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Exposure assessment of potentially toxic trace elements via consumption of fruits and vegetables grown under the impact of Alaverdi's mining complex

Davit Pipoyan^a, Meline Beglaryan^a, Liana Sireyan^a, and Nicolò Merendino^b

^aInformational Analytical Center for Risk Assessment of Food Chain of the Center for Ecological Noosphere Studies of NAS RA, Abovyan, Yerevan, Armenia; ^bDepartment of Ecological and Biological Sciences (DEB), Tuscia University, Largo dell'Università snc, Viterbo, Italy

ABSTRACT

This study is aimed to investigate the transfer of potentially toxic trace elements from soils to plants grown under the impact of Alaverdi's mining complex and assess the related dietary exposure to local residents. Contamination levels of potentially toxic trace elements (Cu, Ni, Pb, Zn, Hg, As, Cd) in soils and plants were determined and afterwards, transfer factors, estimated daily intakes, target hazard quotients, and hazard indexes were calculated.

Some trace elements (Pb, Zn, Cd) exceeded the maximum allowable levels. EDIs of Cu, Ni, Hg for the majority of studied fruits and vegetables exceeded the health-based guideline values. Meanwhile, in case of combined consumption of the studied food items, the estimated cumulative daily intakes exceeded health-based guideline values not only for the aforementioned trace elements but also for Zn in the following sequence: Zn > Hg > Ni > Cu. HI > 1 values highlighted the potential adverse health effects for local population through more than one trace element.

Detailed investigations need to be done for the overall assessment of health risks, taking into consideration not only adverse health effects posed by more than one toxic trace element but also through other exposure pathways.

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soil to plant transfer; trace elements; fruits and vegetables; exposure assessment

Introduction

Due to the impact of frequent and sustained mining activities, soil contamination around mining areas has become a severe problem worldwide (Ding *et al.* 2017) and in Armenia particularly (Saghatelyan *et al.* 2010, 2013). The activity in mining complexes is carried out without treatment facilities, dumping the superficial waterways of miner waters, abandonment of tailings dams, and many other violations have a negative impact on the environment (Saghatelyan *et al.* 2010).

Also, it is stated that excessive accumulation of some essential trace elements (*e.g.*, Zn, Cu, Ni) or low concentration of toxic elements (*e.g.*, Cd, Pb, Hg, As) in agricultural soils may not

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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only result in environmental concerns but also affect food quality and safety (US EPA 2014; Yang *et al.* 2007), as these trace elements can enter food chain and accumulate in fruits and vegetables (De Roma *et al.* 2017; Pipoyan *et al.* 2018; Takáč *et al.* 2009).

Fruits and vegetables which are considered to be an essential part of human diet can accumulate trace elements from soil in their edible and nonedible parts (Guerra *et al.* 2012). For this reason, the transfer of trace elements from soil to plant cannot be underestimated as it is the major pathway to human exposure (Ding *et al.* 2018; Garg *et al.* 2014; Roba *et al.* 2016; Sultana *et al.* 2017). Previous investigations in some mining areas of Armenia showed that trace elements enter the local food chain and can pose health risk problems (Pipoyan *et al.* 2018).

Various international studies have been undertaken to assess the transfer of trace metals from soil to plants and possible health risks caused by their consumption (Garg *et al.* 2014; Jolly *et al.* 2013; Lu *et al.* 2017, Vrovnik *et al.* 2016; Zhou *et al.* 2016).

It should be stressed that in Armenia such investigations are needed for Alaverdi in particular, as it is one of the largest mining regions of Armenia. Alaverdi district located in the Lori province, in the north of Armenia, is one of the main areas of copper mineralization. Of the current generation of mines, copper mining began in the northern Alaverdi district in the 1770s. Since 1980s, Alaverdi copper smelter plant has been functioning as a major metallurgical plant (Petrosyan *et al.* 2004). Currently, the only facility for copper smelting in Alaverdi, Armenia, has a total capacity of 40,000 tonnes of copper concentrate per year. Despite its relatively small production volume, Alaverdi frequently raises concerns regarding the environmental damage it causes. According to plant management, there are currently no provisions in place to reduce the environmental impact from the smelter operations. Filters to capture dust and toxic fumes were once in place, but they have been out of order for years without any replacement. The company blames the absence of environmental protection measures on the lack of financial resources owing to the shortage of copper concentrate that the smelter receives to process (Zoï Report 2012). Recent investigation carried out in Alaverdi region revealed anthropogenic origin including historical contamination and current industrial contamination. Pollution levels were classified from moderate to strongly polluted, with high concentrations of arsenic and lead (Akopyan *et al.* 2018). However, it should be stressed that, there is no data on possible adverse health effects to local residents through dietary exposure to contaminants.

Taking into consideration the aforementioned issues, the present study is aimed to investigate the transfer of potentially toxic trace elements from agricultural soils to plants grown under the impact of Alaverdi's mining complex and assess the related possible health risks to local residents.

