Health Risk Assessment of Potentially Toxic Trace and Elements in Vegetables Grown Under the Impact of Kajaran Mining Complex



Davit Pipoyan¹ · Seda Stepanyan¹ · Stella Stepanyan¹ · Meline Beglaryan¹ · Nicolò Merendino²

Received: 22 December 2018 / Accepted: 11 February 2019 / Published online: 20 February 2019 © Springer Science+Business Media, LLC, part of Springer Nature 2019

Abstract

Mining industry is one of the priority sectors of Armenia's economy. However, mining complexes without treatment facilities, such as those in Armenia, have adverse environmental impact. Moreover, soil contamination can pose a potential risk to human health, particularly, through the consumption of food crops. In this study, 12 soil and 32 vegetable composite samples were collected from the city of Kajaran where Armenia's biggest copper and molybdenum mine is located. The concentrations of Cu, Mo, Cd, Hg, As, and Pb were analyzed using atomic absorption spectrophotometer. Diet study was conducted using food frequency questionnaire. Non-carcinogenic and carcinogenic risks to human health through vegetable consumption were assessed. The results indicated that different vegetables have different trace element uptakes. Also, the transfer factors (TFs) for each vegetables, the concentrations of Hg, Cd, and Pb exceeded the maximum allowable levels. THQ of Mo exceeded 1 for all the studied vegetables, while THQ of Cu exceeded 1 for potato and bean, indicating a potential health risk posed by chronic exposure. Exceedingly high levels of Mo exposure can be related to high incidence of anemia among Armenians, since Mo interacts with Cu and is a potential cause of copper deficiency-induced anemia. With regard to cancer risk, none of the carcinogenic risk values exceeded the threshold level.

Keywords Mining · Transfer factor · Trace element · Risk

Introduction

Nicolò Merendino

merendin@unitus.it

Mining and industrial activities such as smelting is one of the common causes of waste accumulation and contaminant

Davit Pipoyan david.pipoyan@cens.am Seda Stepanyan seda.stepanyan@cens.am Stella Stepanyan stella.stepanyan@cens.am Meline Beglaryan

meline.beglaryan@cens.am

Informational Analytical Center for Risk Assessment of Food Chain of the Center for Ecological Noosphere Studies of NAS RA, Abovyan 68, 0025 Yerevan, Armenia

² Department of Ecological and Biological Sciences (DEB), Laboratory of Cellular and Molecular Nutrition, Tuscia University, Largo dell'Università snc, 01100 Viterbo, Italy leaching [1]. These types of activities represent a major health concern over the world since it results to the widespread metal pollution of soils and sediments [2, 3]. While there are two sources of soil contamination with trace elements, natural and anthropogenic, the latter has the most severe impact on the environment and human health [4].

In Armenia, the mineral industry represents a big part of the economy and accounts for approximately 3% of annual GDP. In 2017, it accounted for 30% of exports [5]. The history of mining in Kajaran town goes back to 1935, when the first geological excavations took place in the region. Zangezur Copper-Molybdenum Combine (ZCMC) started its production in 1951 [6]. It is the largest and most stable operating mine in Armenia that possesses the largest molybdenum reserves in the country, concentrated in Kajaran deposit. Moreover, ZCMC is the 100th largest copper mine in the world [7]. It is notable that Armenia is in the 7th place in the world with molybdenum production and in the 31th place with copper production [8]. Besides Mo and Cu, Armenia has rich deposits of Au, Pb, Ag, and Zn, as well as industrial minerals (basalt, diatomite, granite, gypsum, limestone, and perlite) [9].

It is important to state that the contamination of soils with trace elements negatively influences soil characteristics by limiting its productive functions up until desertification and, eventually, can potentially have toxic effects on living organisms [10]. The transfer of heavy metals from soil to vegetables and the consumption of those vegetables is the major exposure route for humans [11].

There are several studies reporting that heavy metals such as Cd and Pb have high transfer capability from soil to edible tissues of vegetables and highly contribute to health risks through vegetable consumption [12–14]. Pb, Cd, Hg, and As are non-essential elements and can cause mutagenic, teratogenic, and carcinogenic effects even at low concentrations [11]. Mo, Cu, and Zn are essential elements at low levels, but the excess of these trace elements can lead to disorders in the biological functioning of the body [15]. Mo has some implications in agriculture, particularly for seed treatment or in fertilizer formulations [16]. However, at certain levels, molybdenum can have toxic effects on health.

In order to ensure that potentially toxic trace elements do not pose a risk to human health, institutions, such as World Health Organization (WHO) and European Food Safety Authority (EFSA) have developed risk analysis as a tool for strengthening food safety systems and reducing diseases linked to food consumption [17, 18]. To evaluate human health risk, exposure needs to be assessed and compared with health-based guidance values (HBGV).

