, and Cu, while corn soils exhibited lower contamination levels, although some sites still showed considerable HMs accumulation. These findings highlight the need for continuous monitoring of soils, irrigation water, and agricultural inputs. The findings are consistent with earlier studies reporting extreme HMs

Table 2

Level of pollution (*CF*), individual metal potential ecological risk index (*ERI*) and total ecological risk (*RI*) for HMs in soils according to type of agricultural crops.

Heavy metals	Soils under crops	<i>CF</i> (mean ±SD)	Categories (<i>CF</i>)	<i>ERI</i> (mean ±SD)	Categories (<i>ERI</i>)
As	Artichoke	11.35 ± 2.91	Very high	113.5 ± 29.1	Considerable
	Corn	5.39 ± 0.74	Considerable	53.9 ± 7.4	Moderate
	Broad beans	12.8 ± 2.32	Very high	128 ± 23.2	Considerable
	Alfalfa	8.27 ± 1.12	Very high	82.7 ± 11.2	Considerable
		30.8 ± 10.24		923.6 ± 37.1	
Cd	Artichoke	11.0 ± 1.96	Very high	330.5 ± 58.7	Very high
	Corn	23.2 ± 5.47	Very high	697.4 ± 164	Very high
	Broad beans	12.2 ± 2.15	Very high	371.1 ± 64.4	Very high
	Alfalfa	0.42 ± 0.08	Low	0.85 ± 0.16	Low
		0.68 ± 0.071	Low	1.37 ± 0.14	Low
Cr	Artichoke	0.64 ± 0.08	Low	1.27 ± 0.17	Low
	Corn	0.55 ± 0.05	Low	1.10 ± 0.11	Low
	Broad beans	20.31 ± 7.25	Very high	101.5 ± 36.24	Considerable
	Alfalfa	5.52 ± 1.05	Considerable	27.6 ± 5.26	Low
		15.73 ± 3.97	Very high	78.6 ± 19.85	Moderate
Cu	Artichoke	10.44 ± 1.96	Very high	52.2 ± 9.82	Moderate
	Corn	1.15 ± 0.12	Moderate	1.15 ± 1.12	Low
	Broad beans	0.84 ± 0.04	Low	0.84 ± 0.04	Low
	Alfalfa	1.11 ± 0.08	Moderate	1.11 ± 0.08	Low
		0.92 ± 0.05	Low	0.92 ± 0.05	Low
Fe	Artichoke	0.31 ± 0.02	Low	1.53 ± 0.12	Low
	Corn	0.41 ± 0.01	Low	2.03 ± 0.08	Low
	Broad beans	0.38 ± 0.02	Low	1.89 ± 0.10	Low
	Alfalfa	0.37 ± 0.01	Low	1.89 ± 0.07	Low
		59.7 ± 24.34	Very high	298.3 ± 121.7	High
Ni	Artichoke	29.2 ± 6.27	Very high	66.5 ± 14.5	Moderate
	Corn	13.3 ± 2.9	Very high	222.4 ± 64.1	High
	Broad beans	44.5 ± 12.83	Very high	145.8 ± 31.3	Considerable
	Alfalfa	41.6 ± 14.11	Very high	41.6 ± 14.11	Moderate
		38.2 ± 9.16	Very high	12.7 ± 2.31	Low
Pb	Artichoke	27.1 ± 4.85	Very high	38.2 ± 9.16	Low
	Corn	12.7 ± 2.31	Very high	27.1 ± 4.85	Low
	Broad beans	1482.06 ± 1535.81	93.49	3505.13	Very high risk
	Alfalfa	495.48 ± 620.47	93.49	3505.13	High risk
<i>RI</i>	Crops	<i>RI</i> mean ± SD	Minimum	Maximum	Categories (<i>RI</i>)
	Artichoke				
	Corn				

Table 2 (continued)

Heavy metals	Soils under crops	<i>CF</i> (mean ±SD)	Categories (<i>CF</i>)	<i>ERI</i> (mean ±SD)	Categories (<i>ERI</i>)
	Broad beans	1168.79 ± 1293.84	95.28	4069.87	Very high risk
	Alfalfa	679.22 ± 653.10	104.53	3068.64	Very high risk

contamination exceeding ecological thresholds in agricultural regions (Keshavarzi et al., 2021; Pizarro et al., 2025). The very high Cu contamination observed in soils under artichoke, broad beans, and alfalfa cultivation may be associated with the use of Cu-based fertilizers or fungicides (Sharafi and Salehi, 2025).

The ecological risk assessment showed pronounced metal-and crop-specific patterns, with Cd being identified as the main ecological risk factor in all agricultural systems (Table 2). Cd consistently produced very high *ERI* values, particularly in artichoke soils, where 70% of sites fell into the very high-risk category, reflecting the strong influence of intensive management practices on Cd accumulation. Corn soils exhibited substantially fewer high-risk sites (29%), consistent with lower external contamination sources. Pb was the second most influential contributor to ecological risk, especially in artichoke and broad beans systems, where 40% and 30% of sites, respectively, reached high risk-levels—patterns aligned with proximity to road networks and legacy atmospheric deposition. As and Cu also contributed to considerable risk in several crops, indicating the presence of multi-metal contamination pressures. Conversely, Cr, Fe, and Ni consistently exhibited low ecological risk across all sampling sites, reflecting their lower mobility under the prevailing soil conditions and suggesting minimal anthropogenic enrichment.

