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Risk assessment of population exposure to toxic trace elements via consumption of vegetables and fruits grown in some mining areas of Armenia

Davit Pipoyan[a], Meline Beglaryan[a], Lara Costantini[b], Romina Molinari[b], and Nicolò Merendino[b]

[a]Informational Analytical Center for Risk Assessment of Food Chain of the Center for Ecological Noosphere Studies of NAS RA, Yerevan, Armenia; [b]Department of Ecological and Biological Sciences (DEB), Tuscia University, Largo dell'Università snc, Viterbo, Italy

ABSTRACT
Consumption of unsafe food is one of the most important public health concerns. Trace elements' contamination caused by direct or indirect activities of mining industries is of importance in this respect. The present study was conducted to assess the chronic dietary exposure and related health risks of trace elements through the intake of selected vegetables and fruits grown under the impact of mining industry in Syunik region (Armenia). Consumption data were obtained via food frequency questionnaire and the concentrations of Cu, Mo, Ni, Cr, Pb, Zn, Hg, and Cd in different fruits and vegetables were determined. Moreover, by combining concentration data with consumption data, estimated daily intake, and target hazard quotient were assessed for each element. The results obtained showed that mean concentrations for Pb and Hg in some vegetables exceeded maximum acceptable levels set by international organizations. Hazard indexes $>$ 1 have been obtained in some cases indicating that for some vegetables (particularly for potato, carrot, maize, onion leaf, grape, bean, beet, sweet pepper, eggplant, and tomato) habitual consumption has a potential to pose adverse health effect to the local population.

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Introduction

The general population is exposed to a large number of contaminants, such as toxic trace elements, through food consumption, water and other environmental matrices. Diet is the main route of exposure to trace elements taken up in different amounts (D'Amato et al. 2013; Yusà et al. 2008). Based on their nutritional significance in humans, trace elements are divided into three groups (1) essential elements; (2) elements, which are probably essential; and (3) potentially toxic elements (WHO 1996). Trace elements such as copper (Cu), zinc (Zn), and molybdenum (Mo) are known for their essentiality as micronutrients useful for normal physiological functions (FNB/IOM 2006), but metabolic disorders are encountered in case

CONTACT Nicolò Merendino merendin@unitus.it Department of Ecological and Biological Sciences (DEB), Laboratory of Cellular and Molecular Nutrition, Tuscia University, Largo dell'Università snc, 01100 Viterbo, Italy.
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of excess of these essential elements (Khan et al. 2014). In contrast, dietary exposure of trace elements such as lead (Pb), cadmium (Cd), arsenic (inorganic As), mercury (Hg), chromium (Cr III), and nickel (Ni) has been associated with toxic and adverse effects to human health (JECFA 2012; Marín et al. 2016). Even though trace elements are ubiquitous and, thus, naturally present in a diet, higher levels may occur as a result of environmental pollution from anthropogenic activities (D'Amato et al. 2013), such as mining and smelting operations, industrial productions and industrial, domestic, and agricultural uses of metals and metal-containing compounds.

Previous reports highlighted that excessive accumulation of metals in agricultural soils around mining areas, resulting in elevated metal uptake by food crops, is of great concern because of potential health risk to the local inhabitants (Zhuang et al. 2014; Zhou et al. 2016; Antoniadis et al. 2017; Ding et al. 2017).

The mining industry is one of the priority branches of Armenia's economy. In the country, production of fruits and vegetables is developed and is a major source of food for the local population. Previous investigations in some mining areas of Armenia showed that trace elements enter the local food chain, which can have both short- and long-term health impacts (Saghatelyan et al. 2013). It is therefore necessary to ensure that the levels of potentially toxic trace elements in food do not present an unacceptable risk for consumers. International organizations such as WHO or EFSA have incorporated risk analysis as a useful methodology to strengthen food safety systems and reduce diseases linked to food consumption (European Commission 2002; FAO/WHO 2006, 2009). In order to evaluate food safety, exposure needs to be assessed and compared with health-based guidance values. The estimation of dietary exposure is a critical step for risk assessment, which is defined as a process of evaluating the possibility of adverse health effect (IPCS/WHO 2004).

The present study was conducted to assess the chronic dietary exposure and related health risks of trace elements (Pb, Cd, Hg, Cr VI, Mo, Zn, Ni, Cu, and As) through the intake of selected vegetables and fruits grown under the impact of mining industry in Syunik region (Armenia).

Firstly, food consumption survey was carried out and trace elements' contents in vegetables and fruits were estimated. Then estimated daily intake (EDI) and target hazard quotient (THQ) for the local population were calculated. In order to assess the overall potential risk of adverse health effects posed by more than one trace element, the hazard index (HI) was estimated.

