Original article

Human risk associated with the ingestion of artichokes grown in soils irrigated with water contaminated by potentially toxic elements, Junin, Peru

María Custodio *, Richard Peñaloza, Salomé Ochoa, Walter Cuadrado

Universidad Nacional del Centro del Perú, Facultad de Medicina Humana, Centro de Investigación en Medicina de altura y Medio Ambiente, Av. Mariscal Castilla N° 3909, Huancayo, Peru

A R T I C L E   I N F O

Article history:
Received 11 December 2020
Revised 12 June 2021
Accepted 20 June 2021
Available online 24 June 2021

Keywords:
Soil
Artichoke
Potentially toxic elements
Carcinogenic risk
Non-carcinogenic risk

A B S T R A C T

The contamination of water, air and soil with potentially toxic elements (PTE) compromises the supply of contaminant free food. Vegetables grown in contaminated soils can absorb and accumulate PTE at concentrations that are toxic to human health. In this context, the human risk associated with the intake of artichokes grown in soils irrigated with PTE contaminated water was assessed. 120 samples of surface soil and artichoke heads were collected and the concentrations of Cu, Fe, Pb, Zn and As were determined. The results showed that the concentrations of Cu, Fe and Zn in soil did not exceed the standards of the Ministry of Environment of Peru, but they did exceed those of Pb (125.45 mg kg$^{-1}$) and As (28.70 mg kg$^{-1}$). The decreasing order of mean PTE concentration in artichoke heads was Fe > Zn > Cu > Pb > As, exceeding the permissible levels of FAO/WHO CODEX Alimentarius. However, the concentrations of As comply with the maximum limits of inorganic contaminants in vegetables (0.3 mg kg$^{-1}$) established in the MERCOSUR regulations. The non-carcinogenic and carcinogenic risk of Pb and As indicated that the ingestion of artichoke heads does not represent a health risk.

1. Introduction

Water and soil contamination by potentially toxic elements (PTE) is a global concern because it threatens food security and human health (Bui et al., 2016; da Silva Júnior et al., 2019; Deng et al., 2021; Pereira et al., 2021). Soil contamination comes mainly from industrial and urban waste, excessive use of fertilizers and pesticides, and air pollution (Ahmed et al., 2019); as well as, soil erosion, lithogenesis, weathering, and geological processes (Alfaro et al., 2019). Irrigation of agricultural soils with water contaminated with PTE in the long term can influence the metal speciation and sorption capacity of the soil favoring its availability. The uptake of PTE from soil by plants depends on the physicochemical properties and solubility of the metal element, soil pH, redox potential, soil type and plant species (Ali and Al-Qahtani, 2012; Khan et al., 2019). PTE are not degradable, are not metabolized, can accumulate and persist for years (Bortey-Sam et al., 2015; Gruszeczka-Kosowska, 2019; Pehoiu et al., 2020), increasing their persistence in soil.

Vegetables grown in soils irrigated by PTE contaminated water can absorb and accumulate these elements in concentrations that are toxic to human health. Pb accumulates mainly in roots and As can be concentrated in grains and fruits (Fagnano et al., 2020). Some metals such as copper (Cu), zinc (Zn), manganese (Mn), iron (Fe) and nickel (Ni) are micronutrients and enzyme cofactors essential for the normal development of biochemical and physiological processes (Jan et al., 2015; Arévalo-Gardini et al., 2017; Tyopine et al., 2020). However, excessive accumulation of toxic and essential elements in vegetables as well as excessive intake can induce negative effects on human health (Yin et al., 2017). High concentrations of Fe have been associated with Parkinson's disease (Hussien et al., 2018), of Cu with liver disorders and of Zn with reduced immune system activity (Jomova et al., 2010; Adimalla, 2020).

The central region of Peru is one of the regions that bases its economy on the mining industry and agricultural activity. Envir-
mental contamination problems due to the development of the mining-metallurgical industry almost a century ago have affected the environmental quality of the region, especially the Mantaro River basin. In addition, the Mantaro River receives wastewater discharges throughout the basin. The waters of the Mantaro River are contaminated by PTE (Mantaro Water Management Authority, 2015), but are used for irrigation of large agricultural extensions of the Mantaro Valley. Different types of food crops are grown throughout the year, such as potatoes, corn, quinoa, barley, wheat, and vegetables. Artichoke (Cynara scolymus L.) is a highly valued vegetable for its nutritional and therapeutic properties (Pagnotta et al., 2017). It is hepatoprotective, choleretic, cholagogue, hypocholesterolemic and adjuvant in diets aimed at weight control. As a nutrient it is very suitable to avoid the excesses of the diet poor in vegetables and fiber and excessively rich in fats (Zayed, et al., 2020).

Exposure to PTE through direct ingestion of soil, water and food crops, inhalation of soil particles and dermal contact with contaminated soil and water has a major impact on human health (US EPA, 2011; Gruszeczka-Kosowska, 2019). The present study applied the EPA (2004) methodology that considers exposure dose (ingestion dose, dermal contact and inhalation), non-carcinogenic risk assessment (hazard quotient and hazard index) and carcinogenic risk (chronic daily intake and cancer risk). Although the health risk of toxic metals has been extensively studied (Yan et al., 2018; Natasha et al., 2021), most research has focused on ingestion as a pathway to assess potential health risks (Woldetsadik et al., 2017; Kumar and Prasad, 2018; Afonne and Ibedio, 2020; Xie et al., 2021), revealing little attention to the other exposure pathways in the soil-crop system.

Since the use of PTE contaminated water in agricultural soil irrigation is a common practice that threatens food security, economic development and human health, there is a great need for information on the concentrations of these toxic elements in agricultural soil and this crop. In addition, there is a lack of available information on potential health risks in areas where PTE contaminated water is being used for agricultural production in central Peru. In this context, the objective of the present study was to evaluate the human risk associated with the ingestion of artichoke grown in soils irrigated with water contaminated by potentially toxic elements in the Junín region, Peru.