Firstly, food consumption survey was developed and trace element contents in soils and plant species were determined, and transfer factors (TFs) were calculated. Afterward estimated daily intakes (EDIs), target hazard quotients (THQs) and hazard indexes (HIs) were calculated.

Methods and materials

Study site choice

This study covered Neghoc and Qarkop rural communities located near the town of Alaverdi (N 41° 5' 42", E 44° 39' 21").

The main food source for local rural communities includes home-grown produce and barter with neighbors. Highly probable risks of contamination are common among rural communities as they are not covered under the state control of food safety as chalked out by

national authorities. Armenia is a member of Custom's Union and Technical Regulation on Food Safety but it does not cover food products produced by individuals at home, in private household farms, or by individuals who engage in horticulture and gardening (EAEU 2011).

Sample collection and treatment

Sampling procedures were done between July and September 2014. In each studied rural community, several farmlands and home gardens were selected taking into consideration the availability of cultivated vegetables and fruits.

Topsoil (0–15 cm) sampling was done according to Standard Operation Procedures (SOPs) developed in the Center for Ecological-Noosphere Studies of NAS, RA (Tepanosyan *et al.* 2016, 2017). A stainless steel hand auger was used. From each sampling point (Figure 1), 3–5 randomly collected subsamples were taken and mixed thoroughly in special clean polyethylene bags to obtain the bulk sample.

Since this was the first ever attempt to study dietary exposure in Alaverdi's mining region, individual food approach was selected. Taking into consideration the data of National Statistical Service of Armenia (NSS RA) and also seasonal availability of the locally grown plants, the most common and widely consumed plant samples were collected from the same soil sampling points. A total of 15 plant species, including nine species of fruits, two species of seeds, one species of fruiting vegetable, one species of root vegetable, and two species of leafy vegetable were sampled. Additional details on the sampled fruits and vegetables are given in Table 1. These plant species were cultivated on the experimental farmlands during spring and summer seasons and fruits and vegetables were collected during the harvest season (summer and autumn, 2014). The seven subsamples of the same plant species were randomly taken from all the selected home gardens and farmlands to form the composite samples (Table 1) and ensure their representativeness, according to WHO and FAO recommendations (WHO/FAO 2008). At least three replications were conducted for each fruit and vegetable.

Overall, seven samples of soil and 45 samples of fruits and vegetables were collected and then placed in special clean polyethylene bags and transported to the laboratory. Soil samples were air-dried, homogenized and sieved (<2 mm), milled according to ISO 11464 (ISO

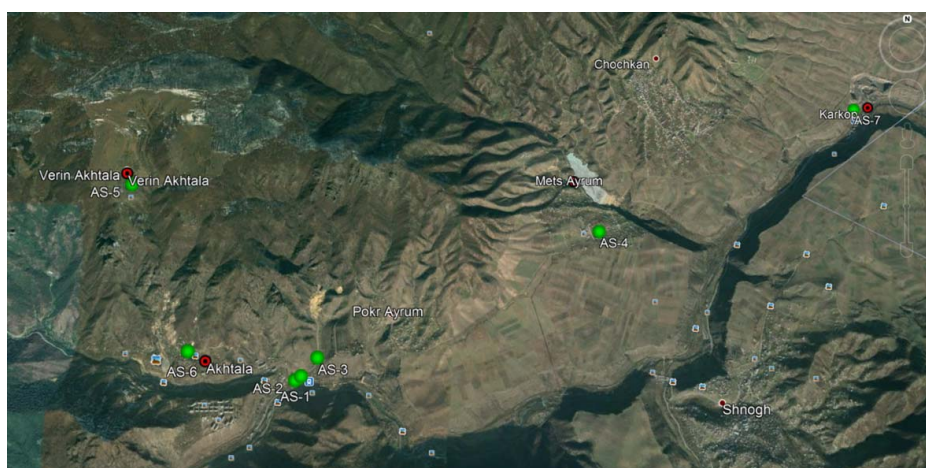


Figure 1. Soil sampling points.

Table 1. Plant samples collected from the studied sites.

Edible part of sample	Common name	Botanical name
Fruit	Apple	<i>Malus</i>
Fruit	Peach	<i>Prunus persica</i>
Fruit	Pear	<i>Pyrus</i>
Fruit	Plum	<i>Prunus domestica</i> L.
Fruit	Cornel	<i>Cornus mas</i>
Fruit	Fig	<i>Ficus carica</i>
Fruit	Cherry	<i>Prunus avium</i>
Fruit	Raspberry	<i>Rubus idaeus</i>
Fruit	Grape	<i>Vitis vinifera</i> L.
Seed	Maize	<i>Zea mays</i> L.
Fruit	Cucumber	<i>Cucumis sativus</i> L.
Root	Potato	<i>Solanum tuberosum</i> L.
Seed	Bean	<i>Phaseolus vulgaris</i> L.
Leaf	Onion leaves	<i>Allium cepa</i> L.
Leaf	Greens	–

2006), and then stored in sealed bags until analysis. Plant samples were washed with distilled water to remove surface dust and soil particles, and then ground until 1-mm-sized 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. All samples (1 g) were digested after addition of 15 mL of triacid mixtures (HNO_3 , H_2SO_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.