Methods and materials

Study site choice

This study covered cities of Kapan (N 39°12'15.60", E 46°27'59.75") and Kajaran (N 39° 9'4.52", E 46° 9'35.71") located in the Republic of Armenia and recognized as large mining centers with own mining bases. Another source of contamination are active and idle tailing repositories and untreated industrial wastewater used in watering either directly or when mixed with irrigation waters (Saghatelyan et al. 2013). These facts largely predetermine specificities of native agroecosystems located within natural biogeochemical provinces in mountain river Voghchi valley.

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The main minerals of the minefield are molybdenite and chalcopyrite with associated pyrites, magnetite, hematite, sphalerite as well as native tellurium (Te) and gold (Au). Concentrates contain significant amounts of rhenium (Re), selenium (Se), and silver (Ag).

The main food source for local rural communities includes homegrown produce and barter with neighbors. Highly probable risks of contamination are common among rural communities, which are out of state control of food safety realized by national authorities.

Plant sampling

With an intention to conduct chronic risk assessment, this research included random sampling of fruits and vegetables, which was done in compliance with WHO and FAO requirements (WHO/FAO 2008).

This was the first ever attempt to study dietary exposure in one of Armenia's mining regions; therefore, individual food approach was selected. The approach allows to estimate the contribution of individual food to exposures as well as assures the greater flexibility in calculating dietary exposures for various segments of population when appropriate food consumption information is available. In order to get the best representative sample across the diet, multiple samples of the same food were gathered from rural sites throughout the mining region.

All major fruits and vegetables grown in home gardens and intended for food purpose and home consumption were collected between July and September 2014. Additional details on the sampled plants are given in Table 1. Agricultural lands selected for this research lie close to mining areas of Kajaran and Kapan, and nearby rural communities. From each sampling site, seven subsamples of the same fruit or vegetable types were collected and then mixed to obtain a composite sample to ensure its representativeness. Due to availability of fruits and vegetables during sampling at least three samples of each fruit and vegetable were collected. The number of samples of few food items (widely spread and widely consumed throughout the region and largely contributing to the diet) reached 10.

Table 1. Plant samples collected from the studied sites.

Edible part of sample	Common name	Botanical name
Leaf	Cabbage	*Brassica oleracea*
Leaf	Onion leaves	*Allium cepa L.*
Leaf	Basil	*Ocimiumbasilicum L.*
Leaf	Fennel	*Foeniculum vulgare*
Root	Carrot	*Daucus carota L.*
Root	Onion bulb	*Allium cepa L.*
Root	Beet	*Beta vulgaris L.*
Root	Potato	*Solanum tuberosum L.*
Seed	Maize	*Zea mays L.*
Seed	Bean	*Phaseolus vulgaris L.*
Fruit	Sweet pepper	*Capsicum annuum L.*
Fruit	Plum	*Prunus domestica L.*
Fruit	Grape	*Vitis vinifera L.*
Fruit	Eggplant	*Solanum melongena L.*
Fruit	Tomato	*Solanum licopersicum L.*
Fruit	Cucumber	*Cucumis sativus L.*

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Total 68 samples were collected and then placed in special clean polyethylene bags intended for plant-origin samples. After transportation to the lab, the samples were washed with distilled water to remove surface dust and soil particles, and then ground until 1-mm-size particle was reached, and kept at a room temperature for subsequent analysis.

Digestion of samples

For destruction of organic matter, wet digestion was used. Acids that have been used in these procedures include nitric acid (HNO_3), sulfuric (H_2SO_4), and perchloric ($HClO_4$) acids. The acids were obtained from authorized distributor of Sigma Aldrich. Plant samples (1 g) were digested after addition of 15 mL of triacid mixtures (HNO_3, H_2S0_4, and $HClO_4$ in 5:1:1 ratio) at 80°C until transparent solution was obtained (Allen et al. 1986). Digested samples were cooled and filtered using Whatman No 42 filter paper and the filtrate was maintained to 50 mL with distilled water.

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Analysis of trace elements

Concentrations of Cu, Mo, Ni, Cr, Pb, Zn, Hg, As, and Cd in the filtrate of digested plant samples were estimated by using atomic absorption spectrophotometer (AAS). A Perkin Elmer Analyst 800 AAS was used to quantify the total metal concentrations. The instrument was fitted with specific lamp for chemical elements and was calibrated using manually prepared standard solution of respective element as well as blank standards for the instrument drift calibration. Standard stock solution of 1000 ppm for all the metals was obtained from SchelTec Authorized Distributor of Perkin Elmer. These solutions were diluted for different concentrations to calibrate the instrument. As a fuel, acetylene gas was used. Support was provided through distribution of air.

