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# Heavy metals and metalloids in organic and conventional vegetables from Chile and Mexico: Implications for human health

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ABSTRACT

The present study assessed the levels of heavy metals (HM; Hg, Cd, Pb, and Cu) and a metalloid (As) in commonly consumed vegetables (lettuce, tomato, green pepper, chard, and spinach) in Chile and Mexico. In Chile the HM and metalloid concentrations were generally lower than those in Mexico and higher in organic crops than in conventional crops. Moreover, the detection frequency of Cd and As in Chilean vegetables was 100%. In Mexico, the Pb levels in organic vegetables (lettuce, tomato, chili, and spinach) and conventional vegetables (spinach and tomato) exceeded the international regulation (IR). In Chile, only tomato showed Pb levels that exceeded the IR. The estimated dietary intake (EDI) values for Mexico were lower than the reference dose, although the EDI values were higher for As in all age ranges and mainly associated with tomato and lettuce in Chile. The target hazard quotient and hazard index values were < 1 (Chile and Mexico). Although the potential health risk is low, prolonged exposure to average concentrations of As (0.2 mg kg-1) in Chile may constitute a potential risk factor for the development of certain cancers. Additional research is necessary to properly regulate As levels in vegetables to ensure food safety.

## 1. Introduction

Rapid urban and industrial growth has introduced various contaminants into the environment with the potential to adversely affect human health. Globally, HM and metalloid pollution of soils, water for human consumption and irrigation, and vegetables has rapidly increased and generated great scientific interest. The HM, such as Cd, Pb, Hg, Ni, and Cu, and metalloids, such as As, are non-biodegradable elements that can accumulate in organs like the liver and kidneys (Tomno et al., 2020; Chen et al., 2021). The consumption of foods contaminated with HM and metalloids has been found to generate severe neurological and muscular damage that can result in diseases such as Parkinson's, muscular dystrophy, Alzheimer's, and multiple sclerosis (Gebrekidan et al., 2013; Huang et al., 2014; Shaheen et al., 2016; Chen et al., 2021). In fact, according to the World Health Organization (WHO), the consumption of contaminated foods is one of the main causes of diseases and deaths worldwide (WHO, 2020).

More than 90% of HM and metalloid exposure is due to the ingestion of contaminated foods and to a lesser extent to dermal contact or inhalation (Haque et al., 2021). These contaminants primarily enter the food chain via natural or anthropogenic pollution associated with irrigation water, industrial emissions, and the use of agrochemicals. Indeed, the excessive application of fertilizers in crop systems is an important means by which these elements enter soils, after which they are either retained in the soil or absorbed and accumulated by plants (Molina et al., 2009; Corradini et al., 2017; Gan et al., 2017; Calderon et al., 2020). Organic farming forgoes the use of conventional agrochemicals and has become an alternative to conventional agricultural production

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methods given that it is generally considered to be environmentally friendly. However, organic farming methods have yielded inconclusive results with regard to the contaminant levels in the cultivated foods (Hadayat et al., 2018; Hattab et al., 2019).

Fresh vegetables are considered essential components of the human diet due to their low cost and high protein, vitamin, mineral, and fiber content (Liang et al., 2018). Worldwide, multiple studies have reported variable levels of microplastics and metalloids in vegetables and fruits (Hu et al., 2017; Kumar et al., 2019; Affum et al., 2020). However, little information is available for fruits or vegetables produced in either Chile or Mexico, despite these countries having the potential to become food powerhouses due to their ability to generate and export fresh and processed produce year-round (Muñoz et al., 2002; Mireles et al., 2004; Leyva Morales et al., 2014; Sawut et al., 2018; Canales et al., 2019; Mahmood et al., 2020; Sayo et al., 2020; Servicio de Información Agroalimentaria y Pesquera SIAP, 2020). Countries that export fruits and vegetables must comply with the strict regulations of international markets aimed at safeguarding consumers (European Union, 2006). Nonetheless, products that do not comply with these regulations are sold in informal domestic markets, which puts the health of consumers, especially those in vulnerable age groups, at risk.

In Chile and Mexico, agriculture is mainly conducted by small and medium-sized producers who employ heterogeneous agronomic practices, which strongly influence food security (Calderon et al., 2020). In Chile, the National Board of School Assistance and Scholarship (JUNAEB) provides more than 4 million meals a day to around 2 million children, which are mainly based on vegetables like chard, spinach, and lettuce (Junta Nacional de Auxilio Escolar y Becas JUNAEB, 2019). Meanwhile, newborns and infants, which are a vulnerable age group, consume notable quantities of fresh or processed chard and spinach in homemade or processed baby foods. In Mexico, the National System for Integral Family Development (SNDIF) provides more than 6 million breakfasts to at-risk and vulnerable children (SNDIF, 2021).

