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ORIGINAL ARTICLE

Accumulation of As and Pb in vegetables grown in agricultural soils polluted by historical mining in Zacatecas, Mexico

Silvia Salas-Muñoz[1] · Elvia Valdez-Valdez[2] · Jorge Armando Mauricio-Castillo[2] · Fatima Berenice Salazar-Badillo[2] · Hector Rene Vega-Carrillo[3] · Miguel Angel Salas-Luevano[4]

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Abstract

Historical mining activities are a source of environmental pollution that affects the food chain and the health of human beings. This study aimed to assess the accumulation of arsenic (As) and lead (Pb) in vegetables grown in agricultural soils polluted by historical mining in Zacatecas, Mexico. The concentration of As and Pb in agricultural soil and edible parts of carrot (*Daucus carota* L.), garlic (*Allium sativum* L.), and pepper (*Capsicum annum* L.) were analyzed by atomic absorption spectrometry. Also, the As and Pb pollution index and soil-vegetable bioconcentration factor were determined. The pH values of the farmland were moderately alkaline. The concentration of As in agricultural soil exceeds the permissible limit of Mexican and international standards representing public and environmental health risks. The Pb content in most soil samples was low, and only two soil samples exceeded the permissible limit of Mexican and international standards. The As and Pb content in edible parts of vegetables exceeded the national standards from various countries and values established by Codex Alimentarius (FAO-WHO). The highest As concentration was found in *C. annum* (111 mg kg^{-1}) and *A. sativum* (100 mg kg^{-1}). The highest concentration of Pb was in pepper fruits. The pollution index indicates that the soil sample is classified as polluted, and its quality is not suitable for agricultural use; thus, the vegetables cannot safely be consumed. Among vegetables, the higher BCF value was for As, ranging from 2.33 to 0.64, and the average for all vegetable samples was 1.01. According to the findings, the state and national agricultural and health authorities should not recommend cultivating vegetables in agricultural soil located in this region. Likewise, preventive measures must be taken to avoid consuming polluted vegetables and certifying their safety grade.

Keywords Historic mining waste · As · Pb · Vegetables · Pollution load index · Bioaccumulation factor

Introduction

Soil pollution by potentially toxic elements (PTEs) is one of the most critical environmental problems because of its effect on human health and ecosystems (Kabata-Pendias 2011). Mining activities are well known for their damaging effects on the environment due to the deposition of large volumes of waste on the soil (Ashraf et al. 2011). One of the main concerns regarding mining activities especially abandoned mines is a waste composed of a multifaceted mixture of metals and dust particles containing a large amount of PTEs (Agboola et al. 2020). Accordingly, the geochemical composition of the soil is considerably changed at nearby mining areas (Du et al. 2018).

In Mexico, millions of tons of tailings are abandoned and dispersed across the mining regions, and their potential to affect the environment is still unknown (Ramos-Arroyo and Siebe-Grabach 2006). In particular, the opencast coal mining method has been associated with the generation of millions of tons of sulfide-rich tailings (Bhattacharya et al. 2006; Masto et al. 2011).

Additionally, waste and tailings of abandoned mines are deposited inappropriately, with a scarce layer of the

✉ Miguel Angel Salas-Luevano
masalas@uaz.edu.mx

1 CONACYT-Campo Experimental Zacatecas-INIFAP Calera de VR, Zacatecas, Mexico

2 Unidad Académica de Ciencias Químicas, Universidad Autonoma de Zacatecas, Zacatecas, Zacatecas, Mexico

3 Unidad Académica de Estudios Nucleares, Universidad Autonoma de Zacatecas, Zacatecas, Zacatecas, Mexico

4 Unidad Académica de Agronomía, Universidad Autonoma de Zacatecas, Zacatecas, Zacatecas, Mexico

original land, without reforestation programs, lack of protective systems (Salas et al. 2017), and no continuing management (Salari et al. 2012). These wastes are usually deposited on the ground that occupies large surface areas (Conesa et al. 2007). The tailings generate spoils, effluents, and dust with high concentrations of metal and metalloid elements (Wiegleb and Felinks 2001). In this way, extractive mining activities degrade the environment, affecting the neighboring population's health. This problem is even getting more serious worldwide, especially in developing countries (Bagdatlioglu et al. 2010).

