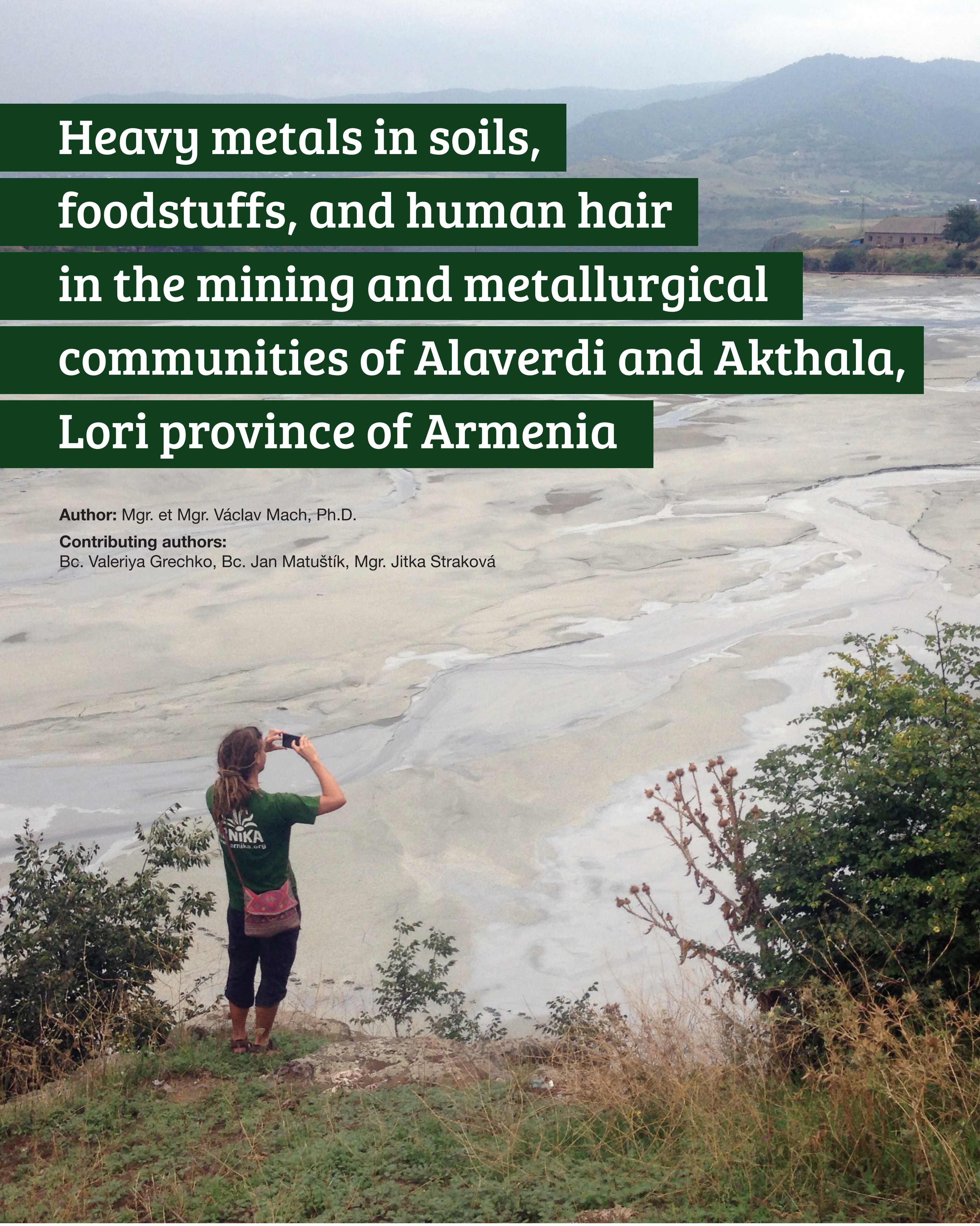
Heavy metals in soils, foodstuffs, and human hair in the mining and metallurgical communities of Alaverdi and Akthala, Lori province of Armenia



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This report was prepared and published as a part of the project "Empowering civil society in Alaverdi and Akhtala in addressing problems with industrial pollution", with the financial assistance of the Ministry of Foreign Affairs of the Czech Republic under the Transformation Cooperation Programme. The production of this publication was also made possible thanks to the Global Greengrants Fund.