In both Mexico and Chile, notable efforts have been made to monitor the presence of HM, metalloids, and other contaminants in commonly consumed vegetables to reduce exposure via ingestion. In Chile, the Food Sanitation Regulation (Decree 977/1996) of the Ministry of Health controls the levels and types of HM and metalloids allowed in food matrices. However, this regulation is limited to a small group of HM, metalloids, and food matrices, which do not include leafy vegetables. In Mexico, the National Service of Agri-Food Health, Safety, and Quality (SENASICA) regulates the levels of HM (Cd, Pb, and Hg) and metalloids (As) in animal-derived foods. However, regulations only exist for fresh vegetables when they are used as raw materials in processed products, and these regulations do not consider As levels (DOF, 2014; SENASICA, 2019).

Currently, information of the levels and types of HM and metalloids in vegetables produced in Chile and Mexico is scarce. To our knowledge, our study is the first to investigate the HM and metalloid content in vegetables that are highly consumed in these two countries. The objectives of this study were to a) quantify and compare the levels of HM and metalloids in chard, spinach, lettuce, green pepper, and tomato produced in Chile and Mexico and b) to estimate the health risks to different age groups (6–70 years) of ingesting contaminated vegetables. The results of this study provide information about the current state of HM and metalloid levels in these commonly consumed vegetables that may be used to strategically modify the existing regulations in Chile and Mexico, which are lax and outdated.

## 2. Materials and methods

### 2.1. Sample collection

In all, 101 samples of vegetables that were produced in different locations throughout Chile and Mexico were collected from informal markets and supermarkets from 2018 to 2019. In Chile, the samples (n = 40) consisted of conventional vegetables [lettuce (10), chard (10), green pepper (10), and tomato (10)] from the metropolitan region and Valparaíso (V). In Mexico, vegetables labelled as "organic" [n = 26; green pepper (5), lettuce (7), spinach (7), and tomato (7)] and conventional vegetables [n = 35; green pepper (8), tomato (9), lettuce (9), and spinach (9)] were collected in nine states (Baja California, Mexico City, Guerrero, Nayarit, Nuevo León, Sinaloa, Sonora, Tlaxcala, and Yucatan; Fig. 1). The samples were stored in individual plastic bags, labeled, and refrigerated at 4 ºC until analysis, which took place within 24 h of collection.

### 2.2. Sample treatment

The fresh vegetable samples (3–5 kg) were crushed and homogenized according to internationally adopted standards of the Codex Alimentarius (Organización de las Naciones Unidas para la Alimentación y la Agricultura FAO, 2023). Briefly, 100 ± 1.0 g samples were frozen for 24 h and then dried at − 15 °C for 3–4 days using a lyophilizer (LABCONCO, Kansas City, MO, USA). Briefly, 0.5 ± 0.05 g of the previously dried vegetable (composite) samples were transferred to a pre-conditioned Teflon flask. Then, 5 mL of suprapur nitric acid was added and allowed to react for 60 min before 2 mL of hydrogen peroxide (Merck, Darmstadt, Germany) was added and allowed to reach for an additional 60 min and then 5 mL of Milli-Q water was added. The flasks containing samples from Chile were closed and placed in the carousel of an Ethos 1 microwave oven (Milestone, Sorisole, Italy) for digestion, while those from Mexico were digested in an Anton Paar Multiwave Pro microwave (Ostfildern, Germany). The digestion procedures were the same for the samples from both countries and were conducted with the following program: step 1 (time: 2 min, power: 250 W), step 2 (time: 2 min, power: 500 W), step 3 (time: 10 min, power: 1000 W), step 4 (time: 10 min, power: 1500 W), and step 5 (cooling to 55 °C; EPA, 1996). Finally, the digested samples were brought up to a final volume of 25 mL with Milli-Q water for further analysis.

### 2.3. Instrumental analysis and quality assurance

The samples from Chile were analyzed for Pb, As, and Cd content using a PinAAcle™ 900 T atomic absorption spectrometer with graphite furnace (Perkin Elmer, Waltham, MA, USA). Meanwhile, Hg was quantified using a DMA-80 direct mercury analyzer (Milestone). Calibration curves with five points plus a blank for each metal were prepared to evaluate linearity and determine the limit of detection (LOD) and limit of quantification (LOQ). The regression coefficient of the calibration curve for all analytes was > 0.99. The LOQ values for Pb, As, Cd, and Hg were 0.030, 0.060, 0.003, and 0.001 mg $kg^{-1}$, respectively. As a means of quality control, blank and duplicate samples were also injected and analyzed (Fig. S2). Metals were not detected in blank samples, and the relative standard deviation of the duplicates was < 5%. Finally, the reference material SRM 1570a was used to validate the method, and all recovery values for all metals met the standards of the Official Methods of Analysis (AOAC 2023).

The samples from Mexico were analyzed by anodic stripping voltammetry (ASV) using a VA 797 Computrace (Metrohm, Herisau, Switzerland). The methods used to detect Cd, Pb, and Cu were those of Application Bulletin 113/2 (Metrohm), whereas Hg was detected with the methods described in Application Note V-89 (Metrohm). The LOQ values for Pb, Cd, Cu, and Hg were 0.013, 0.027, 0.089, and 0.010 mg $kg^{-1}$, respectively (Fig. S1). No metals or metalloids were detected in blank samples, and the relative standard deviation of the duplicates was < 10%.