2. Material and methods

2.1. Description of the study area

The study area is located in the Mantaro river basin in central Peru, between 75°18′ 33″ west longitude and 11° 54′ 59″ south latitude, between 2500 and 4000 m altitude. The Mantaro river is the main river in the basin that is fed by tributaries that run through the central Andean Mesozoic belt (Petersen, 1965). For decades, the Mantaro river has experienced contamination by potentially toxic elements that exceed the environmental quality standards for water from rivers in the sierra (National Water Authority, 2014). Most of the agricultural area of the Mantaro valley in the dry season is irrigated with water from the Mantaro river (Agriculture Ministry, 2008). The climate is semi-frigid and humid with temperatures ranging from 7 to 12°Celsius. The highest rainfall occurs during the rainy season, on average it rains about 280 mm per month, equivalent to 80% of the annual rainfall. The relative humidity varies from 52 to 71% (Rodbell et al., 2014). The sampling areas were established in sectors with artichoke cultivation. Sector 1 (S1) was established in the Mantaro district of Jauja province and sectors S2, S3 and S4 were established in the Matahuasi, Mito and Orcotuna districts of Concepción province in the Junín region, respectively (Fig. 1). These four districts have a long history of agricultural production with the Mantaro river as their water source.

2.2. Sampling and pre-treatment of samples

The sampling was carried out in agricultural areas with artichoke cultivation in sectors S1, S2 and S3 and S4 established in districts of the provinces of Jauja and Concepción, in September 2020. A total of 120 samples of surface soil and artichoke heads were collected. In each sector five plots were sampled and in each of them five sub-samples of soil were collected from the 20 cm depth using a stainless steel drill type device. The soil subsamples were mixed to obtain three composite samples for each plot according to the standard method of the Ministry of Environment. Artichoke head samples were collected from the same soil sampling sites of the respective plots (FAO, 2004). The samples were placed in zippered 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 sieve to remove stones and plant debris. The sieved soil was placed in a Binder electric oven (model FD-115) at 80°C for 48 h. The completely dry samples were ground in a Fritsch Pulverisette 2 mortar mill (with zirconium oxide chamber and 0.074 mm mesh). The resulting soil was stored in 250 ml high density polyethylene (HDPE) containers until further analysis. Bracts from artichoke heads were separated and washed with deionized water and air-dried for 10 days at room temperature. The dried samples were ground and transferred to HDPE containers for PTE analysis.

2.3. Digestion and analytical procedures

In soil samples, the digestion was performed from one gram of the sample contained in a 250 ml beaker and 10 ml of concentrated HNO3 was added. The beakers with the mixture were heated at 100°C for 45 min to oxidize all oxidizable matter. After cooling, 5 ml of 70% HClO4 was added and the mixture was brought to boiling until the appearance of white fumes. These were allowed to cool and 20 ml of distilled water was added and again brought to boiling. The digested samples were allowed to cool and filtered through Millipore filters. The filtrates were transferred to 25 ml volumetric flasks and made up to volume with distilled water.

Samples of powdered artichoke heads (1 g) were digested with 10 ml of a mixture of HNO3 and HClO4 in a 2:1 ratio and left overnight. The next day, the samples treated with the mixture of the acids were heated until the brown fumes turned white. The digested samples were filtered into 50 ml graduated tubes and transferred to volumetric flask and the final volume was adjusted to 50 ml with distilled water (Mahmood et al., 2013). The concentration of Cu, Fe, Pb and Zn (mg L⁻¹) was analyzed using flame atomic absorption spectrophotometry (F-AAS) and As using graphite furnace atomic absorption spectrophotometry (GF-AAS) with an Atomic Absorption Spectrophotometer (Varian AA240). All samples were analyzed in triplicate.

2.4. Quality control and assurance

Quality control and quality assurance was performed by quality control methods that included replication, the use of norms for each metal investigated as indicated by the standard method, considering the detection limit, accuracy procedures or optimal recovery percentage of the instrument (Table S1). All chemicals and standard solutions for heavy metals and metalloid were of analytical grade (99.98% purity level) purchased from Merck (Germany). With the 1000 mg L⁻¹ standard for Pb, Cu, Fe, Zn and As, an average
standard of 100 mg L⁻¹ concentration was prepared. Working standards were prepared with 1% nitric acid.

2.5. Statistical analysis

The statistical analyses were performed with the Vegan package of the R software. The Kruskal-Wallis test was used as a non-parametric method to compare PTE concentrations in artichoke heads by sector. To quantify the distinct absorption capacity of artichoke heads in relation to soils, transfer factors (TF) were calculated that result from the ratio of the mean PTE concentrations in the heads to the soil multiplied by 100. In addition, TF are used in several studies to determine the relationship between PTE content in crops and soil content (Peris et al., 2007). Redundancy analysis (RDA) was used to investigate relationships between PTE levels in artichoke heads and soil concentrations (Gan et al., 2017), using canonical ordination analysis in the Canoco 5 software. Spearman’s rho correlation analysis was used to identify the interaction of environmental and physiological parameters of the metals. The analysis of permutational multivariate variance test (PERMANOVA) was used to determine the significant differences (α = 0.05) at multivariate level of the sectors under study either for PTE concentration in soils and artichoke heads.