Quality assurance and quality control

To ensure the appropriate quality of data, standard operational procedure was established and several procedures were implemented in order to verify reliability of the results. Appropriate cleaning of glassware was provided by washing with 10% HNO_3. Double distilled deionized water was used for solution preparation. Double distillation and deionization of water was done by using Simplicity Ultrapure Water System (MILLIPORE S.A.S., 67120 Molsheim, France).

Blank standards obtained from authorized distributor of Perkin Elmer were run after five determinations to calibrate the instrument. The coefficients of variation of replicate analysis were determined and variation less than 10% was considered correct.

Precision and accuracy of analyses were guaranteed by repeated analysis of samples against National Institute of Standard and Technology Standard Reference Materials (SRM 1570a, SRM 1573a).

The replicate analyses of samples were carried out. The results were found to be within ± 2% of the certified values, which declare the accuracy of the achieved results.

Diet assessment methods

For a diet study, individual-based approach was selected. This study included the development of a food frequency questionnaire (FFQ), which was used as a "list-based diet history" consisting of a structured listing of individual foods (WHO/FAO 2008).

The whole set of examined food commodities was included to understand not only portion size but also frequency of consumption. To avoid from misleading and not correct data, standardized FFQ and pictures were used for indication of serving portions. Two hundred males and females at the age of 25–70 residing in mining areas participated in this study and filled out the FFQ. The data-collection phase of the research was carried out in August–September, 2015. All the collected data were coded, inputted into a relevantly developed data entry field, processed, and analyzed with the help of SPSS software (SPSS Ins., version 11). The food consumption survey involved both male and female respondents in order to implement exposure assessment by gender.

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Data analysis

Estimated daily intake

The average EDI of the assessed trace elements by human subjects was calculated using the following equation, which is recommended by the United States Environmental Protection Agency (USEPA) (US EPA 1997).

$$EDI = (C \times IR \times EF \times ED)/(BW \times AT), \quad (1)$$

where EDI is the average daily intake or dose through ingestion (mg/kg body weight (BW)/day); C is the trace element concentration in the exposure medium (mg/kg); IR is the ingestion rate (kg/day); EF is the exposure frequency (except potato (365 days/year), for all other investigated fruits and vegetables 183 days/year); ED is the exposure duration (was set to 63.6 for males and 69.7 for females based on the average life expectancy, starting from 8 years of age); BW is the body weight (kg). According to our polling survey in the studied region, BWs for males and females were considered to be 70 and 60 kg, respectively; AT is the time period over which the dose is averaged (days/year multiplied number of exposure years).

A questionnaire-based survey was conducted in the studied villages to determine key risk factors such as dietary behaviors, daily activities, and lifestyle of local people. In this study area, most foodstuffs are self-produced.

Target hazard quotient

Human health risk due to trace elements exposure can be expressed in terms of THQ (US EPA 1997). THQ, based on noncancer toxic risk, is determined by the ratio of the average EDI resulting from exposure to site media compared to the oral reference dose (R_fD) for an individual pathway and chemical.

$$THQ = EDI/R_fD. \quad (2)$$

Oral reference dose is an estimation of maximum permissible risk to human population through daily exposure when taking into consideration a sensitive group during a lifetime.

The applied R_fD for Mo, Ni, Zn, As, and Cd were 0.005, 0.02, 0.3, 0.0003, and 0.001 mg/kg/BW/day, respectively (US EPA 1989, 1991a, 1991b, 1992, 2005; Giri 2017). Taking into consideration tolerable daily intake (TDI) proposed by EFSA (EFSA 2014), the oral reference dose for Cr(III) was 0.3 mg/kg/BW/day. Taking into consideration provisional tolerable weekly intake (EFSA 2010), the oral reference dose for Pb was 0.0035 mg/kg/BW/day. For Hg the tolerable weekly intake (0.004 mg/kg/BW/day) was considered (EFSA 2012). Dietary reference intake (0.01 mg/kg/BW/day) was used as a reference dose for Cu (ATSDR 2004).

If the value of THQ is less than 1, the risk of noncarcinogenic toxic effects is assumed to be low. When it exceeds 1, there may be concerns for potential health risks associated with overexposure. To assess the overall potential risk of adverse health effects posed by more than one metal, the THQs can be summed across contaminants to generate a HI to estimate the risk of a mixture of contaminants. The HI refers to the sum of more than one THQ for multiple substances and/or multiple exposure pathways (Zhuang et al. 2014). In the present study, the HI was used as a screening value to identify whether there is significant risk caused by trace elements through average dietary consumption for the residents living in rural communities in Syunik region.