### 2.4. Evaluation of potential health risk

Multiple routes of exposure to HM exist, with food ingestion being the principal route. The estimated daily intake (EDI) values of HM (Pb,

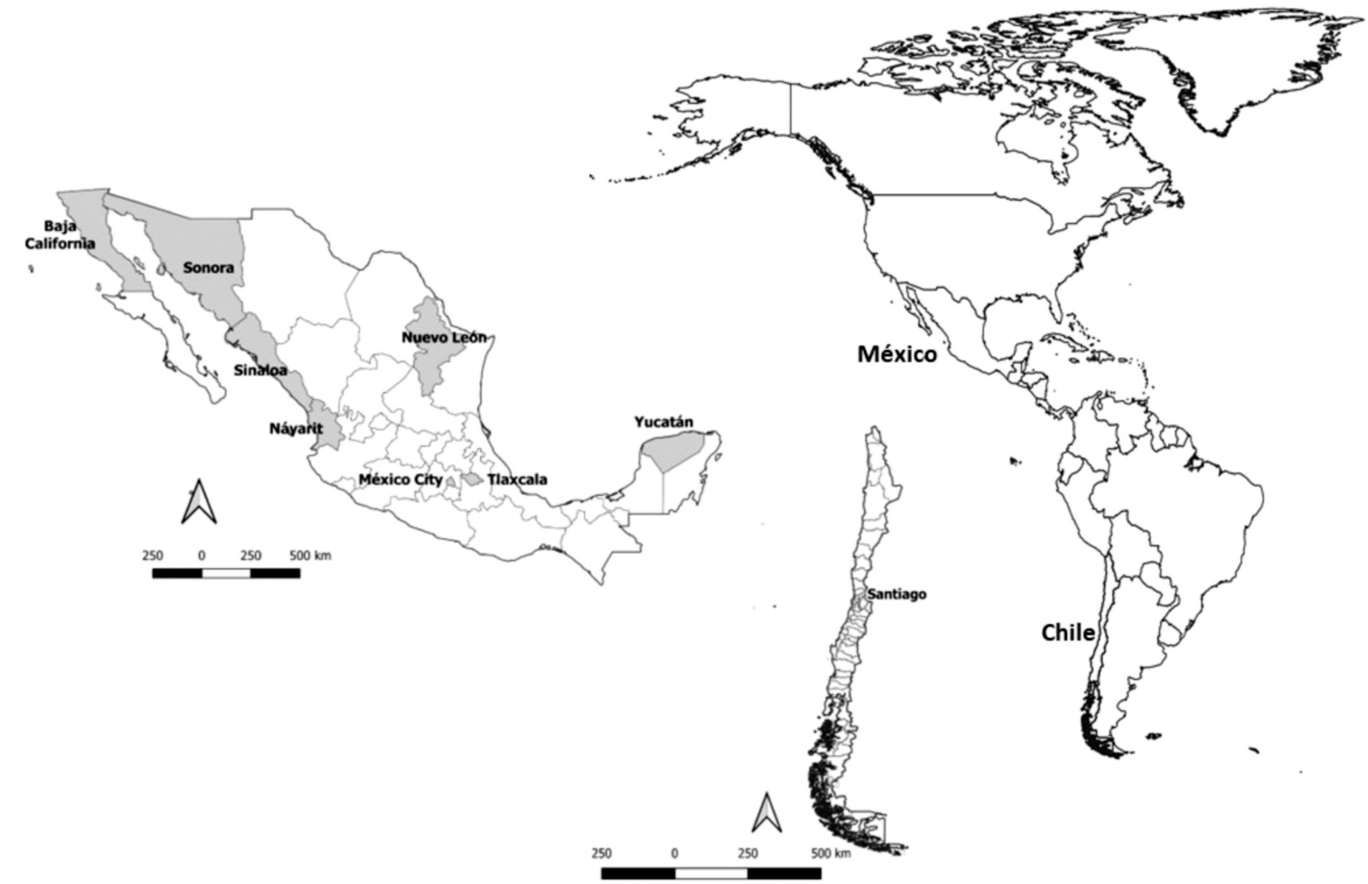


**Fig. 1.** Vegetable sampling sites in Chile and Mexico (2018–2019).

Cd, and Cu) and metalloids (As) were calculated according to the average concentration of each HM and metalloid in each vegetable and the corresponding consumption rates of each age group (6–20, 21–50, and 51–70 years) using Eq. (1):

$$EDI = \frac{C \times IR}{B_{wa}} \quad (1)$$

where C is the average concentration of each metal in a vegetable (fresh weight [FW] in mg kg$^{-1}$), IR is the ingestion rate (average daily consumption in g day$^{-1}$), and $B_{wa}$ is the body mass based on the age group. We utilized the information from the Food Commodity Intake Database (FCID 2005–2010) of the United States in our study, as no information on vegetable consumption by age group is available for either Chile or Mexico.