2.6. Human health risk assessment

2.6.1. Exposure dose

The risk assessment was conducted on the basis of exposure doses to PTE in artichoke soil using equations (1), (2) and (3) (EPA, 2004) and their respective parameters (Table 1).

\[
D_{\text{ing}} = \left( \frac{C_s \times \text{IngR} \times EF \times ED}{BW \times AT} \right) \times 10^{-6} 
\]

\[
D_{\text{der}} = \left( \frac{C_s \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \right) \times 10^{-6} 
\]

\[
D_{\text{inh}} = \frac{C_s \times \text{inhR} \times EF \times ED}{PEF \times BW \times AT} 
\]

Where, \( D_{\text{ing}} \) is the exposure dose through ingestion, \( D_{\text{der}} \) is the exposure dose through dermal absorption and \( D_{\text{inh}} \) is the exposure dose through inhalation of the element from the soil (mg kg⁻¹ body weight-day). \( C_s \) is the concentration of the element in the soil (mg kg⁻¹).

2.6.1.1. Non-carcinogenic risk assessment. The non-carcinogenic risk has been evaluated through the hazard quotient (HQ), calculated by dividing the average daily intake value by the reference dose (Antoniadis et al., 2019).

\[
HQ_{\text{ing/der/inh}} = \frac{D_{\text{ing/der/inh}}}{R\text{D}_{\text{ing/der/inh}}} 
\]

Where, \( HQ_{\text{ing/der/inh}} \) is the hazard quotient for ingestion, dermal contact or inhalation.

If \( HQ \leq 1 \) means that adverse health effects are unlikely, \( HQ > 1 \) reveals probable adverse health effects. \( HQ > 10 \) indicates high chronic risk (Khalli et al., 2019).

The overall potential for non-cancer effects has been assessed by integrating the HQs calculated for each element and expressed as a hazard index (HI) (Al-bagawi, 2019).

\[
HI = \sum_{i=1}^{n} HQ_{\text{ing/der/inh}} 
\]
3. Results

3.1. Content and distribution of potentially toxic elements in soil and artichoke heads

The mean and standard deviation of PTE concentrations determined in soil samples and artichoke heads from sectors S1, S2, S3, and S4 of the provinces of Jauja and Concepción in the Junín region are presented in Table 3. The decreasing order of mean PTE concentrations in soil samples of artichoke cultivation was: Fe > Zn > Pb > Cu > As. The highest mean concentration of Cu (62.68 mg kg\(^{-1}\)) was recorded in S3. Pb (125.45 mg kg\(^{-1}\)) in S4, Zn (681.60 mg kg\(^{-1}\)) in S1, Fe (1498.80 mg kg\(^{-1}\)) in S1 and As (28.70 mg kg\(^{-1}\)) in S3. The mean concentrations Cu in soil samples recorded in all sectors did not exceed the limit values of international environmental quality standards, except for the standard values of soil protection of the Ministry of Environmental Protection of China (EPMC) in their lower range values (50–200 mg kg\(^{-1}\)) (EPMC, 2014). The mean Pb concentrations recorded in all sectors under study did not exceed the standard values of the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) (100 mg kg\(^{-1}\)) (WHO/FAO, 2011a), Environmental Protection Agency (200 mg kg\(^{-1}\) (US EPA, 2002) and Ministry of Environment Canada (200 mg kg\(^{-1}\)) (CME, 2004) but were higher than the standard values of the EPMC (80 mg kg\(^{-1}\)) and the Ministry of Environment of Peru (MINEN) (70 mg kg\(^{-1}\)) (MINEN, 2017). As well as, to that reported by Guan et al., (2018) who report that metals may continue to accumulate in the study area reveal
the safe and unsafe zones for agricultural production. The spatial patterns of these toxic elements are dissimilar in their geographic distribution (Fig. S1). The spatial distribution maps of Cu and As show concentrations in the S3 and S4 sectors and that of Pb in the S4 sector on the right bank of the Mantaro River. While the highest Fe concentrations extended to the S1 sector. The spatial distribution of Zn was similar in the four sectors.

The decreasing order of mean PTE concentration recorded in artichoke heads was Fe > Zn > Cu > Pb > As. Artichoke heads obtained from S1 plots recorded the lowest mean concentrations of Cu (4.61 mg kg\(^{-1}\)), Pb (0.42 mg kg\(^{-1}\)) and As (0.14 mg kg\(^{-1}\)) and the highest concentrations of Fe (93.59 mg kg\(^{-1}\)) and Zn (31.91 mg kg\(^{-1}\)). In contrast, artichoke heads obtained from S3 and S4 plots recorded the highest mean concentrations of the PTE studied, except for Fe. All registered PTE in artichoke heads exceeded the maximum permissible levels (MPL) established by CODEX Alimentarius (FAO/WHO, 2011b). However, the concentrations of As recorded in artichoke heads comply with the maximum limits of inorganic contaminants in vegetables (0.3 mg kg\(^{-1}\) for As) established in the MERCOSUR regulation (acronym of the Southern Common Market in Spanish) (MERCOSUR/GMC/RES. No 12/11).

The transfer factor (TF) result reflects the potential ability of PTE to move from soil to edible parts of artichoke from sectors irrigated by PTE contaminated water (Table S2) (Custodio et al., 2021). The transfer of PTE from soil to food crops is one of the key processes through which humans are exposed (Kumar et al., 2019). The transfer factor (TF) values recorded in this study indicate that Cu and Zn are elements that tend to have greater mobility in the artichoke and a bioavailability proportional to their concentration in the soil (Table 3). The TF of the PTE in the four study sectors showed an order of Cu > Zn > As > Fe > Pb, which is consistent with the conclusions of other studies (Latif et al., 2018). The TF showed a maximum of 0.132 for copper and 0.055 for Zn, in line with other research indicating Zn as having a high transfer rate from soils (Peris et al., 2007).