Overall ecological risk (*RI*) patterns were dominated by Cd (61%) and Pb (19%), consistent with previous reports identifying these metals as key ecological stressors in agricultural soils affected by mining, industrial emissions, and agrochemical inputs (Jing et al., 2023; Pan et al., 2024; Vasudhevan et al., 2025; Wu et al., 2023). The spatial and crop-specific differences in *RI* likely reflect a combination of crop management intensity, external anthropogenic inputs, and soil physicochemical characteristics that affect metal retention and mobility (Chen et al., 2023). High and very high *RI* values in artichoke, broad beans, and alfalfa systems suggest that these crops may act as indicators of cumulative contamination processes linked to both historical industrial emissions and contemporary agricultural practices. Given the significant ecological risks associated with Cd and Pb, targeted mitigation measures are required, including restricting the use of Cd-rich agrochemicals, applying amendments to reduce metal bioavailability, and implementing monitoring programs for irrigation water and soil quality to prevent further ecological degradation and ensure safe and sustainable agricultural practices in the valley.

3.3. Concentración de HMs en los cultivos agrícolas

The concentrations of HMs in the four crop species are shown in Fig. 2 and Table S7. Significant differences were observed among crops. Cu, Fe, and Zn were detected in all species, whereas some metals were absent in specific crops (As, Cd, Ni, and Pb in corn; Cr in broad beans; and Ni in artichoke). Alfalfa was the only crop containing all eight metals. The highest Fe and Zn concentrations occurred in alfalfa (39.47 and 11.34 mg kg⁻¹) and broad beans (15.74 and 16.52 mg kg⁻¹), respectively, whereas the lowest As and Cd levels (0.01–0.14 mg kg⁻¹) were found in artichoke, alfalfa, and broad beans. As, Cd, and Pb were significantly higher in alfalfa and artichoke than in broad beans, while Cu and Zn were higher in broad beans. Ni concentrations were similar between alfalfa and broad beans, and Cr was higher in alfalfa. These differences reflect crop-specific metal uptake and variation in metal

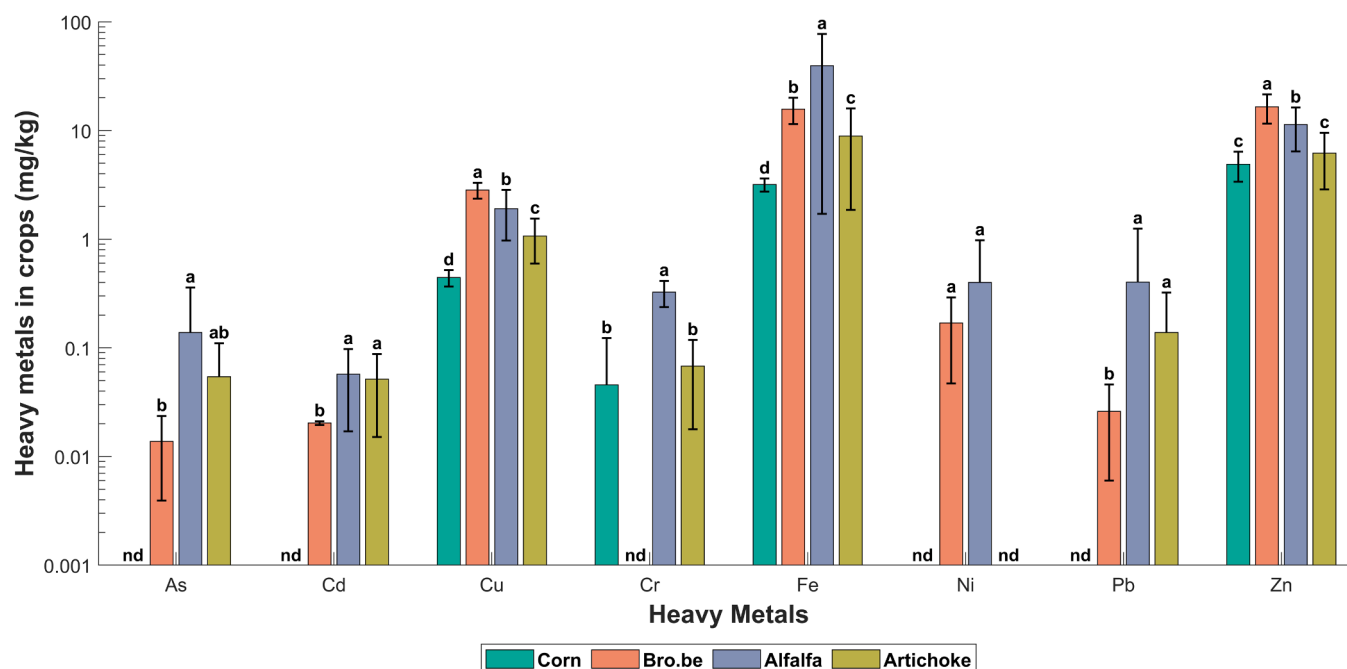


Fig. 2. Concentration of heavy metals in agricultural crops (alfalfa, artichoke, broad beans, and corn).

availability in soil, water, and air (Zhao et al., 2024). When compared with international standards (Table S7), Pb exceeded Codex Alimentarius limits in artichoke (0.1 mg kg^{-1}) and alfalfa (0.3 mg kg^{-1}) (FAO/WHO, 2015, 2024). Regulatory limits for Cr, Cu, Fe, Ni, and Zn are not defined by FAO/WHO, and Peru lacks national food contaminant standards.

Comparison with previous studies (Table 3) shows substantial variability in crop metal concentrations globally. Similar to our findings, corn grains in Peru and Ghana showed non-detectable levels of As, Pb, and Cd. Most studies in China reported mean levels of Pb, Cd, As, Cr, Cu, Ni, and Zn in corn below national limits, though some studies documented exceedances for Pb, Cd, As, and Cr. Pb exceedances in artichoke have been reported in Peru and Colombia. For broad beans, our Cd and Pb levels were below safety limits, consistent with findings from Gansu (China), whereas studies in Serbia and Saudi Arabia reported exceedances for Pb and Cr. Higher Cr, Fe, and Zn levels in broad beans were reported in Slovenia. Metal concentrations in alfalfa were generally lower than those reported in Pakistan, South Africa, and China, where Cd and Pb frequently exceeded safety thresholds. In Tunisia, Ni, Cd, and Pb were below detection limits, and Zn was lower than in the present study. Overall, cross-study comparisons highlight substantial variability in HMs concentrations across regions, likely driven by differences in crop varieties, environmental conditions, and anthropogenic inputs (Li et al., 2018; Zhao et al., 2024).