There are several, however insufficient, studies reporting about the serious contamination of agricultural soil with heavy metals in inhabited areas of Kajaran, Alaverdi, Akhtala, and Agarak towns. Common contamination sources include dust and waste coming from mining activities [7].

In Armenia, fruits and vegetables are an essential part of human diet and a significant source of human exposure to trace elements [19]. Vegetables are the most exposed food to environmental pollution [20]. The transfer of trace elements from soil to vegetables is a major pathway to human exposure and should be evaluated [19].

The aim of this study was to assess the dietary exposure to potentially toxic trace elements, particularly Cu, Mo, Hg, Cd, As, and Pb through the intake of selected vegetables grown under the impact of Kajaran's mining complex. For this, dietary surveys were carried out and the contents of trace elements in vegetables were determined. Moreover, the estimated daily intake (EDI), transfer factor (TF), target hazard quotient (THQ), and cancer risks (CRs) for the local population were calculated.

Materials and Methods

Study Site Choice

The study was carried out in the mining complex of Zangezur Copper-Molybdenum Combine located in the Vokhchi valley, Kajaran town (N 39° 09' 04", E 46° 09' 36"). ZCMC's mine produces approximately 18.5 million tons of ore per year, which is more than 60% of the turnover of Armenia's whole mining sector. There are 21 tailing dams in Armenia, 13 of which are active. ZCMC's Artsvanik dam is the largest one among the active dams, with a current volume that makes up 75% of the total volume of all tailings in the country [7].

The geological composition of Kajaran includes tertiary volcanogenic, intrusive rocks such as porphyrites, porphire granites, and monzonites. Approximately 80% of the territory is covered by soil and diluvium layers of 1–5 m. Brown soil is available up to 1800 m a.s.l., while chestnut soil at 1800–2400 m a.s.l. Soils of the north facing slopes are covered by mountain-forest gray skeletal soil. South facing slopes are covered by mountain-xerophile vegetation [21].

Sample Collection and Treatment

The sampling of topsoil (with a depth of 0–15 cm) was done in accordance with Standard Operating Procedures (SOPs) based on ISO 1038-1 and United States Environmental Protection Agency (US EPA) standards [10]. The SOPs were developed at the Center for Ecological Noosphere Studies of the Republic of Armenia.

Vegetable sampling was done taking into account the seasonal availability as well as the high consumption rate of the investigated food types. All the vegetable samples (potato, carrot, bean, fennel, and pumpkin) were taken from the exact same soil sampling points, according to WHO and FAO requirements [22]. In total, 12 samples of soil (Fig. 1) and 32 composite samples (3 subsamples for each vegetable) of available cultivated vegetables (potato, carrot, bean, fennel, and pumpkin) were collected and taken to laboratory with special clean bags. Both soil and vegetable sampling was carried out in September 2015.

Analysis of Trace Elements and QA/QC

The total concentrations of trace elements (Cu, Mo, Hg, Cd, As, Pb) in soils were determined using X-ray fluorescence spectrometry (EDXRF X-5000) (Innov-X Systems, 2003, USA). For quantifying trace element concentrations in vegetables, Perkin Elmer Analyst 800 AAS was used [23]. For all trace elements, the standard stock solution of 1000 ppm was used. The latter was obtained from the authorized distributor of PerkinElmer, SchelTec AG [23]. The analysis was conducted at the Central Analytical Laboratory of Center for Ecological Noosphere Studies, which is accredited by ISO-IEC 17025 [10].

In order to obtain reliable results, appropriate quality assurance and quality control (QA/QC) procedures were carried out for soil and vegetable analyses. The required standard reference materials (NIST 2711a, NIST 2710a, SRM 1570a, SRM 1573a) were purchased from the National Institute of Standards and Technology (NIST), USA. To get precise and accurate analyses, samples were repeatedly analyzed [10].



Data Collection and Analysis

To get vegetable consumption data, food frequency questionnaire (FFQ) was developed and used for conducting surveys [22]. FFQ is used commonly as a part of large dietary assessment study to obtain data on consumption frequency, portion size, etc. [24]. Two hundred people (18–65 years old) residing in Kajaran town took part in the survey. The FFQ was paper based and interviewer administered. The intervieweradministered food frequency questionnaire method was without any possibility of identification (incognito interview) and thus, a statement on ethical approval was not necessary.

The average daily consumption of vegetables was calculated by multiplying daily consumption frequency (portions/day) with portion size and quantity.

Transfer Factor (TF)

Transfer factor is the major pathway for human exposure to trace elements and is used to measure the transfer of trace elements from soil to plants [25]. The calculation was made by dividing the content of trace element in studied vegetables by the average content of trace element in soil samples.

$$TF = C_{\text{vegetable}}/C_{\text{soil}} \tag{1}$$

where $C_{\text{vegetable}}$ indicates the concentration of trace elements in vegetables, while C_{soil} represents the concentration of metals in soil [26].