### 2.5. Estimation of health risk

The human health risk associated with the ingestion of foods contaminated with HM and metalloids was evaluated according to the guidelines of the United States Environmental Protection Agency Risk Assessment Guidance for Superfund (RAGS) Volume III: Part A (USEPA, 2001). The health risk was calculated based on the target hazard quotients (THQ) and the hazard index (HI) for both non-carcinogenic and carcinogenic HM according to Eqs. (2, 3):

$$THQ = \frac{C \times IR_{food} \times E_{fr} \times ED_{tot}}{Rfd \times Bw_a \times AT_n} \quad (2)$$

and

$$HI = \sum THQ \quad (3)$$

where C is the average concentration of the HM or metalloid (mg kg$^{-1}$ FW), $IR_{food}$ is the daily ingestion rate (g day$^{-1}$), $E_{fr}$ is the exposure frequency (144 days year$^{-1}$ considering a consumption rate of 3 times per week), $ED_{tot}$ is the total exposure (70 years), $Bw_a$ is the average body weight, and $AT_n$ is the average time ($ED_{tot}$ x 365 years$^{-1}$) equivalent to 2550 days. The RfD values for Cd, Pb, As, and Cu were 0.001, 0.004, 0.0003, and 0.04 mg kg$^{-1}$, respectively (Guadie et al., 2021). THQ and HI values $< 1$ indicate that there is no severe risk to exposure to HM or metalloids via the consumption of contaminated foods, while values $\geq 1$ indicate adverse health effects in people.

### 2.6. Data Analysis

Descriptive statistics (minimum, maximum, mean, and standard deviation) were calculated for each vegetable. The LOD was taken to be the minimum concentration for samples with values < LOD. A non-parametric Wilcoxon test was performed to compare concentrations between Mexico and Chile and between conventional and organic production. Significance was determined at $p < 0.05$.

## 3. Results and discussion

### 3.1. Metal concentrations in vegetables

#### 3.1.1. Mercury

Tables 1 and 2 show the HM and metalloid content in the vegetables included in this study. In Chile, the highest detection frequencies were found in green peppers (80%), chard (40%), and tomatoes (40%). In addition, maximum concentrations (0.009 mg kg$^{-1}$) were observed in chard and tomato. No Hg was detected in lettuce.

In Mexico, Hg was detected in all vegetables [spinach (100%),

**Table 1**
Minimum, maximum, mean, and standard deviation of the concentrations of heavy metals and metalloid and maximum residue limits (MRL; mg kg$^{-1}$ wet wt.) in vegetables from Chile.

| Heavy metal /Metalloid | Vegetable Conventional | n | Min | Max | Mean | Std. Dev. | MRL (UE) |
|---|---|---|---|---|---|---|---|
| Cd | chard | 10 | 0016 | 0019 | 0017 | 0001 | 0,20 |
| | green pepper | 10 | 0015 | 0019 | 0017 | 0002 | 0,05 |
| | lettuce | 10 | 0016 | 0019 | 0018 | 0001 | 0,20 |
| | tomato | 10 | 0014 | 0019 | 0017 | 0029 | 0,05 |
| Pb | chard | 10 | 0030 | 0154 | 0049 | 0038 | 0,30 |
| | green pepper | 10 | 0018 | 0324 | 0080 | 0099 | 0,10 |
| | lettuce | 10 | 0030 | 0152 | 0051 | 0039 | 0,30 |
| | tomato | 10 | 0030 | 0528 | 0133 | 0156 | 0,10 |
| Hg | chard | 10 | 0001 | 0009 | 0002 | 0003 | - |
| | green pepper | 10 | 0001 | 0006 | 0003 | 0002 | - |
| | lettuce | 10 | 0001 | 0001 | 0001 | 0000 | - |
| | tomato | 10 | 0001 | 0009 | 0003 | 0003 | - |
| As | chard | 10 | 0142 | 0281 | 0241 | 0038 | - |
| | green pepper | 10 | 0145 | 0273 | 0228 | 0047 | - |
| | lettuce | 10 | 0219 | 0310 | 0250 | 0028 | - |
| | tomato | 10 | 0161 | 0248 | 0207 | 0026 | - |

lettuce (100%), tomato (100%), and green pepper (93.75%)] in concentrations higher than those of samples from Chile ($p < 0.0001$; Figs. 2A and 2B). The highest concentrations were found in conventional lettuce (1.057 mg kg$^{-1}$) and organic spinach (0.450 mg kg$^{-1}$). Interestingly, the Hg concentration in organic lettuce (0.128 mg kg$^{-1}$) was 50% lower than that of conventional lettuce (0.279 mg kg$^{-1}$). However, no significant differences in Hg levels were detected between organic and conventional crops ($p > 0.06$). When comparing the levels of Hg in our study with those reported in China (0.015 mg kg$^{-1}$), a highly industrialized country, they were 10–20 times lower than the average values for conventional and organic crops (Zhang et al., 2018).