The concentrations of Cu, Pb and Zn differ significantly from one sector to another according to the Kruskal Wallis test (Fig. 2). The highest Cu and Pb concentrations were significantly (p < 0.05) in the areas that were closest to the Mantaro river. The highest concentrations of Zn were recorded in the most distant sectors of the river where agricultural activity is intensive and the application of fertilizers and insecticides is frequent. Several studies indicate that Zn is a component of fertilizers and pesticides (Naz et al., 2018; Gupta et al., 2019). Therefore, the indiscriminate use of these agrochemicals would be another important source of Zn in the soil of the study area. The behavior of Cu and Pb would be due to continuous irrigation with water from the Mantaro river with a history of contamination from copper mining activity. The proximity of agricultural areas to the main road (hydrocarbon burning) with high vehicle traffic and atmospheric deposition would also be contributing to the Pb content.

The Pb concentrations recorded in artichoke heads were not homogeneous. This could be attributed to the fact that the highest value of PTE accumulation in vegetables occurs in the roots, which would indicate a limited translocation rate of the toxic systemic level. However, the accumulation will depend on the mechanism of heavy metal absorption, the plant species, age and part of the plant. The interaction between PTE is another reason for the non-homogeneous. This could be attributed to the fact that the highest value of PTE accumulation in vegetables occurs in the roots, which would indicate a limited translocation rate of the toxic systemic level. However, the accumulation will depend on the mechanism of heavy metal absorption, the plant species, age and part of the plant. The interaction between PTE is another reason for the non-homogeneous.
exaggerated use of agrochemicals among other factors (Machado et al., 2017).

Fig. 4 shows the ordination biplot of the redundancy analysis of PTE concentrations in soil and artichoke heads. The two axes represented a variation of 38.62% of the distribution, showing for the first and second axis an explanation value of 24% and 14%, respectively. Distance analysis based on redundancy indicates that Pb and Zn concentrations in soil explain the distribution of concentrations in artichoke heads. Pb in soil has a greater contribution in the distribution and correlates significantly and positively with the concentration of Pb in artichoke heads, with an explanation percentage of 18.3% of the total (39.4%). Zn in soil has an explanation percentage of 13% and is the second metal that determines the distribution, with positive correlation with the concentration of Zn in artichoke heads. Pb and Zn enter the roots from the soil through the intake of water mixed with minerals and nutrients and then they are mobilized to the shoots and other organs. Cu, Fe and As showed no spatial correlation, indicating that soil was not their only source.

Spearman’s correlation analysis for both factors individually explains this contrast. In the artichoke head, Pb only correlates positively and significantly with Cu at a rho of 0.49. In the soil, As correlates positively and significantly with Cu, with a rho of 0.72. The PERMANOVA analysis for PTE concentrations in artichoke heads indicates that S1 is significantly different from S3 and S4 (p < 0.05). While for PTE concentrations in soil S3 is significantly different from the other sectors.

3.2. Health risk assessment for exposure to potentially toxic elements

In Peru, many studies focus on assessing heavy metal and metalloid contamination of water and soil, but information on health risks from eating vegetables contaminated with heavy metals is quite limited. The results of the non-carcinogenic risks to humans from exposure to Pb and As for children, adults and farmers are shown in Table 4 and the carcinogenic risk in Table 5. The non-carcinogenic risks were determined by the hazard quotient and hazard index. In general, the HQ of ingestion was the most significant with respect to HQing and HQder. In children, the HQing of Pb in soil was higher than the HQing of adults and farmers. Los valores del HQing values in all sectors sampled indicated that adverse health effects are unlikely (HQing < 1). Similar behavior to the HQing of Pb showed the values of the HQing of As in sectors S1 and S2. However, the HQing of As in sectors S3 and S4 indicated probable adverse health effects (HQing > 1). In adults and farmers, the HQing de Pb and As indicated that adverse health effects are unlikely (HQing < 1).

The Pb hazard index recorded HI < 1 values, indicating that there is no evident risk for the population to suffer from non-carcinogenic effects in the study sectors. However, in the S4 sector the HI registered values of 0.52 for children, 0.04 for adults and 0.13 for adult farmers, indicating that this sector is the one with the highest HI value; since the risk quotients for the metal exposure pathways are high. The sectors S1, S2 and S3 have a homogeneous distribution of risk indexes, with values close to the third decile of the maximum recommended value for children, the third percentile for adults and the first decile of the maximum value for farmers. These results indicate that there is a probable risk for children whose risk index values are significantly higher than those of an adult or a farmer. The As hazard index for children recorded HI values ≥ 1, indicating evident risk of non-carcinogenic effects in the S1-S4 sectors of the study area.

The carcinogenic risk (CR) of Pb to children through soil ingestion from sectors included in the study ranged from $1.80 \times 10^{-3}$ to
Carcinogenic risks to humans by exposure to lead and arsenic in soil from artichoke cultivation in the Junin region of Peru.