The greater HMs accumulation observed in alfalfa relative to the other crops is attributable to its intrinsic morphological and physiological traits. Alfalfa is recognized for its strong capacity to absorb, tolerate, and sequester heavy metals, particularly within root tissues, which underpins its frequent use in phytoremediation (Chen et al., 2015, 2022). This species can accumulate substantial amounts of potentially toxic elements during growth, aided by legume-specific traits that enhance tolerance to Cd and Pb, promote Cd and Cu phytoextraction, increase Zn accumulation in roots, and contribute to the stabilization of Cu, Pb, and Zn in soils (Ayub et al., 2022). Broad beans also exhibited elevated Zn and Cu concentrations, consistent with its known tendency to accumulate higher levels of Zn, Fe, and Cu than other legume species (Sinković et al., 2023). Although these elements are essential micronutrients, excessive accumulation can pose risks to human health.

The absence of As, Cd, Pb, and Ni in corn grains, of Cr in broad beans,

and of Ni in artichoke may be attributed to restricted metal translocation. Corn, for instance, tends to retain HMs in its roots, preventing their transfer to aerial tissues (Wei et al., 2020). In general, crops accumulate metals more readily in roots than in above-ground tissues (Lyu et al., 2022; Shahid et al., 2015). Nonetheless, HMs accumulation in crops is strongly influenced by the very high soil concentrations of As, Cd, Pb, Cu, and Zn, as well as the high and very high ecological risk levels identified for Cd and Pb. Although total metal concentrations in soil are elevated, only a small fraction is bioavailable to plants (Sun et al., 2009). Even so, the presence of elevated HMs in broad beans and artichoke may pose potential health risks to consumers.

3.4. Accumulation factor (AF) of HMs in crops

The average AF values of the eight HMs across the four crop types are presented in Fig. 3 and Table S8. The AF is commonly used to assess the capacity of plants to absorb HMs from soil. Significant differences were detected in the mean AF values among crops. Higher mean AF values were observed for Cd (0.202) in the aerial tissues of alfalfa. Artichoke, corn, and broad beans exhibited AF values for Fe lower than 0.0005, while the AF for Pb in broad beans was significantly lower than in the other crops. Overall, AF values varied according to crop species and metal type. The general AF trend across the studied HMs followed the order alfalfa > broad beans > corn > artichoke. AF values for Cd and Ni were significantly higher in alfalfa, whereas AF values for Cu and Zn were higher in broad beans. As and Cr showed similar mean AF values ($p < 0.05$) among the four crops. AF values for Cd, Fe, Ni, and Pb were highest in alfalfa tissues.

Corn grains did not accumulate As, Cd, Ni, or Pb, which is consistent with the fact that, in most plants, only a small fraction of HMs is translocated from roots to shoots (Shahid et al., 2015). However, previous studies have reported AF values > 1 for Cd, Cr, Pb, and Zn in corn grains (Sharma et al., 2018). These toxic elements tend to accumulate mainly in roots or remain bound in soil (Islam et al., 2024; Wang et al., 2016). Studies on corn have shown that Cd is absorbed and transported through the apical regions of the roots, retained largely in the rhizodermis and cortex of the outer root tissues, and only a small portion is transferred to the stem (Rizwan et al., 2017). Some metals, such as Pb, Ni, and As, tend to remain concentrated in roots and are transported less

Table 3

Comparison of heavy metals concentrations in crops in different countries (mg kg⁻¹).

Crops	Metals evaluated	Location	References
Corn (<i>Zea mays</i>)	As (nd), Cd (nd), Cu (0.44), Cr (0.05), Fe (3.16), Ni (nd), Pb (nd) and Zn (4.87)	Junín, Perú	This study
	As(nd), Cd (0.10) and Pb (nd)	Arequipa, Perú	(Bedoya-Perales et al., 2025)
	Cu (2.12), Pb (nd), Zn (36.86), Fe (174.37) and As (0.078)	Concepción, Perú	(Custodio et al., 2020)
	As (9.28), Cd (0.35), Cr (66.0), Hg (0.10), Ni (27.60), Cu (25.38) and Zn (67.41)	Liaoning, China	(Zhao et al., 2022)
	Cr (0.471), Cu (1.868), Zn (19.77), Ni (0.61), Pb (0.03)	Guizhou, China	(Zhao et al., 2023)
	As (0.021), Cd (nd), Hg (nd), Pb (nd) and Cr (nd)	Gansu, China	(Xie et al., 2022)
	Pb (0.16), Cd (0.02), Zn (24.32), Cu (9.38), Cr (0.08) and Ni (0.33)	Shandong, China	(Wen et al., 2025)
	As (0.05), Pb (nd), Cd (nd), Cu (0.039) and Zn (nd)	Tamale, Ghana	(Adam et al., 2022)
	Pb (0.034), Cd (0.004), As (0.004) and Cr (0.023)	Jiyuan, China	(Liu et al., 2024)
	Ni (0.37), Cr (0.13), Cd (0.006), Mn (4.96), As (0.09), Cu (1.64), Zn (20.11), and Pb (0.052)	Patuakhali, Bangladesh	(Islam et al., 2024)
	Pb (1.84), As (1.57) and Cr (4.92)	Khuzestan, Iran	(Gholami et al., 2025)
	As (0.009), Cr (0.169), Cd (0.018), Hg (0.001) and Pb (0.019)	Nanyang Basin, China	(Liu et al., 2025)
	Cd (2.26) and Pb (4.6)	Pakistan	(Alhaj Hamoud et al., 2024)
			This study
Artichoke (<i>Cynara scolymus</i>)	As (0.05), Cd (0.05), Cr (0.07), Cu (1.07), Fe (8.97), Ni (nd), Pb (0.14) and Zn (6.19)	Junín, Perú	
	Cu (5.27), Pb (0.47), Zn (28.63), Fe (75.04) and Cr (0.05)	Concepción, Perú	(Custodio et al., 2021)
	Cd (0.16), Co (0.43), Zn (3.97), As (2.36), Pb (7.07), Ni (nd), Cu (13.1) and Cr (12.1)	Sibaté, Colombia	(Lizarazo et al., 2020)
Broad beans (<i>Vicia faba</i>)	As (0.01), Cd (0.02), Cr (nd), Cu (2.83), Fe (15.74), Ni (0.17), Pb (0.03) and Zn (16.52)	Junín, Perú	This study
	Fe (26.00), Cu (3.00), Zn (25.2), Mn (7.90), Cd (0.03), Pb (1.00), Ni (35.4) and Cr (2.30)	Vojvodina, Serbia	(Pastor et al., 2024)
	Cu (0.052), Mn (0.134), Pb (0.251) and Zn (0.140)	Saudi Arabia	(Alyemeni and Almohisen, 2014)
	As (0.008), Cd (nd), Hg (nd), Pb (nd) and Cr (nd)	Gansu, China	(Xie et al., 2022)
	Cr (1.51), Mn (45.63), Fe (53.86), Zn (41.44) and Mo (4.5)	Slovenia	(Sinković et al., 2023)
Alfalfa (<i>Medicago sativa</i>)	As (0.14), Cd (0.06), Cr (0.33), Cu (1.91), Fe (39.47), Ni (0.40), Pb (0.40) and Zn (11.34)	Junín, Perú	This study
	Cd (2.16) and Pb (5.67)	Pakistan	(Alhaj Hamoud et al., 2024)
	Pb (6.75), Cd (0.11), Cr (18.10), Cu (2.7), Zn	Inner Mongolia, China	(Ren et al., 2025)