In Mexico, some productive areas are located adjacent to coal or nonferrous metal mining activities, which are known to increase the levels of HM and metalloids in vegetables (Wu et al., 2010). Indeed, Li et al. (2017) confirmed that high Hg levels in vegetables were related to the transport of Hg in the air from industrial to agricultural areas. Another potential source of Hg entry into agricultural systems is associated with the use of NPK fertilizers (Zhao and Wang, 2010). Finally, the Hg concentrations in tomatoes and green peppers were relatively similar between vegetables and production method.

### 3.1.2. Cadmium

Unlike Hg, Cd is a recognized contaminant in fertilizers (Peng et al., 2022). In Chile, all vegetable matrices contain variable concentrations of Cd (Fig. 2B), although they do not exceed 0.019 mg kg$^{-1}$ (Table 1) and are lower than those reported for spinach and lettuce in China, the UK, Greece, and Saudi Arabia (Huang et al., 2017). The Chilean vegetables in this study are safe to consume, as their Cd levels do not exceed the international standard of 0.050 mg kg$^{-1}$ (European Union, 2006).

In Mexico, the detection frequency of Cd varied depending on the vegetable as follows: lettuce (56%) > green pepper = tomato (31.25%) > spinach (25%; Fig. 2A). The average Cd levels in organically and conventionally produced vegetables (except tomato) exceeded the international standard, even though the maximum value was 0.134 mg kg$^{-1}$ (Table 2).

The detection frequency of Cd in vegetables from Mexico was lower than that of Chile (Figs. 2A and 2B), although maximum values were detected in Mexican vegetables. Significant differences were detected in the Cd levels of tomatoes between Chile and Mexico, with higher values observed in Mexico ($p = 0.042$). The maximum Cd levels for organic and conventional vegetables were 0.569 and 0.523 mg kg$^{-1}$ in spinach and green pepper (Table 2), with no significant differences due to production method ($p > 0.05$).

**Table 2**
Minimum, maximum, mean, and standard deviation of the concentrations of trace metals and maximum residue limits (MRL; mg kg$^{-1}$ wet wt.) in vegetables produced via conventional and organic methods in Mexico.

| Heavy metal /Metalloid | Vegetable | n | Min | Max | Mean | Std. Dev. | MRL (MEX) | MRL (EU) |
|---|---|---|---|---|---|---|---|---|
| **Conventional** | | | | | | | | |
| Cd | spinach | 7 | < LOD | 0301 | 0051 | 0104 | 2,0 | 0,20 |
| | green pepper | 8 | < LOD | 0523 | 0065 | 0173 | 2,0 | 0,05 |
| | lettuce | 9 | < LOD | 0174 | 0039 | 0053 | 2,0 | 0,20 |
| | tomato | 9 | < LOD | 0395 | 0055 | 0124 | 2,0 | 0,05 |
| Pb | spinach | 7 | < LOD | 2256 | 0431 | 0765 | 150 | 0,30 |
| | green pepper | 8 | < LOD | 0271 | 0067 | 0115 | 150 | 0,10 |
| | lettuce | 9 | < LOD | 0483 | 0111 | 0161 | 150 | 0,30 |
| | tomato | 9 | < LOD | 2109 | 0303 | 0651 | 150 | 0,10 |
| Hg | spinach | 7 | < LOD | 0350 | 0186 | 0079 | 1,5 | - |
| | green pepper | 8 | 0097 | 0331 | 0142 | 0101 | 1,5 | - |
| | lettuce | 9 | 0113 | 1057 | 0279 | 0296 | 1,5 | - |
| | tomato | 9 | 0106 | 0192 | 0146 | 0031 | 1,5 | - |
| Cu | spinach | 7 | < LOD | 9391 | 3006 | 3246 | 300 | - |
| | green pepper | 8 | < LOD | 5913 | 2114 | 2049 | 300 | - |
| | lettuce | 9 | < LOD | 6468 | 2465 | 1793 | 300 | - |
| | tomato | 9 | < LOD | 3924 | 1759 | 1342 | 300 | - |
| **Organic** | | | | | | | | |
| Cd | spinach | 9 | < LOD | 0569 | 0108 | 0185 | 2,0 | 0,20 |
| | green pepper | 5 | < LOD | 0296 | 0187 | 0105 | 2,0 | 0,05 |
| | lettuce | 7 | < LOD | 0176 | 0060 | 0069 | 2,0 | 0,20 |
| | tomato | 7 | < LOD | 0134 | 0038 | 0055 | 2,0 | 0,05 |
| Pb | spinach | 9 | < LOD | 1605 | 0668 | 0586 | 150 | 0,30 |
| | green pepper | 5 | < LOD | 0573 | 0174 | 0230 | 150 | 0,10 |
| | lettuce | 7 | < LOD | 1595 | 0315 | 0541 | 150 | 0,30 |
| | tomato | 7 | < LOD | 0872 | 0156 | 0302 | 150 | 0,10 |
| Hg | spinach | 9 | 0116 | 0450 | 0196 | 0103 | 1,5 | - |
| | green pepper | 5 | 0072 | 0138 | 0100 | 0023 | 1,5 | - |
| | lettuce | 7 | 0103 | 0152 | 0128 | 0014 | 1,5 | - |
| | tomato | 7 | 0068 | 0247 | 0189 | 0061 | 1,5 | - |
| Cu | spinach | 9 | < LOD | 23,61 | 8384 | 6820 | 300 | - |
| | green pepper | 5 | < LOD | 2988 | 1782 | 1000 | 300 | - |
| | lettuce | 7 | < LOD | 11,52 | 3602 | 3572 | 300 | - |
| | tomato | 7 | < LOD | 5864 | 2451 | 2040 | 300 | - |