Analysis of trace elements

For the trace element analysis, only the edible parts of vegetables and fruits were used.

Concentrations of trace elements (Cu, Ni, Pb, Zn, Hg, As, and Cd) in soil and plant samples were estimated by using X-ray fluorescence spectrometry (Olympus Innov-X-5000 (USA)) and atomic absorption spectrophotometer (AAS, PerkinElmer AAnalyst 800), respectively. A PerkinElmer Analyst 800 AAS was used to quantify the total metal concentrations in plant samples. 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 PerkinElmer. 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 using Simplicity Ultrapure Water System (MILLIPORE S.A.S., 67120 Molsheim, France).

Standard reference materials (NIST 2711a and NIST 2710a, USA) and blank (SiO_2) obtained from the National Institute of Standards and Technology of the USA were analyzed as part of the quality assurance and quality control (QA/QC) procedures for soil analysis.

Blank standards obtained from authorized distributor of PerkinElmer 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 plant analyses were guaranteed by repeated analysis of samples against National Institute of Standard and Technology Standard Reference Materials (SRM 1570a, SRM 1573a).

The replicate analysis of samples was carried out. The results were found to be within $\pm 2\%$ 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 following steps were undertaken for the development of FFQ: (1) constructing the food list, (2) assigning consumption frequency and portion sizes, and (3) developing a pilot test. So, the whole set of examined food commodities was included to understand not only portion size but also frequency of consumption. To avoid misleading and incorrect data standardized FFQ and pictures were used for indication of serving portions. All participants voluntarily took part in face-to-face surveys. The survey was interviewer administered, and a paper-based questionnaire was used. Prior to filling the FFQ, each participant was given a brief oral introduction about the procedure of the survey, final aim of the study, and the institution conducting it. Two hundred males and females between the age of 25 and 70 residing in mining areas participated in this study and filled out the FFQ. The data collection phase of the research was carried out during 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 Inc., version 11). The food consumption survey involved both male and female respondents in order to implement exposure assessment by gender.

Data analysis

Transfer factor (TF)

The ability of a trace element to migrate from the soil through the plant parts and make itself available for consumption was represented by the index called TF. So, in this study, transmission of trace elements from soil to edible part of plant was calculated as follows:

$$\text{TF} = C_{\text{plant}} / C_{\text{soil}} \quad (1)$$

where C_{plant} and C_{soil} represent the potentially toxic trace element concentration in extracts of plants and soils on dry weight basis, respectively (Jolly *et al.* 2013; Rai *et al.* 2015; Tasrina *et al.* 2015).

Estimated daily intake (EDI)

The average estimated daily intake (EDI) of the assessed trace elements by human subjects was calculated using the following equation, which is recommended by the US EPA (US EPA 1997).

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

where EDI is the average daily intake or dose through ingestion (mg/kg body weight (BW)/d); C is the trace element concentration in the exposure medium (mg/kg); IR is the ingestion rate (kg/d); EF is the exposure frequency (except potato (365 d/year), for all other investigated fruits and vegetables 183 d/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 diet survey (FFQ) in the studied region, body weights for males and females were considered to be 70 and 60 kg, respectively; AT is the time period over which the dose is averaged (365 d multiplied number of exposure years).

Cumulative daily intakes were calculated as the sum of individual EDI values for each trace element.

Target hazard quotient

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

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

The applied RfD for Ni, Zn, As, and Cd were 0.02, 0.3, 0.0003, and 0.001 mg/kg/ BW/d, respectively (US EPA 1989, 1991a,b, 2005). Taking into consideration provisional tolerable weekly intake (EFSA 2010), the oral RfD for Pb was 0.0035 mg/kg/BW/d. For inorganic Hg, the tolerable weekly intake (0.004 mg/kg/BW/d) was considered (EFSA 2012). Dietary reference intake (0.01 mg/kg/BW/d) was used as a RfD 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 (Zhuang *et al.* 2014).

Statistical analysis

The significance of difference between food consumption of males and females were analyzed by using Student's *t*-test. All the statistical tests were performed using Excel and SPSS software (SPSS Inc., version 11).

All the data are presented in terms of mean (M) and standard deviation (SD) of triplicates.

Results and discussion

Levels of trace elements in fruits and vegetables

Contents of trace elements (Cu, Ni, Pb, Zn, Hg, As, and Cd) in studied plant species are presented in Table 2. Each value corresponds to the average for the selected plant species from different locations.

The detected contents of **Cu** in studied fruits and vegetables (Table 2) were highly variable (0.3–20.8 mg/kg). The content of **Ni** in studied fruits and vegetables was in the range of 0.08–3.55 mg/kg. The detected contents of **Pb** (Table 2) in some studied fruits and vegetables exceeded the maximum level (0.1 mg/kg) in the following sequence: fig > bean > potato. Pb content in grape was equal to maximum level (0.1 mg/kg) set by EU Commission Regulation (European Commission 2006).