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Statistical analysis

The significance of difference between food consumption of male and female was analyzed by using Student's *t*-test. The data of trace elements concentrations in vegetables and fruits were subject to analysis of variance test to assess the content of trace elements between different food groups. All the statistical tests were performed using Excel and SPSS software (SPSS Ins., version 11).

Results and discussion

Levels of trace elements in vegetables and fruits

Contents of Cu, Mo, Ni, Cr, Zn, Pb, Hg, As, and Cd in different vegetables grown in the mining areas of Armenia and intended for self-consumption are given in Table 2.

Mean contents of Cu in investigated plants ranged from 0.5 to 24 mg/kg. Onion bulb uptake was less (0.5 mg/kg) than in other vegetables. The highest content was detected in onion leaf samples (24 mg/kg). Determined contents can be explained by two important factors: (1) this area is one of Armenia's natural biogeochemical regions to which copper-molybdenum province belongs; (2) presence of three tailing repositories (Darazami, Voghchi, Pkhrut) in the surroundings of the Zangezur copper-molybdenum mining where several farmlands are located. Since, our results indicate that there is intensive accumulation in leafy vegetables, particularly, in onion leaf widely used in this region as a foodstuff.

Mean contents of Mo are highly variable (0.1–44 mg/kg) depending also on the geochemical peculiarities of the farmlands. As described earlier, Kajaran is a geochemical region of molybdenum and actively exploits local mines, so vegetables growing in the vicinity of the city show noticeable difference in uptake. Onion leaf uptake was higher than in other vegetables (44 mg/kg). Relatively high contents were detected in onion leaf and in vegetables such as carrot, maize, and potato (11.3, 6, and 4.7 mg/kg, respectively), which were taken from farmlands closed to Kajaran city.

Table 2. The contents of contaminants in vegetables and fruits from investigated areas.

		Contents (mg/kg fresh matter)								
Species	Mean/SD	Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
					Fruits, vegetables, and seeds					
Bean	M	8.78	0.56	2.67	0.33	0.26	8.50	0.002	0.002	0.001
	SD	4.16	0.17	1.18	0.08	0.12	3.27	0.001	0.001	0
Sweet pepper	M	9.53	1.13	1.80	0.184	0.18	8.68	0.004	0.004	0.002
	SD	3.57	0.36	0.54	0.05	0.05	2.25	0.003	0.003	0.001
Maize	M	15.73	6.00	3.87	0.28	0.03	11.77	0.001	0.003	0.001
	SD	0.87	2.78	0.81	0.04	0.01	3.36	0	0.001	0
Plum	M	2.07	0.23	0.63	0.13	0.019	2.80	0.001	0.001	0.001
	SD	0.90	0.06	0.15	0.04	0.002	0.35	0.001	0	0
Grape	M	7.40	1.13	1.60	0.11	0.01	5.68	0.058	0.012	0.003
	SD	1.10	0.51	0.80	0.05	0.005	2.59	0.002	0.008	0.002
Eggplant	M	4.68	0.73	1.18	0.17	0.12	6.32	0.002	0.003	n/d
	SD	1.71	0.33	0.28	0.04	0.06	1.71	0.001	0.003	–
Tomato	M	3.46	0.44	0.88	0.1	0.07	3.22	0.002	0.001	0.002
	SD	1.73	0.25	0.41	0.02	0.02	0.89	0.001	0.001	0.001
Cucumber	M	0.63	0.05	0.14	0.11	0.04	0.49	0.001	0.001	n/d
	SD	0.17	0.01	0.05	0.01	0.01	0.05	0	0.001	-
					Root vegetables					
Beet	M	3.20	0.50	1.40	0.24	0.172	4.00	0.12	n/d	0.002
	SD	1.71	0.20	0.72	0.04	0.03	2.00	0.03	–	0.001
Potato	M	9.30	4.67	1.61	0.18	0.182	4.53	0.004	0.003	0.002
	SD	2.33	1.61	0.50	0.03	0.03	0.31	0.001	0.001	0.001
Onion bulb	M	0.45	0.43	0.08	0.1	0.007	2.84	0.003	0.002	0.001
	SD	0.04	0.23	0.03	0.02	0.002	1.35	0	0	0
Carrot	M	10.33	11.25	1.49	0.3	0.079	5.38	n/d	n/d	0.01
	SD	1.67	4.75	0.62	0.08	0.009	0.68	–	–	0
					Leafy vegetables					
Fennel	M	6.20	0.77	2.57	0.71	0.24	5.63	0.002	0.006	0.001
	SD	0.40	0.21	0.70	0.08	0.07	2.84	0	0.001	0
Basil	M	6.30	0.62	1.58	0.63	0.23	6.54	0.002	0.001	0.002
	SD	3.11	0.28	0.83	0.05	0.04	3.17	0.001	0	0.001
Cabbage	M	0.99	0.38	0.33	0.16	0.07	3.03	0.001	0.003	n/d
	SD	0.28	0.13	0.06	0.06	0.02	0.15	0.001	0.001	–
Onion leaves	M	24.03	44.10	3.73	0.42	0.1	9.17	n/d	n/d	n/d
	SD	2.24	16.60	0.15	0.09	0.04	1.25	–	–	–

