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Heavy Metals and Arsenic in Soil and Cereal Grains and Potential Human Risk in the Central Region of Peru

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ABSTRACT

The objective of this study was to analyze the content of heavy metals and arsenic in soil and cereal grains as well as to evaluate the possible human risk in the central region of Peru. The soil samples of corn and barley grains were collected from seven agricultural zones and the concentrations of Cu, Fe, Pb, Zn and As were determined with the method of atomic absorption flame spectrophotometry. PERMANOVA showed that the effect of the type of crop and the sampling zone significantly influence the concentrations of heavy metals and As in soil and corn and barley grains ($p < 0.05$). PCA for heavy metals and As in soil and grain samples of the cereals studied showed that the first two main components represented 81.03% and 94.77% of the total variance, respectively. Hazard Quotient (HQ) for ingestion was the most significant. The HQ values of Pb and As in crop soils indicated that detrimental health effects are unlikely (HQ < 1). The soil hazard index (HI) values of both crops did not exceed the threshold value of 1 (HI < 1). The carcinogenic risk level (CR) of As from ingestion of corn and barley crop soils contaminated by As was higher in children than in farmers and adults. The bioconcentration factor (BCF) of As was higher in barley grains than in corn grains. The THQ of As exceeded the target value of 1 in 100% of the barley and corn sampling sites. The RC of As in grains exceeded the acceptable risk level of 10^{-6} in all sampling zones.

Keywords: soil, cereals, heavy metals, arsenic, human risk.

INTRODUCTION

Environmental contamination by heavy metals and metalloids is a global problem of great concern in today's society, due to the rapid growth of urbanization, changes in land use and industrialization (Rai et al., 2019). The concentration of these metals in the soil has increased exponentially in the last three decades (Kumar and Prasad, 2018) and contributed to soil contamination as a consequence. This effect generated by toxic metals is one of the worrying aspects of this growing ecological and health crisis, due to their non-biodegradability and persistence. These metals enter the food chain through contaminated soil, water and atmospheric deposition (França et al., 2017). Soil contamination is accelerated by the continuous and excessive use of agrochemicals, such as pesticides, phosphate fertilizers and fertilizers, and the use of wastewater for irrigation (Branco et al., 2015). The accumulation of toxic metals in the soil negatively affects food security and poses a threat to the human and animal health. The ingestion of soil by livestock may also represent another entry point of toxic metals into the food chain (Cai et al., 2009).

Vegetables can absorb toxic metals from contaminated soils, wastewater and by atmospheric deposition of particles from various sources. The absorption of metals by roots is determined by several factors, such as metal content in the soil, pH and type of soil, organic matter, cation exchange capacity, species and genotype (Fan et al., 2017). The accumulation of toxic metals in the food chain can be dangerous for the human health. Prolonged ingestion of the plants contaminated with toxic metals can alter biochemical processes, lead to their accumulation in the liver and kidneys, and induce toxicity in many organs of the human body (Rai et al., 2019). However, the toxicity of toxic metals depends on the forms and routes of exposure, the interruptions of intracellular homeostasis as well as oxidative deterioration of biological macromolecules (Woldetsadik et al., 2017).

Globally, numerous investigations have reported on the contamination of agricultural soils with toxic metals (Hang et al., 2009; Branco et al., 2015). These metals can be easily absorbed and accumulate in high concentrations in the edible parts of vegetables. Very high levels of toxic metals have been found in tomatoes, carrots, cabbage, turnips, radishes, cauliflowers, cucumbers, spinach and other vegetables (Yang et al., 2009; Antoniadis et al., 2017). Crops such as rice, corn, wheat, potatoes, and soybeans irrigated with wastewater can be a significant source of toxic metals in the human and animal diet (Amin et al., 2013). Other studies reveal that the absorption and accumulation of toxic metals not only differs between species, but also within each species (Zhu et al., 2007; Shahid et al., 2018).

The ingestion of food contaminated with toxic metals is an important route that contributes to approximately 90% of human exposure (Khan et al., 2013). The gastrointestinal tract is the main route of Pb absorption and adults absorb about 10% of the lead content in food, while children absorb 3 or 4 times more Pb (Bui et al., 2016). Most Pb is concentrated in bones, teeth, and fatty tissue, leading to the depletion of essential nutrients and immune defenses. The toxicity at the risk dose level of Pb can cause increased blood pressure, nervous system difficulties, and bone weakness. It can also negatively affect mental development, causing neurological and cardiovascular disorders in humans (Zhou et al., 2016). In adults, it can cause kidney dysfunction, hypertension, and other serious diseases of the liver, lung, nervous system, and immune system (Chaoua et al., 2018). At excessive levels, As can cause cancer, skin, respiratory, cardiovascular, gastrointestinal, hematological, liver, kidney, neurological, developmental, reproductive and immune problems (Zhao et al., 2014; Shah et al., 2020).

The human exposure to contaminated food is a concern worldwide. In the South American context, food safety has become an issue of great interest due to the high levels of heavy metals in the environment, which reveals the need to assess food safety with respect to the presence of non-essential metals in the edible parts of principal food crops (Arisseto-Bragotto et al., 2017). In Peru, this type of assessment is necessary for crops in the areas with limited availability of good quality water where crops are irrigated with water from the rivers contaminated with heavy metals. The central region of Peru is an important agricultural production area irrigated with the water from the Mantaro River that contains high concentrations of toxic metals. In this sense, this study aims to analyze the content of heavy metals and arsenic in the soil and in cereal grains and to evaluate the possible human risk in the central region of Peru.

MATERIAL AND METHODS

Study area

The Mantaro river watershed is located in the Central Andes of Peru, between 10° 30' to 13° 30' South Latitude and between 74°00' to 76° 30' West Longitude. The Mantaro river is the main river of the basin, its flow depends on rainfall, the level of Lake Junin and the lakes located at the foot of the snow-capped mountains of the western cordillera and the snow-capped mountains of Huaytapallana. The tributaries of the Mantaro river run through many of the mining areas in the basin (Geophysical Institute of Peru, 2010). Along its course, the Mantaro River is the recipient of wastewater from many of the mining and urban industries of central Peru. Throughout the valley, during the dry season, the polluted waters of the Mantaro river are used for irrigation of large agricultural areas of importance to the Peru's economy. The agricultural area with the main food crops, such as potatoes, barley, corn and wheat is 56,314.00 ha. In the highlands of the Junín region, 74.9% of the agricultural surface is dry land, while 25.1% is irrigated (Agriculture Ministry, 2008). The sampling sites were defined in seven agricultural zones in the province of

Concepción in the Junín region that are irrigated with the contaminated water from the Mantaro River (National Water Authority, 2014).