| PTE | Crop sector | Pathways exposure | CDI | HQ | HI |
|-----|-------------|-------------------|-----|----|----|
| Pb  | S1          | Ingestion         | 1.21 × 10⁻³ | 3.47 × 10⁻¹ | 3.9 × 10⁻¹ |
|     |             | Inhalation        | 6.70 × 10⁻⁴ | 1.91 × 10⁻⁵ | 3.9 × 10⁻⁴ |
|     |             | Dermal            | 1.53 × 10⁻⁴ | 3.42 × 10⁻⁴ | 3.9 × 10⁻⁴ |
|     | S2          | Ingestion         | 1.20 × 10⁻³ | 1.89 × 10⁻⁵ | 3.9 × 10⁻⁴ |
|     |             | Inhalation        | 6.60 × 10⁻⁸ | 1.89 × 10⁻⁵ | 3.9 × 10⁻⁴ |
|     |             | Dermal            | 1.51 × 10⁻⁴ | 4.31 × 10⁻⁵ | 3.9 × 10⁻⁴ |
|     | S3          | Ingestion         | 1.25 × 10⁻³ | 3.58 × 10⁻⁵ | 4.0 × 10⁻¹ |
|     |             | Inhalation        | 6.92 × 10⁻⁸ | 1.98 × 10⁻⁵ | 4.0 × 10⁻¹ |
|     |             | Dermal            | 1.58 × 10⁻⁴ | 4.52 × 10⁻⁵ | 4.0 × 10⁻¹ |
|     | S4          | Ingestion         | 1.60 × 10⁻³ | 4.58 × 10⁻⁵ | 5.2 × 10⁻¹ |
|     |             | Inhalation        | 8.85 × 10⁻⁸ | 2.53 × 10⁻⁵ | 5.2 × 10⁻¹ |
|     |             | Dermal            | 2.02 × 10⁻⁴ | 5.77 × 10⁻⁷ | 5.2 × 10⁻¹ |
| As  | S1          | Ingestion         | 2.70 × 10⁻⁴ | 8.99 × 10⁻⁴ | 1.0 |
|     |             | Inhalation        | 1.49 × 10⁻⁴ | 4.96 × 10⁻⁶ | 1.0 |
|     | S2          | Ingestion         | 3.40 × 10⁻⁵ | 1.13 × 10⁻¹ | 1.1 |
|     |             | Inhalation        | 2.85 × 10⁻⁴ | 9.50 × 10⁻⁰ | 1.1 |
|     | S3          | Ingestion         | 1.57 × 10⁻⁴ | 5.24 × 10⁻⁴ | 1.1 |
|     |             | Inhalation        | 3.59 × 10⁻⁵ | 6.20 × 10⁻⁰ | 1.1 |
|     | S4          | Ingestion         | 2.02 × 10⁻⁴ | 6.75 × 10⁻⁰ | 1.4 |
|     |             | Inhalation        | 4.62 × 10⁻⁵ | 1.54 × 10⁻⁰ | 1.4 |
|     |             | Dermal            | 3.57 × 10⁻⁵ | 1.19 | 1.3 |

2.41 × 10⁻³ (high cancer risk). These results reveal that the CR of Pb from ingestion of soil contaminated by this PTE is higher in children than from adults and farmers. The CR of As for children ranged from 4.05 × 10⁻⁴ to 5.50 × 10⁻⁴ (medium cancer risk) and for farmers ranged from 1.14 × 10⁻⁴ to 1.56 × 10⁻⁴ (medium cancer risk). The CR of Pb and As for children and adults (including farmers) through inhalation of soils from the sectors evaluated qualified as high and medium risk, respectively (US EPA 2011). Pb CR for children qualified as low cancer risk and in adults and farmers as very low cancer risk. The As TCR for children qualified as high cancer risk and in adults and farmers as medium cancer risk (Table 5).

The concentration of Pb and As in artichoke heads determined by the TF showed a homogeneous trend, except in the S1 sector that registered minimum TF values of 0.004 and 0.006 for Pb and As, respectively (Table 6). In all study sectors, artichoke head samples showed a TF value <1 for Pb and As, indicating that artichoke absorbs heavy metal, but it does not concentrate it in the heads. This result coincides with several studies that indicate that edible plant organs are not the main site of heavy metal accumulation (Tóth et al., 2016; Yañez et al., 2018). Other studies that support our findings refer to Pb as one of the low-mobility PTE that can accumulate in the root and shoots (Gatta et al., 2018). The non-carcinogenic risk (THQ) and the carcinogenic risk (CR) were also quantified. In children, adults and farmers, the THQ of Pb and As was lower than the target value (THQ <1), indicating that in this population group they do not represent a potential health risk after ingestion of artichoke heads. The RC of Pb in artichoke heads for
the three groups of the population under study showed an acceptable risk of $10^{-6}$ (US EPA, 2011). In contrast, the CR of As obtained revealed a low $10^{-5}$ cancer risk from exposure to As through ingestion. Therefore, frequent consumption of vegetables contaminated with Pb results in a high body accumulation of Pb that will increase the risk of neurological disorders and anemia. The high concentration of As has impacts on human health such as: skin disorders and respiratory and dermatologic problems.

4. Discussion

4.1. Content of potentially toxic elements in soil and artichoke heads

The contamination of water and soil by PTE is a problem of great concern worldwide, as it compromises the supply of food free of these contaminants (Neumann, 2016). Access to good quality water for agriculture is decreasing due to the degradation of water bodies. Soil contamination through irrigation with PTE contaminated water leads to cross-contamination of food. In the Mantaro River basin in the central region of Peru, large extensions of agricultural soils are irrigated with PTE contaminated water for more than eight decades (Custodio et al., 2021). The continuous use of these waters for irrigation has led to the accumulation of PTE in the agricultural soils of the study area, asrevealed by our findings.

The results obtained reveal that soils in sectors S3 and S4 recorded PTE concentrations that exceeded the maximum permitted limits of the national and international standard (MINEN, 2017; FAO/WHO, 2011a; CME, 2004; EPMC, 2014), which means that the soils in these sectors are undergoing degradation processes. The mean concentrations of As, Pb and Zn in this study were higher than the concentrations reported by Orellana et al. (2020) in high Andean areas with rainfed agriculture in the central region of Peru. The high concentration of Pb and As in sectors S3 and S4 reveal that the bioavailable concentration of heavy metals is higher in soils irrigated with contaminated water than in soils irrigated with rainwater. Soil quality is affected by the accumulation of Pb and As, which is one of the consequences of the mining and metallurgical activity that has been going on for more than eight decades in the Mantaro basin (Ministry of Agriculture, 2010). However, industrial waste, excessive use of agrochemicals and untreated urban effluents also contribute to soil contamination with PTE.

The results of the present study are supported by many studies around the world that report that irrigation with water contaminated with heavy metals and metalloids increases the mobile fraction of these contaminants in the soil (Marrugo-Negrete et al., 2017; Xiao et al., 2017; Keshavarzi and Kumar, 2019; Kumar et al., 2019; Adimalla et al., 2020; Filimon et al., 2021). The mean concentrations of Cu, Zn and As recorded in the study area were similar to the concentrations reported by Xiao et al. (2017) for agricultural soils with mining influence. Marked differences were only observed in comparison to mean Pb concentrations. However, all PTE concentrations recorded in this study did not exceed the maximum allowable concentrations for agricultural soils in China (350 mg kg$^{-1}$), revealing that the soils are safe for agricultural production.