According to data presented in Table 3, the contents of **Zn** in studied food items varied from 1.13 to 51 mg/kg. The higher contents reported for the majority of investigated plant species showed a decreasing order of greens > raspberry > onion > maize > bean > cucumber > fig > potato > grape > apple > peach > cherry > plum > pear > cornel and

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

Plant species	Mean/SD ^a	Contents (mg/kg fresh matter)						
		Cu	Ni	Pb	Zn	Hg	As	Cd
Fruits, vegetables, and seeds								
Apple	M	0.725	1.46	0.082	6.4	0.0015	0.003	0.0013
	SD	0.246	0.615	0.041	2.015	0.001	0.001	0.001
Peach	M	0.802	1.573	0.003	6.03	0.001	0.002	0.01
	SD	0.21	0.23	0.001	0.13	0	0.001	0.003
Pear	M	0.64	0.117	0.001	2.02	0.002	0.0017	0.003
	SD	0.13	0.03	0	0.67	0.001	0.0008	0.001
Plum	M	0.635	0.156	0.005	2.25	0.0015	0.0005	0.0013
	SD	0.096	0.012	0.002	0.88	0.001	0.0001	0.001
Cornel	M	0.29	0.08	0.013	1.14	0.0013	0.0027	n/d
	SD	0.05	0.01	0.002	0.23	0.001	0.001	—
Fig	M	7.8	2.01	0.18	15.19	0.094	0.0017	n/d
	SD	1.47	0.35	0.06	2.27	0.013	0.001	—
Cherry	M	1.2	1.87	0.005	2.32	n/d	n/d	0.012
	SD	0.35	0.33	0.001	0.55	—	—	0.004
Raspberry	M	13.48	3.55	n/d	34.51	n/d	0.005	n/d
	SD	5.13	0.89	—	11.06	—	0.004	—
Grape	M	7.77	0.52	0.1	7.41	0.0017	0.002	0.0013
	SD	1.75	0.09	0.09	2.98	0.001	0.001	0.001
Maize	M	1.58	0.68	0.05	21.32	0.07	0.027	0.114
	SD	0.6	0.19	0.01	6.44	0.02	0.01	0.05
Cucumber	M	0.47	0.33	0.0015	19.48	0.0015	0.004	0.0017
	SD	0.05	0.07	0	2.07	0.001	0.002	0.0006
Bean	M	10.7	1.7	0.129	20.85	0.0015	0.004	0.0013
	SD	3.97	0.48	0.09	2.51	0.001	0.001	0.001
Root vegetable								
Potato	M	12.43	0.68	0.12	12.41	0.0012	0.005	0.001
	SD	4.56	0.21	0.04	3.55	0.0005	0.002	0
Leafy vegetables								
Onion leaves	M	9.34	0.263	0.022	22.51	0.0012	0.012	0.141
	SD	1.01	0.036	0.016	1.97	0.001	0.009	0.024
Greens	M	20.78	1.43	0.068	51	0.003	0.1	n/d
	SD	3.09	0.3	0.028	15.1	0.001	0.012	—

Note: Data are means of $n = 3$ replicates. ^aSD: Standard deviation. n/d: not detected.

Table 3. The contents of trace elements in soil samples from investigated areas.

Soil samples	Contents (mg/kg)						
	Cu	Ni	Pb	Zn	Hg	As	Cd
	MAC (mg/kg)						
	132	80	65	220	2.1	2	2
As-1	808	65.64	147.3	1127	<0.05	6.01	<0.07
As-2	1223	74.94	116	801	<0.05	3.07	<0.07
As-3	811	82.77	123.8	642	0.09	3.75	7.66
As-4	470	37.8	50.9	831	0.176	3.8	0.22
As-5	390	35.8	43	619	<0.05	6.7	0.26
As-6	733	22.8	40.1	816	<0.05	8.7	0.33
As-7	1847	28.4	117.9	877.8	<0.05	7.4	<0.07
Average	897.43	49.74	91.29	816.26	0.13	5.63	2.12

Note: MAC – maximum allowable concentrations, exceeded contents are highlighted.

were significantly higher than the recommended safe level (0.3 mg/kg) (FAO/WHO 1993). Zn is well known as an essential element for normal body function, but at exceedingly high concentrations can have adverse effects on human health. It can also be noted that among the estimated trace elements, in quantitative terms, the higher contents were reported for Zn and lower ones for Hg and As.

The contents of Cd in onion (0.14 mg/kg) and in maize (0.11 mg/kg) were exceeding the maximum level set by EU Commission Regulation (European Commission 2006). Cd contents in cherry (0.012 mg/kg), peach (0.01 mg/kg), pear (0.003 mg/kg), and in cucumber (0.002 mg/kg) were below the maximum level (European Commission 2006). Cd contents were not exceeding the maximum level (European Commission 2006) in apple, plum, grape, potato, and bean (0.001 mg/kg) samples also. In cornel, fig, raspberry, and greens Cd were not detected.