Collection of soil samples and food grains

The sampling was carried out in four agricultural zones with maize cultivation and three zones with wheat cultivation, during May and June 2019. There were 168 samples of corn soil and grains consisted of 168 as well as 126 samples of barley soil and grains. Seven samples of approximately 100 g of surface soil were collected in each sampling area using a 20 cm deep stainless steel drill type device. The soil samples from each zone were mixed to obtain a composite sample of approximately 500 g. The corn and barley grain samples were collected from the same soil sampling sites in the respective agricultural zones prior to harvest. The samples were placed in zipper plastic bags, labeled and then transferred to the laboratory.

The soil samples were air dried at room temperature, disaggregated and sieved through a 2 mm stainless steel mesh screen to remove stones and plant debris. The sieved soil was placed in an electric oven at 60°C for 24 hours and the completely dried samples were crushed in a mortar. The resulting soil was stored in 250 ml HDPE bottles until further analysis. The food grains were dried for 10 days, then husked and placed in an oven at 100°C for 6 h. The dried samples were ground using a stainless steel mill and transferred to high density polyethylene (HDPE) containers for the heavy metal and metalloid analysis.

Digestion and analytical procedures

The soil samples (1 g) were placed in a beaker with 10 ml HNO_3 and 5 ml H_2SO_4 concentrate. The beakers were then heated to 100°C in the microwave digestion system until almost all the nitrogen dioxide was evaporated. A blank was also prepared for each digestion batch using 10 ml HNO_3 and 5 ml of concentrated H_2SO_4 to check its homogeneity and processing efficiency. The digested samples were then cooled and filtered through acid-treated Millipore filters (0.45 mm mesh). They were transferred into graduated test tubes and deionized water was added up to the 50 ml mark. The digested 50-ml filter solution was transferred to an acid-rinsed polyethylene sample container with a label for analysis (USEPA, 1996). The food grains (1 g) were digested with 10 ml of concentrated HNO_3 for 1 h at 80°C and then for 20 h at 120°C (Khan et al., 2019). The digested samples were filtered in 50 ml graduated plastic tubes and the final volume was adjusted

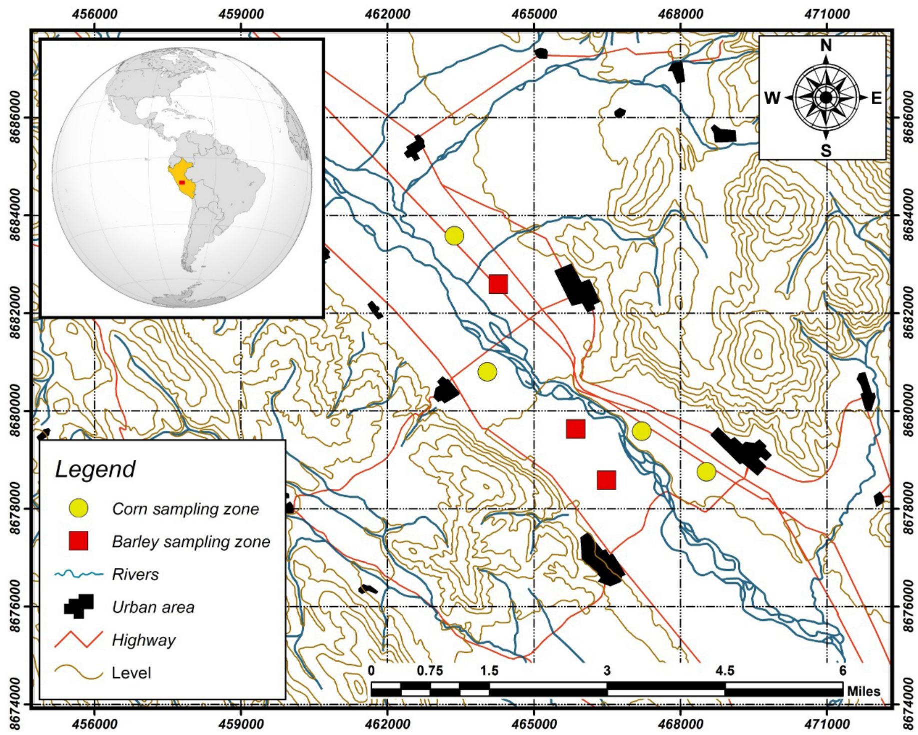

Figure 1. Map of location of sampling zones in the province of Concepción, Peru

to 50 ml with deionized water. The analysis of heavy metals and arsenic was performed by flame atomic absorption spectrophotometry. All samples were analyzed in triplicate.

Quality control and assurance

Quality control was performed through the application of standard laboratory and quality control protocols that included replication, the use of national and international standards for each metal investigated, and the determination of the accuracy of the instrument (APHA, 2012). The glassware was thoroughly cleaned with detergent and rinsed several times with deionized water before use. Standard solutions of 100 mg/L concentration for heavy metals and As were prepared from the 1000 mg/L standard. Then, working standards were prepared with 1% nitric acid.

Statistical analysis

A permutational multivariate variance analysis (PERMANOVA) was performed to test the effect of type of crop and sampling sector on the Pb, Cu, Fe, Zn and As concentrations in crop soil and corn and barley grains, using the Adonis function in the vegan R-package. The heavy metal and As concentrations in crop and grain soils were further explored by principal component analysis (PCA). VARIMAX rotation was performed to improve the interpretability of uncorrelated components (Gottfried et al., 2009). All significant loads (i.e. loads > 0.45) were included in the interpretation of the main components (PC). Spearman's correlation coefficient (rho) was used as correlation measure (dependence) between soil and grain variables, giving a value between +1 and –1, where 1 represents the total positive correlation, 0 means no correlation and –1 represents the total negative correlation. The rho coefficient is based on the ranges of the observations; Spearman's range correlation coefficient does not assume that the relationship between variables is linear.