On the other hand, the spread of fine particles has caused damage to ecosystems including pollution of adjacent agricultural soils, deterioration of the food chain, economic and social injury that poses severe health risks to humans and grazing animals (Clemente et al. 2007; Martínez-Sánchez et al. 2012). The accumulation of PTEs in agriculture is an increasing concern nowadays (Jolly et al. 2013). As moves slowly in polluted and near-surface soils being redistributed by tilling, burrowing animals, or overland runoff (MDEP 1995; Barringer et al. 2001). While Pb is generally immobile in soil; therefore, it accumulates in the top layer of soil (Berglund et al. 2000) and can remain there for thousands of years (Kumar et al. 1995).

On the other hand, fresh vegetables and fruits are vital to our diet because they contain essential nutrients for the human body and its health, such as carbohydrates, proteins, minerals, vitamins, and trace elements (Itanna 2002; Zhong et al. 2018). Also, have multiple health benefits: rich in fibers, antioxidants, and medicinal properties. For example, carrot has a massive accumulation of carotenoids in the root (Klein and Rodriguez-Concepcion 2015); pepper crop is considered the second most economically important vegetable worldwide after tomato. This is used as a spice in different countries (Aluko 2016). Also, pepper is the source of capsaicinoids, vitamins A (ascorbic acid), B and C (carotenoids), polyphenols, phosphorus, and calcium (Andrews 1995; Topuz and Ozdemir 2007). Garlic contains more than 70 organosulfur compounds (Randle and Lancaster 2002). Vegetables uptake PTEs from soil and air polluted and accumulate them in different organs in high quantities enough to cause potential health risks to the consumers (Wang et al. 2005; Yang et al. 2007; Singh et al. 2010).

In this way, the ingestion of polluted vegetables suspended tailings, and soil particles (geophagia) are common in populated areas near mines (Ngole-Jeme and Fantke 2017). Food chain pollution is the main pathway of PTEs exposure for humans through various routes such as inhalation, dermal contact, and oral ingestion (Khan et al. 2008; Komárek et al. 2008; Rout et al. 2014). Therefore, PTEs represent a potential threat to the environment and impact soil properties, causing surface and subsurface water pollution, uptake by plants, and adverse effects on living organisms (Arenas-Lago et al. 2014; Lago-Vila et al. 2017).

It should be highlighted that toxic elements such as As (first) and Pb (second) stand out among the CDC rank substance priority list pose the most significant potential threat to human health (ATSDR 2021). Long-term health effects of exposure to As are skin and lung cancer, kidney disease, hypertension, cardiomyopathy, neuropathy, affect the liver, bladder, and lymphatic system (Vahidnia et al. 2007). While the complications related to Pb toxicity are damage to the nervous system in children, such as intellectual deficits, neurological damage, cognitive dysfunction, neurobehavioral disorders, and encephalopathy. Also, hypertension, renal impairment, abdominal colic, cancer, anemia, low blood levels, and death (Lanphear et al. 2005; Patrick 2006; Flora et al. 2012).

So, it is essential to monitor food quality, given that plant uptake is one of the main pathways through which PTEs enter the food chain (Antonious and Kochhar 2009). Nowadays, increasing food demand and security is of great concern worldwide due to toxic metals polluted foodstuffs and their associated health risks (Rehman et al. 2017; Nawab et al. 2018). Thus, vegetables cultivated in soil pollution without environmental restrictions and inefficient mining activities may accumulate PTEs above those expected. Therefore, information about toxic element concentrations in vegetables is essential to assessing the potential risks to human health and ecological systems. The present study aimed to determine the accumulation of As and Pb in vegetables grown in agricultural soils polluted by historical mining in Zacatecas, Mexico.

Materials and methods

Description of the study area

The study was carried out in agricultural soils of four rural communities: El Bordo (22°54′34″ N, 102°24′45″ W), El Lampotal (22°54′43″ N, 102°24′10″ W), La Era (22°51′17″ N, 102°25′03″ W) and Santa Rita (22°54′42″ N, 102°25′06″ W) located in Guadalupe and Vetagrande municipalities in Zacatecas, Mexico; a polluted region since colonial and postcolonial times with high natural deposits of As and Pb (Santos-Santos et al. 2006) (Fig. 1). This region presents an arid tropical climate with an average temperature of 16.6 °C, annual precipitation from 400 to 500 mm, altitude ranges from 2,000 to 2,300 m above sea level (Medina et al. 2009), and different types of soils among which are Kastanosems, Luvisols, Calcisols, and Fluvisols (Krasilnikov et al. 2013; INEGI 2022).

