



Heavy metals in soils and edible tissues of *Lepidium meyenii* (maca) and health risk assessment in areas influenced by mining activity in the Central region of Peru

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ABSTRACT

Heavy metal contamination of soil and agricultural products is an environmental problem, has an adverse effect on the quality of food crops, and is a danger to food security and public health. The concentration of arsenic (As), cadmium (Cd), lead (Pb), iron (Fe) and zinc (Zn) in surface soils and edible hypocotyls tissues of two ecotypes of *Lepidium meyenii* Walpers (maca) was evaluated in three districts of the Junín province, Peru. In addition, the risk to human health due to exposure to heavy metals from maca consumption was evaluated. Soil samples and maca hypocotyls were collected in areas influenced by mining and metallurgical activity. The mean concentration of Cd (0.32 ± 0.23 mg/kg) and Pb (0.20 ± 0.12 mg/kg) in maca samples exceeded the values established by the Food and Agriculture Organization and the World Health Organization. The bioconcentration factor was less than 1. The estimated daily intake of each metal was below the oral reference dose. The hazard quotient and hazard index were less than 1, it is unlikely to cause non-cancer adverse health outcome. The cancer risk for As and Cd was higher than the tolerable limit (1×10^{-6}) in children and adults. In the district of Ondores, the cancer risk for As in children was higher than the acceptable limit (1×10^{-4}). Residents of the Ondores district would be more exposed to As and Cd from consumption of maca hypocotyls. It is very important to carry out continuous monitoring of other toxic metals in different ecotypes of maca (red, black, yellow, purple, creamy white, pink) in order to evaluate the variation in the accumulation of heavy metals and the level of toxicity of each metal between ecotypes.

1. Introduction

Environmental contamination by toxic metals is a food safety risk and a global problem for human health [1]. Mining and metallurgical activity, irrigation of crops with wastewater, leaching from landfills, application of organic and inorganic fertilizers, and mining wastes have contributed to the accumulation of toxic metals in soils [2–6]. As a result of these anthropogenic activities, heavy metals are released into the atmosphere, water and soil, threatening natural ecosystems and the exposed population [7,8]. In contaminated areas, these toxic elements

can enter the human body through inhalation, ingestion of soil and water, dermal contact and consumption of contaminated vegetables [9]. On the other hand, the accumulation of metals in high concentrations above physiological requirements could have a serious effect on the health of all living beings in general [10].

Heavy metals are characterized by their long persistence period and have many adverse health effects, and exposure to these chemicals continues to increase in many regions of the world [11]. These can cause a variety of negative health effects, for example: long-term exposure to arsenic (As) causes cancers, neurological problems, lung diseases

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[11–13]. Exposure to cadmium (Cd) leads to renal dysfunction, bone demineralization, hepatotoxicity and hypertension [14]. Likewise, lead (Pb) exposure leads to brain and kidney damage and negative hematological effects in children, and chronic effects on the nervous system [13, 15].

Soluble heavy metal ions in soil are the main source of heavy metals in plants [16]. Therefore, these elements can be transferred and accumulate in agricultural crops, with the likelihood that they can enter the food chain and accumulate in the human body [17,18]. The ingestion of crops loaded with toxic metals such as As, Cd and Pb for prolonged periods of time, even in very low concentrations, constitutes a health risk to consumers [19–21]. An important tool for estimating the nature and likelihood of adverse health effects in humans exposed to toxic chemicals is human health risk assessment through bioaccumulation factor, hazard quotient, daily intake, health risk index [6,9,22].

Several scientific reports have shown that edible root vegetables or tubers are susceptible to absorb and accumulate heavy metals in their tissues and may have adverse effects on the health of people who consume them [23–29]. In this context, it is assumed that maca (*Lepidium meyenii*) bioaccumulates toxic metals in its vegetative parts because it is grown in soils contaminated by the mining activity in the departments of Junín and Pasco in the central region of Peru. Therefore, the ingestion of maca by local inhabitants would not be safe.

Maca is a native plant that belongs to the Brassicaceae family [30–32]. Its hypocotyls are cultivated and consumed as native food and medicinal product [33]. In the Junín region there are 13 maca ecotypes according to the color of their hypocotyls [34]. Its nutritional value is composed of carbohydrates (55–60 %), protein (10–14 %), dietary fiber (8.5 %) and fat (1.2 %). It is rich in minerals such as calcium, potassium, iron, manganese, copper, zinc, sodium, as well as fatty acids and secondary metabolites of pharmacological and nutritional importance such as macaene, macamides, macaridin and alkaloids that are only found in this plant [35–38]. In addition, maca has nutritional, energizing and male and female fertility enhancing properties, has effect on sexual dysfunctions, prostatic hyperplasia, alleviates menopausal syndrome, improves memory and learning, improves skin health [30,36,37,39–41], prevents osteoporosis [42], has antioxidant and antitumor properties [43]. Therefore, maca is a great food that improves the health of people who consume it.

Maca production in Peru covers an area of approximately 8,000 ha, with more than 10,000 producers dedicated to its cultivation [44]. In 2015, according to reports from the exporters' association (Adex), more than 870 tons of maca were exported, distributed mainly in 15 countries (Hong Kong, United States, China, Canada, United Kingdom, Australia, among others) [45].