Human health risk assessment

Exposure doses

The Mantaro Valley population are potential receptors of pollution; as agricultural areas are interspersed with peri-urban areas. Considering that agriculture is the main activity of the Andean population, the subjects were divided into three groups: adults, farmers or shepherds and children. The exposure to soil contamination can occur through the ingestion of soil, dermal contact and inhalation (USEPA, 2011). The risk of exposure to heavy metals and arsenic in soil was assessed using equations (1), (2) and (3).

$$D_{ing} = \left(\frac{C_s\ x\ IngR\ x\ EF\ x\ ED}{BW\ x\ AT}\right) x\ 10^{-6} \quad (1)$$

where: D_{ing} is the dose of exposure by ingestion of the element from soil (mg kg^{-1} body weight-day);
Cs is the concentration of the element in soil (mg kg^{-1});
$IngR$ is the rate of soil ingestion (100 mg day^{-1} for adults, 330 mg day^{-1} for adult farmers or herders and 200 mg day^{-1} for children);
EF is the frequency of exposure (350 days per year^{-1});
ED is the duration of the exposure to non-carcinogenic (30 years for adults and 6 years for children) and carcinogenic contaminants (24 years for adults and 6 years for children);
BW is the average body weight of the exposed person (70 kg for adults and 15 kg for children).
AT is the average time of exposure (10,950 days for adults and 2,190 days for children).

$$D_{der} = \left(\frac{C_s\ x\ SA\ x\ SL\ x\ ABS\ x\ EF\ x\ ED}{BW\ x\ AT}\right) x\ 10^{-6} \quad (2)$$

where: D_{der} is the dose of exposure through the dermal absorption of the element from soil (mg kg^{-1} body weight-day);
Cs is the concentration of the element in the soil (mg kg^{-1});
SA is the surface area of exposed skin (5,700 cm^2 for adults; 3,300 cm^2 for farmers or herders and 2,800 cm^2 for children);
SL is the factor of adherence of the soil to the skin (0. 07 mg cm^{-2} day^{-1} for adults, 0.3 mg cm^{-2} day^{-1} for farmers or herders, and 0.2 mg cm^{-2} day^{-1} for children),
ABS is the dermal absorption factor (0.03 for As and 0.001 for other elements),
EF, ED, BW, and AT as detailed in equation (1) (EPA, 2004).

$$D_{inh} = \frac{C_s \; x \; inhR \; x \; EF \; x \; ED}{PEF \; x \; BW \; x \; AT} \quad (3)$$

where: D_{inh} is the dose of exposure through the inhalation of the element from soil (mg kg^{-1} body weight-day);
Cs is the concentration of the element in soil (mg kg^{-1});
$InhR$ is the inhalation rate from soil (20 mg day^{-1} for adults and 7.6 mg day^{-1} for children).
PEF is the particulate emission factor (1.36 x 109). EF, ED, BW and AT are detailed in equation (1).

Non-carcinogenic risk assessment

The non-carcinogenic risk has been evaluated using the hazard ratio (HQ), which was calculated by dividing the exposure value by the reference dose (Antoniadis et al., 2019).

$$HQ_{ing/\mathrm{inh/der}} = D_{ing/\mathrm{inh/der}} / \mathrm{Rf}D_{ing/\mathrm{inh/der}} \quad (4)$$

where: $HQ_{ing/inh/der}$ is the hazard quotient for ingestion, inhalation and dermal contact.
$RfD_{ing/inh/der}$ is the reference dose for ingestion, dermal contact or inhalation (mg kg^{-1} body weight day-1), which is the threshold value for the toxicity of each element obtained from the literature (Haidong et al., 2017).

If the HQ ≤ 1 means that detrimental health effects are unlikely. HQ > 1 reveals likely detrimental health effects. HQ > 10 indicates high chronic risk. The calculated HQs were integrated and expressed as a hazard index (HI) (Al-bagawi, 2019)

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{HQ}_{ing/\mathrm{inh/der}} \quad (5)$$

where: $HI_{ing/inh/der}$ is the total chronic hazard index for each route of exposure. "n" is the total number of chemicals.

If HI < 1, it is assumed that the non-cancer adverse effect due to a given exposure pathway or chemical is negligible, while the potential for chronic effects may be a concern when HI > 1.

Carcinogenic risk assessment

The carcinogenic risk was evaluated considering the USEPA risk assessment guide (EPA, 2004). The chronic daily intake (CDI) was calculated with the equation (6).

$$\mathrm{CDI}_{ing} = \mathrm{C_s \; x \; DI/BW} \quad (6)$$

where: C_s, DI and BW represent the concentration of trace metal in soil in (mg kg^{-1}), mean daily soil intake and body weight, respectively.

Cancer risk (CR) was calculated using the formula:

$$\mathrm{CR}_{ing} = \mathrm{CDI}_{ing} / \mathrm{SF_{ing}} \quad (7)$$

where: SF_{ing} is the cancer slop factor.
SF_{ing} As is 1.5 mg kg^{-1} day^{-1} (Kamunda et al., 2016).

If risk > 1.0 x 10^{-4} is considered unacceptable;1.0 x 10^{-4} < risk < 1.0 x 10^{-6} is considered an acceptable range; risk < 1.0 x 10^{-6} is considered as no significant health effects.

Human health risk from heavy metals in cultivated grains

The bioconcentration factor (BCF) was calculated using equation (8).

$$BCF = \frac{C_{grain}}{C_{soil}} \quad (8)$$

where: C_{grain} and C_{soil} are the total concentrations of a given heavy metal and metalloid in the grain and soil of the crop (mg kg^{-1}), respectively.

The potential human risk of exposure to heavy metals and metalloids from the consumption of cultivated grains was evaluated using THQ (EPA, 2000).

If THQ > 1, the ratio reveals a potential health risk associated with the contaminant. If THQ < 1, there is no potential health risk associated with the contaminant. In order to evaluate the carcinogenic risk of heavy metals and metalloids in cultivated grains, only the risk of ingestion was considered, and was calculated using the following equations (9) and (10).

$$THQ = \frac{\mathrm{EDI}}{RfD_{ing}} = \frac{\mathrm{EF \; x \; ED \; x \; IngR \; x \; C}}{RfD_{ing} \; x \; BW \; x \; AT_{nc}} \; x \; 10^3 \quad (9)$$

$$\mathrm{CR}_{ing} = \mathrm{EDI \; x \; SF_{ing}} \quad (10)$$

where: EDI is the estimated daily intake of each heavy metal and metalloid and
$IngR$ = 402 g d^{-1}.