Fig. 1 Map of the sampling sites of soil and vegetables located in Guadalupe and Vetagrande municipalities at the state of Zacatecas in Mexico

Historical mining and origin of the soil pollution

In Zacatecas, after discovering silver veins in 1548, its extraction was carried out from 1570 to 1820 in haciendas of benefit through the "amalgamation method" (Santos-Santos et al. 2006). The wastes were placed on the shores of streams and for centuries dragged by the rains through the mountains and released directly towards the agricultural lands. Nowadays, agricultural soil and subsoil layers of approximately 1.0–2.0 m until a few centimeters thickness contain millions of tons of alluvial wastes, representing the primary source of waste from historical mining. These wastes contain remaining valuable minerals and metals that were not recovered in the past and are objects of assessment studies (Alcaldea et al. 2018). In this way, previous studies have reported that the soils of this region have high concentrations of Ag, Au, As, Cd, Hg, and Pb (Flores 2003; Ogura et al. 2003; Santos-Santos et al. 2006). In addition, a reprocessing factory for these minerals and metals deposits the amalgamated sediments in a tailing within its facilities (Fig. 2), and the other two abandoned tailings out in the open without control, contributing to the pollution of agrosystems and nearby communities affecting proximally 6500 people. These lands are mainly used for agriculture, and there are no restrictions by agriculture and Mexican environmental agencies.

Soil and vegetable sampling

The sampling area at the nine study sites covers an area of approximately 1250 ha (Fig. 1), and representative samples of surface soil and vegetables (carrot, garlic, and pepper) were collected randomly for each established plot. Habitants use these vegetables for self-consumption also supply retail and wholesale country markets. At each sampling site, soil samples were taken from the upper 0–25 cm of the profile representing the rhizosphere and arable layer, and 10 random subsamples were collected in a restricted circle of 60 cm around the vegetal species with a distance of 20 m between each sub-sample. A total of nine composed samples composed of 10 random subsamples from every sampled place were taken. Each composed sample used for analyses weighed one kg. The rhizosphere soil samples were isolated from the roots and vegetative organs, shaking them in a plastic bag. Soil samples brought to the laboratory were mixed and left dried naturally in clean plastic trays for a week at ambient temperature (26 °C) followed by an oven-dry until a constant weight was obtained. Then samples were stored in polyethylene bags until used for acid digestion.

All vegetables at the stage of maturity and for fresh consumption were collected before harvest. Vegetable composed samples (about five kg) were collected into polyethylene bags jointly where the soil samples were. Individual crop samples include tissue collected from four locations within each sampling site to obtain representative samples and as well as to obtain sufficient dried tissue (0.5 g) for analysis. Vegetable samples were mixed and washed thoroughly with tap water twice; the dust and soil particles adhering to the carrots were removed but not peeled. The remaining particles adhering to the plant surfaces were extracted with distilled water, deionized water, and dried with tissue paper. The edible parts of all vegetable samples were cut into small pieces, fresh tissue was

Fig. 2 View of the tailing processing company near to crop lands belonging to Guadalupe and Vetagrande municipalities at the state of Zacatecas in Mexico

weighed separately and recorded, and then were heated in an oven at 70 °C for 48 h to a constant weight. Samples ground using a porcelain mortar and then a stainless-steel mill, mixed and sieved with a 2-mm mesh, re-dried, weighed, and stored in plastic bags at ambient temperature before digestion (McBride et al. 2015).

Physical–chemical parameters of agricultural soil

The < 2-mm fraction of composite samples of soil was used to determine the physicochemical properties. Soil particle-size composition (sand, silt, and clay) was determined using the micropipette method (Miller and Miller 1987). Soil pH was measured in a soil paste saturated with deionized water at a ratio of 1:2.5 using a glass electrode (McLean 1982; McCauley et al. 2017). The electrical conductivity (EC) of the soil was measured using a conductivity meter on an extract of soil obtained by shaking it with deionized water at a 1:1 (w/v) soil: water ratio (Janzen 1993). Organic matter (OM) was determined by the Walkley and Black method (1934). All parameters were evaluated by triplicate.