In Perú, the mining is an ancestral activity that has been going on since the pre-Inca era, with extensive reserves yet to be exploited, currently, it is the second world producer of silver, copper and zinc, and third in lead [46,47]. However, this mining extractive activity has caused a high environmental impact on ecosystems such as soil degradation by toxic elements [48]. According to statistical data as of 2015 from the Ministry of Energy and Mines, for decades mining activity has caused environmental liabilities mainly in six regions that represent more than 71 % of the accumulated total, Junín with 7.39 % and Pasco with 5.27 % [49]. These abandoned environmental liabilities in Peru represent a permanent potential risk to human health and ecosystems surrounding the Lake Junín National Reserve.

From the literature review, it has been verified that researchers have studied extensively on the medicinal properties of maca, but there are few related studies on the concentration of heavy metals in soils and the cultivation of maca. The objective of this study was to evaluate the concentration of heavy metals in soils and edible tissues of two maca ecotypes (yellow and purple) collected from three districts of the Junín province. In addition, the potential health risk from exposure to heavy metals was evaluated by estimating the estimated daily intake (EDI), hazard quotient (HQ), hazard index (HI) and cancer risk (CR) from

consumption of hypocotyls of maca.

2. Materials and methods

2.1. Area of study

The study area corresponds to agricultural plots with cultivation of *L. meyenii* (maca), which is grown between altitudes of 4000–4500 meters above sea level (masl) in the Central mountain range of Peru [40,50] in the regions of Junín and Pasco (Fig. 1). The area corresponds to the puna ecological floor, with temperatures ranging between 4 and 7 °C during the day and can drop at dawn to –10 °C. The area is exposed to high solar irradiation, frequent frosts, strong winds and strongly acidic soils (pH < 5), slightly saline and a sandy loam texture [51,52], with an average annual rainfall of 740 mm. Maca cultivation is the main activity in Ondores (OND), Carhuamayo (CAR) and Junín (JU), in addition to cattle ranching. The community of Ondores has the largest extensions of land with maca cultivation in the Bombón plateau.

2.2. Sample collection and preparation

Samples of soils were collected from three maca-producing areas in the province of Junín. Soils were collected from plots with maca cultivation, and the choice of sampling sites was based on the authorization of the plot owners for sampling. In total, 20 composite soil samples were collected from the topsoil (0–20 cm depth), in each sampling plot five randomly taken subsamples were pooled to obtain a representative composite sample (1 kg) [53,54]. The composite samples were placed in polyethylene zipper bags, labelled and taken to the laboratory. Finally, soil samples were first air-dried and then oven-dried at 80 °C for 72 h, ground and sieved with a 2 mm mesh sieve and kept in polyethylene bags prior to analysis.

The mature maca hypocotyls were harvested at harvest time (June and July of each year), once they had completed their vegetative period (after 8 months of being sown). The samples of soils and maca hypocotyls were collected from the same sampling points. Five subsamples of maca hypocotyls were mixed at each soil sampling point. In total, 40 composite samples (1 kg) were collected from two ecotypes of maca (20 yellow maca and 20 purple maca, both ecotypes growing in the same plot). The samples were cleaned and washed several times with potable water and rinsed with deionized water, air-dried, and then dried in an oven at 60 °C for 48 h. The dried samples were ground and sieved, and placed in airtight plastic containers and stored in desiccators until digestion.

The number of replicates for soil and maca samples was in Junín (n = 5), Carhuamayo (n = 5) and Ondores (n = 10). Ten replicates were chosen in the Ondores locality because this area has the largest number of plots with maca cultivation and the highest maca production.

2.3. Heavy metal analysis

The homogenized and pulverized soil sample (0.5 g) was placed in beakers, and digestion was performed at 80 °C for 120 min using 10 mL of nitric acid (HNO₃) and 3 mL of hydrochloric acid (HCl). The digested and cooled sample was filtered into a 100 mL volumetric flask and the volume was made up with deionized water. In the same way, each sample of maca powder (1.0 g) was digested in a mixture of 10 mL of HNO₃ and 3 mL of HCl, and the solution was heated on an electric stove at a temperature of 150 °C for 90 min. Then, 10 mL of perchloric acid (HClO₄) was added to the digesting solution, allowed to cool and transferred to a 100 mL flask, rinsed and diluted with ultrapure water and shaken, finally filtered with N°42 paper of 200 mmØ. The total digested and diluted samples were refrigerated at 4 °C until analysis.

After digestion of the samples, the concentration of heavy metals in the soil samples and two ecotypes of maca were analysed using an atomic absorption spectrophotometer (Varian model AA240). The

