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RESEARCH ARTICLE

# Comparison of exposure to trace elements through vegetable consumption between a mining area and an agricultural area in central Chile

Marcelo Aguilar[1] · Pedro Mondaca[1] · Rosanna Ginocchio[2] · Kooichi Vidal[1] · Sébastien Sauvé[3] · Alexander Neaman[1]

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## Abstract

Human exposure to trace elements has been a large concern due to the potential health issues. Accordingly, this study aimed to compare the concentrations of arsenic, copper, and zinc in the edible parts of vegetables grown in a mining-agricultural area and in an exclusively agricultural area and to compare the potential human health risks of consuming vegetables from both areas. The consumption habits of the studied population were extracted from the 2010 National Alimentary Survey of Chile. In most cases, the concentrations of trace elements in the edible tissues of vegetables (lettuce, spinach, garlic, onion, carrot, potato, sweet corn, and tomato) were higher in the mining-agricultural area than those in the control area. This difference was most pronounced for leafy vegetables, with arsenic being the trace element of concern. Specifically, the arsenic concentrations in the edible tissues of lettuce and spinach were 8.2- and 5.4-fold higher, respectively, in the mining-agricultural area than in the control area. Lettuce was the vegetable of concern due to its relatively high consumption and relatively high concentration of trace elements. Nevertheless, there was no health risk associated with vegetable consumption in either the mining area or the control area because none of the HQ values surpassed 1.0.

**Keywords** Hazard quotient · Arsenic · Health risk · Food safety · Daily intake

**Highlights**
?Leafy vegetables exhibited the highest TE content in tissues.
Arsenic was the TE of greatest concern.
Local alimentary habits are a key factor for health risk assessments.
None of the HQ values surpassed 1.0.
There was no health risk associated with vegetable consumption in any of the studied areas.

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✉ Alexander Neaman
alexander.neaman@pucv.cl

[1] Escuela de Agronomía, Pontificia Universidad Católica de Valparaíso, Quillota, Chile

[2] Departamento de Ecosistemas y Medio Ambiente, Center of Applied Ecology and Sustainability, Pontificia Universidad Católica de Chile, Santiago, Chile

[3] Department of Chemistry, Université de Montréal, Montréal, Canada

## Introduction

Human exposure to trace elements (TEs) has been a subject of worldwide concern due to the potential health issues (Hu et al. 2014; Park and Choi 2013; Zhuang et al. 2014). Specifically, several studies have reported that mining activities may increase TEs in the soils of central Chile (Aguilar et al. 2011; González et al. 1984). Once in the soils, TEs may potentially accumulate in vegetable tissues and enter the human food chain (Ahumada et al. 2004). Additionally, the consumption of vegetables grown in mining areas has been shown to be the main source of human TE intake in several locations (e.g., Ávila et al. 2016; Hu et al. 2014; Lion and Olowoyo 2013). However, in these studies, human exposure to TEs cannot be clearly linked to mining activities since agriculture may also contribute to the high amounts of TEs in soils (Amin et al. 2013; Arao et al. 2010; Gupta et al. 2012). On the other hand, the TEs in the soils may be associated with their natural concentration, which tends to be elevated in mining areas (De Gregori et al. 2003; PGS 2015).

Different vegetables may contribute to the intake of TEs at different magnitudes (Khan et al. 2015). For example, Muñoz et al. (2002) reported that spinach contributed more As to the intake of TEs than did cabbage, lettuce, and chard. On the other hand, certain organs in the same plant may have different concentrations of TEs. For example, Smith et al. (2009) documented that the concentration of As was higher in the roots of vegetables than in their aboveground parts. In addition, Amin et al. (2013) stated that onion exhibits a higher accumulation of Zn in the bulb than in the roots and that garlic shows a higher accumulation of Cu in the leaves than in the fruit. Therefore, the contribution of TEs to humans through vegetable consumption depends not only on the TE concentration in the soil but also on the species and organs consumed and the actual consumption. Thus, previous studies are not clear about whether exposure to TEs through vegetable consumption is caused by the characteristics of the vegetables studied or if it is related to the soil quality.