Hg contents in investigated plant species were in the range of 0.0012–0.09 mg/kg; however, these values did not exceed the general limit (1 mg/kg) proposed by JECFA (2002). The relatively high contents were reported for fig (0.09 mg/kg) and maize (0.07 mg/kg). Hg contents in cherry and raspberry samples were not detected.

Taking into consideration the aforementioned results, it can be stressed that all the investigated fruits and vegetables showed detectable contents of more than one studied trace element.

Levels of trace elements in soils

The contents and maximum allowable concentrations (MACs) of trace elements (Cu, Ni, Pb, Zn, Hg, As, and Cd) in studied soil samples are presented in Table 3. Among the other studied trace elements, the contents of Cu, Zn, and As in all investigated soil samples exceeded the MAC values (CENS/OSCE 2011). Meanwhile, the content of Hg in all studied soil samples was below the MAC value (Table 3). The obtained contents of Cd and Ni exceeded the allowable concentrations (2 mg/kg and 80 mg/kg, respectively) only for one soil sample (As-3). Pb contents obtained for three investigated soil samples (As-5, As-6, As-7) were higher than MAC value (65 mg/kg).

Transfer of trace elements from soil to plant

For the evaluation of the accumulation of potentially toxic trace elements in edible parts of plant samples in relation with soils, the TF was calculated, which provided the proper information on contents of trace elements in edible parts of plants.

Table 4. Transfer factor from soils to fruits and vegetables.

Plant species	Transfer factor						
	Cu	Ni	Pb	Zn	Hg	As	Cd
Fruits, vegetables, and seeds							
Apple	0.001	0.03	0.001	0.01	0.01	0.001	0.0005
Peach	0.001	0.032	0.00004	0.01	0.008	0.0003	0.005
Pear	0.001	0.002	0.00001	0.002	0.011	0.0003	0.00142
Plum	0.001	0.003	0.00006	0.003	0.01	0.0001	0.0005
Cornel	0.0003	0.002	0.0001	0.001	0.01	0.0005	—
Fig	0.01	0.04	0.002	0.02	0.71	0.0003	—
Cherry	0.0013	0.038	0.0001	0.003	—	—	0.006
Raspberry	0.02	0.1	—	0.042	—	0.001	—
Grape	0.01	0.01	0.001	0.01	0.013	0.0004	0.001
Maize	0.002	0.014	0.0004	0.03	0.51	0.005	0.054
Cucumber	0.0005	0.007	0.00002	0.024	0.011	0.0007	0.001
Bean	0.012	0.034	0.002	0.03	0.01	0.0006	0.0005
Root vegetable							
Potato	0.01	0.014	0.001	0.015	0.01	0.001	0.0005
Leafy vegetables							
Onion leaves	0.01	0.005	0.0002	0.03	0.01	0.002	0.07
Greens	0.023	0.03	0.001	0.06	0.02	0.02	—

Some researchers (Rai *et al.* 2015; Vrhovnik *et al.* 2016) reported that plants undergo the bioaccumulation of trace elements from the environment in cases when TFs are higher than 1, while a $TF < 1$ indicates that the plant only absorbs but does not accumulate the trace element. On the other hand, Tasrina *et al.* (2015) stated that uptake of metals by plants tends to increase with increasing concentration, as long as it is within a certain range. When the concentration goes beyond the range, the uptake will decrease because plant roots are injured, thus leading to a lower absorbing ability.

Soil to plant TF values for Cu, Ni, Pb, Zn, Hg, As, and Cd for consumed fruits and vegetables are given in Table 4. From Table 4 it is obvious that the TF values for all trace elements varied between investigated plant species and are less than 1. The smallest value of TF was obtained for Pb (plum) and the highest one for Hg (fig). The relatively high TF values are obtained for Hg, Zn, and Ni, which range from 0.01 (apple, plum, cornel, potato, bean, and onion) to 0.71 (fig), 0.001 (cornel) to 0.06 (greens), 0.002 (cornel) to 0.1 (raspberry), respectively.

TFs > 0.5 for fig (0.71) and maize (0.51) indicate that a significant amount of the element has been transferred from soil to plant, while TFs of 0.1 indicate that the plant is excluding the element from its tissue (Rai *et al.* 2015).

The TF values of Cu, Pb, As, and Cd are quite low for all investigated fruits and vegetables. Cornel, fig, raspberry, and greens did not show transfer of toxic trace element Cd. The investigated fruits, particularly cornel, peach, pear, and plum were found to show a lower TF compared to other plants.

Estimated daily intake

Estimation of the level of trace element exposure to population living in studied communities is of great importance for observing the possible health risks. Therefore, combining concentration data with consumption data (Table 5), in this study EDIs and cumulative daily

Table 5. Fruit and vegetable consumption data for males and females.