The Project was implemented by Arnika – Toxics and Waste Programme, based in Prague, Czech Republic, Center for Community Mobilization and Support (CCMS), based in Alaverdi, Armenia, and Ecolur, based in Yerevan, Armenia.

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Summary

The study was focused on the monitoring and evaluation of pollution by heavy metals in the industrial region of Alaverdi and Akhtala in the north-east of Armenia. A set of samples of soil, foodstuffs (home-grown vegetables, fruits, and honey), and human hair was carried out to monitor the distribution of industrial contamination with respect to various legislative limits and potentially hazardous effects on human health. The samples were taken on nine farms on an area that covers the close surroundings of industrial facilities in Alaverdi (the Alaverdi metallurgical plant) and community of Akhtala (copper mines and tailing ponds) in July 2019. These are located on or near the River Debed. All of these facilities can be potential sources of heavy metal contamination, not only for their close surroundings but also for more distant regions.

Increased levels of arsenic, cadmium, copper, molybdenum, nickel, and lead were found in the soils of the area that was investigated. Most of the sites that were sampled can be considered as polluted. The levels of these pollutants could represent a threat to the environment and human health in some cases. The concentrations of heavy metals in multiple soil samples exceed various legal standards, most frequently the Armenian soil standard, but in many cases also the Dutch soil standard, French soil standard, Czech soil standard, and the United States Environmental Protection Agency (US EPA) level of the pollution limit for non-industrial areas. The concentrations of heavy metals in the samples show pollution caused by copper processing plants.

According to the results, all the presumed potential sources (the Alaverdi copper smelter, the Akhtala mines, and the tailing dams) seem to be threats to the environment. Analysis using the Risk-Integrated Software for Cleanups (RISC) indicated that the most risky heavy metal in the area of interest was arsenic, followed by cadmium. Higher concentrations of heavy metals in garden soils indicate anthropogenic pollution with potential hazardous effects on the health of the local population.

The maximum levels of cadmium and lead in foodstuffs set by the FAO/WHO and the European Union were met in our samples of fruits and vegetables. In the case of the food safety requirements set by an Order of the Minister of Healthcare of Armenia, one leaf vegetable sample (Malva) exceeded the maximum permissible level of cadmium. We did not find significantly higher levels of heavy metals in vegetables and fruits than other studies from the same mining area, except one leaf vegetable sample (Malva). The calculations show that none of the heavy metals exceed the reference value of the target hazard quotient when a mix of the foodstuffs that were investigated is consumed.

From thirteen hair samples taken in the mining area, most of them show good or normal results comparable with other studies investigating pollution with heavy metals from around the world. One sample contained a significantly higher mercury concentration, but safely below the US EPA recommendation of a 1.0 mg/kg reference dose not to be exceeded in women of childbearing age.

Three hair samples from one farm located in Akori contained elevated levels of nickel in comparison with levels found in studies conducted in various sites around the world.

Continuous environmental monitoring should be performed to monitor the level of heavy metals and help with implementing strategies to reduce the impact of contamination on the inhabitants. Detailed investigations need to be performed for the overall assessment of the health risks posed by heavy metals, taking into consideration not only adverse health effects posed by the ingestion of vegetables but also through other exposure pathways. Moreover, it would be useful to monitor the presence of heavy metals in other human tissues in addition to hair. To mitigate the health risks, community members' awareness on the issue and their training in risk mitigation and involvement in solving the problem should be prioritized. If BAT/BEP standards are not yet in place in mining and metallurgical operations, we can recommend their implementation, which could reduce the additional burden of heavy metal exposure for local residents.

This document has been produced with the financial assistance of the Ministry of Foreign Affairs of the Czech Republic under the Transformation Cooperation Programme.