The highest concentrations of PTE in artichoke heads were recorded in sectors S3 and S4. The result observed in S1 and S2 may be due to the continuous extraction of these toxic elements by the food crops grown during the year. Generally, PTE availability and mobility in the rhizosphere are influenced by root exudates and microorganisms (Kharazi et al., 2021). Other studies indicate that plants in soils irrigated by PTE contaminated water can absorb and accumulate these elements in concentrations that pose a potential threat to human health (Jan et al., 2015; Rehman et al., 2016). The high TF values of Cu and Zn reflect the high bioavailability of these elements in artichokes from the evaluated sectors. The TF values for all PTE in this crop were $< 1$, revealing that their uptake by the crop did not increase linearly with increasing metal concentrations in the soil of the study area. However, this behavior is determined by parameters, such as soil texture, soil pH, plant species, translocation and transpiration rate of metals, bioavailability of metals (Gupta et al., 2019).

4.2. Health risk assessment for exposure to potentially toxic elements

The HQing of soil contaminated with PTE in the central region of Peru is the most significant with respect to HQing Pb, HQing As and HQing Zn, which values in children, farmers and adults revealed that adverse health effects are unlikely (HQing $< 1$). The results indicate that children have a higher Pb ingestion than farmers and adults. These results coincide with those of (Ghasemidehkordi et al., 2018) who reported HQing Pb values of Pb in children older than adults. The same was also found in other similar works (Yang et al., 2018; Gruszeczka-Kosowska, 2019; Gruszeczka-Kosowska et al., 2020; Rehman et al., 2020; Haghnejaz et al., 2021), indicating the high vulnerability of children’s exposure to ingestion of PTE contaminated soil. An increased risk in children could also be attributed to low body weight.

Many studies indicate that Pb intake can cause significant changes in several biological processes at the cellular and molecular level, such as interfering with enzyme function, protein synthesis, biochemical defects, and blocking the release of neurotransmitters and encephalopathies. There is great evidence of the relationship of Pb exposure with various disorders. Exposure to Pb in the prenatal period can cause miscarriages, premature births, low birth weight and neonatal deaths (Sanders et al., 2018). In children, Pb exposure affects cognitive abilities, intelligence, memory, processing speed, and motor functions (Ji et al., 2018; Donzelli et al., 2019). Other diseases associated with Pb exposure are diabetes, hypertension, and cardiovascular disease (Thayer et al., 2012).

Table 6

| PTE | Crop sector | HQing | CR |
|-----|-------------|-------|----|
|     | Children    | Adult | Farmer |
| Pb  | S1          | 0.03  | 0.03 |
|     | S2          | 0.03  | 0.03 |
|     | S3          | 0.05  | 0.05 |
|     | S4          | 0.05  | 0.05 |
| As  | S1          | 0.11  | 0.10 |
|     | S2          | 0.14  | 0.14 |
|     | S3          | 0.16  | 0.15 |
|     | S4          | 0.11  | 0.10 |

The highest concentrations of PTE in artichoke heads were recorded in sectors S3 and S4. The result observed in S1 and S2 may be due to the continuous extraction of these toxic elements by the food crops grown during the year. Generally, PTE availability and mobility in the rhizosphere are influenced by root exudates and microorganisms (Kharazi et al., 2021). Other studies indicate that plants in soils irrigated by PTE contaminated water can absorb and accumulate these elements in concentrations that pose a potential threat to human health (Jan et al., 2015; Rehman et al., 2016). The high TF values of Cu and Zn reflect the high bioavailability of these elements in artichokes from the evaluated sectors. The TF values for all PTE in this crop were $< 1$, revealing that their uptake by the crop did not increase linearly with increasing metal concentrations in the soil of the study area. However, this behavior is determined by parameters, such as soil texture, soil pH, plant species, translocation and transpiration rate of metals, bioavailability of metals (Gupta et al., 2019).

4.2. Health risk assessment for exposure to potentially toxic elements

The HQing of soil contaminated with PTE in the central region of Peru is the most significant with respect to HQing Pb, HQing As and HQing Zn, which values in children, farmers and adults revealed that adverse health effects are unlikely (HQing $< 1$). The results indicate that children have a higher Pb ingestion than farmers and adults. These results coincide with those of (Ghasemidehkordi et al., 2018) who reported HQing Pb values of Pb in children older than adults. The same was also found in other similar works (Yang et al., 2018; Gruszeczka-Kosowska, 2019; Gruszeczka-Kosowska et al., 2020; Rehman et al., 2020; Haghnejaz et al., 2021), indicating the high vulnerability of children’s exposure to ingestion of PTE contaminated soil. An increased risk in children could also be attributed to low body weight.

Many studies indicate that Pb intake can cause significant changes in several biological processes at the cellular and molecular level, such as interfering with enzyme function, protein synthesis, biochemical defects, and blocking the release of neurotransmitters and encephalopathies. There is great evidence of the relationship of Pb exposure with various disorders. Exposure to Pb in the prenatal period can cause miscarriages, premature births, low birth weight and neonatal deaths (Sanders et al., 2018). In children, Pb exposure affects cognitive abilities, intelligence, memory, processing speed, and motor functions (Ji et al., 2018; Donzelli et al., 2019). Other diseases associated with Pb exposure are diabetes, hypertension, and cardiovascular disease (Thayer et al., 2012).
Arsenic $HQ_{\text{ing}}$ values in sectors S3 and S4 indicated probable adverse health effects. These results indicate that continued exposure to soils contaminated by this metalloid can cause serious health disorders. Several studies have shown that arsenic induces cognitive deficits in children, even at low concentrations (Karri et al., 2016; Kuo et al., 2017). Higher concentrations of arsenic exposure can alter children’s growth and development, leading to neurological deficits. In general, acute and sub-acute arsenic toxicity involves the gastrointestinal, dermal, nervous, renal, ophthalmic, and other systems (Tyler and Allan, 2014; Emenike et al., 2019); this will depend on the magnitude of the dose and the time of exposure. The HI values of As for children were $HI > 1$ in the study area, indicating an obvious health risk for children. These results are similar to those reported by Tang et al. (2017), who found $HI$ of 1.40 and Antoniadis et al. (2017), who reported an $HI$ ranging from 0.63 to 1.66.