Table 3 (continued)

Crops	Metals evaluated	Location	References
	(13.26), Ni (4.84), and Hg (0.005)	Tunisia	(Helaoui et al., 2023)
	Cd (nd), Ni, Pb (nd), Cu (19.95) and Zn (61.76)	South Africa	(Hantsi et al., 2025)
	Cr (1034.53), Mn (108.67), Ni (74.2) and Zn (75.4)		

efficiently to aerial tissues (Gholami et al., 2025).

Although $AF < 1$ in three crops suggests limited translocation, 9% of alfalfa samples showed $AF > 1$ for Cd, reflecting its high uptake capacity and the high mobility of Cd in the soil–plant system (Shahid et al., 2015; Zunaide et al., 2023). Rhizobia in legumes may also influence HMs availability via chelation and rhizosphere processes (Ayub et al., 2022). Variations in AF among crops reflect species and element specific uptake and detoxification mechanisms (Pasricha et al., 2021). Soil properties, particularly pH (7.4–7.6) and organic matter (3.1–4.0%), influenced HMs mobility and availability (Wei et al., 2025). Each crop also exhibits distinct physiological requirements and metal uptake mechanisms, influenced by soil properties, the amount and type of trace metals present (Kaur et al., 2025; Sharma et al., 2018). Despite $AF < 1$, Pb concentrations in artichoke and alfalfa exceeded FAO/WHO limits, indicating that low accumulation efficiency does not guarantee food safety. Compliance with environmental and food quality standards remains essential.

3.5. Human health risk from HMs

3.5.1. Non-carcinogenic and carcinogenic risk

Table 4 summarizes non-carcinogenic risk (HQ), hazard index (HI), and carcinogenic risk (CR) values for the metals analyzed in corn, broad beans, and artichoke, in both children and adults. The main finding, according to the deterministic method, is that the mean values of HQ and HI for all elements were below the risk threshold of 1, suggesting a low probability of adverse health effects from individual exposure to each metal. It was observed that As consistently contributed the highest HQ values in all scenarios. Systematically, the child group presented a greater risk than adults for the same crop and element.

At the metal-specific level, As showed the highest contribution to both HQ and CR values, particularly in children consuming artichoke ($HQ = 0.357$; $CR = 1.61 \times 10^{-4}$) and broad beans ($HQ = 0.287$; $CR = 1.29 \times 10^{-4}$), consistent with studies identifying As as the main toxicant in crops irrigated with contaminated water (Ferré-Huguet et al., 2008; Islam et al., 2014). Ni was the second most critical element, yielding the highest carcinogenic risk ($CR = 1.36 \times 10^{-3}$ in children consuming broad beans), a pattern previously reported in cereals and leafy vegetables from industrial regions (Wang et al., 2014). Cd caused moderate non-carcinogenic effects ($HQ = 0.167$ in broad beans; $HQ = 0.087$ in artichoke), and although its CR remained below 1×10^{-4} . Nevertheless, Cd remains a cumulative nephrotoxin and has been identified as a major contributor to chronic kidney disease in populations consuming Cd-enriched crops (Huang et al., 2017). El Pb presented low CR values but exceeded the Codex Alimentarius maximum limit for fruit vegetables ($0.14 \text{ mg kg}^{-1} > 0.1 \text{ mg kg}^{-1}$), denoting direct non-compliance with food-safety standards. Pb's cumulative neurotoxicity, even at trace levels, has been emphasized by the World Health Organization (WHO, 2023) and confirmed in recent dietary exposure assessments (Ding et al., 2016). Finally, Zn and Cu though essential micronutrients, contributed noticeably to total HQ ($Zn = 0.159$; $Cu = 0.199$ in broad beans), suggesting bioaccumulation consistent with long-term agricultural inputs and fertilizer use.