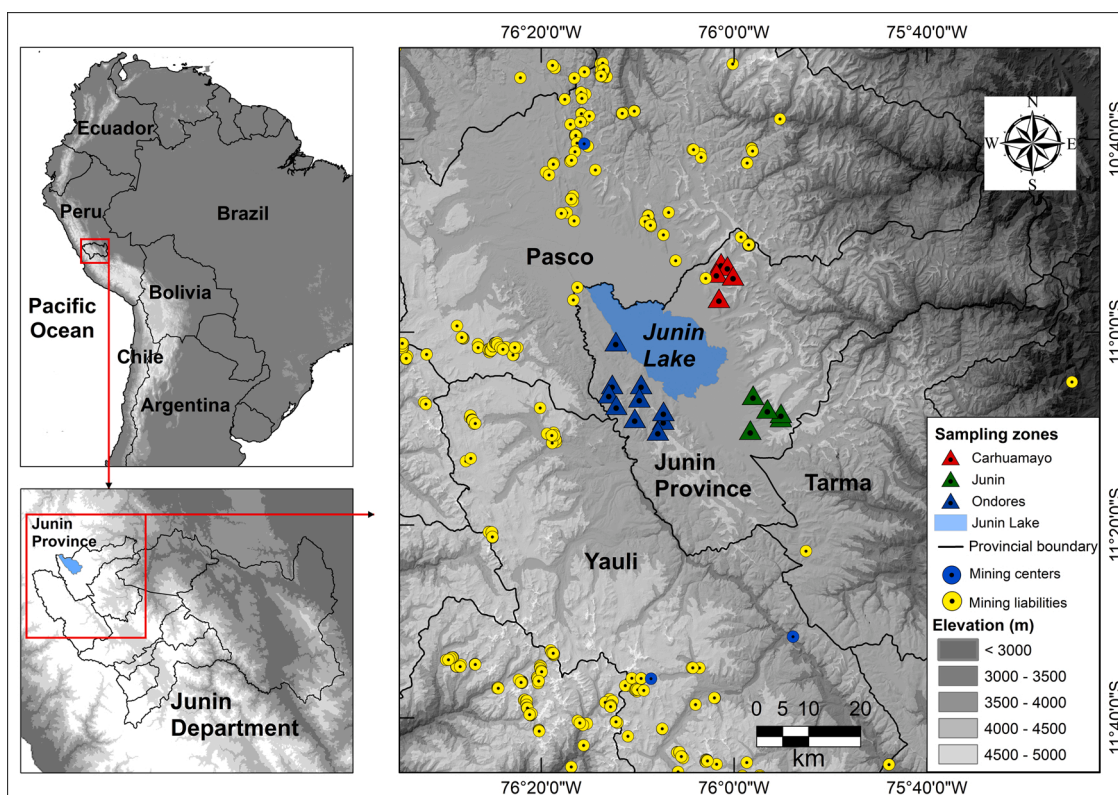


Fig. 1. Location of soil sampling sites and maca hypocotyls in three districts (zones) of Junín province, Peru.

instrument was operated in flame mode with air and acetylene. The calibration curve was prepared with solutions in 1% HNO₃ medium (Table 1) with acceptable correlation coefficient (> 0.9978). Blank solutions were prepared following the same procedure; the result of the blanks were below the detection limit. For each batch of samples, a duplicate assay was performed to see the precision of the results obtained. The duplicate samples showed less than 10 % of the relative standard deviations in all treatments. The limit of detection (LOD) and the limit of quantification (LOQ) for As, Cd, Pb, Fe and Zn (mg/kg) are shown in Table 2.

2.4. Bioaccumulation of heavy metals in maca tissues

The bioconcentration factor (BCF) is an indicator that measures the ability of maca hypocotyls to accumulate in their tissues a type of metal from a soil with several metals. The transfer of metals from the soil to the hypocotyls of maca was calculated according to the Eq. (1) [55–59]:

$$BCF = \frac{C_{root}}{C_{soil}} \tag{1}$$

where C_{root} is the concentration of As, Cd, Pb, Fe and Zn in the hypocotyls of maca and C_{soil} in the soil.

Table 1 Concentrations used for calibration curve for the heavy metals analysis.

Heavy metals	Standard concentrations (mg/L)					
As	0.000	0.001	0.005	0.010	–	–
Cd	0.000	0.010	0.050	0.100	0.300	–
Pb	0.000	0.100	0.250	0.500	0.800	1.000
Fe	0.000	0.100	0.300	0.500	1.000	–
Zn	0.000	0.100	0.300	0.500	–	–

Table 2 The limit of detection (LOD) (mg/kg) and limit of quantification (LOQ) (mg/kg) values of each metal for soil and maca.

Elements	Soil		Maca	
	LOD	LOQ	LOD	LOQ
As	0.05	0.20	0.01	0.06
Cd	0.006	0.03	0.003	0.01
Pb	0.02	0.12	0.01	0.03
Fe	1.00	3.80	0.10	0.28
Zn	0.50	1.60	0.50	1.20

2.5. Human health risk assessment

2.5.1. Estimated daily intake (EDI)

The estimated daily intake (EDI) of each element was quantified according to the Eq. (2) [60,61]:

$$EDI = \frac{C_m \times FIR \times C_f \times EF \times ED}{BW \times AT} \tag{2}$$

where C_m is the mean concentration of each metal (mg/kg); FIR is the average consumption of maca (0.096 and 0.180 kg/person/day for children and adults), which was obtained from the application of a questionnaire to families in the study area. We selected 97 volunteer families who consume maca hypocotyls in the three districts (30 in Junín, 25 in Carhuamayo and 42 in Ondores). A representative of each family was asked and requested to show the actual amount of daily consumption of maca hypocotyls of a 50 year old adult and a 7 year old child. The food was then weighed and the average daily consumption of maca per person was determined. C_f is the conversion factor (0.085) [6, 54,62]; EF is the frequency of exposure (350 days/year); ED is the duration of exposure (70 years in adults and 7 years in children); Bw is body weight (21 and 66 kg for children and adults respectively); AT is the mean exposure time (350 days x 50 years for adults and 350 days x 7

years for children).