The THQ values of Pb and As for artichoke in the four study sectors showed that the population is exposed to a relatively high health risk. However, Zhuang et al. (2009) point out that the ingested dose of heavy metals is not equal to the absorbed contaminant dose in reality, since a fraction of the ingested heavy metals can be excreted, and the rest accumulates in body tissues where it affects human health. Our results indicate that Pb and As represent a potential health risk from ingestion of artichoke contaminated with these elements (US EPA, 2007). As was the main contributor to total CR in all sectors of the study area. The present results are similar to those reported by Wu et al. (2020), who found that children had a higher risk of developing cancer than adults. Therefore, the results of the health risk assessment reveal the need to implement measures to control PTE contamination in soil and reduce the translocation of metals from soil to edible crops in the Mantaro watershed.

5. Conclusions

In Peru, as well as in other regions of the world, the shortage of water for irrigation is becoming increasingly evident. Large agricultural areas are irrigated with water contaminated by PTE that in the long term would be favoring its availability for absorption by food crops. Cu, Zn and Fe in soil presented concentrations in the range of national and international regulatory limits. In artichoke heads all PTE exceeded the maximum allowable levels established in the FAO/WHO CODEX Alimentarius. However, the concentrations of As recorded in artichoke heads comply with the maximum limits of inorganic contaminants in vegetables (0.3 mg kg$^{-1}$ for As) established in the MERCOSUR regulation. Our findings indicate that Cu and Zn are the elements that tend to have greater mobility in artichokes and a bioavailability proportional to their concentration in soil.

In the human risk assessment for PTE exposure in artichoke soil, Pb $HQ_{\text{ing}}$ values in all sectors sampled indicated that adverse health effects are unlikely ($HQ_{\text{ing}} < 1$). The Pb hazard index recorded HI $< 1$ values, indicating that there is no evident risk for the population to suffer from non-carcinogenic effects in the study sectors. The Pb TCR for children rated as low cancer risk and in adults and farmers as very low cancer risk. The As TCR for children qualified as high cancer risk and in adults and farmers as medium cancer risk. In all study sectors, samples of artichoke heads showed a value of BCF $< 1$ for Pb and As, indicating that artichoke absorbs heavy metal, but does not accumulate it. The THQ of Pb and As in children, adults, and farmers was lower than the target value (THQ $< 1$), indicating that in this population group does not represent potential health risk after ingestion of artichoke heads. The CR of Pb in artichoke heads for the three groups of the population under study showed an acceptable risk and the CR of As a low risk of cancer.

These findings suggest the implementation of continuous monitoring strategies for soil, food crop and water quality in order to prevent health problems caused by the ingestion of contaminated vegetables. It is recommended that farmers in the study area be informed about the appropriate use of agrochemicals. Also, conduct a more detailed study and on several crops to ensure that contaminant free food reaches consumers.

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.

Acknowledgments

The authors would like to acknowledge the Universidad Nacional del Centro del Perú for the study grant through FEDU/012020357694. Also, to the Laboratory of Chemistry and Environment of the Faculty of Applied Sciences for facilitating the use of the equipment and instruments.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sbsj.2021.06.054.

References

Adimalla, N., 2020. Heavy metals pollution assessment and its associated human health impact evaluation of urban soils from Indian cities: a review. Environ. Geochem. Health, (May). 42, 173–190. https://doi.org/10.1007/s10653-019-00324-4.

Afonne, O.J., Ifediba, E.C., 2020. Heavy metals risks in plant foods – need to step up precautionary measures. Current Opinion in Toxicology 22, 1–6. https://doi.org/10.1016/j.cotox.2019.12.006.

Agriculture Ministry, 2008. Regional agricultural sector strategic plan 2009 - 2015. Regional Direction of Agriculture Junín.

Ahmed, M., Matsumoto, M., Ozaki, A., Thinh, N. Van, 2019. Heavy Metal Contamination of Irrigation Water, Soil, and Vegetables and the Difference between Dry and Wet Seasons Near a Multi-Industry Zone. Water 11, 583. https://doi.org/10.3390/w11030583.

Al-bagawi, A.H., 2019. Assessment of Trace Elements Contamination of Irrigation Water and Agricultural Soil in Hail Region. Saudi Arabia. IOSR J. Appl. Chem. 12, 7–15.

Alfar, J.A., Carreras, N.M.E.A., Mitre, G.B., 2019. Arsenic accumulation in lettuce (Lactuca sativa L.) and broad bean (Vicia faba L.) crops and its potential risk for human consumption. Heliyon 5, https://doi.org/10.1016/j.heliyon.2019.e01152.

Ali, M.H.H., Al-Qahrami, K.M., 2012. Assessment of some heavy metals in vegetables, cereals and fruits in Saudi Arabian markets. Egypt. J. Aquat. Res. 38, 31–37.

Antoniadis, V., Golia, E.E., Liu, Y.T., Wang, S.L., Shaheen, S.M., Rinklebe, J., 2019. Soil and maize contamination by trace elements and associated health risk assessment in the industrial area of Voles. Greece. Environ. Int. 124, 79–88.