Specifically, the highest mean HQ was recorded for As in children consuming artichoke ($HQ = 0.357$) and broad beans ($HQ = 0.287$). However, Gholami et al. (2025) reported HQ values for Pb and As in

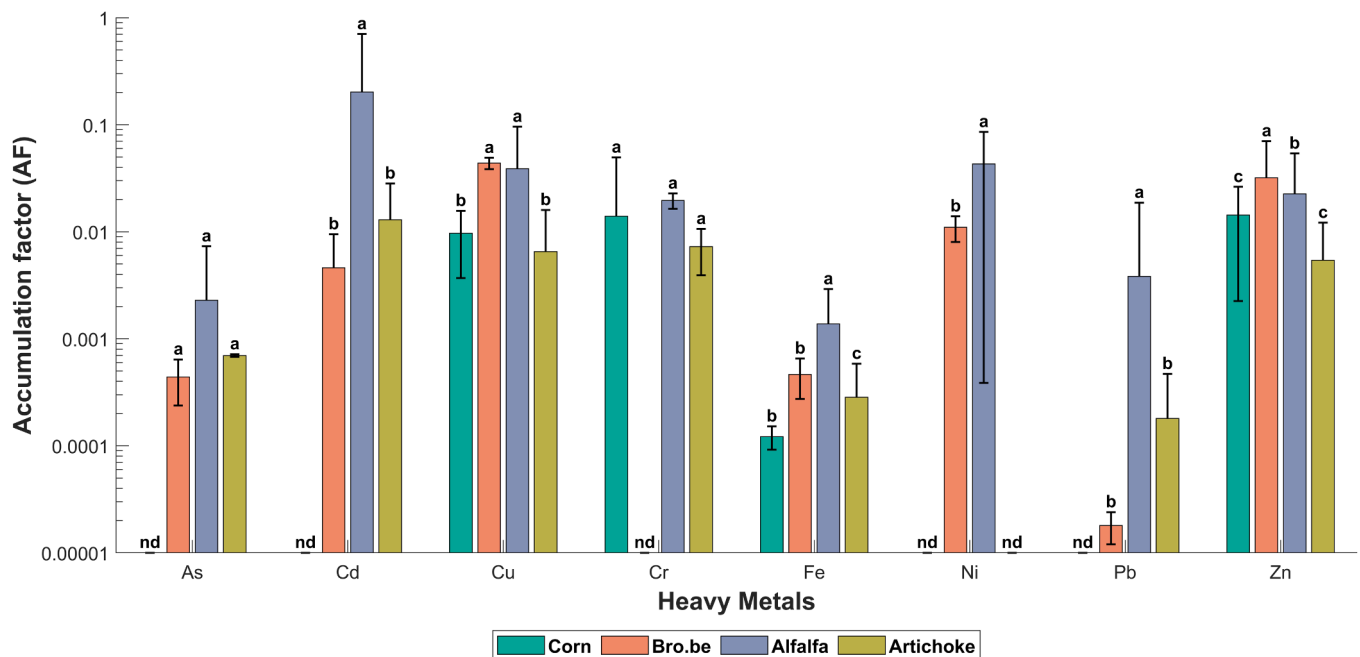


Fig. 3. Accumulation factor (AF) of HMs in crops (alfalfa, artichoke, broad beans and corn).

Table 4

Estimated daily intake (EDI/mg/kg.day⁻¹), non-carcinogenic risk (HQ), and carcinogenic risk (CR) of heavy metals by crop type in children and adults.

Heavy metals	Crops	EDI		HQ		CR	
		Children	Adult	Children	Adult	Children	Adult
As	Artichoke	1.07E-04	8.27E-05	0.357	0.276	1.61E-04	1.24E-04
	Broad beans	8.61E-05	3.57E-05	0.287	0.119	1.29E-04	5.36E-05
	Corn	-	-	-	-	-	-
Cd	Artichoke	8.71E-05	7.17E-05	0.087	0.072	5.23E-05	4.30E-05
	Broad beans	1.70E-04	1.07E-04	0.167	0.107	1.00E-04	6.43E-05
	Corn	-	-	-	-	-	-
Cr	Artichoke	8.41E-05	6.49E-05	0.028	0.022	4.20E-05	3.24E-05
	Broad beans	-	-	-	-	-	-
	Corn	1.54E-04	7.93E-05	0.051	0.026	7.71E-05	3.96E-05
Cu	Artichoke	1.10E-03	8.77E-04	0.028	0.022	-	-
	Broad beans	8.00E-03	4.10E-03	0.199	0.102	-	-
	Corn	1.78E-03	9.17E-04	0.045	0.023	-	-
Fe	Artichoke	1.04E-02	8.02E-03	0.015	0.011	-	-
	Broad beans	4.65E-02	1.63E-02	0.066	0.023	-	-
	Corn	1.49E-02	7.65E-03	0.011	0.010	-	-
Ni	Artichoke	-	-	-	-	-	-
	Broad beans	7.99E-04	4.11E-04	0.040	0.021	1.36E-03	6.99E-04
	Corn	-	-	-	-	-	-
Pb	Artichoke	1.80E-04	1.39E-04	0.045	0.035	1.53E-06	1.18E-06
	Broad beans	1.22E-04	6.29E-05	0.031	0.016	1.04E-06	5.34E-07
	Corn	-	-	-	-	-	-
Zn	Artichoke	7.14E-03	5.51E-03	0.024	0.018	-	-
	Broad beans	9.18E-02	5.90E-02	0.159	0.082	-	-
	Corn	1.94E-02	9.98E-03	0.065	0.033	-	-
HI-TCR	Artichoke	-	-	0.585	0.455	2.57E-04	2.01E-04
	Broad beans	-	-	0.948	0.470	1.59E-03	8.17E-04
	Corn	-	-	0.172	0.094	7.71E-05	3.96E-05

corn for both adults and children above 1, while HQ values for Cr were below 1. The trend of HI for all elements studied by food crop was: broad beans > artichoke > corn. The highest risk index was recorded in children consuming broad beans (HI = 0.948), a value close to the risk threshold, indicating a potentially concerning exposure mainly associated with the contribution of As, Cd, Cu, and Zn. Although the values found in our study did not exceed the threshold of 1, they were sufficiently close to warrant concern, since chronic exposure to inorganic As, even at low levels, is associated with a range of severe non-carcinogenic effects, including skin lesions, cardiovascular diseases, diabetes, and,

critically, neurological developmental deficits (González et al., 2020; Tchounwou et al., 2023).