Note: Data are means of $n = 3–10$ replicates. n/d, not detected; SD, standard deviation.

The mean contents of Ni in investigated plants ranged from 0.1 to 3.9 mg/kg. The contents of Ni detected in maize (3.9 mg/kg) and onion leaf (3.7 mg/kg) were higher than in other investigated plants. The minimum concentration of Ni was detected in onion bulb (0.1 mg/kg).

The mean contents of Cr in studied plants ranged from 0.1 to 0.7 mg/kg. The concentrations in fennel (0.7 mg/kg) and basil (0.6 mg/kg) were higher than in other investigated plants.

The mean contents of Zn in studied plants are highly variable (0.5–11.8 mg/kg). The contents of Zn detected in maize, onion leaf, sweet pepper, and bean were 11.8, 9.2, 8.7, and 8.5 mg/kg, respectively. The minimum concentration for Zn was detected in cucumber (0.49 mg/kg).

The mean contents of Pb in investigated plants ranged from 0.01 to 0.3 mg/kg. The concentrations of Pb in bean (0.3 mg/kg), potato (0.2 mg/kg), sweet pepper (0.2 mg/kg), and beet (0.2 mg/kg) were higher than the maximum level (0.1 mg/kg) set by EU Commission Regulation (European Commission 2006).

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Hg concentration in beet (0.1 mg/kg) exceeds the general limit (1 mg/kg) proposed by JECFA (FAO/WHO 2002). For the other plants, the contents of Hg were below 1 mg/kg.

The contents of As and Cd in investigated samples were less than the contents of other determined toxic trace elements. Besides, the contents of Cd in investigated plants were below the maximum level set by EU Commission Regulation (European Commission 2006).

Estimated daily intake and target hazard quotient

Dietary exposure of potentially toxic trace elements in humans depends on daily intake. The EDI values for trace elements are firmly based not only on contamination level but also on consumption of vegetables and fruits grown in contaminated areas.

THQ was calculated to assess the potential of investigated vegetables and fruits in causing adverse health effects.

EDI and THQ values both for males and females are generalized in Tables 3 and 4.

The highest EDI of Cu, both for females and males, was detected in maize (5.77E-02 and 5.17E-02 mg/kg/BW/per day, respectively), which is higher than dietary reference intake of the metal (1.00E-02 mg/kg/BW/day) (ATSDR 2004). For both male and female, the EDI for bean and potato was also higher than dietary reference intake value. The minimum EDI was obtained for onion bulb, for male 2.57E-04 mg/kg/BW/day and for female 3.00E-04 mg/kg/BW/day, respectively. Cumulative daily intakes (Table 3) both for male and female exceeded the dietary reference intake of Cu.

THQ for Cu was more than 1 in maize, potato, bean, sweet pepper, grape, carrot, eggplant, tomato, and onion leaves both for males and females. It means that consumption of those vegetables can have negative health effect. Some vegetables (particularly plum and beet for male) have THQ values, which are very close to 1. Although for some investigated fruits and vegetables THQ values were less than 1, they can substantially contribute to total THQ when combined among them.

According to Yu et al. (Yu et al. 2006) the EDI amounts of the Cd, Pb, and Cu toxic elements from the vegetables grown at three villages near to Baiyin, a Chinese mining and smelting site, have exceeded the recommended dietary allowance levels and thus have a health hazard for human consumption. The HI values for adults and children were 10.25 and 11.11, respectively. The article highlights the importance of multiple pathways in studying health risk assessment of heavy metal exposure in China.