Estimated Daily Intake (EDI)

To get the estimated daily intake values for all trace elements, the following equation was used. The latter is recommended by the US EPA [27].

$$EDI = (C \times IR \times EF \times ED)/(BW \times AT)$$
(2)

where C is the trace element content in vegetable samples; EF is the exposure frequency taken as 183 days per year; ED is

the exposure duration (63.6 year for males and 69.7 year for females, based on the average life expectancy, starting from 8 years of age); BW is the body weight (kg) for males and females (70 kg and 60 kg, respectively); AT is the time period over which the dose is averaged (25,550 days (70 years)). According to the FFQ-based dietary surveys conducted in Kajaran town, the ingestion rates (IR) for potato, carrot, bean, fennel, and pumpkin were 0.21, 0.09, 0.11, 0.01, and 0.03 kg per day, respectfully. To get the cumulative daily intakes, individual EDI values for each trace element were summed up.

Non-carcinogenic and Carcinogenic Risk Assessment

Target Hazard Quotient was used for determining noncarcinogenic risk level resulting from trace element exposure. Human health risk exposure was assessed using the following formula suggested by US EPA, 1997. THQ was calculated as the ratio of the EDI to the oral reference dose (RfD).

$$THQ = EDI/RfD$$
(3)

For the RfD of Cu, dietary reference intake of 0.01 mg/kg/ bw/day was used [28]. For Mo, the RfD was taken as 0.005 mg/kg/bw/day [29]. For As and Cd, the RfDs were considered to be 0.0003 and 0.001 mg/kg/bw/day, respectively [29, 30]. The RfD for Pb was considered to be 0.0035 mg/kg/bw/day, taking into consideration provisional tolerable weekly intake (PTWI) [31]. For the RfD of Hg, the tolerable weekly intake of 0.004 mg/kg/bw/day was used [32]. When the value of THQ is less than or equal to 1, the probability of non-carcinogenic adverse effects is low and the hazard is regarded as negligible. When the value of THQ exceeds 1, adverse health effects are possible due to overexposure.

To evaluate the risk to human health from exposure to multiple trace elements in contaminated sites, hazard index (HI) was used. The latter is equal to the total sum of THQs across contaminants [33]. It also refers to the sum of more than one THQs for multiple substances and/or multiple exposure pathways [34].

Carcinogenic risk indicates the probability of a person to develop cancer over a lifetime of exposure to the contaminant. CR is calculated using contaminant intakes and toxicity values (slope factors) [35]. In this study, the carcinogenic risk was calculated with the following formula [36].

$$CR = SF \times EDI$$
 (3)

where SF is the slope factor. SFs for Cd, As, and Pb were 0.38, 1.5, and 0.0085 $(mg/kg/day)^{-1}$ respectively [36, 37]. According to the US EPA, the acceptable limit of carcinogenic risk is less than 1×10^{-6} [35].

Statistical Analysis

The data analysis period ranged from August to December 2016. The statistical tests were conducted using SPSS software (version 22.0).

Results and Discussion

Levels of Trace Elements in Soils

Table 1 summarizes the contents of trace elements in agricultural soils collected from 12 different points of study area. The average contents were found to be in the order of Cu > Mo >As > Hg > Cd. The values reported for Cu and Mo were higher than the maximum allowable concentrations (MACs), while the values reported for other elements were within their respective allowable concentrations [10, 38].

Levels of Trace Elements in Vegetables

Table 2 summarizes the contents of six trace elements (Cu, Mo, Hg, Cd, As, and Pb) in studied vegetables.

Among all the studied vegetables, Cu contents were the highest in fennel (27.63 mg/kg) and the lowest in carrot (5.78 mg/kg). The presence of Kajaran's copper-molybdenum

mine can provide an explanation for high contents of Cu in local food. Although Cu is an essential element for human body, its high contents can seriously damage human health [39]. Hence, Cu contents in local food shall be monitored and kept under state control for ensuring consumer health protection.

The levels of Mo were significantly high, ranging from 6.93–47.93 mg/kg. The highest Mo content was observed for bean (47.93 mg/kg), while the lowest for carrot (6.93 mg/kg). A significant share of world's Mo deposits is concentrated in just one small region of Armenia, Syunik. The operation of Kajaran's mine in this region results in migration of Mo from agricultural soils to vegetables which are widely consumed by local people and, consequently, can be a significant source of Mo exposure.

The levels of Hg were relatively low, ranging from 0 to 0.1 mg/kg. Only the value detected in fennel (1 mg/kg) was equal to the maximum acceptable limit of 1 mg/kg proposed by FAO/WHO [40] thus, raising some concerns.