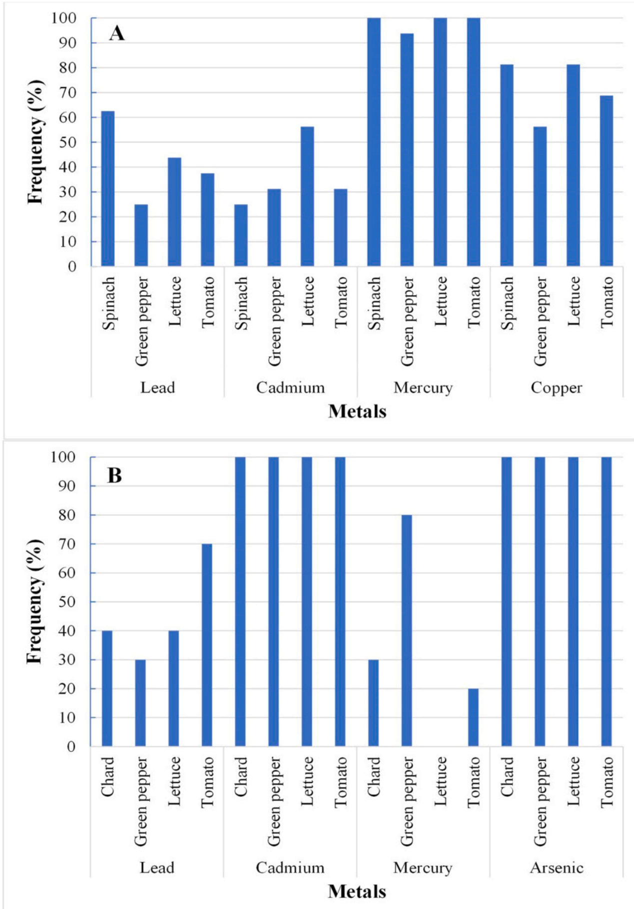


**Fig. 2.** Detection frequency of metals and metalloids in vegetables in A) Mexico and B) Chile.

Similar Cd levels were reported in spinach from Australia (~ 0.361 mg $kg^{-1}$ FW; Kachenko and Singh, 2006). For conventional tomatoes (Chile), the average Cd level (0.055 mg $kg^{-1}$) was equal to the maximum reported in Poland (Rusin et al., 2021). Studies of crops grown near mining areas in China have reported average Cd levels in lettuce and spinach of ~ 0.460 and 0.513 mg $kg^{-1}$, respectively, which may explain the high Cd levels found in Mexico (Zhou et al., 2016). Similar trends in these matrices have also been reported in countries such as Macedonia and Italy (Huang et al., 2017). Interestingly, previous studies have also reported differences in the accumulation levels of HM and metalloids between conventional and organic crops. Lee et al. (2017) found that the use of organic amendments was associated with higher concentrations of HM and metalloids in organic fruits than those present in conventional crops. However, Hattab et al. (2019) reported that HM levels in conventional lettuce and tomatoes were 15–24 times higher than the levels present in those that were organically produced. Similar results have been reported in vegetables grown with conventional and organic agriculture methods in the United States (Hadayat et al., 2018). However, in this study, the average levels of Cd in organic vegetables were 2–3 times higher than those of conventional vegetables.

In addition, the average Cd levels reported in China for spinach (0.513 mg $kg^{-1}$) and lettuce (0.460 mg $kg^{-1}$) are lower than those reported in our study for both countries and production methods (Zwolak, 2019). The types and levels of HM and metalloids in agri-food products mainly depend on the matrix and cropping system (Krejcova et al., 2016).