RESULTS

Analysis of heavy metals and arsenic in soil and grains from the Concepción province

Table 1 shows the mean concentration and standard deviation of heavy metals and arsenic determined in the soil and grain samples from the corn and barley crops in the province of Concepción in central Peru. The overall data showed that the mean concentration of heavy metals and arsenic varied by sampling site and type of crop. The decreasing order of average concentrations of heavy metals and metalloid in the soil samples of corn and barley crops was: Fe > Zn > Pb > Cu > As. In corn crop soil, the highest mean concentration of Fe (29733.72 mg kg^{-1}) was recorded in Sc4, Zn (1164.89 mg kg^{-1}) in Sc3, Pb (96.49 mg kg^{-1}) in Sc2, Cu (70.80 mg kg^{-1}) in Sc3 and As (12.66 mg kg^{-1}) in Sc1. In the barley soils, the highest mean concentration of Fe (29400.36 mg kg^{-1}) was recorded in Sb1, Zn (1414.06 mg kg^{-1}) in Sb1, Pb (185.31 mg kg^{-1}) in Sb3, Cu (78.48 mg kg^{-1}) in Sb1 and As (9.36 mg kg^{-1}) in Sb1.

The concentrations of Fe and As in the corn soils were higher than the concentrations of these elements in the barley soils. Similar behaviors were found in the Cu, Pb and Zn concentrations in the barley soils compared to the concentrations of these elements in the corn soils. The crop soils located in the northern Mantaro River valley (Sc1 and Sc2) showed higher mean As and Pb concentrations, respectively, and a high standard deviation compared to the other corn sampling sites. The barley soils with higher mean As and Pb concentrations were also located in the north of the valley (Sb1). Fe, Cu and Zn in the corn and barley soils showed no significant differences between their mean concentrations.

Pb is the only element that exceeds the environmental quality standards for soils in Peru (70 mg kg^{-1}) (Ministry of the Environment, 2017) and threshold values of the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) (100 mg kg^{-1}) (FAO/WHO, 1993), with the sampling sites located south of the valley having the highest concentrations of Pb (185.31 mg kg^{-1}). However, the average concentrations of Cu, Pb, Zn and As in the soils of both types of crops did not exceed the threshold values of the United States Department of Agriculture (USDA) (4300, 420, 7500 and 75 mg kg^{-1}; Cu, Pb, Zn and As, respectively)

Table 1. Mean concentration and standard deviation of heavy metals and arsenic in soils and grains of the Concepción province and safety limit values, expressed in mg kg^{-1}

Sample	Sampling zone	Cu			Pb			Zn			Fe			As		
		Mean ± SD			Mean ± SD			Mean ± SD			Mean ± SD			Mean ± SD		
Soil corn	Sc1	63.45	±	2.59	88.49	±	1.32	1079.70	±	36.93	27589.16	±	723.31	12.66	±	1.95
	Sc2	56.18	±	4.96	96.49	±	3.80	1026.50	±	25.25	28427.42	±	806.66	11.18	±	0.31
	Sc3	70.80	±	4.86	88.09	±	2.31	1164.89	±	83.33	28507.36	±	1343.16	10.57	±	0.10
	Sc4	59.15	±	3.03	93.50	±	5.59	1164.16	±	89.97	29733.72	±	574.58	10.65	±	1.14
Soil barley	Sb1	78.48	±	1.0113	154.95	±	27.59	1414.06	±	90.45	29400.36	±	1372.40	9.36	±	0.76
	Sb2	77.48	±	1.7125	151.05	±	6.33	1296.69	±	53.28	28796.21	±	851.59	9.32	±	0.44
	Sb3	77.67	±	2.0615	185.31	±	18.38	1345.34	±	99.47	27852.47	±	617.99	9.16	±	0.49
Safety limits																
USDA		4300			420			7500						75		
FAO/WHO		100			100									20		
EQS soil Peru					70									50		
Grain corn	Gc1	2.18	±	0.12	nd			29.00	±	4.78	137.08	±	4.87	0.070	±	0.008
	Gc2	2.04	±	0.09	nd			32.35	±	3.64	146.75	±	2.75	0.083	±	0.009
	Gc3	2.21	±	0.09	nd			40.88	±	1.41	205.64	±	5.10	0.061	±	0.004
	Gc4	2.05	±	0.09	nd			45.22	±	3.01	207.31	±	13.29	0.100	±	0.015
Grain barley	Gb1	18.71	±	0.85	nd			58.85	±	1.23	69.70	±	7.84	0.124	±	0.022
	Gb2	19.97	±	1.09	nd			56.16	±	1.12	69.99	±	9.38	0.142	±	0.003
	Gb3	17.41	±	0.81	nd			65.58	±	0.96	72.97	±	7.91	0.142	±	0.016
Safety limits																
FAO/WHO		5			5											
EPA		1			0.2									0.15		

(USDA, 2000) nor the maximum permissible values of Cu and As in soils of FAO and WHO (FAO/WHO, 2011) (100 y 20 mg kg^{-1}, respectively).

The decreasing order of the maximum mean concentration of heavy metals and As in corn and barley grains was: Fe (207.31 mg kg^{-1} in corn and, 72.97 mg kg^{-1} in barley) > Zinc (45.22 mg kg^{-1} in corn and 65.58 mg kg^{-1} in barley) > Cu (2.21 mg kg^{-1} in corn to 19.97 mg kg^{-1} in barley) > As (0.100 mg kg^{-1} in corn to 0.142 mg kg^{-1} in barley). The results of this study also revealed that the type of crop has a significant influence on the concentrations; since barley grain had a higher concentration of these heavy metals and metalloids compared to corn. In addition, it was found that the sampling sites located in the southern part of the Mantaro Valley are characterized by corn grain production with higher concentrations of Fe compared to the northern sectors ($p < 0.05$). This is the only element in corn grain that has mean concentrations higher than the mean concentrations of barley grains.

The mean concentrations of Cu, Zn and As in barley grains were significantly higher than the mean concentrations of these heavy metals and metalloids in corn grains. The Zn concentrations changed significantly ($p < 0.05$) due to the effect of the sampling site on corn grains. The sampling sites located in the southern part of the Mantaro valley have higher concentrations of Zn in the grain than the other two sites evaluated. The mean Cu concentrations exceeded the safety limits of FAO (5.0 mg kg^{-1}) and the U.S. Environmental Protection Agency (1.0 mg kg^{-1}) [37]. In contrast, mean As concentrations in grains from these cereals did not exceed the EPA limits (0.15 mg kg^{-1}).

Permutational multivariate variance analysis (PERMANOVA) showed that the effect of the type of crop and the sampling zone influence the concentrations of Pb, Cu, Fe, Zn and As in soil and grains significantly ($p < 0.05$). However, the concentrations of these toxic elements in the barley cultivation soils in the northern, central and southern sampling zones did not show significant differences ($p > 0.05$). In contrast, the concentrations of heavy metals and As in the corn growing soil showed significant differences due to the effect of the sampling zone (Table 2).