Species	Ingestion rate, kg/d	
	For males	For females
Fruits, vegetables, and seeds		
Apple	0.2	0.23
Peach	0.2	0.18
Pear	0.2	0.19
Plum	0.26	0.22
Cornel	0.12	0.1
Fig	0.2	0.2
Cherry	0.15	0.16
Raspberry	0.15	0.16
Grape	0.3	0.25
Maize	0.23	0.22
Cucumber	0.22	0.2
Bean	0.26	0.22
Root vegetable		
Potato	0.32	0.28
Leafy vegetables		
Onion leaves	0.03	0.02
Greens	0.05	0.05

Note: Body weights for males and females were considered to be 70 and 60 kg, respectively.

intakes were assessed and compared with an available health-based guidance values (HBGVs) set by international organizations.

A description of the EDIs of potentially toxic trace elements is presented in [Table 6](#).

Although **Cu** is an essential micronutrient, normally subject to effective homeostatic control, excess dietary intakes can be toxic in some circumstances. Mean dietary Cu intakes from food for adults in different European countries have been estimated to be within a range of 1.0–2.3 mg/day for males and 0.9–1.8 mg/day for females (EFSA 2015b). Besides, according to IOM the upper level (UL) for adults is 10 mg/d (equivalent to 0.16 mg/kg/BW/d), a value based on protection from liver damage as a critical adverse effect (EGVM 2003; IOM 2001). According to data presented in [Table 4](#), the EDI of Cu obtained for some investigated fruits and vegetables showed a decreasing order of potato > bean > grape > raspberry > fig > greens and was higher than the dietary reference intake (0.01 mg/kg/BW/d) (ATSDR 2004), but was below the UL (0.16 mg/kg/BW/d). On the other hand, for the combined consumption of studied fruits and vegetables, the estimated cumulative daily intake (2.32E-01mg/kg/BW/d) exceeded not only the dietary reference intake, but also the UL.

According to the Scientific Committee for Food (SCF 2006), in the absence of adequate dose-response data for adverse health effects it is not possible to establish a tolerable upper intake level for **Ni**. Meanwhile, according to EFSA scientific opinion (EFSA 2015a) on the risks to human health from Ni in food, the tolerable daily intake (TDI) is 0.0028 mg/kg/BW/d (2.80E-03 mg/kg/BW/d). Besides, European Food Safety Authority also stated that the mentioned value may not be sufficiently protective of individuals sensitized to Ni (EFSA 2015a). According to data presented in [Table 6](#), the EDI of **Ni** obtained for some investigated fruits and vegetables showed a decreasing order of raspberry > fig > peach > apple > cherry > potato > maize and was higher than the TDI (0.0028 mg/kg/BW/d). The obtained results ([Table 6](#)) also suggested that in case of combined consumption



Table 6. Estimated daily intake (EDI) of trace elements in vegetables and fruits.

Plant species	Cu		Ni		Pb		Zn		Hg		As		Cd	
	Oral reference doses (RfDs)													
	1,00E-02		2,00E-02		3,50E-03		3,00E-01		1,00E-04		3,00E-04		1,00E-03	
	Estimated daily intake (mg/kg body weight (BW)/d)													
	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female
Fruits, vegetables, and seeds														
Apple	2,07E-03	2,78E-03	4,17E-03	5,60E-03	2,35E-04	3,15E-04	1,83E-02	2,45E-02	3,43E-06	4,60E-06	9,43E-06	1,27E-05	2,86E-06	3,83E-06
Peach	1,83E-03	1,92E-03	4,49E-03	4,72E-03	9,71E-06	1,02E-05	1,72E-02	1,81E-02	2,86E-06	3,00E-06	4,86E-06	5,10E-06	2,86E-05	3,00E-05
Pear	1,81E-03	2,01E-03	3,34E-04	3,71E-04	2,86E-06	3,17E-06	5,77E-03	6,40E-03	5,71E-06	6,33E-06	4,86E-06	5,38E-06	8,57E-06	9,50E-06
Plum	2,36E-03	2,33E-03	5,78E-04	5,71E-04	1,97E-05	1,94E-05	8,36E-03	8,25E-03	4,46E-06	4,40E-06	1,86E-06	1,83E-06	3,71E-06	3,67E-06
Cornel	4,95E-04	4,82E-04	1,36E-04	1,32E-04	2,28E-05	2,22E-05	1,95E-03	1,89E-03	2,23E-06	2,17E-06	4,63E-06	4,50E-06	0	0
Fig	2,23E-02	2,60E-02	5,73E-03	6,69E-03	5,05E-04	5,89E-04	4,34E-02	5,06E-02	2,69E-04	3,14E-04	4,86E-06	5,67E-06	0	0
Cherry	2,57E-03	3,20E-03	4,00E-03	4,98E-03	1,05E-05	1,31E-05	4,97E-03	6,19E-03	0	0	0	0	2,57E-05	3,20E-05
Raspberry	2,89E-02	3,59E-02	7,61E-03	9,48E-03	0	0	7,40E-02	9,20E-02	0	0	1,01E-05	1,25E-05	0	0
Grape	3,33E-02	3,24E-02	2,23E-03	2,17E-03	4,29E-04	4,17E-04	3,18E-02	3,09E-02	7,29E-06	7,08E-06	9,00E-06	8,75E-06	0	0
Maize	5,20E-03	5,81E-03	2,22E-03	2,48E-03	1,33E-04	1,49E-04	7,00E-02	7,82E-02	2,22E-04	2,48E-04	8,77E-05	9,79E-05	3,76E-04	4,19E-04
Cucumber	1,47E-03	1,56E-03	1,05E-03	1,11E-03	4,71E-06	5,00E-06	6,12E-02	6,49E-02	4,71E-06	5,00E-06	1,26E-05	1,33E-05	0	0
Bean	3,98E-02	3,92E-02	6,31E-03	6,23E-03	5,34E-04	5,27E-04	7,74E-02	7,65E-02	4,46E-06	4,40E-06	1,34E-05	1,32E-05	3,71E-06	3,67E-06
Root vegetable														
Potato	5,68E-02	5,80E-02	3,12E-03	3,19E-03	5,51E-04	5,62E-04	5,67E-02	5,79E-02	5,49E-06	5,60E-06	0	0	4,57E-06	4,67E-06
Leafy vegetables														
Onion leaves	4,00E-03	3,11E-03	1,13E-04	8,78E-05	9,21E-06	7,17E-06	9,65E-03	7,50E-02	5,14E-07	4,00E-07	5,01E-06	3,90E-06	6,04E-05	4,70E-05
Greens	1,48E-02	1,73E-02	1,02E-03	1,19E-03	4,88E-05	5,69E-05	3,64E-02	4,25E-02	0	0	0	0	0	0
Cumulative daily intake	2,18E-01	2,32E-01	4,31E-02	4,90E-02	2,52E-03	2,70E-03	5,17E-01	6,34E-01	5,32E-04	6,11E-04	1,68E-04	1,85E-04	5,14E-04	5,53E-04