### 3.1.3. Lead

Like Cd, Pb is another non-essential element present in fertilizers (Nacke et al., 2013). In Chile, the highest Pb detection frequency was found in tomatoes (70%), followed by lettuce (40%), chard (40%), and green pepper (30%). In Mexico, the highest Cd detection frequency was found in lettuce (62.5%), followed by spinach (43.75%), tomato (37.5%), and green pepper (25%). Once again, the Pb levels in vegetables from Chile were lower than those in vegetables from Mexico (Tables 1 and 2), although no significant differences were present ($p > 0.07$). The Pb levels in the vegetable samples from Chile did not exceed those of international regulations for chard, green pepper, and lettuce (0.30 mg $kg^{-1}$), although the average concentration in tomatoes (0.133 mg $kg^{-1}$) exceeded the international standard of 0.100 mg $kg^{-1}$ (European Union, 2006). Interestingly, the highest Pb concentrations were found in non-leafy vegetables, namely green pepper (0.324 mg $kg^{-1}$) and tomatoes (0.528 mg $kg^{-1}$), which also showed the highest detection frequencies (Table 1, Fig. 2B). In this regard, the Pb levels reported in our study are higher than those reported in the United States for conventional and organic tomatoes (0.0072 vs. 0.00495 mg $kg^{-1}$) and lettuce (0.0253 vs. 0.012 mg $kg^{-1}$; Hadayat et al., 2018). A similar pattern was found in tomatoes (0.003 mg $kg^{-1}$) and lettuce (0.033 mg $kg^{-1}$) that had been produced in urban community gardens in Slovakia (Hiller et al., 2022).

Anthropogenic activities, such as mining and fertilizer application, may be some of the principal pathways for Pb entry into crop systems in Chile (Molina et al., 2009; Tume et al., 2019). In Mexico, Pb levels in conventional and organic crops (except conventional tomatoes) exceed those of international regulations (Table 2), and no differences were found between production methods ($p > 0.2$). The average Pb concentrations in organic spinach, chard, and green pepper were twice as high as those of their conventionally produced counterparts, with spinach (0.668 mg $kg^{-1}$) and lettuce (0.315 mg $kg^{-1}$) showing the highest accumulation levels. When comparing Pb levels in tomatoes, the levels detected in our study are 10 and 20 times higher for organic and conventional crops, respectively, than those reported for supermarket tomatoes in Poland (0.016 mg $kg^{-1}$; Rusin et al., 2021). Interestingly, the rate of Pb accumulation in vegetables grown in soils fortified with 800 and 200 mg $kg^{-1}$ of Pb followed the order of carrot > lettuce > bean > tomato, which is contrary to what is reported in our study (Mc Bride et al., 2015).

### 3.1.4. Copper

In our study, Cu levels were only analyzed in vegetables from Mexico. The detection frequency varied among the vegetable samples, with spinach and lettuce showing the highest frequencies (81.25%), followed by tomato (68.75%) and green pepper (56.25%; Fig. 2A). The maximum Cu concentrations among organic and conventional vegetables were found in spinach and lettuce. For lettuce, the Cu levels in organic vegetables (11.5 mg $kg^{-1}$) were twice as high as those of conventional vegetables (6.47 mg $kg^{-1}$), with the Cu level of organic spinach (23.6 mg $kg^{-1}$) being nearly three times higher than that of conventional spinach (9.39 mg $kg^{-1}$), but no significant differences were observed in Cu levels between production methods ($p > 0.07$; Table 2).

Feseha et al. (2021) reported an average Cu level of 16.6 mg $kg^{-1}$ in lettuce irrigated with wastewater that was more than 5 times higher than what was reported in our study. Interestingly, a study in Chile compared the accumulation rates of Cu in lettuce grown in areas near a copper smelter and found lower Cu levels in the control treatment (20 mg $kg^{-1}$ dry weight) than those of lettuce grown in the industrial zone (37 mg $kg^{-1}$ dry weight). A similar pattern was identified in chard (control: 13 mg $kg^{-1}$; industrial zone: 37 mg $kg^{-1}$; Lizardi et al., 2020). In China, the average Cu levels in leafy vegetables (0.239–7.024 mg $kg^{-1}$ FW) grown in greenhouses or fields were lower than those in our study (Hu et al., 2014), although the study does not indicate which levels correspond to greenhouse or field crops. In Bangladesh, the Cu levels reported in spinach range from 1.10 to 2.10 mg $kg^{-1}$ and are comparatively lower than those in our study.

*3.1.5. Arsenic*

In our study, As was only analyzed in vegetables from Chile. Interestingly, the detection frequency in all vegetable matrices was 100% (Fig. 2B). The maximum As levels for each vegetable were similar and ranged from 0.219 to 0.310 mg $kg^{-1}$ (Table 1). Lizardi et al. (2020) evaluated As levels in lettuce grown in a non-industrial zone and reported an average As value of 0.23 mg $kg^{-1}$, which is similar to what we have reported in our study. However, when compared to the value reported by Lizardi et al. (2020) for lettuce grown in an industrial zone (1.1 mg $kg^{-1}$), our results are lower, which highlights the importance of anthropogenic sources to As accumulation. A similar pattern was observed for the average As levels in chard grown in an industrial zone (Lizardi et al., 2020).

In China, a study was conducted that evaluated the levels of As accumulation in areas subject to intensive human intervention and reported maximum As levels of 0.88 mg $kg^{-1}$ (Su et al., 2023). Similarly, Zwolak et al. (2019) reported As levels that were three times higher (0.660 mg $kg^{-1}$) in lettuce of Chinese origin compared to those in lettuce from other countries. In contrast, Chen et al. (2021) reported lower levels (0.043–0.0796 mg $kg^{-1}$ FW) than those reported by Zwolak et al. (2019). Interestingly, the As levels in spinach (0.13 mg $kg^{-1}$) from Bangladesh are lower than the average reported for Chile (IslaM et al., 2016).