The results of the present investigation showed that the highest EDI of Mo was obtained for carrot, for female 4.31E-02 mg/kg/BW/day and for male 2.89E-02 mg/kg/BW/day, respectively, which exceeded the R_fD of metal (5.00E-03 mg/kg/BW/day) (US EPA 1992). The obtained results also suggested that in case of consumption of potato, onion leaf, and maize the EDI values exceeded the R_fD. The minimum EDI was obtained for cucumber for female and male, 2.33E-04 mg/kg/BW/day and 2.29E-04 mg/kg/BW/day, respectively. THQ for Mo ranged from 0.05 to 5.79 for males and from 0.05 to 8.63 for females. It should be stressed that the cumulative daily intake of Mo (Table 3) does not exceed the reference dose, so consumption of several vegetables does not have a significant potential in causing adverse health effects. For selected vegetables, such as carrot, potato, onion leaf, THQ value is more than 5, which proves that risks are obvious and precautions must be undertaken. For maize consumption, THQ is higher than 1 for male and female (3.94 and 4.40). The results of investigation show that cucumber and onion bulb do not have any significant

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Table 3. Estimated daily intake (EDI) of trace elements in vegetables and fruits.

	Estimated daily intake (mg/kg body weight per day)																	
	Cu		Mo		Ni		Cr		Pb		Zn		Hg		As		Cd	
Species	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female
Fruits, vegetables, and seeds																		
Bean	4.52E-02	4.68E-02	2.88E-03	2.99E-03	1.37E-02	1.42E-02	1.70E-03	1.76E-03	1.34E-03	1.39E-03	4.37E-02	4.53E-02	1.03E-05	1.07E-05	1.03E-05	1.07E-05	5.14E-06	5.33E-06
Sweet pepper	3.40E-02	3.49E-02	4.04E-03	4.14E-03	6.43E-03	6.60E-03	6.57E-04	6.75E-04	6.43E-04	6.60E-04	3.10E-02	3.18E-02	1.43E-05	1.47E-05	1.43E-05	1.47E-05	7.14E-06	7.33E-06
Maize	5.17E-02	5.77E-02	1.97E-02	2.20E-02	1.27E-02	4.42E-02	9.20E-04	1.03E-03	9.86E-05	1.10E-04	3.87E-02	4.32E-02	3.29E-06	3.67E-06	9.86E-06	1.10E-05	3.29E-06	3.67E-06
Plum	7.69E-03	6.56E-03	8.54E-04	7.28E-04	2.34E-03	2.00E-03	4.83E-04	4.12E-04	7.06E-05	6.02E-05	1.04E-02	8.87E-03	3.71E-06	3.17E-06	3.71E-06	3.17E-06	3.71E-06	3.17E-06
Grape	3.17E-02	3.08E-02	4.84E-03	4.71E-03	6.86E-03	6.67E-03	4.71E-04	4.58E-04	4.29E-05	4.17E-05	2.43E-02	2.37E-02	2.49E-04	2.42E-04	5.14E-05	5.00E-05	1.29E-05	1.25E-05
Eggplant	2.41E-02	2.57E-02	3.75E-03	4.02E-03	6.07E-03	6.49E-03	8.74E-04	9.35E-04	6.17E-04	6.60E-04	3.25E-02	3.48E-02	1.03E-05	1.10E-05	1.54E-05	1.65E-05	0	0
Tomato	1.88E-02	2.02E-02	2.39E-03	2.57E-03	4.78E-03	5.13E-03	5.43E-04	5.83E-04	3.80E-04	4.08E-04	1.75E-02	1.88E-02	1.09E-05	1.17E-05	5.43E-06	5.83E-06	1.09E-05	1.17E-05
Cucumber	2.88E-03	2.94E-03	2.29E-04	2.33E-04	6.40E-04	6.53E-04	5.03E-04	5.13E-04	1.83E-04	1.87E-04	2.24E-03	2.29E-03	4.57E-06	4.67E-06	4.57E-06	4.67E-06	0	0
Root vegetables																		
Beet	8.23E-03	1.07E-02	1.29E-03	1.67E-03	3.60E-03	4.67E-03	6.17E-04	8.00E-04	4.42E-04	5.73E-04	1.03E-02	1.33E-02	3.09E-04	4.00E-04	0	0	5.14E-06	6.67E-06
Potato	5.05E-02	4.65E-02	2.54E-02	2.34E-02	8.74E-03	8.05E-03	9.77E-04	9.00E-04	9.88E-04	9.10E-04	2.46E-02	2.27E-02	2.17E-05	2.00E-05	1.63E-05	1.50E-05	1.09E-05	1.00E-05
Onion bulb	2.57E-04	3.00E-04	2.46E-04	2.87E-04	4.57E-05	5.33E-05	5.71E-05	6.67E-05	4.00E-06	4.67E-06	1.62E-03	1.89E-03	1.71E-06	2.00E-06	1.14E-06	1.33E-06	5.71E-07	6.67E-07
Carrot	2.66E-02	3.96E-02	2.89E-02	4.31E-02	3.83E-03	5.71E-03	7.71E-04	1.15E-03	2.03E-04	3.03E-04	1.38E-02	2.06E-02	0	0	0	0	2.57E-05	3.83E-05
Fennel	4.43E-03	5.17E-03	5.50E-04	6.42E-04	1.84E-03	2.14E-03	5.07E-04	5.92E-04	1.71E-04	2.00E-04	4.02E-03	4.69E-03	0	1.67E-06	4.29E-06	5.00E-06	7.14E-07	8.33E-07
Basil	4.50E-03	5.25E-03	4.43E-04	5.17E-04	1.13E-03	1.32E-03	4.50E-04	5.25E-04	1.64E-04	1.92E-04	4.67E-03	5.45E-03	1.43E-06	1.67E-06	7.14E-07	8.33E-07	1.43E-06	1.67E-06
Cabbage	3.39E-03	3.30E-03	1.30E-03	1.27E-03	1.13E-03	1.10E-03	5.49E-04	5.33E-04	2.40E-04	2.33E-04	1.04E-02	1.01E-02	3.43E-06	3.33E-06	1.03E-05	1.00E-05	0	0
Onion leaves	1.37E-02	1.60E-02	2.52E-02	2.94E-02	2.13E-03	2.49E-03	2.40E-04	2.80E-04	5.71E-05	6.67E-05	5.24E-03	6.11E-03	0	0	0	0	0	0
Cumulative daily intake	3.28E-01	3.52E-01	1.22E-01	1.42E-01	7.60E-02	1.11E-01	1.03E-02	1.12E-02	5.64E-03	6.00E-03	2.75E-01	2.94E-01	6.44E-04	7.30E-04	1.48E-04	1.49E-04	8.75E-05	1.02E-04