Note: For Ni, Zn, As, and Cd the US EPA oral reference doses were used (US EPA 1989, 1991a, b, 2005). For Hg and Pb, the tolerable weekly intake and provisional tolerable weekly intake were considered (EFSA 2010, 2012). For Cu, the dietary reference intake was used as a reference dose (ATSDR 2004). Estimated and cumulative daily values > RfDs are in bold.

Table 7. Target hazard quotients (THQs) and hazard indexes (HIs) of trace elements.

Plant species	Males/Females	Target hazard quotients							HI
		Cu	Ni	Pb	Zn	Hg	As	Cd	
Fruits, vegetables, and seeds									
Apple	M	0,21	0,21	0,07	0,06	0,03	0,03	0,003	0,61
	F	0,28	0,28	0,09	0,08	0,05	0,04	0,004	0,82
Peach	M	0,18	0,22	0,003	0,06	0,03	0,02	0,029	0,54
	F	0,19	0,24	0,003	0,06	0,03	0,02	0,030	0,57
Pear	M	0,18	0,02	0,001	0,02	0,06	0,02	0,009	0,31
	F	0,20	0,02	0,001	0,02	0,06	0,02	0,010	0,33
Plum	M	0,24	0,03	0,01	0,03	0,04	0,01	0,004	0,36
	F	0,23	0,03	0,01	0,03	0,04	0,01	0,004	0,35
Cornel	M	0,05	0,01	0,01	0,01	0,02	0,02	0	0,12
	F	0,05	0,01	0,01	0,01	0,02	0,02	0	0,12
Fig	M	<u>2,23</u>	0,29	0,14	0,14	<u>2,69</u>	0,02	0	<u>5,51</u>
	F	<u>2,60</u>	0,33	0,17	0,17	<u>3,14</u>	0,02	0	<u>6,43</u>
Cherry	M	<u>0,26</u>	0,20	0,003	0,02	0	0	0,026	<u>0,51</u>
	F	0,32	0,25	0,004	0,02	0	0	0,032	0,63
Raspberry	M	<u>2,89</u>	0,38	0	0,25	0	0,03	0	<u>3,55</u>
	F	<u>3,59</u>	0,47	0	0,31	0	0,04	0	<u>4,41</u>
Grape	M	<u>3,33</u>	0,11	0,12	0,11	0,07	0,03	0	<u>3,77</u>
	F	<u>3,24</u>	0,11	0,12	0,10	0,07	0,03	0	<u>3,67</u>
Maize	M	<u>0,52</u>	0,11	0,04	0,23	<u>2,22</u>	0,29	0,38	<u>3,79</u>
	F	0,58	0,12	0,04	0,26	<u>2,48</u>	0,33	0,42	<u>4,23</u>
Cucumber	M	0,15	0,05	0,001	0,20	<u>0,05</u>	0,04	0	<u>0,49</u>
	F	0,16	0,06	0,001	0,22	0,05	0,04	0	0,53
Bean	M	<u>3,98</u>	0,32	0,15	0,26	0,04	0,04	0,004	<u>4,79</u>
	F	<u>3,92</u>	0,31	0,15	0,25	0,04	0,04	0,004	<u>4,71</u>
Root vegetable									
Potato	M	<u>5,68</u>	0,16	0,16	0,19	0,05	0	0,005	<u>6,25</u>
	F	<u>5,80</u>	0,16	0,16	0,19	0,06	0	0,005	<u>6,38</u>
Leafy vegetables									
Onion leaves	M	0,40	0,006	0,003	0,03	0,01	0,017	0,060	0,53
	F	0,31	0,004	0,002	0,03	0,004	0,013	0,047	0,41
Greens	M	<u>1,48</u>	0,05	0,01	0,12	0	0	0	<u>1,66</u>
	F	<u>1,73</u>	0,06	0,02	0,14	0	0	0	<u>1,99</u>