The result of the principal component analysis (PCA) for heavy metals and As in the soil samples from corn and barley crops showed that the first two principal components represented 81.03% of the total variance in the data set. The first major component (PC1) represented 58.57% of the total variance. The Cu, Pb and Zn concentrations showed high positive charges (0.75 to 0.95) and the As concentrations showed high negative charges (–0.75 to –0.95) at the PC1. The Fe concentrations showed high positive charges (0.70 to 0.91) at PC2. The crop soils with higher concentrations of Zn, Cu and Pb corresponded to the zones with barley crops and soils with higher concentrations of As to the zones with corn crops. The small differences with significant trend from one agricultural area to another are explained by PC2. The Fe concentrations determined the difference between geographically distributed agricultural zones. In the case of barley soils, the northern zones of the Mantaro River valley showed

Table 2. Permutational multivariate variance analysis of crop sectors according to the metal and metalloid concentration in soils and grains

Sample	Sampling zone	Gc4	Gc3	Gc2	Gc1	Gb3	Gb2	Gb1
Soil	Gc4							
	Gc3	0.0071						
	Gc2	0.0086	0.0081					
	Gc1	0.0254	0.0685	0.0845				
	Gb3	0.0084	0.0093	0.0088	0.0077			
	Gb2	0.0081	0.0067	0.0084	0.0085	0.0581		
	Gb1	0.0066	0.0072	0.008	0.007	0.0888	0.2554	
Grain	Gc4							
	Gc3	0.0079						
	Gc2	0.0082	0.0093					
	Gc1	0.0076	0.0075	0.0636				
	Gb3	0.0092	0.0069	0.0098	0.0069			
	Gb2	0.0066	0.0086	0.0073	0.0089	0.0067		
	Gb1	0.01	0.0078	0.0081	0.0084	0.0676	0.1206	

higher concentrations of Fe. The corn soils from the zones located in the southern part of this valley showed higher Fe concentrations (Figure 2).

PCA of heavy metals and arsenic in barley and corn grains showed that the first two main components represented 94.77% of the total variance in the data set. PC1 represented 85.75% of the total variance. The Cu, Zn and As concentrations showed high positive charges (0.75 to 0.95) and the Fe concentrations showed high negative charges (–0.75 to –0.95) in PC1. Barley grains showed higher concentrations of Zn, As and Cu compared to the corn grains with higher Fe concentration. No significant effects were observed due to the geographical location of the agricultural areas. However, the concentrations of some toxic elements in the grains of certain areas were slightly higher. Barley grains from the areas located south of the Mantaro River Valley had higher concentrations of Zn, As and Cu compared to the concentrations of these elements in the grains of this cereal in the agricultural areas located in the north of the valley. Corn grains from the areas located in the southern part of the valley showed higher concentrations of Zn than the areas located in the northern part of the valley, with a tendency to have a higher concentration of Fe of the same equivalence (Figure 3).

Spearman correlation coefficients between heavy metals and arsenic in the corn crop soils showed that Cu and Pb indicated a significant negative correlation (–0.43 a −0.71) with reflectance spectra at a significance level of 0.01. In turn, As and Zn showed significant positive correlation (0.43 to 0.71). In the soils with barley crops it was found that Zn and Cu showed positive significant correlation (0.43 to 0.71) and, Fe and Pb – negative significant correlation (–0.43 a −0.71). In corn grains it was found that As and Cu revealed negative significant correlation (–0.43 a −0.71) and, Fe and Zn highly positive significant correlation (0.71 to 0.9). Barley grains only revealed significant negative correlation between Zn and Cu.

Health risk assessment for exposure to heavy metals and arsenic from soil and cereal grains

The results revealed that the concentrations of heavy metals and As in corn and barley soil did not exceed the environmental quality standards (EQS) for soil in Peru (Ministry of the Environment, 2017) and the international threshold values (USDA, 2000); (FAO/WHO, 1993) except for Pb, the mean concentrations of which exceeded the EQS for Peru and the FAO/WHO threshold values. However, due to their toxicological effect and the carcinogenic nature of some of them, the risk they pose to the health of children, adults and farmers was determined. As was the only carcinogenic element detected in the soil and grains of the cereals under study. Therefore, both the carcinogenic and non-carcinogenic risks of this metalloid were determined through equations (1) to (8) (USEPA, 2011; Zhao et al., 2014) (Table 3). The non-carcinogenic risk of Pb and As was determined by the hazard quotient (HQ) and the hazard index (HI).

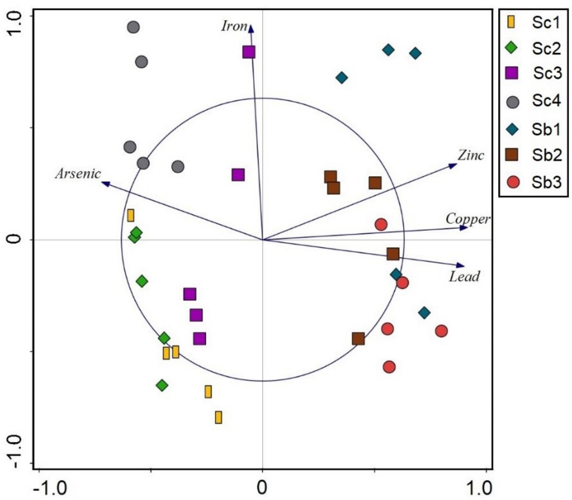

Figure 2. Perceptual map f principal component analysis for metals and metalloids in corn and barley soils

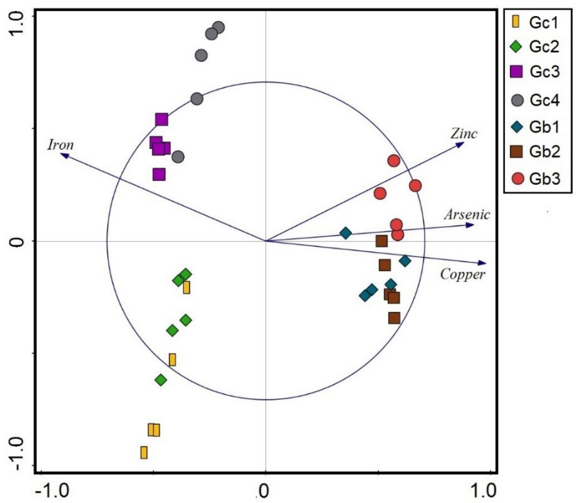

Figure 3. Perceptual map of principal component analysis for metals and metalloids in corn and barley grains