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1. Introduction

Heavy metal pollution has pervaded many parts of the world. Although heavy metals are natural components of the earth's crust, certain activities on the part of mankind, such as mining and smelting, have caused increased concentrations of heavy metals in the environmental compartments.[i] In some areas heavy metal concentrations have reached potentially harmful levels. In addition to mining and smelting, sources such as vehicle emissions, industrial waste, and fertilizers also contribute to the accumulation of heavy metals in the soil, atmosphere, and surface water.[ii] The various heavy metals can cause adverse effects on the human body, having toxic and carcinogenic effects and causing the oxidative deterioration of biological macromolecules.[iii] Exposure to pollutants such as heavy metals is one of the major environmental and public health concerns.

This study is focused on the presentation and assessment of data related to contamination by heavy metals in a mining area in the vicinity of the towns of Alaverdi and Akhtala in the Lori region in Armenia. In this mining region the production of food of plant origin is developed and the fruits and vegetables that are produced are the major source of food for the local population. With regard to the fact that in the study region the consumption of food of plant origin in the overall diet is significantly higher, the monitoring of heavy metals in vegetables and fruits that are consumed can be considered as an efficient tool for health risk assessment, simultaneously with providing appropriate information about any threat and risk regarding exposure to heavy metals. Previous research studies conducted in the mining region found heavy metal pollution in different environmental compartments. These works dealt with soil pollution[iv v vi], concentrations of heavy metals in the river water of the River Debed and their effect on aquatic life[vii viii] , levels of heavy metals in agricultural crops[ix x], and the burdening of humans by some heavy metals[xi xii xiii]. The river ecosystem in the catchment basin of the River Debed was exposed to heavy metal pollution to a degree that may have posed health risks to aquatic life as well as to humans because of mining and metallurgical industrial activities and the inadequate management of industrial waste and wastewater.xiv Moreover, concentrations of the trace elements that were studied in fruits and vegetables demonstrated that some trace elements (Cu, Ni, Pb, Zn) among most samples exceeded the maximum allowable limits set by international organizations. It may be concluded that habitual and combined consumption of the above-mentioned fruits and vegetables can pose a health risk to the local population.[xv] The potential sources of pollution that were discussed are the Alaverdi copper smelter, the copper mine in Akhtala and the copper and molybdenum mine in community of Shnogh, Teghut, and tailing dams in Akhtala, Teghut, and Mets Ayrum. The study follows up and continues the work of previously published studies and expands their findings with additional results from sites which were not monitored.

The present study was conducted to assess the risk to human health posed by heavy metals through the intake of vegetables and fruits grown on farms in the mining region. Nine selected farms that provide vegetables and fruit as sources of alimentation for the families living on them are located in and around the municipalities of Alaverdi and Akhtala. For that purpose, a set of environmental and biological samples from nine rural farms in the area of interest was taken and analysed. Soil samples were taken in vegetable gardens or other agricultural fields of the nine farms that were investigated. Biological samples included vegetables and fruits grown on the farms that were investigated, human hair from people living on the farms that were investigated, and honey from two bee-keepers who live near the farms. The environmental and biological samples were analysed for their heavy metal content and the results of the analysis are reported in this study. The aim of the study is to monitor the presence of heavy metals in the surroundings of industrial areas and to analyse its effects on both human health and the quality of the environment.

The sampling was followed by chemical analyses of heavy metals in all the samples of soil and hair that were collected, and in the majority of samples of fruits and vegetables. Some samples of fruits and vegetables were not analysed for the reason of limited financial resources. Samples of soil, vegetables and fruits, honey, and human hair were analysed for their content of various heavy metals (mercury, arsenic, cadmium, copper, molybdenum, nickel, lead, and chromium). The analyses of the soil samples took place at the University of Chemistry and Technology in Prague (Czech Republic); the samples of honey, vegetables, and fruits were analysed by the National Institute of Public Health in Prague (Czech Republic); and the samples of human hair were analysed by the National Institute of Public Health in Ústí nad Labem (Czech Republic).