Sample preparation and analysis

Separately, representative samples for both soil and vegetable for digestion procedures were taken. All digested samples were diluted to 50 ml with 0.5% HNO_3 and stored at 4 °C until As and Pb analysis concentration. Then, weighed a sample of fine powder (0.5 g) for digestion (Cao et al. 2014) using a microwave oven 3000, Microwave Reactor System (MARS), digestion techniques following the standard Method: SW 846: 3050AB (US. EPA 1996a). The total soil As and Pb concentrations were measured in composite samples using atomic absorption spectrometer (AAS, model 800) Perkin Elmer, according to previously described EPA Method: SW 846: 3050/6010B three replicates by vegetable were analyzed (US. EPA 1996b). Procedures used to ensure precision and accuracy in the measurements of As and Pb included the use of Standard Reference Materials (SRM) from the National Institute of Standards and Technology (NIST) localized in the USA. Trace reagent analysis grade reagents were used.

Table 1 Arsenic and lead concentration in agricultural soil impacted by historical mining in Zacatecas, Mexico

Communities /site	pH	EC (dS m^{-1})	OM (%)	Particle size (%)			PTEs (mg/kg^{-1})	
				Sand	Loam	Clay	As	Pb
Santa Rita								
Site (1)	7.65	4.94	3.30	65	22	13	135 ± 20.18	179 ± 27.32
Site (2)	7.77	4.12	3.11	43	36	21	39 ± 6.99	90 ± 4.5
El Bordo								
Site (3)	7.89	3.58	2.06	37	24	39	75 ± 6.43	63 ± 3.40
Site (4)	8.18	3.87	2.22	45	24	31	91 ± 8.50	72 ± 6.47
Site (5)	8.18	1.97	3.34	37	38	25	141 ± 19.21	1201 ± 130.24
Lampotal								
Site (6)	7.95	2.60	2.72	53	30	17	138 ± 8.43	25 ± 3.83
Site (7)	7.78	3.88	2.70	47	28	25	70 ± 9.22	185 ± 13.5
La Era								
Site (8)	8.07	2.64	3.24	57	22	21	127 ± 14.4	177 ± 19.32
Site (9)	8.44	1.52	3.16	43	26	31	165 ± 7.37	1206 ± 155

All parameters were evaluated by triplicate

Soil-vegetable bioconcentration factor

The bioconcentration factor (BCF) is the ratio of PTEs concentration in vegetables to that in the soil. The bioconcentration factor (BCF) was calculated as follows:

$$\mathrm{BCF} = \frac{C_{\mathrm{vegetable}}}{C_{\mathrm{soil}}} \tag{1}$$

where $C_{\mathrm{vegetable}}$ is the total concentration of a particular PTEs in the edible part (mg kg^{-1} dw), and C_{soil} represents PTEs concentration in the soil habitat of the vegetable (mg kg^{-1}) (Chang et al. 2014).

Pollution load index

The suitability of soils for agricultural uses can be further assessed by using the pollution index (PI) which assesses the environmental risk caused by the polluted soils. The PI expressed as the single index method can be calculated as follows:

$$PI = \frac{C_{PEM}}{C_0} \tag{2}$$

where PI, C_{PEM}, and C_0 represent the pollution index, the potentially toxic metal (loid) content in planting media and the standard value of the element, respectively. Where PI > 1, the soil sample is classified as polluted, while PI ≤ 1 suggests unpolluted soil (Li et al. 2006; Yang et al. 2011; Hu et al. 2013; Wu et al. 2015). A PI value that is greater than 1 but not greater than three suggests that the soil is slightly polluted, a PI value greater than three but not greater than five suggests that the soil is moderately polluted, and a PI value greater than five suggests that the soil is seriously polluted (Wu et al. 2015).