In contrast to the non-carcinogenic risk (HQ), mean carcinogenic risk (CR) values exceeding the unacceptable risk threshold (1.0E-04) were found in the food crops. The main elements contributing to this risk were Ni and As, both classified by the International Agency for Research on Cancer (IARC) as Group 1 carcinogens, i.e., “carcinogenic to humans” (IARC., 2012; Tchounwou et al., 2015). The highest CR value was observed in children consuming broad beans, attributed to Ni (mean CR = 1.36E-03). As also presented unacceptable risk levels for children

consuming artichoke (mean CR = $1.61\text{E}-04$) and broad beans (mean CR = $1.29\text{E}-04$), as well as for adults consuming artichoke (mean CR = $1.24\text{E}-04$). Our results are consistent with those reported by Pan et al. (2024) and Zhao et al. (2024), who identified As and Ni as having high contribution rates to health risk. The confirmation of the carcinogenicity of inorganic As by the IARC, with sufficient evidence for lung cancer, gives considerable toxicological weight to these risk estimates (Lewis et al., 2015).

In the present study, the child group exhibited higher carcinogenic risk than adults for the same exposure pathways, since children, due to their lower body weight and smaller body surface area, absorb more HMs compared to adults (Gholami et al., 2025). On the other hand, Cr and Pb showed risk levels that remained within the precautionary range (between $1.0\text{E}-06$ and $1.0\text{E}-04$). The total cancer risk (TCR) exceeded the acceptable range in both children and adults consuming broad beans and artichoke, being highest in children consuming broad beans (TCR = $1.59\text{E}-03$). These results demonstrate that the consumption of broad beans constitutes the main factor of both non-carcinogenic and carcinogenic risk, particularly in the child population.

The Monte Carlo simulation (Fig. 4) showed that the probability of exceeding the non-carcinogenic risk threshold (HI = 1) was low across all crops, consistent with the deterministic results. Children consistently exhibited higher risk than adults, as indicated by the rightward shift of their HI distributions. Corn showed no probability of exceeding the threshold (0%), while artichoke and broad beans presented slightly elevated risks. For artichoke, the probability of HI > 1 was 1.8% in children and 0.7% in adults. Overall, although mean HI values remained below 1, the probabilistic analysis indicates a small but measurable likelihood of risk particularly among children and individuals with high consumption or greater sensitivity.

This discrepancy between the deterministic (HI < 1) and probabilistic (HI > 1 = 1.8%) results is critically important. The deterministic approach, which relies on mean values, suggests a scenario of acceptable risk. However, this point-estimate model is recognized for possessing a high degree of uncertainty stemming from variations in individual characteristics and environmental differences. The Monte Carlo (MC) simulation is employed to overcome this limitation by analyzing the uncertainty of the results. The MC simulation, by contrast, provides a more realistic risk profile, demonstrating that a deterministic average

can provide a false sense of security. This is consistent with findings such as those by Wang et al. (2023), where deterministic HI values for several individual food groups (such as vegetables, HI=0.8726, and fruits, HI=0.8170) were below the threshold of 1, yet the 90th percentile of the probabilistic simulation for those same groups (HI=2.98 for vegetables; HI=2.62 for fruits) was well above it. Therefore, the 1.8% probability found in this study indicates that a subset of the population, particularly individuals at the upper extremes of the consumption distribution or those with higher sensitivity, face a real risk of adverse health effects.

Unlike the non-carcinogenic risk assessment, the cancer risk analysis reveals an alarming situation and one of clear concern for public health. The results indicate that the consumption of the food crops studied entails a total carcinogenic risk (TCR) that frequently exceeds the unacceptable risk threshold of 1.0×10^{-4} (USEPA, 1989), a limit recognized above which risk is considered unacceptable and requires intervention. Fig. 5 illustrates the probability distribution of total carcinogenic risk (TCR) derived from the consumption of three food crops. A central finding is that a significant portion of the simulated population exceeds the unacceptable risk threshold (TCR > 1.0×10^{-4}) in all scenarios analyzed. It is shown that the child group presents a considerably higher risk profile than adults, as evidenced by a larger proportion of this population exceeding the risk limit. When comparing crops, broad beans and corn present the highest risks, with probabilities of unacceptable risk greater than 55% in both children and adults. Specifically, corn shows the highest-risk scenario, with a probability of 99.2% in children and 61.3% in adults of exceeding the threshold. Artichoke presents a slightly lower risk, with probabilities of 56.5% in children and 41.4% in adults. Previous studies indicate that human health risk is associated with crop varieties, types of heavy metals, and age groups (Zhao et al., 2024). Therefore, these findings suggest that the majority of the consumer population is exposed to a potential cancer risk through this dietary pathway.