Note: THQ > 1 and HI > 1 values are highlighted.

of the investigated fruits and vegetables, the estimated cumulative daily intake (4.90E-02 mg/kg/BW/d) exceeded the TDI (EFSA 2015a).

Pb is a nonessential element, which can be toxic even at trace levels. The nervous system is the main target organ for Pb toxicity (EFSA 2010). However, the EDI and estimated cumulative daily intake values for each studied fruit and vegetable did not exceed the health-based guideline value (0.0035 mg/kg/BW/d).

Zn being an essential element in human diet required for normal body function is the least toxic among all the metals (Amin *et al.* 2013; EFSA 2014). The safe UL of Zn for daily consumption over a lifetime is 25 mg/d (equivalent to 0.42 mg/kg/BW/d) (EGVM 2003). The results of the present study (Table 6) showed that the EDI of Zn for each studied fruit and vegetable did not exceed the UL and oral RfD values (0.3 mg/kg/BW/d), meanwhile for combined consumption of these food items the estimated cumulative daily intake both for males and females (5.17E-01 and 6.34E-01 mg/kg/BW/d, respectively) exceeded the noted health-based guideline values.

The obtained results of the present study showed that among the other investigated fruits and vegetables, the EDI value for **Hg** exceeded the health-based guideline value (0.004 mg/kg/BW/d) only for fig and maize. However, it should be noted also, that for the combined consumption of

studied fruits and vegetables the estimated cumulative intake both for males and females ($5.32\text{E-}04$ and $6.11\text{E-}04$ mg/kg/BW/d, respectively) exceeded the aforementioned guideline value.

EDI and estimated cumulative daily intake values for **As** and **Cd** did not exceed the reference values (0.0003 mg/kg/BW/d and 0.001 mg/kg/BW/d, respectively).

Target hazard quotient and hazard index

The data on THQ and HI (combined THQ) for studied fruits and vegetables are summarized in Table 7. The data presented in Table 7 showed that among the other studied trace elements $\text{THQ} > 1$ values were obtained only for **Cu** and **Hg**. $\text{THQ} > 1$ values obtained for **Cu** for males showed a decreasing order of potato > bean > grape > raspberry > fig > greens and for females: potato > bean > raspberry > grape > fig > greens. THQ values of Hg both for males and females exceeded 1 in the case of consumption of fig and maize. From Table 7 it is also obvious that there is a potential risk to local population's health through more than one studied trace elements. The HI value expresses the combined noncarcinogenic effects of multiple elements. $\text{HI} > 1$ values obtained for investigated fruits and vegetables showed a decreasing order of fig > potato > bean > raspberry > maize > grape > greens.

Conclusions

The safety of agricultural products growing in metal mining areas is of wide concern. Accumulation of trace metals in plants occur by various sources but soil is considered the major one, as the transfer of trace elements from soil to plant is one of the key factors of human exposure through food chain. In the present study, the soils to plant TFs varied from element to element depending on the types of investigated fruits and vegetables and are less than 1. However, it should be stressed that there were trace elements (Ni, Pb, Zn, and Cd) that exceeded the maximum allowable levels, meanwhile others either did not exceed or did not have established maximum allowable levels. It can also be emphasized that studied fruits and vegetables had high contribution in dietary exposure of trace elements. EDIs of Cu, Ni, and Hg for the majority of studied fruits and vegetables exceeded the health-based guideline values. Meanwhile, in case of combined consumption of the studied food items, the estimated cumulative daily intakes exceeded health-based guideline values not only for the aforementioned trace elements but also for Zn in the following sequence: $\text{Zn} > \text{Hg} > \text{Ni} > \text{Cu}$. Besides, $\text{HI} > 1$ values highlighted the potential adverse health effects for local population through more than one trace element *via* consumption of fig, potato, bean, raspberry, maize, grape, and greens. Furthermore, detailed investigations need to be done for the overall assessment of health risks, taking into consideration not only adverse health effects posed by more than one toxic trace elements but also other exposure pathways (inhalation, dermal, *etc.*).

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Declaration of interest

The authors declare that they have no conflicts of interest.

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