Results and discussion

Physicochemical parameters of agricultural soil

The physicochemical results generated in this study are shown in Table 1. The pH values in the agricultural soil samples from all the sites ranged in a narrow interval from 7.7 to 8.44, with an average of 7.99. The electrical conductivity (EC) found ranged from 1.52 to 4.94 with a mean of 3.2 dS m^{-1}, while the organic matter (OM) oscillated from 2.06 to 3.34 and a mean of 2.8%. As observed in Table 1, the soil samples collected from the northern sites displayed the highest EC value, and the south sites had the lower value. However, the OM value in the soil samples was higher in both the northern and southern areas than places from the center of the Communities of El Bordo and El Lampotal. Analysis of the soil textural the relative percentages of sand, loam, and clay was in the range (37–65%) for sand, (22–38%) for loam, and (13–39%) for clay. According to the USDA, the region samples showed a certain degree of homogeneity with a predominance of clay sandy loam, sandy loam, and clay loam. In general, the pH of the soil analyzed was close to 8.0 at all sites. In this regard, Merry et al. (1986) stated that increasing soil pH decreased Pb concentrations in vegetable crops; since Pb is relatively immobile and As very slowly leaches through soils (Hood 2006). In this context, Alam et al. (2003) suggest that in the relatively neutral soil pH (7.6–8.5) As will be immobile in the local soil profile.

Therefore, the alkaline range of soil (> 8.0) restricts the mobilization of PTEs, thus reducing their uptake and transference from soil to crops (Cheng 2007; Sharma et al. 2007). The EC value indicates soil salinity. Horneck et al. (2011) reported that soil with EC values less than 1 mS cm^{-1} is suitable for crop production. Although values of EC showed a range from 1.52 (normal) to 4.94 (slightly saline); Also, vegetables did not show symptoms by salinity.

As and Pb concentration in agricultural soil

The analysis of PTEs concentration in agricultural soil is shown in Table 1. In this study, As concentrations in the soil from all the sampled sites range from 39.02 to 165 mg kg^{-1}, with an average of 109.22 mg kg^{-1} did exceed the critical level (> 20 mg kg^{-1}) of Mexican standard for agricultural soil and residential (NOM-147-SEMARNAT/SSAI-2004). In addition, the As concentrations are higher and surpass environmental critical limit concentrations of the WHO permissible limit for As in agricultural soils (0.5 mg kg^{-1}) (WHO 2004).

Our results are similar with As concentrations reported in Guadalupe, Zacatecas, with average of 109 mg kg^{-1} (Santos–Santos et al. 2006; Gonzalez et al. 2012) and, old mining region of Guanajuato, Mexico, with range from 21 to 36 mg kg^{-1} (Mendoza-Amezquita et al. 2006). Although, differ from the As concentrations reported in the old mining area in Zimapan, Hidalgo, Mexico (2,550–14,600 mg kg^{-1}) (Ortega-Larrocea et al. 2010).

On the other hand, several sources of toxic elements may increase PTEs in agricultural soils (Gupta et al. 2012; Amin et al. 2013), including mineral fertilizers (Nziguheba and Smolders 2008). The PTEs concentrations confirm that the rock phosphates are the primary source of these elements in mineral fertilizers (Nziguheba and Smolders 2008; Kratz et al. 2011). In this regard, Molina et al. (2009) found that the long-term use of these P-fertilizers in some agricultural systems may increase PTEs concentration in soil. There is little information about the use of fertilizers, dosage, and their impact in the analyzed area. However, approximately 30–35% of vegetable producers apply P-bearing fertilizers, N-bearing fertilizers, S-bearing fertilizers, and micronutrients. The use of fertilizers is not widespread in the region but their long-term use may affect soil and groundwater geochemistry increasing the level of As and other PTEs (Kratz et al. 2016; Papazotos et al. 2019).

Pb concentrations in agricultural soils analyzed in this study were low in most soil samples from four Communities, except at El Bordo and La Era (Table 1). These levels show that pollution by Pb was not very extensive. However, the minimum and maximum Pb concentrations were 25 and 1206 mg kg^{-1}, respectively, and the mean concentration was 355.4 mg kg^{-1}. In this regard, the concentration of Pb in El Bordo (1201.4 mg kg^{-1}), and La Era (1205.8 mg kg^{-1}) was three times higher than the maximum limits of Pb in Mexico (400 mg kg^{-1}) (WHO 1993). Therefore, the soil is unsuitable for agricultural use. In Mexico, previous studies reported different Pb concentrations in diverse crop soils in the Valley of the Mezquital, Mexico (22.86 mg kg^{-1}) (Prieto-Garcia et al. 2007); in agricultural soils near mining regions in Guadalupe, Zacatecas, Mexico (100 and 400 mg kg^{-1}) (Santos–Santos et al. 2006; Gonzalez et al. 2012); Yaqui and Mayo agricultural valleys in Sonora, Mexico (10–56 mg kg^{-1}) (Meza-Montenegro et al. 2012) and rural communities in Fresnillo, Zacatecas, Mexico (4,940 mg kg^{-1}) (Salas and Vega 2016). Our results corroborate other studies on mining activities, which also reported that elevated Pb levels in soil were ubiquitous in the vicinities of mines (Zhuang et al. 2009b; Luo et al. 2011).