2.5.2. Hazard quotient (HQ)

The risk of non-carcinogenic effects (HQ) is expressed as the ratio of the dose from metal exposure (EDI) to the oral reference dose (RfD). The HQ value for each metal was calculated using Eq. (3) [60,63,64]:

$$HQ = \frac{EDI}{RfD} \quad (3)$$

where RfD is the oral reference dose for each chemical element (mg/kg/day) [65]. If the HQ value is <1, the exposed inhabitants are assumed to be safe; if the HQ > 1, it is assumed that the inhabitants are exposed to non-cancer risks [63].

The hazard index (HI) was expressed as the sum of the HQ values of individual metals [23,66,67] according to the Eq. (4):

$$HI = \text{Total HQ} = \sum_{i=1}^n HQ; i = 1, 2, 3, \dots, n \quad (4)$$

2.5.3. Cancer risk (CR)

Cancer risk (CR) assesses the potential risk associated with the exposure to carcinogenic elements (As, Cd and Pb) throughout lifetime after the exposure. It was calculated according to Eq. (5) [54,68]. The total cancer risk (TCR) was expressed as the sum of the CRs of As, Cd and Pb, and is shown in Eq. (6) [69,70]:

$$CR = EDI \times CPSo \quad (5)$$

$$TCR = \sum_{i=1}^n CR; i = 1, 2, 3, \dots, n \quad (6)$$

where CPSo is the oral cancer factor for As, Cd and Pb of 1.5, 0.38 and 0.0085 (mg/kg/day)⁻¹ respectively [65]. A CR less than or equal to 1×10^{-6} means there is no risk of cancer, but a value greater than 1×10^{-4} indicates a significant carcinogenic risk for people [1,71]. CR in children and adults from exposure to carcinogenic contaminants was calculated based on lifetime risk (365 days x 70 years) [72].

2.6. Statistical analysis

The results were expressed as the mean, standard deviation of heavy metal concentrations in soil and maca. A one-way ANOVA was used to compare heavy metal concentrations between soil sampling sites, and a two-way ANOVA to compare heavy metal concentrations and the bio-concentration factor between maca ecotypes and localities. The comparison of means was carried out using the Tukey test with a significance level of $p < 0.05$.

3. Results and discussion

3.1. Heavy metals in soils under maca cultivation

The results of the analysis of metals in the soils under maca cultivation are presented in Table 3. The results revealed that the mean concentration of Cd (1.42 ± 0.88 mg/kg) and Pb (72.11 ± 15.43 mg/kg) in the soil samples exceeded the limit allowed by the national and Canadian standard [73,74]. In the analysed soil samples, 45 % of Cd and 60 % of Pb exceeded the regulated limits in all three soil sampling locations. All the soil samples exceeded the limits regulated by the Canadian standard for As (12.00 mg/kg), but did not exceed that regulated by the Peruvian standard (50 mg/kg). Iron and zinc elements were the most abundant, but these values were below the recommended limits, which would indicate that there was no anthropogenic contamination associated with these chemical elements.

Soil samples from the district of Ondores (producing area with the largest extension of maca cultivation) exhibited the highest

Table 3

Concentration of As, Cd, Pb, Fe and Zn in soils under maca cultivation (mg/kg) in three districts of Junín province.

Heavy metal	JU (n = 5)	CAR (n = 5)	OND (n = 10)	Mean ± SD	Reference values (mg/kg)
As	17.90 ± 3.74 ^a	21.27 ± 6.42 ^a	22.11 ± 6.30 ^a	20.85 ± 5.79	12 [73] – 50 [74]
Cd	0.63 ± 0.20 ^a	0.71 ± 0.11 ^a	2.17 ± 0.61 ^b	1.42 ± 0.88	1.4 [73,74]
Pb	59.96 ± 18.39 ^a	67.03 ± 11.95 ^{ab}	80.73 ± 10.49 ^b	72.11 ± 15.43	70 [73,74]
Fe	16528.40 ± 2104.06 ^a	19496.80 ± 1334.17 ^a	25243.52 ± 4087.44 ^b	21628.06 ± 4913.21	–
Zn	90.92 ± 26.48 ^a	140.68 ± 33.74 ^b	154.54 ± 20.26 ^b	135.179 ± 36.09	200 [73] – 300 [77]

Different superscript letters within columns indicate significant differences by Tukey's post-hoc tests ($p < 0.05$).

concentrations of As, Cd, Pb, Fe and Zn, results that could suggest that the soils of this locality would be more enriched with the five metals than the localities of Carhuamayo and Junín. If these chemical elements were mobilized from the soil to the edible parts of the plant it would be a threat to human health [6]. The higher content of As, Cd and Pb in Ondores could be attributed to the increased discharge and diffusion of atmospheric particles by wind, water and rainfall [14] resulting from the Pb and Zn mining and smelting processes of the La Oroya Metallurgical Complex, mining operations at Cerro de Pasco, environmental liabilities and other potential sources. The presence of the Fe element in the soil would have the geological parent material as the main source as reported by [20,75]. The addition of organic manure (sheep manure) in the maca crop would be one of the potential sources of As, Cd and Zn contribution to the soil, the adding cattle manure is the predominant source of heavy metals in agricultural soils [76].