The levels of Cd were the lowest among the studied trace elements, ranging from 0 to 0.01 mg/kg. However, when comparing with the maximum acceptable level set by EU Commission Regulation [41], it can be observed that Cd contents in fennel (0.01 mg/kg) exceeded the acceptable level (0.001 mg/kg).

The levels of Pb ranged from 0.54–1.18 mg/kg. In all the mentioned food items, the contents of Pb were above the maximum acceptable level (0.1 mg/kg for vegetables, 0.3 mg/kg for leafy vegetables) set by EU Commission Regulation [41].

The contents of As ranged from 0 to 0.1 mg/kg. Even though As levels in food were not that high, they shall be monitored and kept under state control, since International Agency for Research into Cancer (IARC) classified inorganic arsenic as a human carcinogen and Armenian population is vulnerable in terms of high cancer incidence. In fact, according to WHO, Armenia ranks the second in the world with "all cancers" incidence relative to its population size [42].

Overall, among the studied trace elements, the contents of Hg, Cd, and Pb exceeded the recommended safety level, while

 Table 1
 The contents of trace elements in soil samples from investigated areas (mg/kg fresh matter)

Trace elements	MAC (mg/kg)	Soil	Soil samples											Average (mg/kg)	SD
		K1	K2	K3	K4	K5	K6	K7	K8	K9	K10	K11	K12		
Cu	132	540	580	480	440	340	420	380	320	280	330	220	260	382.5	112.2
Мо	132	140	220	240	260	180	130	220	240	140	300	180	320	214.2	62.2
Hg	2.1	n/d	n/d	n/d	0.045	0.078	0.141	n/d	n/d	n/d	n/d	n/d	n/d	0.088	0.049
Cd	2	n/d	n/d	n/d	0.17	0.21	0.16	n/d	n/d	n/d	n/d	n/d	n/d	0.045	0.082
As	2	n/d	n/d	4.406	n/d	7.317	4.316	n/d	n/d	n/d	n/d	n/d	n/d	1.34	2.53
Pb	65	8.1	9.6	10.2	12.4	13.4	15	17.8	18	24.2	18.4	12.2	28.8	15.68	5.88

n/d not detected

Table 2 The contents of trace elements in vegetables from investigated areas, (mg/kg)

	Contents	Contents (mg/kg, fresh matter) Trace element													
	Trace ele														
	Cu		Мо		Нg		Cd		As		Pb				
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD			
Potato	12.01	3.28	26.59	9.13	0.02	0.003	n/d	_	0.03	0.01	0.54	0.13			
Carrot	5.78	1.76	6.93	1.78	0.01	0.005	n/d	-	n/d	_	0.69	0.05			
Bean	12.00	2.79	47.93	8.77	n/d	_	n/d	-	n/d	_	0.91	0.09			
Fennel	27.63	7.02	46.42	17.56	0.10	0.016	0.01	0.002	0.10	0.01	1.06	0.16			
Pumpkin	13.17	2.33	28.87	10.64	n/d	—	n/d	-	n/d	_	1.18	0.36			

Data are means of n = 3 replicates. SD, standard deviation; n/d, not detected

the contents of other trace elements (Cu, Mo, and As) did not have maximum tolerable limits established by EFSA or WHO.

Soil-to-Plant Transfer of Trace Elements

Soil-to-plant TFs of trace elements are presented in Table 3. For all the studied vegetables, they were less than 1, except for Hg in potato and fennel. This indicates poor response of plants towards element uptake for the majority of trace elements.

As it can be observed from the table, TFs vary from element to element depending on the type of vegetable. In general, the highest TFs were reported for root vegetables.

A similar study from China also observed TF variations within the vegetable types [43]. The highest TF value of trace elements was found in leaf vegetables and the lowest one in fruit vegetables.

Estimated Daily Intake of Trace Elements

Estimated daily intake was calculated by combining the data on trace element contents with the data on vegetable

Tak	ole	3 5	Soil-to	o-plant	transfer	factor
-----	-----	-----	---------	---------	----------	--------

consumption. Overall, only the EDI values of Mo and Cu exceeded the reference doses (Table 4).

EDI of Mo exceeded the reference value (5.00E–03 mg/kg/ bw/day) for all the investigated vegetables [29] while EDI of Cu exceeded the reference value (1.00E–02 mg/kg/bw/day) only for potato and bean. EDIs of Hg, Pb, Cd, and As did not exceed the tolerable weekly intake of 1.00E–04 mg/kg/bw/day and provisional tolerable weekly intake of 3.50E–03 mg/kg/ bw/day, oral reference doses of 1.00E–03 mg/kg/bw/day, and 3.00E–04 mg/kg/bw/day, respectively [31, 32, 44, 37].

When considering the combined consumption of investigated vegetables, the estimated cumulative daily intakes of four vegetables exceeded the reference values for Cu, Mo, and Pb.