3.5.2. Public health implications and risk management strategies

The findings reveal critical public-health implications, as the total carcinogenic risk (TCR) exceeded the unacceptable threshold (1.0×10^{-4}) in several scenarios, with probabilities surpassing 99% in children consuming corn and 67% for broad beans. According to USEPA criteria, TCR values above 1.0×10^{-4} require management intervention (USEPA,

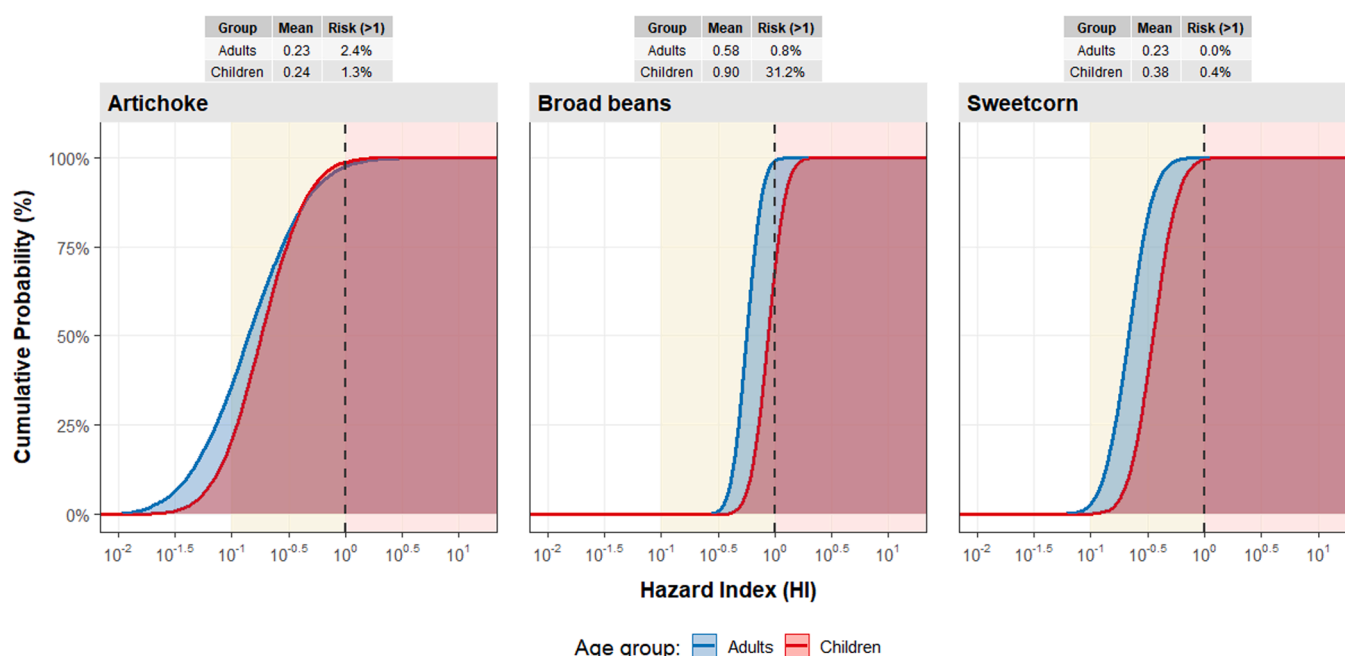


Fig. 4. Cumulative probability distributions of the non-carcinogenic hazard index (HI) by crop and age group, based on a Monte Carlo Simulation.

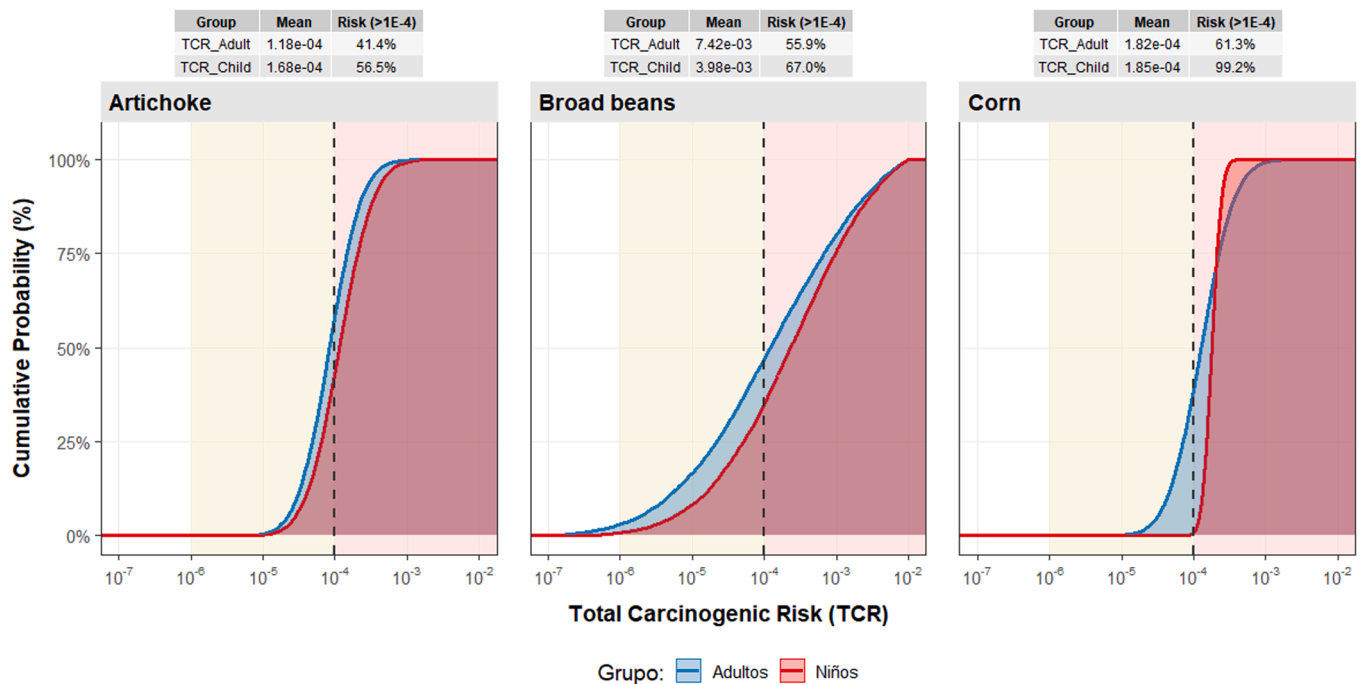


Fig. 5. Cumulative probability distributions of the total carcinogenic risk (TCR) by crop and age group, based on a Monte Carlo Simulation.