Table 4. Fruit and vegetable consumption data for males and females.

	Ingestion rate, kg/day	
Species	Males	Females
	Fruits, vegetables, and seeds	
Bean	0.36	0.32
Sweet pepper	0.25	0.22
Maize	0.23	0.22
Plum	0.26	0.19
Grape	0.30	0.25
Eggplant	0.36	0.33
Tomato	0.38	0.35
Cucumber	0.32	0.28
	Root vegetables	
Beet	0.18	0.20
Potato	0.38	0.30
Onion bulb	0.04	0.04
Carrot		
	Leafy vegetables	
Fennel	0.05	0.05
Basil	0.05	0.05
Cabbage	0.24	0.20
Onion leaves	0.04	0.04

contribution in Mo exposure. In an area in Armenia, where the population is exposed to a high dietary intake of Mo for geophysical reasons with soil levels of 77 mg Mo/kg and 39 mg Cu/kg, aching joints and gout like symptoms have been reported. The daily intakes of Mo and Cu, calculated from analysis of levels in different foods, were 10–15 mg Mo/day (equivalent to 0.14–0.21 mg Mo/kg BW/day for a 70 kg adult) and 5–10 mg Cu/day, compared to intakes of 1–2 mg Mo and 10–15 mg Cu in a control area (SCF 2000). Biochemical investigations showed abnormally high serum uric acid levels in humans and livestock (81 mg/L in humans with symptoms). The US NRC concluded that the involvement of Mo was speculative (SCF 2000).

Because of the deficiencies in the study conducted in Armenia, inadequate data exist for identifying a causal association between excess molybdenum intake in normal, apparently healthy individuals, and any adverse health outcomes.

EDI values of Ni obtained for all investigated plants did not exceed R_fD (2.00E-02 mg/kg/BW/day) (US EPA 1991b) and TDI (2.80E-03 mg/kg/BW/day) of metal (EFSA 2015).

None of the studied vegetables and fruits has a THQ > 1 for Ni, but some vegetables have high contribution. Ni THQ of bean and maize for female is equal to 0.7, while for males it is 0.69 and 0.64, respectively, which declares that mixing of these vegetables in a diet will contribute to THQ more than 1. According to data presented in Table 3, the cumulative daily intakes of Ni both for male and female exceeded R_fD and TDI values. Generalizing obtained data, it is possible to argue that Ni also has a potential to pose adverse health effects.

The highest EDI of Hg for both male and female were found in grape (2.49E-04 and 2.42E-04, respectively) and beet (3.09E-04 and 4.00E-04, respectively), instead, the other analyzed foodstuff did not exceed the reference value (5.40E-04mg/kg/BW/day) (EFSA 2012). THQ values of Hg both for males and females did not exceed 1.