3.2. Heavy metals in edible maca hypocotyls

Maca is a millenary Andean product used as traditional food and medicine by the inhabitants of the Andean region of Peru, and is also in great demand internationally due to its medicinal properties [36,37,78]. The levels of As, Cd, Pb, Fe and Zn in edible hypocotyls of yellow and purple maca grown at three different sites are presented in Table 4. The mean concentrations of Cd and Pb in yellow and purple maca samples were 0.32 ± 0.23 and 0.20 ± 0.12 mg/kg for Cd and Pb, respectively, values that exceeded the limits regulated by the Food and Agriculture Organization and the World Health Organization (FAO/WHO) [79]. The average concentration of As, Cd, Pb, Fe and Zn concentration between the two ecotypes of maca were statistically identical ($p > 0.05$), due to the fact that the cultivation of yellow and purple maca are performed in the same plots with soil of similar physical and chemical characteristics. The results revealed that the content of the selected metals in the ecotypes of maca was statistically different in the three sites. As, Cd, Pb, Fe and Zn recorded the highest concentrations in the hypocotyls of the two maca ecotypes in the Ondores producing area followed by Carhuamayo and Junín. These differences could be attributed to the fact that the variation of element content in the soil between different croplands could be influenced by the variation in the accumulation capacity of the plants [80].

The two ecotypes of maca accumulated more Zn in their hypocotyls compared to the other metals studied, which could be attributed to the amount of bioavailable Zn in the soil and its retention and adsorption capacity in plant roots [17,81]. The high Zn accumulation in maca hypocotyls confirmed that soluble Zn is readily available to plants in soils with high soil Zn content, acidic pH and relatively high organic matter contents [75,81]. Indeed, essential metals such as Zinc tends to be bio-accumulated more in living tissues than the non-essential ones such as

Table 4

Concentration of As, Cd, Pb, Fe and Zn in yellow and purple maca (mg/kg) in three districts of Junín province.

Heavy metal	Yellow maca			Mean ± SD	Purple maca			Mean ± SD	Permissible limit (mg/kg)
	JU (n = 5)	CAR (n = 5)	OND (n = 10)		JU (n = 5)	CAR (n = 5)	OND (n = 10)		
As	0.12 ± 0.01 ^a	0.14 ± 0.04 ^{ab}	0.21 ± 0.08 ^b	0.17 ± 0.07 ^a	0.13 ± 0.03 ^a	0.21 ± 0.05 ^{ab}	0.26 ± 0.08 ^b	0.21 ± 0.09 ^a	0.5 [86]
Cd	0.15 ± 0.02 ^a	0.22 ± 0.04 ^a	0.46 ± 0.17 ^b	0.32 ± 0.18 ^a	0.07 ± 0.01 ^a	0.19 ± 0.04 ^a	0.51 ± 0.18 ^b	0.32 ± 0.23 ^a	0.1 [79]
Pb	0.10 ± 0.02 ^a	0.21 ± 0.05 ^b	0.24 ± 0.14 ^b	0.20 ± 0.11 ^a	0.07 ± 0.02 ^a	0.18 ± 0.05 ^b	0.28 ± 0.13 ^b	0.20 ± 0.12 ^a	0.1 [79]
Fe	4.22 ± 0.63 ^a	4.98 ± 0.53 ^a	6.79 ± 1.66 ^b	5.69 ± 1.67 ^a	4.99 ± 0.97 ^a	5.45 ± 0.54 ^a	6.89 ± 1.78 ^b	6.07 ± 1.53 ^a	425 [87,88]
Zn	30.61 ± 4.39 ^a	36.19 ± 1.75 ^{ab}	37.46 ± 6.33 ^b	35.43 ± 5.66 ^a	30.39 ± 4.85 ^a	33.66 ± 3.07 ^{ab}	35.34 ± 5.72 ^b	33.68 ± 5.17 ^a	100 [87,88]

Different superscript letters within columns indicate significant differences by Tukey's post-hoc tests ($p < 0.05$).

cadmium [82–84]. There are few studies related to the concentration of heavy metals in maca, such as that of Espinoza Dominguez [85] who reported similar concentrations for Cd, Pb and As in samples of maca sold in the “10 de octubre” market in Peru.

The main economic activity in the province of Junín is the production of maca for self-consumption and sale in the local, regional, national and international markets. However, the decrease in production for export purposes of this Andean product is worrying, only 5% of Peruvian maca production is exported [44] presumably due to the heavy metal content in maca hypocotyls, which has been affecting the economy of low-income families.

3.3. Bioconcentration factor

Translocation of chemical elements in the soil-plant system is the main pathway of human exposure, because plants absorb and accumulate metals in their edible and non-edible parts [89]. Plant anatomy and physiology, amount and type of heavy metals, physical and chemical traits of soil determine the process of translocation and storage of heavy metals in plants [25,90]. The bioconcentration factor (BCF) is an indicator of the ability of movement of chemical elements from the soil to the edible part of the plant. Fig. 2 shows the BCF of As, Cd, Pb, Fe and Zn from soil to yellow and purple maca samples. The BCF in yellow and purple maca decreased in the order of Zn (0.278) > Cd (0.257) > As (0.009) > Pb (0.003) > Fe (0.0003) and Zn (0.266) > Cd (0.216) > As (0.010) > Pb (0.003) > Fe (0.0003) respectively. This difference in BCF values could be explained due to variations in metal concentration and soil physicochemical characteristics [54].