In this way, concentrations of As and Pb in the agricultural soil showed heterogeneity, irregular distribution, pollution, not uniform, and a strong influence by historical mining in the selected sites. Furthermore, the layers of soil enriched with different concentrations of metals were subjected to wind and water erosion processes that gave rise to the redistribution of the PTEs in farmland (Renshaw et al. 2006). Resulting in a contaminated zone with variable concentrations of As and a lower risk of Pb. Therefore, these results agree with those reported by Ha et al. (2011), where high PTEs concentrations soil has been continuous dispersal downstream from the tailings mining.

As and Pb concentration in vegetables

The average concentration of total As and Pb (mg kg^{-1} dw) in the selected vegetables is listed in Table 2. The average As concentrations in pepper (95.66 mg kg^{-1} dw) was higher than carrot and garlic (92.33 mg kg^{-1} dw). Whereas the average Pb concentration in pepper was higher (9.6 mg kg^{-1}) than Pb concentrations in carrot and garlic (4.8 mg kg^{-1}). Highest As concentration was measured in *C. annuum* with 111 mg kg^{-1} from site number nine, and the maximum Pb concentration was in *D. carota* 9.9 mg kg^{-1} from site number five.

In general terms, As concentration in vegetables recorded similar concentration from the nine sampled sites belonging the communities El Bordo, El Lampotal, La Era, and Santa Rita (89 ± 9.7, 91 ± 8.7, 90 ± 9.1, 105 ± 12.5 mg kg^{-1} dw, respectively). The As concentration average of vegetables was 93.44 mg kg^{-1} value, which was higher than the maximum limit (ML) established by international standards (1.0 mg kg^{-1}), permitted in many countries, including Mexico (Osuna-Martínez et al. 2021). The highest As concentrations were found in *C. annum* and *A. sativum* (111 ± 11.97 and 100 ± 13.04, respectively, site nine from Community La

Table 2 The average concentration of total arsenic and lead in vegetables, bioaccumulation factor in vegetables and, pollution load index of agricultural soil

Communities: Site	Communities: Vegetable	PTEs (mg/kg^{-1} dw): As	PTEs (mg/kg^{-1} dw): Pb	Bioaccumulation factor (BAF): As	Bioaccumulation factor (BAF): Pb	Pollution index (*Pi*): As	Pollution index (*Pi*): Pb
Santa Rita							
1	Garlic	87 ± 7.38	3.0 ± 0.78	0.64	0.01	6.13	0.44
2	Pepper	91 ± 11.9	< DL	2.33	< DL	1.77	0.22
El Bordo							
3	Carrot	92 ± 8.28	< DL	1.22	< DL	3.40	0.15
4	Carrot	85 ± 7.34	2.1 ± 0.05	0.93	0.02	4.13	0.18
5	Carrot	95 ± 10.42	9.9 ± 1.48	0.67	DNI	6.40	3.00
El Lampotal							
6	Carrot	95 ± 10.91	3.6 ± 1.18	0.68	0.14	6.27	0.06
7	Pepper	85 ± 7.40	9.6 ± 0.25	1.21	0.05	3.18	0.46
La Era							
8	Carrot	100 ± 13.04	5.4 ± 2.14	0.78	0.03	5.77	0.44
9	Pepper	111 ± 11.97	< DL	0.67	DNI	7.5	3.01
*Codex Maximum Levels		1.0	0.1–0.3				

*Codex Maximum Levels (CML) of PTEs in vegetables (FAO/WHO-CODEX, 1995; amended in 2019)

Era). The communities of Santa Rita, El Bordo, and Lampotal registered similar concentrations, with an average of 90 ± 9.09 mg kg^{-1} dw, in all sites.