Non-carcinogenic Risk Assessment

To estimate the potential of studied vegetables to pose noncarcinogenic health risks, target hazard quotient was calculated and presented in Table 5.

THQ values were the highest for potato and bean, in certain cases exceeding the concern level by more than fifteen times. It is particularly interesting that THQs of Mo were the highest

Plant species	Transfer factor												
	Cu		Мо		Hg	Hg		Cd			Pb		
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	
Potato	0.031	0.0027	0.107	0.0235	1.038	0.011	0.052	0.008	0.005	0	0.036	0.0056	
Carrot	0.016	0.0015	0.035	0.0089	0.578	0.023	0.076	0.019	-	-	0.058	0.0173	
Bean	0.031	0.0028	0.182	0.0134	-	-	-	-	-	-	0.055	0.0215	
Fennel	0.072	0.0045	0.252	0.1073	1.8	0.44	0.144	0.0533	0.023	0.008	0.069	0.0267	
Pumpkin	0.037	0.0032	0.104	0.0231	-	-	-	-	-	-	0.065	0.0083	

SD, standard deviation; "-", TFs for elements not detected in samples were not calculated

Table 4	Estimated daily	v intake of trace el	lements in vegeta	bles for male	es and fema	les, (mg/k	cg/bw/c	lay)
---------	-----------------	----------------------	-------------------	---------------	-------------	------------	---------	------

Plant species	Estimated daily intake of trace elements, mg/kg/bw/day											
	Cu		Мо		Hg		Cd		As		Pb	
	М	F	М	F	М	F	М	F	М	F	М	F
Potato	0.0360	0.0420	0.0798	0.0931	0.0001	0.0001	0	0	0.0001	0.0001	0.0016	0.0019
Carrot	0.0074	0.0087	0.0089	0.0104	0	0	0	0	0	0	0.0009	0.0010
Bean	0.0189	0.0220	0.0753	0.0879	0	0	0	0	0	0	0.0014	0.0017
Fennel	0.0039	0.0046	0.0066	0.0077	0	0	0	0	0	0	0.0002	0.0002
Pumpkin	0.0056	0.0066	0.0124	0.0144	0	0	0	0	0	0	0.0005	0.0006
Cumulative EDI	0.0719	0.0839	0.1830	0.2135	0.0001	0.0001	0	0	0.0001	0.0001	0.0046	0.0054

Estimated and cumulative daily intake values above reference values are in italics. M, males; F, females.

among all trace elements and exceeded the concern level (THQ > 1) for all the investigated vegetables. In contrast, THQs of Hg, Cd, As, and Pb were below 1 for all vegetables. Meanwhile, Cu levels exceeded concern level only for potato and bean.

The exceedingly high Mo values indicate that, from the point of view of human health, the consumption of carrot, fennel, pumpkin, and especially potato and bean has a potential to pose adverse effects to local population. People in Armenia, women in particular, are highly vulnerable towards anemia. According to the Food and Nutrition Board of Institute of Medicine, high Mo intake may result in anemia and low white blood cell counts due to lack of Cu [45]. When there is a high Mo intake, the interaction of Mo with Cu can lead to copper deficiency, while copper deficiency is a well described cause of anemia [46, 47]. Thirteen percent of women in Armenia suffer from anemia and this might possibly be linked to the excessive amounts of Mo in local food. Out of 13%, the majority, 12%, are classified as mildly anemic, 1% as moderately anemic, and 0.2% as severely anemic [48]. Hence, it is recommended for the population of Syunik, particularly

for women, to reduce the consumption of potato and bean grown under the impact of Kajaran mining industry and substitute it with potato and bean brought from other places. A similar study regarding the exposure assessment of trace elements in vegetables was recently conducted in another town of Armenia, Kapan [49]. The results indicated that THQ for Cu, Hg, Cd, As, and Pb in bean, potato, and carrot were below 1. Thus, the results of the present study report higher levels of Cu in vegetables from Kajaran relative to those from Kapan. The levels of Mo, however, were not studied in Kapan, thus, no comparisons can be made.

In comparison with studies beyond Armenia, Hu [43] (2014) carried out risk assessment of trace elements in food and found out that Cd was the major element contributing to the potential health risk in Nanjing City of China, followed by As and Pb. The THQ values of Cd reported in China were considerably higher than those in this study, however, the values of Pb and As were higher in the present study. A research from Pakistan also reported high health risk index (HRI \geq 1) for Cd, indicating that vegetable consumption can pose a potential health risk to consumers [50].