Table 3. Non-carcinogenic risks to humans from soil lead and arsenic

Element	Sampling zones	C_{CUL} mg kg^{-1}	Pathways exposure	CDI			HQ			HI		
				Children	Adult	Farmer	Children	Adult	Farmer	Children	Adult	Farmer
Pb	Sc1	92.68	Ingestion	1.18×10^{-3}	1.02×10^{-4}	3.35×10^{-4}	3.39×10^{-1}	2.90×10^{-2}	9.58×10^{-2}			
			Inhalation	6.53×10^{-8}	5.23×10^{-8}	5.23×10^{-8}	4.27×10^{-2}	3.47×10^{-3}	3.47×10^{-3}	9.02×10^{-1}	7.69×10^{-2}	2.35×10^{-1}
			Dermal	1.49×10^{-4}	1.22×10^{-5}	1.22×10^{-5}	1.87×10^{-5}	1.49×10^{-5}	1.49×10^{-5}			
	Sc2	108.36	Ingestion	1.39×10^{-3}	1.19×10^{-4}	3.92×10^{-4}	3.96×10^{-1}	3.39×10^{-2}	1.12×10^{-1}			
			Inhalation	7.64×10^{-8}	6.11×10^{-8}	6.11×10^{-8}	4.99×10^{-2}	4.06×10^{-3}	4.06×10^{-3}	5.83×10^{-1}	4.97×10^{-2}	1.52×10^{-1}
			Dermal	1.75×10^{-4}	1.42×10^{-5}	1.42×10^{-5}	2.18×10^{-5}	1.75×10^{-5}	1.75×10^{-5}			
	Sc3	95.48	Ingestion	1.22×10^{-3}	1.05×10^{-4}	3.45×10^{-4}	3.49×10^{-1}	2.99×10^{-2}	9.87×10^{-2}			
			Inhalation	6.73×10^{-8}	5.39×10^{-8}	5.39×10^{-8}	4.39×10^{-2}	3.58×10^{-3}	3.58×10^{-3}	5.22×10^{-1}	4.45×10^{-2}	1.36×10^{-1}
			Dermal	1.54×10^{-4}	1.25×10^{-5}	1.25×10^{-5}	1.92×10^{-5}	1.54×10^{-5}	1.54×10^{-5}			
	Sc4	111.23	Ingestion	1.42×10^{-3}	1.22×10^{-4}	4.02×10^{-4}	4.06×10^{-1}	3.48×10^{-2}	1.15×10^{-1}			
			Inhalation	7.84×10^{-8}	6.27×10^{-8}	6.27×10^{-8}	5.12×10^{-2}	4.17×10^{-3}	4.17×10^{-3}	6.87×10^{-1}	5.86×10^{-2}	1.79×10^{-1}
			Dermal	1.79×10^{-4}	1.46×10^{-5}	1.46×10^{-5}	2.24×10^{-5}	1.79×10^{-5}	1.79×10^{-5}			
	Sb1	242.53	Ingestion	3.10×10^{-3}	2.66×10^{-4}	8.77×10^{-4}	8.86×10^{-1}	7.59×10^{-2}	2.51×10^{-1}			
			Inhalation	1.71×10^{-7}	1.37×10^{-7}	1.37×10^{-7}	1.12×10^{-1}	9.09×10^{-3}	9.09×10^{-3}	5.64×10^{-1}	4.81×10^{-2}	1.47×10^{-1}
			Dermal	3.91×10^{-4}	3.18×10^{-5}	3.18×10^{-5}	4.89×10^{-5}	3.91×10^{-5}	3.91×10^{-5}			
	Sb2	171.15	Ingestion	2.19×10^{-3}	1.88×10^{-4}	6.19×10^{-4}	6.25×10^{-1}	5.36×10^{-2}	1.77×10^{-1}			
			Inhalation	1.21×10^{-7}	9.65×10^{-8}	9.65×10^{-8}	7.88×10^{-2}	6.41×10^{-3}	6.41×10^{-3}	5.13×10^{-1}	4.37×10^{-2}	1.34×10^{-1}
			Dermal	2.76×10^{-4}	2.25×10^{-5}	2.25×10^{-5}	3.45×10^{-5}	2.76×10^{-5}	2.76×10^{-5}			
	Sb3	243.06	Ingestion	3.11×10^{-3}	2.66×10^{-4}	8.79×10^{-4}	8.88×10^{-1}	7.61×10^{-2}	2.51×10^{-1}			
			Inhalation	1.71×10^{-7}	1.37×10^{-7}	1.37×10^{-7}	1.12×10^{-1}	9.11×10^{-3}	9.11×10^{-3}	5.14×10^{-1}	4.38×10^{-2}	1.34×10^{-1}
			Dermal	3.92×10^{-4}	3.19×10^{-5}	3.19×10^{-5}	4.90×10^{-5}	3.92×10^{-5}	3.92×10^{-5}			
As	Sc1	18.79	Ingestion	2.40×10^{-4}	2.06×10^{-5}	6.80×10^{-5}	8.01×10^{-1}	6.86×10^{-2}	2.27×10^{-1}			
			Inhalation	1.32×10^{-8}	1.06×10^{-8}	1.06×10^{-8}	1.01×10^{-1}	8.22×10^{-3}	8.22×10^{-3}	9.02×10^{-1}	7.69×10^{-2}	2.35×10^{-1}
			Dermal	3.03×10^{-5}	2.46×10^{-6}	2.46×10^{-6}	4.42×10^{-5}	3.53×10^{-5}	3.53×10^{-5}			
	Sc2	12.14	Ingestion	1.55×10^{-4}	1.33×10^{-5}	4.39×10^{-5}	5.18×10^{-1}	4.44×10^{-2}	1.46×10^{-1}			
			Inhalation	8.56×10^{-9}	6.85×10^{-9}	6.85×10^{-9}	6.52×10^{-2}	5.31×10^{-3}	5.31×10^{-3}	5.83×10^{-1}	4.97×10^{-2}	1.52×10^{-1}
			Dermal	1.96×10^{-5}	1.59×10^{-6}	1.59×10^{-6}	2.85×10^{-5}	2.28×10^{-5}	2.28×10^{-5}			
	Sc3	10.89	Ingestion	1.39×10^{-4}	1.19×10^{-5}	3.94×10^{-5}	4.64×10^{-1}	3.98×10^{-2}	1.31×10^{-1}	5.22×10^{-1}	4.45×10^{-2}	1.36×10^{-1}