To protect human health from the exposure to TEs through vegetable consumption, international organizations have established limits for agricultural soils (CCME 1999a, b2001), or food (EU 2006; FAO 1995; MINSAL 1997). Such guidelines are relatively easy to use, but they usually disregard both the physical status and alimentary habits of the targeted population, tending to overestimate risks, and result in alarmist conclusions. Considering this, the US Environmental Protection Agency proposed the use of "hazard quotients" (HQ), which also include the physical status and alimentary habits of the targeted population (USEPA 1989, 2011). Because of its higher certainty, this expression has been widely used to determine human health risks through the consumption of vegetables grown in contaminated areas (Ávila et al. 2016; Noli and Tsamos 2016). However, these studies do not usually consider HQ in uncontaminated areas. Thus, estimated HQ cannot be linked directly to a specific anthropogenic activity.

Soils from central Chile have been historically used for a dual mining and agricultural purpose (BCN 2012; Folchi 2006; INE 2002), leading to an increase in the concentrations of TEs in the soil. In fact, Chile is the main producer of Cu worldwide (SERNAGEOMIN 2016; USGS 2016) and an important producer of fruits and vegetables (INE 2007). Thus, the authors propose that potential human health risk through vegetable consumption should be determined for both the mining area and the agricultural area without mining activities (control). Hence, the results can discern the actual enrichment effect of mining activities on human exposure to TEs. Thus, the present study aims to (1) compare the concentrations of As, Cu, and Zn in the edible parts of different vegetables cultivated in soils near a mining area and a control area and (2) compare the potential human health risk of consuming the vegetables grown in both areas.

## Materials and methods

### Location of the study area

The control area was located in Quillota, central Chile, which represents a traditional agricultural zone that is not associated with mining activities. On the other hand, the mining area was located in Catemu, which represents a traditional mining-agricultural zone. Specifically, the mining area was located near the Chagres copper smelter, which has been in operation since 1917 and emitted significant loads of smelter dust to the atmosphere before the implementation of mitigation measures in 1991 (Folchi 2006). The control and mining areas are comparable since they possess similar soil characteristics (Table 1) and climatic characteristics (Santibañez and Uribe 1990).

Six experimental plots (160 $m^2$ each) were established in the mining area (MA) to the northeast of the smelter (in the direction of the prevailing winds), at an average distance of 2.5 km. Likewise, one plot (160 $m^2$) was established in the

**Table 1** Principal characteristics of the soils in mining and control areas

| Data | *n* | Distance from smelter (km) | Physicochemical characteristics ± SD | | | | Trace element concentration ± SD (mg $kg^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Textural class | pH | EC (dS $m^{-1}$) | OM (%) | As | Cu | Zn |
| Background in soils of the Valparaiso region | | | | | | | 13[a] | 68[a] | 137[a] |
| Average in soils from the control area (C) | 24 | 25 | Loam | 8.1 ± 0.2 | 1.2 ± 0.7 | 2.6 ± 0.3 | 15 ± 3.5 | 101 ± 81 | 142 ± 43 |
| Average in soils from the mining area (MA) | 129 | 2.5 | Loam | 8.0 ± 0.1 | 2.0 ± 1.5 | 3.7 ± 1.5 | 29 ± 5.9 | 343 ± 103 | 112 ± 15 |
| Enrichment factor (MA/C) | – | – | – | – | – | – | 1.9[b] | 3.4[b] | 0.8[b] |

*EC* electrical conductivity, *OM* organic matter

[a] PGS (2015)

[b] Statistically significant difference between mining and control areas according to the Mann-Whitney test

control area (C). In each plot, the same farmer grew vegetables according to traditional local management, using furrow irrigation and no synthetic chemicals. Specifically, only turkey manure from La Calera town (25 km from the mining area) was added.

## Studied vegetables

Eight vegetable species were selected according to the following criteria: domestic consumption, local production (Merlet and D'Etigny 1989), and TE accumulation (Kabata-Pendias 2011; Soudek et al. 2011). Then, vegetables with different edible parts were selected: "Winter Galega" lettuce, "Viroflay" spinach, Chinese garlic, "Sonic" onion, "Abaco" carrot, "Rosara INIA" potato, "Belen" sweet corn, and "Gladiador" tomato. The selected vegetables represent approximately 70% of the vegetables consumed in the region (MINSAL 2010).