Arévalo-Gardini, E., Arévalo-Hernández, C.O., Baligar, V.C., He, Z.L., 2017. Heavy metal accumulation in leaves and beans of cacao (Theobroma cacao L.) in major cacao growing regions in Peru. Sci. Total Environ. 605–606, 792–800. https://doi.org/10.1016/j.scitotenv.2017.06.122.

Bortey-Sam, N., Nakayama, S.M.M., Akoto, O., Ikenaka, Y., Fohli, J.N., Baidoo, E., Mizukawa, H., Ishizuka, M., 2015. Accumulation of heavy metals and metalloid in foodstuffs from agricultural soils around Tarkwa area in Ghana, and associated human health risks. Int. J. Environ. Res. Public Health 12, 8811–8827. https://doi.org/10.3390/ijerph120808811.

Bui, A.T.K., Nguyen, H.T.H., Nguyen, M.N., Tran, T.H.T., Vu, T.V., Nguyen, C.H., Reynolds, H.L., 2016. Accumulation and potential health risks of cadmium, lead and arsenic in vegetables grown near mining sites in Northern Vietnam. Environ. Monit. Assess. 188, 525. https://doi.org/10.1007/s10661-016-5535-5.

CME, 2004. Soil, Ground Water and Sediment Standards for Use Under Part XV. 1 of the Environmental Protection Act. Canadian Ministry of the Environment.

Custodio, M., PeñaLoza, R., Alvarado, J., Chanamé, F., Maldonado, E., 2021. Surface Water Quality in the Mantaro River Watershed Assessed after the Cessation of Anthropogenic Activities Due to the COVID-19 Pandemic. Pol. J. Environ. Stud. 30, 1–14. https://doi.org/10.15244/pjoes/130986.
Pagnotta, M.A., Fernandez, J.A., Sonnante, G., Egea-Gilabert, C., 2017. Genetic diversity and accession structure in European Cynara cardunculus collections. PloS ONE 12, 1–23. https://doi.org/10.1371/journal.pone.0178770.

Pehouï, G., Murarescu, O., Dadués, C., Dulama, I.D., Teodorescu, S., Stîrbescu, R.M., Bucurica, I.A., Stanescu, S.G., 2020. Heavy metals accumulation and translocation in native plants grown on tailing dumps and human health risk. Plant Soil 456, 405–424. https://doi.org/10.1007/s11104-020-04725-8.

Peña, F.D.M., Beltran, E., 2017. Application of phytoremediation in soils contaminated by heavy metals using Helianthus annuus L. at the El Mantaro Experimental Station. Prospect. Univ. 9, 31–45.

Pereira, M., Tissor, F., Facco, R., Ibáñez, R., Pistón, M., 2021. A simple and economical ultrasound-assisted method for Cd and Pb extraction from fruits and vegetables for food safety assurance. Results in Chemistry 3. https://doi.org/10.1016/j.resci.2020.100089 100089.

Peris, M., Mió, C., Recatalà, L., Sánchez, R., Sánchez, J., 2007. Heavy metal contents in horticultural crops of a representative area of the European Mediterranean region. Sci. Total Environ. 378, 42–48. https://doi.org/10.1016/j.scitotenv.2007.01.030.

Petersen, U., 1965. Regional geology and major ore deposits of central Peru. Econ. Geol 60, 407–476. https://doi.org/10.2113/gsecongeo.60.3.407.

Rehman, Z.U., Khan, S., Qin, K., Brusseau, M.L., Shah, M.T., 2016. Quantification of inorganic arsenic exposure and cancer risk via consumption of vegetables in southern selected districts of Pakistan. Sci. Total Environ. 6, 321–329. 10.1016 / j.scitotenv.2016.01.094.

Rehman, I.U., Ishaq, M., Ali, L., Muhammad, S., Din, I.U., Yaseen, M., Ullah, H., 2020. Potentially toxic elements’ occurrence and risk assessment through water and soil of Chitral urban environment, Pakistan: a case study. Environ Geochim Health 42, 4355–4368. https://doi.org/10.1007/s10653-020-00531-4.

Rodbell, D.T., Delman, E., Abbott, M., Besonen, M., Tapia, P., 2014. The heavy metal contamination of Lake Junín National Reserve, Peru : An unintended consequence of the juxtaposition of hydroelectricity and mining. GSA Today 24, 4–10. https://doi.org/10.1130/GST2014.0012.

Sanders, A.P., Svensson, K., Cennings, C., Burris, H.H., Oken, E., Amarasingwardena, C., Priyanaka, B., Pizano-Zarate, M.L., Schnaas, L., Tamayo-Ortiz, M., Baccarelli, A.A., Sarlin, L.M., Tellez-Rojo, M.M., 2018. Prenatal lead exposure modifies the effect of shorter gestation on increased blood pressure in children. Environ. Int. 120, 464–471. https://doi.org/10.1016/j.envint.2018.08.038.

Tang, Z., Chai, M., Cheng, J., Jin, J., Yang, Y., Nie, Z., Huang, Q., Li, Y., 2017. Contamination and health risks of heavy metals in street dust from a coal-mining city in eastern China. Ecotoxicol. Environ. Saf. 138, 83–91. https://doi.org/10.1016/j.ecoenv.2016.11.003.

Thayer, K.A., Heindel, J.J., Bucher, J.R., Gallo, M.A., 2012. Role of Environmental Chemicals in Diabetes and Obesity : A National Toxicology Program Workshop Review. Environ. Health Perspect. 120, 779–789. https://doi.org/10.1289 / ehp.1104597.

Tóth, G., Herrmann, T., Da Silva, M.R., Montanarella, L., 2016. Heavy metals in agricultural soils of the European Union with implications for food safety. Environ. Int. 88, 299–309. https://doi.org/10.1016/j.envint.2015.12.017.