In this context, all edible parts of species vegetables analyzed in this work showed concentrations of As far exceeded maximum permissible level (MPL) of Latin American countries as Chile with 1 µg g^{-1} of ww (Muñoz et al. 2002), Argentine with 1 mg kg^{-1} (CAA 2020) and, Brazil with 1 mg kg^{-1} (MS 2013). Likewise, the limit for edible plants in Mexico is 1.0 mg kg^{-1} (ww) (Osuna-Martínez et al. 2021). Furthermore, plant As concentration tends to increase with increasing soil As and then stabilize at some maximal value at higher concentrations in soil (Tasrina et al. 2015). In this work, our results differ from those reported by Cao and Ma (2004), who suggested that direct soil contact by root vegetables leads to higher concentrations than leafy vegetables, which must translocate As from roots to shoots. Therefore, As concentrations in garlic and carrot roots tissues and pepper fruits were positively proportional to As levels in the soil.

On the other hand, all edible vegetal parts analyzed in this work showed Pb levels ranging from 2.06 to 9.82 mg kg^{-1}. These levels far exceed Codex Maximum Levels (CML) of 0.1 mg kg^{-1} for root crops and 0.3 mg kg^{-1} for leafy vegetables in fresh weight basis (FAO/WHO-CODEX, 1995; amended in 2019). In *A. sativum*: the found mean concentration for Pb in garlic was 3.0 mg kg^{-1}. The MPL Pb in bulb vegetables is 0.1 mg kg^{-1} (FAO/WHO 2014). Therefore, this value was higher than those found in previous studies (Song et al. 2009). Also, confirm comparable Pb values than those of literature reported in garlic (Guerra et al. 2012; Rehman et al. 2016; Roba et al. 2016). However, the results of this study were lower than those found by Türkdoğan et al. (2003), Maleki and Zarasvand (2008) and Senila (2014). *D. carota*: The mean concentration found of Pb to carrot was 5.0 mg kg^{-1}. The permissible limit of Pb in carrots is 0.1 mg kg^{-1} (EU 2006; FAO/WHO 2014). Therefore, this value exceeded MPL in carrots (Knapp et al. 2013; Islam et al. 2016; Rehman et al. 2016; Shaheen et al. 2016; Zhou et al. 2016). Also, they were comparable with the found by Banerjee et al. (2010) and Pančevski et al. (2014). However, concentration was lower than the studied by Senila (2014). *C. annuum*: The found mean concentration for Pb in pepper fruits was 9.6 mg kg^{-1}. These findings indicate that Pb levels were higher than those reported by other authors as Antonious and Kochhar (2009), Guerra et al. (2012), Islam and Hoque (2014), Mirecki et al. (2015), Islam et al. (2016), and Antoine et al. (2017). However, concentration was comparable with Ahmad and Goni (2010).

These dates were higher than those recommended (standard level of 0.1 mg kg^{-1} in root and tuber vegetables) by the European Union (2006) and the Food and Agricultural Organization (FAO)/World Health Organization (WHO) CODEX (2011). In Mexico, the official standard NOM-117-SSa1-1994 does not mention the permissible Pb limit and takes as a reference 0.1 mg kg^{-1}. In this work, the uptake of As and Pb in plants is regulated by chemical speciation, biogeochemical characteristics, other physic-chemical parameters of the soil, microbial activity by mycorrhization, and plant factors (Davies 1995; Feleafel and Mirdad 2013; Abbas et al. 2018). Therefore, the spatial difference in the pollution

Pb of As and Pb in plants was possibly due to different levels of pollution and the previously mentioned parameters.

Soil-vegetable bioaccumulation factor

According to the bioaccumulation factor (BCF) value of plants, these are characterized as excluders (< 1.0), and hyperaccumulators (> 1.0–10.0), respectively (Ma et al. 2001). The BCF values of As and Pb in vegetables are presented in Table 2. These values varied between vegetable species and sites. For example, the highest BCF value for As has ranged from 0.64 to 2.33, and the average for all samples was 1.01. Likewise, root vegetables show the highest BCF. These results suggest that these species pose a higher health risk due to consumption by human beings for a longer time (Alam et al. 2016). The highest BCFs were recorded in *A. sativum* (2.33), followed by *D. carota* (1.22) and *C. annuum* (1.21). Also, these data implicate that vegetables are hyperaccumulators (> 1.0), and those with values close to 1.0 are accumulators of As. These might be due to higher mobility of the As with a natural occurrence in soil (Alam et al. 2003) and its lower retention in the soil than other toxic cations (Zurera et al. 1987).