Plant species	Male/Female	THQ fo	THQ for trace elements							
		Cu	Cu Mo		Cd	As	Pb			
Potato	М	3.6	15.95	0.02	0.01	0.27	0.47	20.32		
	F	4.2	18.61	0.02	0.01	0.32	0.54	23.7		
Carrot	М	0.74	1.78	0	0.01	0	0.25	2.78		
	F	0.87	2.08	0	0.01	0.01	0.3	3.27		
Bean	М	1.89	15.06	0	0	0	0.41	17.36		
	F	2.2	17.57	0	0	0	0.48	20.25		
Fennel	М	0.39	1.33	0	0	0.05	0.04	1.81		
	F	0.46	1.55	0	0	0.05	0.05	2.11		
Pumpkin	М	0.56	2.47	0	0	0	0.14	3.17		
-	F	0.66	2.89	0	0	0	0.17	3.72		

THQ and HI values above 1 are in italics

 Table 5
 Target hazard quotients

 of trace elements
 Image: Target hazard quotients

 Table 6
 Carcinogenic risk of trace elements for males and females

Plant species	Cancer risk f	Cancer risk for trace elements											
	Cd		As		Рb								
	Male	Female	Male	Female	Male	Female							
Potato	2.08E-06	2.66E-06	5.53E-05	7.08E-05	6.31E-06	8.07E-06							
Carrot	8.90E-07	1.14E-06	8.79E-07	1.12E-06	3.44E-06	4.39E-06							
Bean	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.56E-06	7.11E-06							
Fennel	2.47E-07	3.16E-07	9.47E-06	1.21E-05	5.85E-07	7.48E-07							
Pumpkin	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.96E-06	2.50E-06							

THQ values of individual trace elements are summed and presented as hazard index, showing the combined noncarcinogenic effects of multiple elements. As it can be observed from Table 5, all HI values exceeded 1, in certain cases more than 20 times, indicating that all vegetables entail potential health risks posed by chronic exposure.

Carcinogenic Risk Assessment

For estimating the potential carcinogenic risks of studied vegetables, trace element intakes and toxicity values were used [51]. As Table 6 indicates, none of the CR values exceeded the moderate risk level (CR > 10^{-3}) or the threshold level (CR > 10^{-4}) suggested by US EPA. Moreover, the CR values for Cd and As in most of the studied vegetables were under the safe limit (CR < 10^{-6}). It is interesting that the CR values for females are, in general, higher than those for males.

In comparison with the results of similar studies, the carcinogenic risks for Cd and As in bean, potato, and carrot were much lower in this study than in the study from Kapan. The values reported in Kapan exceeded US EPA limit of $CR < 10^{-6}$ for both males and females [49], while the values in this study were below the US EPA limit. This indicates that even though both Kajaran and Kapan are located near Syunik's mining complex, the population of Kajaran is safer in terms of carcinogenic risks than the population of Kapan. In comparison with a study from Pakistan, the CR values reported in this study were lower.

Conclusion

Vegetables are an essential part of human diet, thus, estimating the risks associated with vegetable consumption in mining regions, such as Kajaran, is of particular importance. The investigation of soil-to-plant transfer of Cu, Mo, Hg, Cd, As, and Pb in Kajaran indicated poor response of studied vegetables towards these element uptakes. The contents of Hg, Cd, and Pb in studied vegetables exceeded the safety level, while the contents of other trace elements either did not exceed the maximum allowable levels, or did not have established limits. The health risk assessment of trace elements indicated that local population is exposed to significant non-carcinogenic risks. The hazard index values exceeded 1 for all the studied vegetables. Nevertheless, the carcinogenic risk values were below the US EPA safe limit, indicating that the exposed population is safe in terms of carcinogenic risks.

Overall, this study provides useful information on health risk assessment of potentially toxic trace elements among people in Kajaran's mining region and discusses possible links between high Mo exposure and anemia incidence. Also this research can serve as a basis for future biomarker research in the region that will study the amount of Mo in local people's blood and the incidence of anemia. It is also important to include iron among studied trace elements as its deficiency can lead to anemia as well.

Acknowledgments This study was made with the support of State Committee of Science, Ministry of Education and Science of Armenia.

Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

References

- González-Fernández B, Rodríguez-Valdés E, Boente C, Menéndez-Casares E, Fernández-Braña A, Gallego JR (2018) Long-term ongoing impact of arsenic contamination on the environmental compartments of a former mining-metallurgy area. Sci of the Total Environ 610:820–830
- Lynch SF, Batty LC, Byrne P (2018) Environmental risk of severely Pb-contaminated riverbank sediment as a consequence of hydrometeorological perturbation. Sci Total Environ 636:1428–1441
- Frau I, Korostynska O, Mason A, Byrne P (2018) Comparison of electromagnetic wave sensors with optical and low-frequency spectroscopy methods for real-time monitoring of lead concentrations in mine water. Mine Water and the Environ 37(3):617–624
- Álvarez-Ayuso E, Abad-Valle P (2017) Trace element levels in an area impacted by old mining operations and their relationship with beehive products. Sci of the Total Environ 599:671–678

6. Levine RM, Wallace GJ (2006) The mineral industries of the commonwealth of independent states. Minerals Yearbook 3

5.