Leaf and bulb vegetables were evaluated during autumn–winter, while underground and fruit vegetables were evaluated during spring–summer. Each vegetable was grown in a 40-$m^2$ polygon.

## Soil and vegetable sampling

Each vegetable was harvested according to its commercial harvest index. Sampling considered healthy plants from the inner rows of average size and quality for commercialization. Vegetable samples were collected from edible parts as three composite random samples. Additionally, approximately 2 kg of soil was collected adjacent to the roots of the harvested plants.

## Chemical analysis and quality control

Once in the laboratory, the edible tissues of the vegetables were prepared for analyses. Special care was taken to remove external soil or dust contamination on the surface of the vegetables. Specifically, the lettuce and spinach were thoroughly washed in the following sequence: tap water, 0.1 M HCl, distilled water, 0.05 M EDTA, distilled water, and distilled water again (Steubing 1982). The bulbs of onion and garlic were peeled and washed with distilled water. Similarly, the carrots, potatoes, and tomatoes were washed with tap water, peeled, and washed with distilled water. The corncobs were peeled and washed. Then, the samples were cut into pieces, put into paper bags, and dried in an oven at 70 °C for 48 h. Later, the samples were ground, sieved, and homogenized. The concentrations of metals and nutrients were measured using standard methods (Kalra 1997). A standard reference material (NIST SRM 1570a—spinach leaves) was taken throughout the plant sample digestion process, with the experimental values being within 10% of the certified values.

The soils were separated from vegetal and animal residues, put into paper bags, and dried in an oven at 40 °C. The dry soil samples were ground and sieved through a 2-mm mesh and then homogenized. The general physicochemical characteristics of the soil were determined using routine methods (Sheldrick and Wang 1993; Sparks et al. 1996). The soil total concentrations of As, Cu, and Zn were determined through soil sample digestion in boiling nitric acid followed by the addition of perchloric acid (Maxwell 1968). To prevent volatilization of As during the digestion process, a Teflon stopper with a 30-cm-long glass reflux tube was used (adapted from Verlinden 1982). The total TE concentrations were determined by atomic absorption spectroscopy. Quality was assured by similarly digesting in duplicate the following certified reference samples: PACS-2 obtained from the National Research Council Canada and GRX-2 obtained from the United States Geological Survey. The obtained results for the standard reference materials were within 10% of the certified values.

## Data analyses

A comparison of the TE concentration in the soil and vegetables between the mining area and the control area was performed. First, an analysis of the median was carried out according to Mann-Whitney's test for multiple comparisons ($p < 0.05$) since the data distribution was not normally distributed and differed in the number of samples between the two areas. Second, the enrichment factor (EF) for TEs in the soil and vegetables was calculated using the following equation:

$$\mathrm{EF} = \frac{\text{TE concentration in soil or plant in the mining area}}{\text{TE concentration in soil or plant in the control area}} \tag{1}$$

Statistical analyses were carried out using Minitab 16 software. The tables and figures were created using the Microsoft Excel 2016 software.

## Risk estimation

Local exposure to trace elements was quantified using an indirect quantification method, namely, daily intake (DI) (USEPA 1989), which determined the exposure by relating the quantity of TEs ingested via vegetable consumption to body weight and consumption habits (Supplementary Eq. 1). For that purpose, data from the 2010 National Alimentary Survey of Chile were extracted (MINSAL 2010). Once determined, the DI was compared with a reference dose (RfD) (Supplementary Table 1), i.e., a dose that represents the maximum safe TE intake. Then, the hazard quotient was calculated using Eq. 2, taking into account that there may be a potential risk only if the quotient between DI and RfD is above 1.

$$HQ = \frac{DI}{RfD} \quad (2)$$

## Results and discussion

### Soil properties

The average soil concentrations of TEs and principal soil physicochemical properties are shown in Table 1. The soil pH ranged from neutral to moderately alkaline, which implies a low availability of cationic TEs and a high solubility of As (Ginocchio et al. 2009; McBride 1994). A high SOM content in soil may also reduce TE bioavailability (Ginocchio et al. 2006). Soil organic matter was higher in the mining area, possibly due to its slower decomposition induced by TE contamination (Sauvé 2006) or to the historical addition of organic manure to croplands, which may increase the soil organic matter content (Haynes and Naidu 1998).