1989), indicating that the assessed exposures fall outside acceptable risk ranges. These modeled risks are reinforced by direct non-compliance with food-safety regulations: mean Pb concentrations in artichoke (0.14 mg kg^{-1}) exceed Codex Alimentarius limits (FAO/WHO, 2024), representing an immediate food-safety violation. This means that artichokes from the study area would be unfit for international trade and pose a direct risk of Pb toxicity, regardless of the risk model. The World Health Organization (WHO) has been emphatic that there is no safe level of exposure to Pb and that it is a cumulative toxicant that irreversibly affects multiple body systems, especially neurological development in children (WHO, 2023). Likewise, As identified in this study as one of the main risk drivers, is classified by the WHO as one of the ten chemicals of major public health concern (WHO, 2019).

Therefore, risk-management strategies for the Mantaro Valley should combine short- and long-term measures. Short-term actions include issuing consumption advisories, particularly for children, to limit intake of artichokes and broad beans from highly contaminated areas. Medium-term interventions should focus on reducing metal bioavailability through soil amendments such as phosphates and biochar, both of which have demonstrated efficacy in immobilizing Pb and Cd. For heavily contaminated plots, long-term land-use transitions—such as phytoremediation with accumulator species (e.g., *Medicago sativa*) or conversion to non-food crops—should be considered to disrupt soil-to-crop metal transfer and reduce human exposure.

4. Limitations and recommendations

This study advances the understanding of human health risks from heavy metals in agricultural systems, yet some limitations must be considered when interpreting the findings. First, although the sampling design captured the spatial heterogeneity of the study area, it was not probabilistic or randomized at a large scale, which may introduce selection bias and restrict the extrapolation of results to other regions with different edaphoclimatic conditions or agricultural practices. Sampling was also conditioned by the availability of plots with crops and land-owner permissions.

A major limitation is the absence of local geochemical baseline data for Mantaro Valley soils prior to anthropogenic disturbance. Without

such information, it is not possible to quantify precisely the magnitude of anthropogenic enrichment. Consequently, the contamination indices used here represent relative assessments based on widely applied global reference standards, which facilitate comparison with other contaminated agroecosystems but do not replace a site-specific background.

In crop analysis, the study focused exclusively on edible tissues to align with the objective of assessing oral exposure. Although this approach is appropriate for risk assessment, it does not capture metal accumulation dynamics across plant organs. As such, the study cannot elucidate physiological mechanisms governing uptake, retention, and translocation.

Finally, dietary exposure estimates were based on average consumption values rather than population-specific dietary surveys, which introduces uncertainty. As noted in previous literature, exposure models can lead to both overestimation and underestimation of health risks when local dietary variability is not accounted for (More and Dhakate, 2025).

Future research should adopt probabilistic and spatially stratified sampling frameworks to improve representativeness and reduce selection bias. Establishing robust local soil background concentrations is essential to disentangle natural from anthropogenic contributions and enhance the interpretability of contamination indices. Multi-tissue plant analyses are recommended to characterize metal translocation pathways and clarify physiological mechanisms underlying accumulation in edible tissues. In addition, population-specific dietary surveys should be incorporated to refine exposure estimates and reduce uncertainties in human health risk models. Integrating these improvements will increase the accuracy, comparability, and policy relevance of future assessments in metal-contaminated agroecosystems.

5. Conclusion

Agricultural soils in the Mantaro Valley to accumulate highly significant concentrations of As, Cd, Cu, Pb, and Zn, exceeding the maximum limits recommended by national and international standards. The level of soil contamination under the four crops was very high for Cd, Pb, and Zn. The ecological risk level was very high for Cd, with soils under artichoke cultivation contributing the highest ecological risk. The

elements with the greatest contribution to the ecological risk index were Cd and Pb. The trend of HMs content by crop type was alfalfa > broad beans > artichoke > corn. All crops showed a high concentration of Fe and Zn, but a low concentration of Cd. Artichoke and alfalfa samples exceeded food safety limits for Pb. Artichoke, broad beans and corn are not accumulators of HM, since the accumulation factor (AF) values were less than 1. The highest mean AF was for Cd at 0.202 in alfalfa samples, while the lowest mean AF was for Pb at 0.00002 in broad beans samples. The probabilities of non-carcinogenic risk from the consumption of broad beans were found to be close to the risk threshold of 1, indicating a probability of adverse health effects from exposure to HMs. The consumption of broad beans and corn represents the highest carcinogenic risks, with probabilities of unacceptable risk above 55% in both children and adults. This study provides baseline evidence to support local and regional authorities in implementing periodic monitoring programs for As, Cd, and Pb in soils and agricultural crops of the Mantaro Valley. Additionally, stricter regulation of agrochemical use (fertilizers and pesticides) is needed, promoting safer alternatives such as amendments, mycorrhizal fungi, or biochar to reduce Cd and Pb transfer into edible plant tissues. Awareness campaigns targeting farmers and consumers are also essential to minimize health risks and promote safer and more sustainable agricultural practices in the region.

CRedit authorship contribution statement

Ayllon Reginaldo: Methodology, Investigation. **Javier Aguilar:** Resources, Methodology, Investigation. **Miriam Tames:** Resources, Methodology, Investigation. **Vladimir Camel:** Writing – review & editing, Writing – original draft, Validation, Formal analysis. **Violeta Quispe-Coquil:** Resources, Methodology, Investigation, Conceptualization. **Roberto Cosme:** Resources, Methodology, Conceptualization. **Edith Orellana-Mendoza:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Richard Peñaloza:** Writing – review & editing, Writing – original draft, Validation, Formal analysis. **Ángeles Rojas-León:** Methodology, Investigation. **Sheyla Valero-Maraví:** Resources, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ecoenv.2026.120429](https://doi.org/10.1016/j.ecoenv.2026.120429).

Data availability

Data will be made available on request.

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