- World Bank (2016) Armenia. Strategic Mineral Sector Sustainability Assessment. World Bank, Washington, DC https:// openknowledge.worldbank.org/handle/10986/24756
- IndexMundi (2012) Minerals. Production by Country (Metric tons) https://www.indexmundi.com/minerals/?product=copper&graph= production
- Safirova E (2014) The Mineral Industry of Armenia in 2014. USGS (United States of Geological Survey) https://minerals.usgs.gov/ minerals/pubs/country/2014/myb3-2014-am.pdf
- Tepanosyan G, Sahakyan L, Belyaeva O, Asmaryan S, Saghatelyan A (2018) Continuous impact of mining activities on soil heavy metals levels and human health. Sci Total Environ 639:900–909
- Bi C, Zhou Y, Chen Z, Jia J, Bao X (2018) Heavy metals and lead isotopes in soils, road dust and leafy vegetables and health risks via vegetable consumption in the industrial areas of Shanghai, China. Sci Total Environ 619:1349–1357
- Luo C, Liu C, Wang Y, Liu X, Li F, Zhang G, Li X (2011) Heavy metal contamination in soils and vegetables near an e-waste processing site, south China. J Hazard Mater 186(1):481–490
- Pan XD, Wu PG, Jiang XG (2016) Levels and potential health risk of heavy metals in marketed vegetables in Zhejiang, China. Sci Rep 6:20317
- Nabulo G, Young SD, Black CR (2010) Assessing risk to human health from tropical leafy vegetables grown on contaminated urban soils. Sci Total Environ 408(22):5338–5351
- 15. Gowrishankar R, Kumar M, Menon V, Divi SM, Saravanan M, Magudapathy P, Panigrahi BK, Nair KG, Venkataramaniah K (2009) Trace element studies on Tinospora cordifolia (Menispermaceae), Ocimum sanctum (Lamiaceae), Moringa oleifera (Moringaceae), and Phyllanthus niruri (Euphorbiaceae) using PIXE. Biol Trace Elem Res 133(3):357–363
- WHO (2003) Molybdenum in drinking-water: background document for development of WHO guidelines for drinking-water quality. Switzerland, Geneva
- EC (European Commission) (2002) Regulation (EC) N 178/2002 of 28 January 2002 laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matters of food safety. Off J Eur Comm L 31:1–23
- FAO/WHO (2009) Principles and methods for the risk assessment of chemicals in Food. Environ Health Criteria 240. In: IPCS (International Program on Chemical Safety). Dietary exposure assessment of chemicals in food. WHO Press, pp 6.1–60
- Pipoyan D, Beglaryan M, Sireyan L, Merendino N (2018a) Exposure assessment of potentially toxic trace elements via consumption of fruits and vegetables grown under the impact of Alaverdi's mining complex. Hum Ecol Risk Assess: An Int J:1–16
- Jolly YN, Islam A, Akbar S (2013) Transfer of metals from soil to vegetables and possible health risk assessment. SpringerPlus 2(1): 385–388
- Saghatelyan KA, Arevshatyan GS, Sahakyan VL (2007) The impact of mining production upon the ecosystem and the health of population. In Present Min Environ IV Conf
- WHO/FAO (2008) Dietary exposure assessment of chemicals in food. In: Annapolis. Maryland, USA http://apps.who.int/iris/ bitstream/10665/44027/1/9789241597470 eng.pdf
- Pipoyan D, Beglaryan M, Costantini L, Molinari R, Merendino N (2018b) Risk assessment of population exposure to toxic trace elements via consumption of vegetables and fruits grown in some mining areas of Armenia. Hum Ecol Risk Assess: An Int J 24(2): 317–330