While the Pb recorded the lowest BCF values in all vegetables, it showed a relatively low potential for Pb accumulation in agricultural soil. However, reduced uptake of PTEs is one of the plant's adaptation strategies to avoid metal toxicity (Baker and Walker 1990). Therefore, these results agree with Bui et al. (2016), who found that soil pH slightly alkaline was very similar across sites; we rule out pH as a significant driver of BCF differences in this study. In addition, our results reveal that the responses of vegetables to exposure to As and Pb are complex due to the heterogeneous tolerance and relationships between the polluted soil and plants (Kabata-Pendais et al. 1993). Based on these findings, results agree with Chang et al. (2014), who highlight that the BCF values of PTEs in vegetables from soils near to mining are high. Also, it suggested a high potential for PTEs accumulation in agricultural soils, possibly due to historical mining activities in the region.

Pollution index

A pollution index (PI) indicates whether soil quality is suitable for agricultural use and if vegetables analyzed in this work can be consumed safely (Table 2). The calculated PI values for As in soil samples ranged from 1.77 to 7.5. Site number one showed a PI value of 1.77, suggesting that the soil is slightly polluted; In contrast, sites three (3.40), four (4.13), and seven (3.18) had PI values between three and five, indicating that the soil is moderately polluted; finally, site one (6.13), five (6.4), six (6.27), eight (5.77) and nine (7.5) registered values greater than five suggests that the soil is seriously polluted (Wu et al. 2015). Regarding calculated Pi values for Pb in two soil samples from sites five (3.01) and nine (3.0) were higher than three but lower than five confirming that these sample soils are moderately polluted. On the other hand, the Pi for Pb in the rest of the soil samples was lower than one, indicating that Pb did not pollute the vegetables (Wu et al. 2015). However, the Pi values for As were lower than those reported by Khan et al. (2017b). Therefore, soil samples were classified as polluted and indicated that the studied area is highly polluted (Li et al. 2006). It also showed that the pollution index by As is high and persists a greater possibility of causing health and food safety problems (Khan et al. 2017a). According to the high PI for As, agricultural production should be prohibited in this region. Based on these findings, we can assure that soil quality is unsuitable for agricultural use, and vegetables harvested in this area can not be consumed safely (Li et al. 2006). The results of this study support the urgency of establishing standards for As in food to protect public health (Peralta-Videa et al. 2009; Meharg and Raab 2010) and fulfill the commitments on agri-food safety standards with WHO.

Conclusion

This study brings recent evidence on assessing and accumulating As and Pb in vegetables cultivated in soils polluted by historical mining activities. According to the results, the most relevant findings are that agricultural soils are highly polluted with As and remain available under moderately alkaline conditions. These results indicate that agricultural soils exceed ML safety standards for As and Pb. The concentrations of As compared to the ML in soils for agricultural use in other areas close to mining activities were registered. Also, the concentration of As and Pb in vegetable crops exceeds national and international ML standards for health and food safety. Among vegetables, the highest concentration of As and Pb was recorded in fruit vegetables. The As highest concentration was observed in *C. annuum* followed by *D. carota*. Consequently, vegetables containing high PTEs levels should be considered a hazard for human health. Also, if vegetables are grown, recommend those with low BCF values. Likewise, BCF for *A. sativum*, *C. annuum*, and *D. carota* reveals attributes as tolerant and hyperaccumulators of As. Our findings confirm that the agricultural soils analyzed in this work are not appropriate for food production. Also, considering the high PI value for As, the state and national health and agricultural authorities must take preventive measures against the consumption of polluted edible vegetables and avoid negative consequences for public health. Therefore, high pollution index shows the need to perform permanent monitoring and risk assessment because As and Pb are potentially toxic elements and could be bioaccumulated to human beings through the food chain, and avoid potential problems that could be dangerous to the population. It is recommended that community members living around sources of pollution take steps to assurance public health. Also, needs complete mapping of potentially polluted areas and other routes of exposure should be the subject of future studies to assess their specific contribution to the food chain and the agrosystems.

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