All of the TE concentrations showed significant differences between the mining area and the control area. The highest enrichment factors (EFs) were for Cu and As (3.4 and 1.9, respectively), which may be associated with historical smelter emissions (Alloway 2013; Folchi 2006).

### Trace elements in edible tissues

The average concentrations of TEs in the edible tissues of the vegetables are shown in Table 2. The analysis of EF showed that As has the largest difference between the mining area and the control area and that leafy vegetables are of the highest concern due to their TE accumulations. In particular, As showed the highest EF in lettuce and spinach (8.2 and 5.4, respectively), which are vegetables that show a high specific capacity to absorb As (Díaz et al. 2004; Muñoz et al. 2002; Smith et al. 2009). On the one hand, it has been documented that As in vegetable tissue responds proportionally to the concentration in soil; however, at higher concentrations in the soil, this proportion may increase several times (McBride 2013). On the other hand, the As concentration in spinach was higher than that in lettuce, probably for the following reason. Specifically, the As mobility in plants is low (Shi et al. 2008; Smith et al. 2009), so it tends to accumulate in the roots or old leaves of the vegetables. In addition, the outer (older) leaves of lettuce are commonly removed prior to consumption, in contrast to the leaves of spinach, which are completely consumed. Considering this, the analysis was carried out based on the local treatments before consumption, and such a practice would reduce the As concentration in the leaves of lettuce.

Only Cu in the mining area showed a direct and positive correlation between its concentration in the soil and its concentration in the edible tissue. As shown in Supplementary Table 4, the Cu concentration in soil is correlated with the Cu concentration in the edible tissues of lettuce and spinach, in the case of the mining area. This observation is in agreement with previous studies that demonstrate that the total Cu in soil is a strong indicator of plant Cu availability for leafy vegetables in Cu-enriched soils (Sauvé et al. 1996).

The concentrations of Cu and Zn in tissues of the studied vegetables were similar to other studies with vegetables grown in contaminated soils (Supplementary Table 5). Although Cu and Zn exhibited the highest concentrations in vegetable tissues in this study, Cu and Zn are essential for humans, and their excess can be metabolized by the human body to maintain the balance of Cu and Zn (Turnlund 1998). For example, Cu

**Table 2** Trace element concentrations in edible tissues of vegetables grown in mining and control areas

| Data | TE | Leaf | | Bulb | | Underground | | Fruit | |
|---|---|---|---|---|---|---|---|---|---|
| | | Lettuce | Spinach | Onion | Garlic | Potato | Carrot | Corn | Tomato |
| Average TE concentration in dry vegetables from the control area (C) (mg kg$^{-1}$) | As | 0.10 | 0.18 | u/l | u/l | u/l | *0.21* | 0.03 | u/l |
| | Cu | 11 | *16* | 7.3 | 6.7 | 11 | 9.7 | 1.7 | 3.4 |
| | Zn | 43 | *58* | 24 | 31 | 17 | 19 | 18 | 12 |
| Average TE concentration in dry vegetables from the mining area (MA) (mg kg$^{-1}$) | As | 0.83 | *0.96* | u/l | u/l | 0.06 | 0.33 | 0.06 | 0.10 |
| | Cu | *39* | *34* | 11 | 8.7 | 11 | 9.8 | 1.3 | 2.4 |
| | Zn | *53* | *69* | 35 | 39 | 20 | 37 | 20 | 17 |
| Enrichment factor (MA/C) | As | 8.2[a] | 5.4[a] | – | – | – | 1.7 | 2.6 | – |
| | Cu | 3.5[a] | 2.2[a] | 1.5[a] | 1.3[a] | 1.0 | 1.0 | 0.8 | 0.7 |
| | Zn | 1.2 | 1.2 | 1.5 | 1.2 | 1.2 | 2.0[a] | 1.1 | 1.4 |

The vegetable with the highest TE concentration is shown in italics

*u/l* under limit of detection

[a] Statistically significant difference between the mining and control areas according to the Mann-Whitney test