Ingestion HQ (HQ_{ing}) was most significant with respect to dermal HQ (HQ_{derm}) and inhalation HQ (HQ_{inh}). In children, the HQ_{ing} values corresponding to Pb in the corn-growing soils were lower than the Pb HQ_{ing} values in the barley-growing soils. The HQ_{ing} values of As in the corn soils were higher than the HQ_{ing} values of As in the barley soils. In children, the HQ values of Pb and As in both crop soils for the three exposure pathways were higher than the HQ values in farmers and adults. Overall, the HQ values of Pb and As in maize and barley soils indicated that adverse health effects are unlikely ($HQ_{ing/derm/inh} < 1$). The soil HI values of both crops were below the threshold value of 1 in all evaluated crop areas (HI < 1), indicating that the non-carcinogenic adverse effect is negligible. However, the corn soil HI values were higher than the barley soil HI values, especially for children whose hazard index values are significantly higher than those of farmers and adults.

The carcinogenic risk level (CR) of As from ingestion of corn and barley cropping soil contaminated by this metalloid is higher in children than in farmers and adults. In children, the RC of As from ingestion of contaminated barley and corn soils varied from 2.05×10^{-4} to 3.60×10^{-4} (mean cancer risk). In farmers, the RC of As from ingestion of these contaminated soils ranged from 5.80×10^{-5} low cancer risk) to 1.02×10^{-4} (medium cancer risk) and in adults from 1.76×10^{-5} to 3.09×10^{-5} (low cancer risk). Regarding the CR levels of As by inhalation of contaminated soils from both types of crops for children, farmers and adults, qualified as medium cancer risk. The CR and TCR values were within the range of the safety limit, 10^{-6} to 10^{-4} (USEPA, 2011). However, the CR values for children As were close to the safe limit in the northern part of the study area, indicating a higher risk compared to where corn is predominant, indicating a higher risk with respect to farmers and adults (Table 4).

The bioconcentration of As in grain was determined through the bioconcentration factor (BCF) (Table 5). The bioconcentration capacity determined by the BCF values of As was higher in the barley than in the corn growing areas. The THQ of the As exceeded the target value of 1 in 100% of the barley and corn growing sampling sites. The THQ values of the for farmers and adults were lower than those recorded for children; however, they exceeded the target value of 1

Table 4. Carcinogenic risks to humans from soil arsenic

Sampling zones	C_{CUL}, mg kg^{-1}	Pathways exposure	CR			TCR		
			Children	Adult	Farmer	Children	Adult	Farmer
Sc1	18.79	Ingestion	3.60×10^{-4}	3.09×10^{-5}	1.02×10^{-4}	1.87×10^{-3}	1.54×10^{-4}	2.25×10^{-4}
		Inhalation	4.79×10^{-4}	3.83×10^{-4}	3.83×10^{-4}			
Sc2	12.14	Ingestion	2.33×10^{-4}	2.00×10^{-5}	6.59×10^{-5}	1.21×10^{-3}	9.96×10^{-5}	1.46×10^{-4}
		Inhalation	3.10×10^{-4}	2.48×10^{-4}	2.48×10^{-4}			
Sc3	10.89	Ingestion	2.09×10^{-4}	1.79×10^{-5}	5.91×10^{-5}	1.09×10^{-3}	8.93×10^{-5}	1.30×10^{-4}
		Inhalation	2.78×10^{-4}	2.22×10^{-4}	2.22×10^{-4}			
Sc4	14.32	Ingestion	2.75×10^{-4}	2.35×10^{-5}	7.77×10^{-5}	1.43×10^{-3}	1.17×10^{-4}	1.72×10^{-4}
		Inhalation	3.65×10^{-4}	2.92×10^{-4}	2.92×10^{-4}			
Sb1	11.76	Ingestion	2.26×10^{-4}	1.9×10^{-5}	6.38×10^{-5}	1.17×10^{-3}	9.65×10^{-5}	1.41×10^{-4}
		Inhalation	3.00×10^{-4}	2.40×10^{-4}	2.40×10^{-4}			
Sb2	10.69	Ingestion	2.05×10^{-4}	1.76×10^{-5}	5.80×10^{-5}	1.07×10^{-3}	8.77×10^{-5}	1.28×10^{-4}
		Inhalation	2.73×10^{-4}	2.18×10^{-4}	2.18×10^{-4}			
Sb3	10.70	Ingestion	2.05×10^{-4}	1.76×10^{-5}	5.80×10^{-5}	1.07×10^{-3}	8.78×10^{-5}	1.28×10^{-4}
		Inhalation	2.73×10^{-4}	2.18×10^{-4}	2.18×10^{-4}			

Table 5. Bioconcentration factor and carcinogenic risks to humans from grain arsenic.

Sampling sites	BCF	THQ			CR		
		Children	Adult	Farmer	Children	Adult	Farmer
Gc1	0.005	2.88	1.41	1.41	1.30×10^{-3}	6.32×10^{-4}	6.32×10^{-4}
Gc2	0.009	3.41	1.66	1.66	1.53×10^{-3}	7.48×10^{-4}	7.48×10^{-4}
Gc3	0.007	2.18	1.06	1.06	9.80×10^{-4}	4.78×10^{-4}	4.78×10^{-4}
Gc4	0.010	4.43	2.16	2.16	2.00×10^{-3}	9.73×10^{-4}	9.73×10^{-4}
Gb1	0.016	5.83	2.84	2.84	2.62×10^{-3}	1.28×10^{-3}	1.28×10^{-3}
Gb2	0.014	4.55	2.22	2.22	2.05×10^{-3}	9.98×10^{-4}	9.98×10^{-4}
Gb3	0.018	5.81	2.84	2.84	2.62×10^{-3}	1.28×10^{-3}	1.28×10^{-3}

in 100% of the sampling sites for both crops. The sampling sites with barley cultivation quantified high non-carcinogenic risk, indicating a level of exposure sufficient to cause non-carcinogenic adverse health risks over a lifetime (USEPA, 1995). The carcinogenic risk of As in cereals exceeded the acceptable risk level of 10^{-6} in all sampling zones (USEPA, 2011).