In general, the highest levels of HM and metalloid accumulation are observed in countries with high levels of industrial development that employ fertilizers excessively. In Chile, the production of leafy vegetables is mainly concentrated in regions IV and VII, which are located near region VI, which hosts high mining activity. This may explain the As levels reported in our study. Thus, it is necessary to regulate As content in vegetables and fruits given the current levels of this potentially carcinogenic metalloid (Table S1).

## 3.2. Health risk assessment

The EDI values of HM and metalloids for different age groups are shown in Table S1. In Chile, the EDI values for all age groups followed the order of As > Pb > Cd. The main vegetables that contributed to this order were tomato and chard more so than lettuce and green pepper. It should be noted that the As levels in lettuce and tomato exceeded the RfD (0.0003 mg $kg^{-1}$ $day^{-1}$) for all age and gender groups, which indicates that a high risk to consumers is present. In Mexico, the EDI values for the HM and metalloids in our study did not exceed the corresponding RfD values, thus these vegetables may be considered safe to consume.

Table S2 shows the THQ values for each vegetable and age group. In both Chile and Mexico, these values are less than one. For As, the highest THQ levels were found in tomato in the 6–20 year age group, with the value for women (0.84) being higher than the value for men (0.73). Our results suggest that there are no notable long-term health effects that should be expected due to the consumption of these vegetables. In addition, the HI values were $< 1$ for all vegetables sampled in both Mexico and Chile. In Chile, the HI value for tomato ranged from 0.79 to 0.91 among the age and gender groups, followed by the values for lettuce and green pepper. In Mexico, conventional and organic spinach exhibited the highest HI values compared to those of the other vegetables. Similar results to those reported in our study have indicated that leafy vegetables are the main contributors to the THQ value (Chen et al., 2021).

# 4. Conclusion

We compared HM and metalloid concentrations in highly consumed vegetables from Chile and Mexico and evaluated the associated health risks in terms of EDI, THQ, and HI. The HM and metalloid concentrations varied among vegetables, with higher levels of Cd, Pb, and Hg found in Mexico compared to those found in Chile. Overall, the average Pb levels in tomatoes from Chile and in all sampled vegetables from Mexico exceed the international regulations established for both conventional (2 vegetables) and organic (4 vegetables) crops. Organic crops contained higher HM and metalloid levels than conventional crops, which was evident in spinach and lettuce. Interestingly, similar average levels of As were observed in all vegetable sampled in Chile. In Mexico, organic spinach and lettuce contained higher Cu concentrations than those of conventional crops. When evaluating these results from the perspective of consumption, the EDI values in Mexico did not exceed the RfD; however, the EDI values for As were higher than the RfD for tomato, lettuce, and chard for different age groups in Chile. The THQ and HI values were $< 1$ for all vegetables in Chile and Mexico, which indicates that there are no long-term health risks associated with their consumption. Our study represents a notable contribution to improving food safety in both Chile and Mexico, as our results may be used to develop regulations for metalloids, such as As, in vegetables that will help safeguard consumer safety.

# Author contributions

**Conceptualization:** Calderón R., García-Hernández J. **Data curation:** Palma, P., Godoy, M., Leyva-Morales, J. B., Zambrano-Soria, M., Bastidas-Bastidas, P.J. **Formal analysis:** Palma, P., Godoy, M, Calderón, R., García-Hernández J., Leyva-Morales, J. B., Bastidas-Bastidas, P.J. **Funding acquisition:** Palma, P., Godoy, M, Calderón, R., García-Hernández J., Leyva-Morales, J. B., Bastidas-Bastidas, P.J. **Investigation:** Palma, P., Godoy, M, Calderón, R., García-Hernández J., Leyva-Morales, J. B., Bastidas-Bastidas, P.J., Valenzuela, G. **Methodology:** Palma, P., Godoy, M, Calderón, R., García-Hernández J., Leyva-Morales, J. B., Bastidas-Bastidas, P.J. **Writing – original draft:** Palma, P., Calderón, R., García-Hernández J., Leyva-Morales, J. B. **Writing – review & editing:** Palma, P., Calderón, R., García-Hernández J., Leyva-Morales, J. B.

# CRediT authorship contribution statement

**Calderón, R.:** Funding acquisition, Writing – original draft, Writing – review & editing; Formal analysis; Resources. **García, Hernandez, J.:** Funding acquisition, Formal analysis, Investigation, Methodology. **Palma, P.:** Formal analysis, Supervision, Writing – review & editing. **Leyva-Morales, J.B.:** Formal analysis, Writing – review & editing. **Godoy, M.:** Formal analysis, Investigation. **Bastidas-Bastidas, P.J.:** Formal análisis. **Valenzuela, G.:** Formal analysis.

# 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.

# Data Availability

Data will be made available on request.

# Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2023.105527.

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