- Zalaket J, Wakim LH, Matta J (2017) Development and validation of a semi-quantitative food frequency questionnaire for the assessment of antioxidant vitamins intake in Lebanon. Primary Care Diabetes 11:e3
- Ilic Z, Filipovic-Trajkovic R, Jablanovic M (2001) Transfer factor (coefficient) soil/plant as indicator concentration of heavy metals content in different vegetable species. Contemp Agric
- Adamo P, Iavazzo P, Albanese S, Agrelli D, De Vivo B, Lima A (2014) Bioavailability and soil-to-plant transfer factors as indicators of potentially toxic element contamination in agricultural soils. Sci of the Total Environ 500:11–22
- US EPA (1997) Exposure factors handbook. EPA/600/P-95/002F. Office of Research and Development, Washington
- ATSDR (Agency for Toxic Substances and Diseases Registry) (2004) Toxicological profile for copper https://www.atsdr.cdc.gov/ toxprofiles/tp.asp?id=206&tid=37
- US EPA (1992). Molybdenum; CASRN 7439-98-7, Washington, DC, USA https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm? substance_nmbr=425
- US EPA (2005) Zinc and compounds; CASRN 7440-66-6. Washington DC, USA https://cfpub.epa.gov/ncea/iris/iris_ documents/documents/subst/0426 summary.pdf
- EFSA Panel on Contaminants in the Food Chain (CONTAM) (2010) Scientific opinion on lead in food. EFSA J 8(4):1570 http://www.efsa.europa.eu/en/efsajournal/pub/1570
- EFSA Panel on Contaminants in the Food Chain (CONTAM) (2012) Scientific opinion on the risk for public health related to the presence of mercury and methylmercury in food. EFSA J 10(12):2985 https://www.efsa.europa.eu/en/efsajournal/pub/2985
- EC (European Commission) (2017) New hazard index tool to aid risk assessment of exposure to multiple chemicals. http://ec.europa. eu/environment/integration/research/newsalert/pdf/New_hazard_ index_tool_to_aid_risk_assessment_of_exposure_to_multiple_ chemicals_498na5_en.pdf
- Zhuang P, Lu H, Li Z, Zou B, McBride MB (2014) Multiple exposure and effects assessment of heavy metals in the population near mining area in South China. PLoS One 9(4):e94484
- US EPA (1999) Screening level ecological risk assessment protocol for hazardous waste combustion facilities, appendix E: toxicity reference values. United States Environmental Protection Agency
- Real H, Azam M, Majed N (2017) Consumption of heavy metal contaminated foods and associated risks in Bangladesh. Environ Monit Assess 189(12):651
- US EPA (1991) Arsenic, inorganic; CASRN 7440-38-2. USA, Washington DC https://cfpub.epa.gov/ncea/iris2/ chemicalLanding.cfm?substance_nmbr=278
- CENS/OSCE (Center for Ecological-Noosphere Studies of NAS RA, The Organization for Security and Co-operation in Europe Office in Yerevan) (2011) Risk Assessment of Heavy Metals Contamination in Agricultural Products in Armenia. Report. (in Armenian), Yerevan http://aarhus.am/publications/report_ Alaverdi_2010_Arm1.pdf
- Chi QQ, Zhu GW, Langdon A (2007) Bioaccumulation of heavy metals in fishes from Taihu Lake, China. J Environ Sci 19(12): 1500–1504
- Joint FAO/WHO expert committee on food additives (JECFA) (2002) Limit test for heavy metals in food additive specifications: Explanatory note http://www.fao.org/fileadmin/templates/agns/pdf/ jecfa/2002-09-10 Explanatory note Heavy Metals.pdf
- EC (European Commission) (2006) Regulation (EC) No. 1881/ 2006 of 19 December 2006 Setting maximum levels for certain contaminants in foodstuffs. Off J of the Eur Union 5:24. http:// eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX% 3A32006R1881
- World Life expectancy. WHO, World Bank, UNESCO, CIA. 2014. http://www.worldlifeexpectancy.com/ Accessed 14 December 2018

- 43. Hu W, Chen Y, Huang B, Niedermann S (2014) Health risk assessment of heavy metals in soils and vegetables from a typical greenhouse vegetable production system in China. Hum and Ecol Risk Assess: An International Journal 20(5):1264–1280
- US EPA (1989) Cadmium; CASRN 7440-43-9. Washington, DC, USA https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm? substance_nmbrD141
- Bati K, Masamba WR, Mogobe O (2017) Concentrations of some trace elements in vegetables sold at Maun market, Botswana. J Food Res 6:73–74
- EFSA Panel on Dietetic Products, Nutrition, and Allergies (NDA) (2013) Scientific opinion on dietary reference values for molybdenum. EFSA J 11(8):10 https://www.efsa.europa.eu/sites/default/ files/consultation/nda130426.pdf
- Hayton BA, Broome HE, Lilenbaum RC (1995) Copper deficiency-induced anemia and neutropenia secondary to intestinal malabsorption. Am J Hematol 48(1):45–47
- 48. Armstat (2016) Demographic and Health Survey 2015–2016 https://www.armstat.am/file/article/dhs_kir_2015-16-english.pdf
- 49. Pipoyan D, Beglaryan M, Stepanyan S, Merendino N (2018c) Dietary exposure assessment of potentially toxic trace elements in fruits and vegetables sold in town of Kapan, Armenia. Biol Trace Elem Res:1–8. https://doi.org/10.1007/s12011-018-1522-8
- Khan K, Lu Y, Khan H, Ishtiaq M, Khan S, Waqas M, Wei L, Wang T (2013) Heavy metals in agricultural soils and crops and their health risks in Swat District, northern Pakistan. Food Chem Toxicol 58:449–458
- US EPA (1999) Guidance for performing aggregate exposure and risk assessments. Office of Pesticide Programs. In: Environmental Protection Agency (EPA). DC, Washington