DISCUSSION

Increasing presence of heavy metals and metalloids in water, soil and food is a problem of great environmental, agricultural and health concern worldwide (Yang et al., 2007). The availability of good quality water for agriculture is decreasing due to the strong anthropogenic pressures (e.g., poor waste management, mining and agrochemicals) on aquatic systems. The soil and water contamination is directly related to cross-contamination of food through irrigation. The accumulation of heavy metals and metalloids in agricultural soil is of increasing concern to today's society due to the highly toxic and carcinogenic nature of these elements (Basha et al., 2014). The results obtained reveal that only the Pb concentrations in the soils where both cereals are grown greatly exceeded the Peruvian standard soil EQS (Ministry of the Environment, 2017) and the FAO/WHO threshold values (FAO/WHO, 1993).

Spatial distribution of heavy metals and metalloids in the agricultural soils analyzed in this study depends on the natural and anthropogenic sources. The Andean Mesozoic belt in central Peru represents a rich source of heavy metals and metalloids. Because of this, the intensive exploitation of these minerals began more than a century ago with the consequent generation of waste that ended up contaminating the soil. The contamination of soil and plants at a global level is widely demonstrated in several studies (Ordóñez et al., 2011; Chaoua et al., 2018; Doabi et al., 2018) and very rarely in the soils and food grains in Peru. The high concentrations of Pb in the corn and barley soils recorded in this study are mainly due to the transport of this metal through the waters of the Mantaro River. Monitoring by the Ministry of Agriculture Ministry of Agriculture (2010) of this river reveals high concentrations of heavy metals and metalloids that exceed the water EQS. However, during the dry season, the Mantaro River waters are used for irrigation of large agricultural areas throughout the basin.

Corn and barley are important food crops in the diet of the Andean population, mainly. Corn has been implicated as an important route of exposure to heavy metals and metalloids, especially in the areas with strong mining influence (Apablaza et al., 2017). In grains of these cereals, the heavy metals with toxicological effect such as Pb were not detected. Therefore, the consumption of these cereals from the study area does not represent a danger to human health. As showed mean concentrations lower than the FAO/WHO and EPA safety limits (FAO/WHO, 2011; EPA, 2004). In addition, there is no maximum permitted level of As in cereals and related products established by Codex alimentarius or the European Union (Joint FAO/WHO Food Standards Programme, 2001; Branco et al., 2015). However, the exposure of crops to As, even at very low concentrations, can cause many morphological, physiological and biochemical changes. The results also reveal that the concentration of heavy metals in grains is affected by the chemical speciation of heavy metals in the soil, the soil properties and the genetic characteristics of the crops (Adekiya et al., 2018).

The human exposure to heavy metals and metalloids through ingestion, dermal contact and inhalation of soil and ingestion of contaminated food is a more frequent health problem worldwide (Wang et al., 2019). The HQ values varied by route of exposure, daily intake, age and soil type. The Pb HQ_{ing} values in children, farmers and adults revealed that adverse health effects are unlikely. However, results show that children have a higher lead intake than farmers and adults. Many studies reveal that the lead intake can cause major changes in several biological processes at the cellular and molecular level, such as alteration of the composition of biomembranes, interference with the functioning of enzyme systems, decoupling of biochemical reactions and blocking of release of neurotransmitters and encephalopathies (Dórea, 2019). There is great evidence about the association of the Pb exposure with several disorders or diseases. In the gestation period, the exposure to this heavy metal can cause miscarriages, premature births, low birth weight and neonatal deaths (Claus Henn et al., 2016; Sanders et al., 2018), due to the great facility of Pb to cross the placental barrier. In children, the exposure to Pb causes learning and behavior disorders, lowered intelligence quotient, and hearing disorders (Pebe et al., 2008). Other diseases associated with the Pb exposure are diabetes, hypertension and cardiovascular disease (Thayer et al., 2012).

The exposure routes reveal that ingestion of soil from the arsenic-contaminated cereal crops is the main pathway of exposure to this metalloid, followed by the inhalation pathway. In children, the HQ from ingestion and inhalation of arsenic-contaminated cereal crop soil was higher than the hazard quotient for farmers and adults. Global studies report that the arsenic toxicity affects mainly the digestive, nervous, renal, and skin systems (Mendez et al., 2016; Claus Henn et al., 2016). The health risk indices for ingestion (HI_{ing}) of the soil contaminated by Pb and As were lower than the unit for children, farmers and adults. The CR assessment for As and Pb ingestion in corn and barley grains studied was greater than 1 in a million (10^{-6}), indicating a significant risk according to USEPA (USEPA, 2007).

CONCLUSIONS

The soils of the Mantaro River valley in central Peru are exposed to contamination by heavy metals and metalloids, because large agricultural areas are irrigated with water from the Mantaro River (a river with a high content of toxic elements) during the dry season. The decreasing order of average concentrations of heavy metals and arsenic in the soil samples from corn and barley cultivation was: Fe > Zn > Pb > Cu > As. The concentrations of Fe and As in the corn cultivation soils were higher than the concentrations of these elements in the barley cultivation soils. Similar behaviors were presented by the Cu, Pb and Zn concentrations in the barley soils with respect to the concentrations of these elements in the corn soils. Fe was the only heavy metal in corn grains that presented average concentrations higher than the average concentrations in barley grains. The average concentrations of Cu, Zn and As in barley grains were significantly higher than the average concentrations of these heavy metals and metalloids in corn grains. The PERMANOVA analysis showed that the effect of the type of crop and the sampling sector influence the concentrations of Pb, Cu, Fe, Zn and As in soil and grains significantly ($p < 0.05$).

Health risk assessment showed that the order of exposure was children > farmers > adults. Out of the three routes of exposure to heavy metals and arsenic in soil, ingestion was the main route of exposure, followed by the respiratory exposure and finally by dermal contact exposure. The evaluation of the carcinogenic and non-carcinogenic risks due to the exposure to heavy metals and metalloids in crop soils and corn and barley grains in children, farmers and adults showed that the route of ingestion was the most representative. The soil HI values of both cereals were less than unity in all crop areas evaluated (HI < 1), indicating that the non-carcinogenic adverse effect is negligible. The carcinogenic risk level of As from the ingestion of corn and barley crop soils contaminated by this metalloid is higher in children than in farmers and adults. The carcinogenic risk of As in cereals exceeded the acceptable risk level of 10^{-6} in all sampling zones.

These findings suggest the implementation of strategies for the regular monitoring of contamination by toxic elements of soils and food crops in order to prevent the health problems caused by the ingestion of contaminated vegetables, especially As. It is also recommended that farmers in the study area be informed about the appropriate use of agrochemicals and that they analyze the soils of their agricultural fields before each growing season.

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