The absorption of metals through maca hypocotyls is similar to that reported by [87] for root vegetables. The two ecotypes of maca accumulated the studied metals statistically similarly ($p > 0.05$) (Fig. 2A), because yellow and purple maca were grown in the same plot and with the same physical and chemical soil characteristics. The mean BCF values for As, Pb and Zn in the yellow and purple maca hypocotyls were statistically different in the three sites ($p < 0.05$) (Fig. 2B). Greater accumulation of As and Pb in the maca hypocotyls were observed in samples from Ondores and Carhuamayo districts, while maca hypocotyls from Junín district had a greater accumulation of Zn. These results could indicate that fluctuations in BCF values would be influenced by soil characteristics and the type of metal in each place of study. The BCF of the selected metals was lower than 1, with relatively higher values observed for Zn, due to a higher availability and mobility of Zn in acid

soils [75], Zn and Fe are essential nutrients for plants so they are easily absorbed by them [91], but can be toxic when present in high concentrations. The BCF values for Cd, Pb and As were the lowest, indicating a low intensity accumulation compared to the Zn and Fe elements; this can be explained in that the hypocotyls of the two ecotypes of maca developed special absorption, translocation and accumulation mechanisms in relation to the bioavailability of metals [92]. Toxic elements such as Cd, interact with other essential and trace elements which affects their mobility and bioavailability [25]; for example Cd accumulation in plants is reduced in soils with high Zn contents [93]. High BCF values can cause health risks, because toxic substances with higher BCF values tend to accumulate and move to edible parts of plants than chemicals with low BCF values [94,95].

3.4. Health risk assessment

3.4.1. Non-cancer risk in children and adults

In developing countries such as Peru, health risk assessment should be a priority in places where mining and metallurgical activity is a major contributor to soil, water, air and food contamination. One of the important pathways for entry of toxic elements into the human body is contamination of food crops, therefore, ingestion of contaminated food is a form of exposure with greater contribution to health risk than inhalation and dermal contact pathways [6,96]. Assessing heavy metal intake through maca consumption should be a priority for exposed individuals who are at greatest risk.

The estimated daily intake (EDI), hazard quotient (HQ) and hazard index (HI) for the non-carcinogenic risk of heavy metals from ingestion of maca hypocotyls in children and adults are shown in Tables 5a and 5b. The EDI values of contaminated maca were highest for Zn (1.31×10^{-2} and 7.89×10^{-3}) and Fe (2.15×10^{-3} and 1.29×10^{-3}) in children and adults, respectively, results that agree with the EDI from consumption of contaminated native potato in Junin department [97] and vegetables [54,98]. The results revealed that the EDI of the selected metals was lower than the oral reference dose (RfD) [65]. All EDI values were less than 1, indicating a low risk to the food chain. EDI values were highest for Zn and Fe at Ondores and Carhuamayo and the lowest values were recorded for As, Pb and Cd at both sites. It should be noted that high EDI values for Fe and Zn are beneficial for children and adults, because these two elements are vital micronutrients for humans. Fe functions as a component of a number of proteins such as hemoglobin for the transport of oxygen to tissues throughout the body for

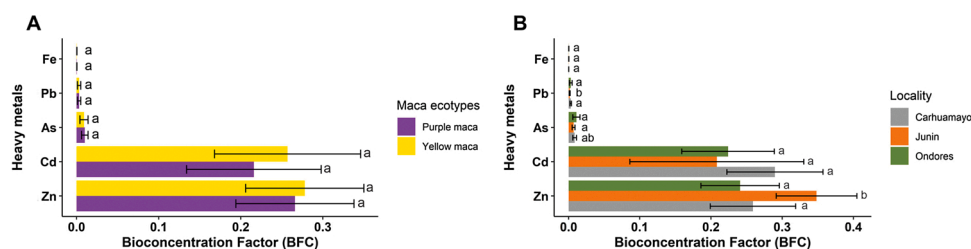


Fig. 2. The bioconcentration factor (BCF) of As, Cd, Pb, Fe and Zn in two maca ecotypes (A) from three localities (B) of Junín province. Different letters indicate significant differences ($p < 0.05$).

Table 5a

Estimated daily intake (EDI) hazard quotient (HQ) and the hazard index (HI) for heavy metals in children from three districts in Junín province.

Heavy metal	EDI Children (mg/kg/day)			Mean EDI (children)	RfD (mg/kg/day)	HQ Children			Mean HQ (children)
	JU	CAR	OND			JU	CAR	OND	
As	4.72E-05	6.76E-05	9.05E-05	6.84E-05	3.00E-04	1.57E-01	2.25E-01	3.02E-01	2.28E-01
Cd	4.35E-05	7.88E-05	1.86E-04	1.03E-04	1.00E-03	4.35E-02	7.88E-02	1.86E-01	1.03E-01
Pb	3.37E-05	7.49E-05	1.01E-04	7.00E-05	3.50E-03	9.64E-03	2.14E-02	2.89E-02	2.00E-02
Fe	1.79E-03	2.01E-03	2.64E-03	2.15E-03	7.00E-01	2.56E-03	2.88E-03	3.77E-03	3.07E-03
Zn	1.18E-02	1.35E-02	1.41E-02	1.31E-02	3.00E-01	3.93E-02	4.49E-02	4.69E-02	4.37E-02
Total	1.37E-02	1.57E-02	1.71E-02	1.55E-02	HI	2.52E-01	3.73E-01	5.67E-01	3.98E-01

Table 5b

Estimated daily intake (EDI), hazard quotient (HQ) and the hazard index (HI) for heavy metals in adults from three districts in Junín province.