**Table 3** Mean vegetable consumption and alimentary habits of the studied population, from the 2010 National Alimentary Survey of Chile (MINSAL 2010)

| Population data | | | Ingestion rate (kg of fresh weight year$^{-1}$) of vegetables | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Age (years old) | Average body weight (kg) | Average exposure time (days) | Leaf | | Bulb | | Underground | | Fruit | |
| | | | Lettuce | Spinach | Onion | Garlic | Potato | Carrot | Corn | Tomato |
| 1 to 10 ($N = 70$) | 27 | 2300 | 11 | 1.9 | 4.7 | 0.3 | 23 | 10 | 7.0 | 14 |
| 11 and older ($N = 159$) | 70 | 16,170 | 15 | 1.2 | 7.6 | 0.5 | 22 | 11 | 7.3 | 18 |

toxicity rarely occurs in humans due to the effective mechanisms of absorption and homeostatic defense against its toxicity, making it almost impossible for Cu to surpass the human body's defense against toxicity by oral ingestion (Scheinberg 1979).

## Daily intake of trace elements by vegetable consumption

As recognized by the USEPA (1989), human exposure to TEs depends not only on the TE concentration in vegetables but also on the quantity consumed (Supplementary Eq. 1). Thereby, the alimentary habits of the studied population were determined (Table 3) based on the data from the 2010 National Alimentary Survey of Chile (MINSAL 2010). The most consumed vegetables were potato, tomato, lettuce, and onion. The estimated daily intakes (DI) are shown in Supplementary Table 2 for children under 11 years old, and those for the remaining population are shown in Supplementary Table 3. Children presented higher DI values than did the older population since ingested TEs are distributed in a lower body mass. Even though spinach showed the highest concentration for almost all TEs (except Zn), spinach had low DI values because of the relatively small quantities consumed. In contrast, lettuce, potato, tomato, and garlic contributed more to DI than spinach did. This difference is explained by the ingestion rate of each vegetable. Thus, local alimentary habits are a key factor for health risk assessments.

## Hazard quotient

The potential human health risk of TE intake through the consumption of vegetables from both areas is shown in Fig. 1. Except for As, HQ values were similar between the mining area and the control area. Thus, this study highlights the necessity of assessing both mining and control areas. If TE exposure is quantified only for a mining area, which is typical in the literature (Islam et al. 2016; Roba et al. 2016; Shen et al. 2017), the results may lead to incorrect assumptions that the entire daily intake of TEs is caused by a presumed contamination source. Nevertheless, the results show that TE exposure through vegetable consumption in the studied population is far from being a risk to human health in both areas.

Although none of the studied TEs resulted in human health risks (none of the HQ values surpassed 1.0), only As showed a large difference between the mining and control areas in both age groups. Specifically, in the population from 1 to 10 years old (Fig. 1a), the HQ of As was 0.4 in the mining area versus