The EDI values of Cr, Zn, Pb, As, and Cd for all investigated plants were below reference values of 3.00E-01, 3.00E-01, 3.50E-03, 3.00E-04, and 1.00E-03 mg/kg/BW/day, respectively (US EPA 1989, 1991a, 2005; EFSA 2010, 2014). Although, according to Table 3, only for Pb

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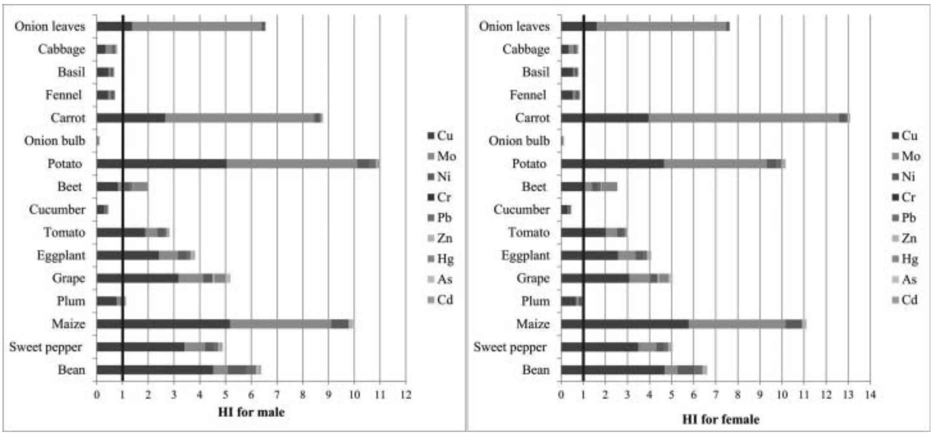

Figure 1. Hazard index (HI) for males (left) and females (right). ***Note:*** The vertical line represents the safety level (HI = 1).

the cumulative daily intake exceeded the reference dose. Zhuang et al. (Zhuang et al. 2014) reported that EDI and THQs for Cd and Pb of rice and vegetables cultivated in vicinity of Dabaoshan mine, China, exceeded the FAO/WHO permissible limit. Cui et al. (Cui et al. 2004) also reported high exposure of Cd and Pb for local residents in Nanning, China. Assessment of potential health risks through intake of vegetables grown in areas of Zhejiang, China indicates that for the general people there is very low health risk to As, Cd, Cr, Pb, Ni, and Hg by vegetable intake (Pan et al. 2016).

In the present study Cr, Zn, As, and Cd were not found to cause any risk to the local population for majority of analyzed vegetables.

In a recent paper, the total health risk index calculated for people in Guizhou, Yunnan, Guangxi, Hunan, Guangdong, Hubei provinces in southern China, and Liaoning province in northeast China, showed a high risk for Pb, Cd, and Hg when consuming vegetables grown in these areas (Zhong et al. 2017).

According to Liu et al. (Liu et al. 2013) the hazard quotient of rape, celery, cabbage, asparagus, lettuce, and carrot intended for diet in the studied sites in China are much higher than the USEPA guideline values, showing that the above-mentioned vegetables are unsafe for human consumption. The authors consider that a large daily intake of these vegetables is likely to cause a significant health hazard to the residents and consumers.

The data on combined THQ (HI) for vegetables and fruits are summarized in Figure 1. It is obvious that there is a potential risk to human health through more than one trace element both for male and female. HI $>$ 1 values obtained for all investigated vegetables showed a decreasing order of potato $>$ maize $>$ carrot $>$ onion leaves $>$ bean $>$ grape $>$ sweet pepper $>$ eggplant $>$ tomato $>$ beet $>$ plum and carrot $>$ maize $>$ potato $>$ onion leaves $>$ bean $>$ grape $>$ sweet pepper $>$ eggplant $>$ tomato $>$ beet for male and female, respectively.

Conclusions

Vegetables and fruits are important source of food in the studied region and they also contribute to exposure to potentially toxic trace elements. It is recommended that intense consumption of vegetables and fruits growing in contaminated areas should be avoided. Our

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investigation pointed out that in this area contamination of vegetables can cause health risk problems. Several elements such as Cu and Mo had EDI values that exceeded the available reference values. It is also noted that some vegetables, particularly leafy vegetables, have intensive uptake of toxic trace elements.

Habitual consumption of contaminated vegetables and fruits results in long-term health effects and the impact becomes apparent after several years. That is why monitoring and risk assessment is crucial for maintaining consumer health protection.

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Declaration of interest

The authors declare that they have no conflicts of interest.

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