Heavy metal	EDI Adults (mg/kg/day)			Mean EDI (adults)	RfD (mg/kg/day)	HQ Adults			Mean HQ (adults)
	JU	CAR	OND			JU	CAR	OND	
As	2.84E-05	4.07E-05	5.45E-05	4.12E-05	3.00E-04	9.47E-02	1.36E-01	1.82E-01	1.37E-01
Cd	2.62E-05	4.75E-05	1.12E-04	6.19E-05	1.00E-03	2.62E-02	4.75E-02	1.12E-01	6.19E-02
Pb	2.03E-05	4.51E-05	6.10E-05	4.22E-05	3.50E-03	5.81E-03	1.29E-02	1.74E-02	1.20E-02
Fe	1.08E-03	1.21E-03	1.59E-03	1.29E-03	7.00E-01	1.54E-03	1.73E-03	2.27E-03	1.85E-03
Zn	7.09E-03	8.12E-03	8.47E-03	7.89E-03	3.00E-01	2.36E-02	2.71E-02	2.82E-02	2.63E-02
Total	8.25E-03	9.47E-03	1.03E-02	9.33E-03	HI	1.52E-01	2.25E-01	3.42E-01	2.40E-01

metabolism, while Zn functions as a component of several enzymes in the structural maintenance of proteins and in the regulation of gene expression [99]. The consumption of maca with heavy metals could present health risks to consumers in the province of Junín, and would be conditioned to the source, exposure time and concentration of the contaminant.

EDI of hazardous heavy metals has been combined with Zn and Fe which are essential nutrients, because toxic metals such as Cd and Pb can interact metabolically with essential nutrients and affect human health. For example, Fe deficiency increases the uptake of Cd, Pb and Al; Pb replaces Zn in heme enzymes; and cadmium replaces zinc in metallothionein [100].

The hazard quotient (HQ) is a non-carcinogenic risk factor that relates the dose of exposure to the toxic element and the reference dose [23]. The HQ sequence for children was As (2.28×10^{-1}), Cd (1.03×10^{-1}), Zn (4.37×10^{-2}), Pb (2.00×10^{-2}) and Fe (3.07×10^{-3}), and for adults it was As (1.37×10^{-1}), Cd (6.19×10^{-2}), Zn (2.63×10^{-2}), Pb (1.20×10^{-2}) and Fe (1.85×10^{-3}). All HQ values were less than 1, the results revealed that exposure to the heavy metals studied is harmless with minimal health risk to children and adults when consuming maca hypocotyls, therefore consumption of maca by local residents is safe. The cumulative hazard exposure (HI) of the metals tested was less than 1 in children (HI = 0.40) and adults (HI = 0.24), suggesting that maca consumption would not have a significant health effect from long-term consumption of maca hypocotyls. The results also indicate that As and Cd were the most important contaminants with the highest contribution to HI in children and adults with 57 % and 25 % (Fig. 3A) respectively, which would mean that these elements would contribute to the potential health risk of people consuming maca.

The higher EDI, HQ and HI values for children than adults is due to the differences in the ingestion rates of food contaminated with heavy

metals, body weights as well as the exposure times [101–103]. Overall, no potential health risk for both children and adults was found. However, accumulation of fine particulate heavy metals in body tissues and organs in the long term may be detrimental to human health [21]. The Ondores locality recorded higher HQ, therefore residents would be relatively more exposed to the analysed metals, and this could be associated with higher levels of metals in maca hypocotyls at this sampling site. In conclusion, EDI, HQ and HI values revealed that no risks of non-cancer effects were associated with the ingestion of heavy metals through the consumption of maca collected at sites above 4000 masl in the districts of Ondores, Carhuamayó and Junín.

3.4.2. Cancer risk in children and adults

The cancer risk (CR) of As, Cd and Pb was assessed according to the estimated daily intake (EDI) and the oral cancer slope factor (CSPO). The results were compared with the acceptable or tolerable threshold limit value for cancer risk established by the United States Environmental Protection Agency (US EPA) ranging from 1.0×10^{-6} to 1.0×10^{-4} [104]. The CR for exposure to the toxic elements of As, Cd and Pb through consumption of contaminated maca hypocotyls is presented in Table 6. Among the three carcinogenic elements, the CR of As and Cd were higher than those of Pb in the maca samples. The CR values for As and Cd in maca were found slightly higher than the safe level (1×10^{-6}) in children (9.84×10^{-5} and 3.75×10^{-5}) and adults (5.54×10^{-5} and 2.26×10^{-5}), respectively. The CR values for Pb in children (5.71×10^{-7}) and adults (3.44×10^{-7}) were lower than the acceptable level (1×10^{-6}) established by US EPA, which would indicate that maca consumption could not present a carcinogenic risk for Pb, a result that agrees with previous studies in other root vegetables [94,105]. In Ondores, the CR value for As (1.30×10^{-4}) was higher than the acceptable level (1.0×10^{-4}) in children, while Cd (6.78×10^{-5}) was

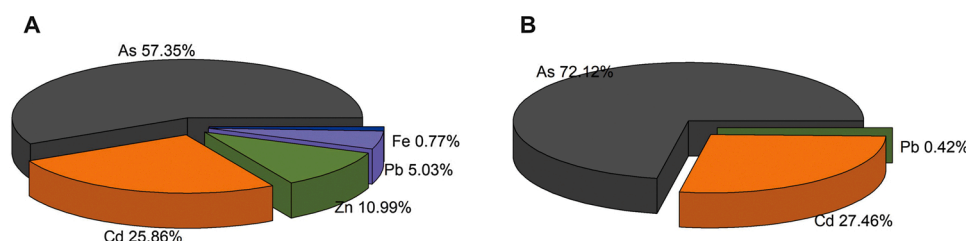


Fig. 3. The contribution of heavy metals to the hazard index (HI) (A) and total cancer risk (TCR) (B) from consumption of maca hypocotyls in children and adults.