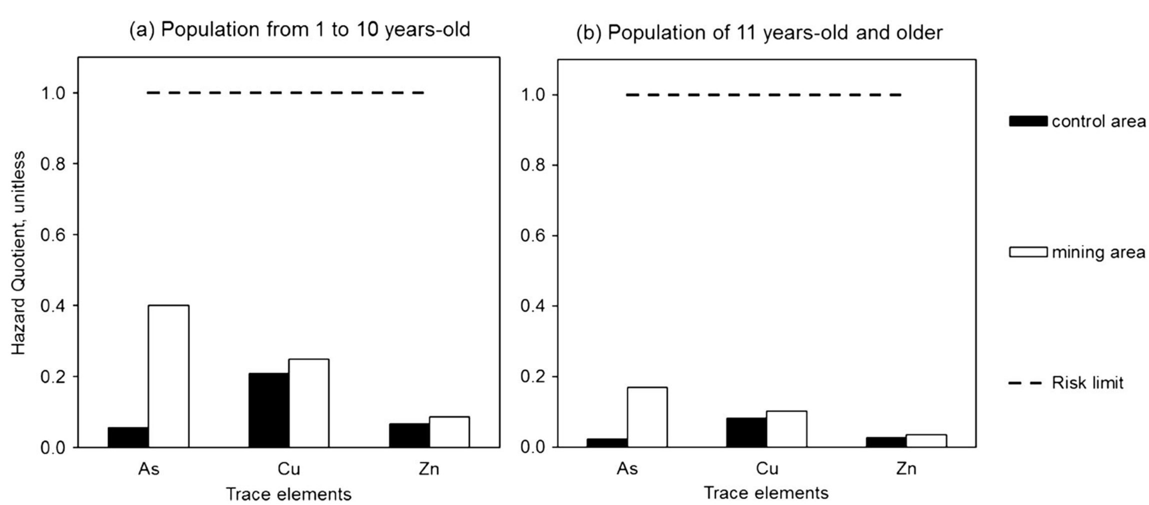


**Fig. 1** Hazard quotient for each trace element in the two age-based scenarios

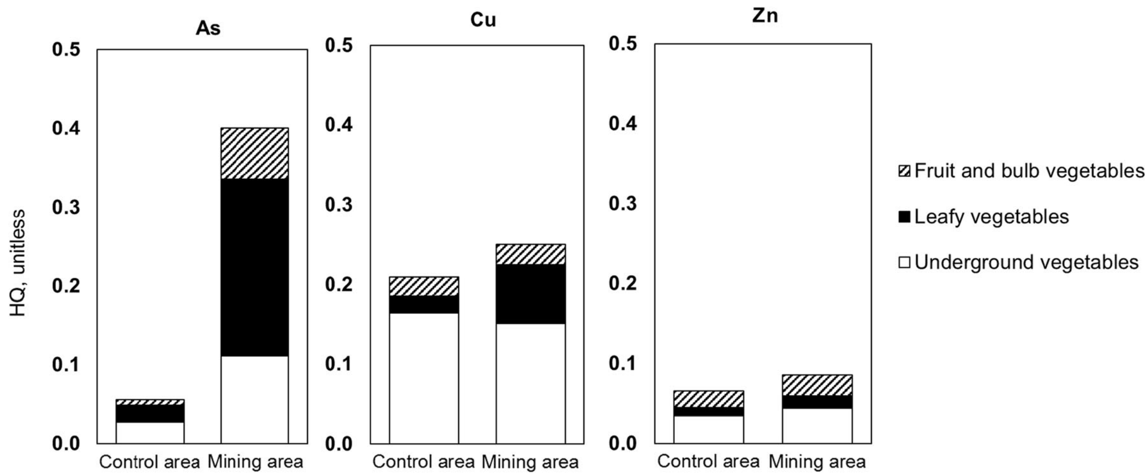


**Fig. 2** Contribution of leafy, underground, and fruit-bulb vegetables to the hazard quotient in the control and mining areas for the age group of people from 1 to 10 years old. References. MINSAL 2010: Base de datos cuantificada de consumo individual, Ministerio de Salud de Chile, Santiago, Chile

0.06 in the control area. Similarly, in the population of 11 years and older (Fig. 1b), the HQ of As was 0.17 in the mining area versus 0.02 in the control area. This increase is related to the influence of historical mining activity, explained by the high capacity of leafy vegetables that accumulate As in As-enriched soils. In the age group of 1–10 years old, for example, the contribution of lettuce and spinach (together) to the HQ of As was 56% in the mining area (Fig. 2) and 38% in the control area (Fig. 2).

It is worth noting that underground vegetables exhibited higher contributions to the HQ of Cu and Zn than leafy vegetables. For instance, potato and carrot together contributed 60 and 51% to the HQ of Cu and Zn, respectively, in the age group of 1–10 years old in the mining area.

## Final considerations

In the present study, the vegetables were thoroughly cleaned; thus, the TEs in the edible tissues were probably lower than those in kitchen conditions (Amir et al. 2016). On the other hand, the mining area exposure scenario was assessed as a worst-case scenario, assuming that all consumed vegetables come from this area. Finally, future research should consider other TE exposure sources, such as the inhalation of and dermal contact with dust and soil and the consumption of drinking water and other locally grown food, in addition to vegetables (Islam et al. 2016; Zhuang et al. 2014).

## Conclusions

According to the objectives, the conclusions are as follows:

1. Concentrations of TEs in the edible tissues of vegetables were higher in the mining area than in the control area, in most cases. The most significant difference was for leafy vegetables, with arsenic being the TE of concern.
2. Lettuce was the vegetable of concern due to its relatively high consumption and relatively high concentration of TEs. Thus, local alimentary habits are a key factor for health risk assessments.
3. In the studied area, there was no health risk associated with vegetable consumption in either the mining area or the control area because none of the HQ values surpassed 1.0.

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