Table 6

Cancer risk (CR) and total cancer risk (TCR) for heavy metals in children and adults from three districts in Junín province.

Heavy metal	CR (children)			Mean CR (children)	CR (adults)			Mean CR (adults)
	JU	CAR	OND		JU	CAR	OND	
As	6.79E-05	9.72E-05	1.30E-04	9.84E-05	4.09E-05	5.86E-05	7.84E-05	5.54E-05
Cd	1.59E-05	2.87E-05	6.78E-05	3.75E-05	9.55E-06	1.73E-05	4.09E-05	2.26E-05
Pb	2.75E-07	6.11E-07	8.26E-07	5.71E-07	1.66E-07	3.68E-07	4.97E-07	3.44E-07
TCR	8.40E-05	1.27E-04	1.99E-04	1.36E-04	5.06E-05	7.62E-05	1.20E-04	7.83E-05

slightly higher than the tolerable level (1.0×10^{-6}). These results could indicate that children would be facing a carcinogenic risk from As and Cd in Ondores from consumption of maca hypocotyls. The cumulative exposure to total cancer risk (TCR) of As, Cd and Pb was higher in children (1.36×10^{-4}) than in adults (7.83×10^{-5}) and the most important contribution would be As followed by Cd. Populations exposed to As from consumption of contaminated water and food could cause gastrointestinal diseases, cardiovascular and central nervous system disorders, and risk for several types of cancer (skin, lung, bladder, kidney) [106,107].

TCR values were higher in children than in adults at all three locations, and increased in the order of Junín > Carhuamayo > Ondores. It is presumed that As could be the most predominant contaminant with 72 % contribution, followed by Cd with 27.5 % (Fig. 3B), and would create a cancer risk relatively higher than the acceptable limit compared to Pb, i.e. there is the probability of occurrence of any type of cancer in a person during his/her lifetime; similar results with what reported by [108]. Therefore, it is important to focus on the possible carcinogenic risks due to As and Cd exposure of maca consumers in the province of Junín. Soils and maca hypocotyls require continuous monitoring in Ondores and Carhuamayo, and follow up on the health status of children and adults in the long term. There are many routes for the transfer of heavy metals to humans, such as ingestion, inhalation, dermal contact with soil, water, air, so the total potential health risk to the general population should be assessed.

4. Conclusions

Concentrations of Cd and Pb in soils and hypocotyls of yellow and purple maca exceeded the permissible limit. Tissues of the two ecotypes of maca accumulated metals and increased in the order of As > Pb > Cd > Fe > Zn. The bioconcentration factor in maca hypocotyls varied for each metal studied, with Zn and Cd showing the highest accumulation but with values less than 1. Although Pb and Cd concentrations in maca hypocotyls were above the permissible limits, maca hypocotyls were considered safe and no potential health risk was found for children and adults ($HI < 1$). The cancer risk for As and Cd was higher than the tolerable limit (1×10^{-6}) in children and adults. In the district of Ondores, the cancer risk for As in children was higher than the tolerable limit (1×10^{-4}), and the residents of this locality would be relatively more exposed to the analysed metals because of higher hazard index and total cancer risk. It is of high priority to evaluate the aggregate exposure of toxic heavy metals in multiple sources: dietary (meat products, dairy, drinking water), soil and air through different exposure routes (inhalation, dermal absorption and oral ingestion), to determine the total harmful risks to local residents and to identify the predominant exposure route with the highest contribution to total hazard index and total cancer risk, and to reduce the risk of harmful effects on the health of the inhabitants of province of Junín. Therefore, it is urgent and necessary that the regional governments of Junín and Pasco implement policies and programs for remediation of soils contaminated by mining activity, to prevent the accumulation of toxic elements in the ecotypes of maca, and to minimize the risk of exposure to contaminants and worry about the food safety of the Andean population and consumers in general. In addition, it is very important to carry out continuous monitoring of other toxic metals in different ecotypes of maca (red, black, yellow, purple,

creamy white, lead, pink) in order to evaluate the variation in the accumulation of chemicals and the level of toxicity of each metal between ecotypes.

Author statement

Authors declare that this research was carried out by all of us and we all agreed to its publication.

Author contribution statement

Edith Orellana-Mendoza: Conceptualization, Methodology, Writing-Original Draft, Writing-Reviewing and Editing. Walter Cuadrado and Diana Bao-Cóndor: Methodology, Investigation. Luz Yallico: Resources, Investigation. Rosa Zárate, Vicky Sarapura: Investigation. Cesar H. Limaymanta: Data curation, Formal analysis. Harold Rusbelth Quispe-Melgar: Reviewing and editing.

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Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.toxrep.2021.07.016>.

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