2. Locality

The area of our interest is located in the surroundings of the municipal communities of Alaverdi and Akhtala, which are located in the Lori Province in the north-eastern part of Armenia, near the border with Georgia. Community of Alaverdi is located along the bank of the River Debed in the gorge of the Small Caucasian chain, at an altitude of 750–1400 m. One of the districts of the town is located above the gorge, while the other parts of the town are scattered across the river inside the gorge. The town has an approximate population of 11,000 (2016). Akhtala is a historical town situated 10 km north-east of Alaverdi, at the base of Mount Lalvar. As in Alaverdi, one of the town districts is separated and located on a hill towards the southern part of the city. The town is located along the River Shamlugh, which enters the Debed. The population of Akhtala is around 1300 (2016).

Because of the geographical position, hypsometric fluctuations, atmospheric circulation, and complicated mountain relief of the Debed basin, a comparatively mild and humid climate is found in the area. Because of the geological and hydrogeological structure, relief characteristics, and heavy precipitation of the Debed catchment area, it is characterized by a dense hydrographic network. The sources of river alimentation in the area include snow, rain, and groundwater. The River Debed is characterized by an unstable flow regime and large fluctuations in water levels.

The potential sources of pollution in the vicinity of municipal communities are the Alaverdi copper smelter, the copper mine and tailing ponds in Akhtala, including Mets Ayrum. These facilities can be potential sources of the leakage of heavy metals into the environment. The main emission from the mines is acidic mine drainage water. The smelting factory contributes to environmental pollution through atmospheric emissions via smokestacks, liquid wastewaters, and also solid emissions such as slag. The tailing ponds, however, should not contribute to emissions if built and operated properly. However, it is a common phenomenon that the dams of tailing ponds leak or polluted water is discharged into nearby watercourses on purpose, so the tailings pond does not overflow, which violates operating standards.

The metallurgical plant in Alaverdi is currently managed by the Russian bank VTB, which acquired the enterprise for debts from Armenian Copper Programme, CJSC, a company that is a member of the Vallex Group. Since the end of the 18th century, the town of Alaverdi has been home to a copper smelting plant. The Alaverdi copper smelter is able to produce about 12,000 tonnes of blister copper annually. The peak of production was achieved in the 1980s, when nearly 55,000 tons of refined copper were produced annually.[xvi] A dominant feature of the factory is a chimney that smokes non-stop on the hill above the factory. The chimney of the plant was transferred from the territory of the city to the forest territory of Lalvar Forestry, not more than a few hundred meters higher than before, and the smoke covers a large part of the town of Alaverdi and the surrounding villages. The smelter is a potential producer and emitter of heavy metals. The operation of the cooper smelter has been suspended since October 2018 because of non-payment of debts of “Armenian Kapr Program” company to VTB Bank. The company was transferred into the ownership of the bank as a pledge.

Near the extended community od Akhtala (urban village Shamlugh) there is Shamlugh copper deposit is located. The ore is processed in the Akhtala Mountain Enrichment Combine, This company also uses an open tailing dam at Nahatak, which is 300 m far from the closest farm located in village of Mets Ayrum. The company previously operated two other tailings, which are considered closed, but in reality, are washed away from the surface as a result of rains and other precipitation. Flushing and leakage of tailings, acid drainage, as well as accumulations of dumps and waste rocks are potential sources of environmental pollution by heavy metals. Residents report cases of contamination of water for irrigation, and even drinking water by contaminants with mud of different colour (yellow or blue). Local residents also claim to suffer from illnesses such as nausea, headaches, or cancer.[xvii]

During the sampling campaign we visited nine sampling sites represented by farms in the area of interest. Samples of soil, foodstuffs, and human hair were taken at these sampling sites. The farms that were visited are located in eight municipal communities: Alaverdi, Akhtala, Akori, Sanahin, Shamlug, Hakhpat, Mets Ayrum, and Chochtan. The sampling sites are presented in Tables 17, 18, and 19 in lists of samples in Annex I. The exact GPS coordinates of the sampling sites are not listed in order to maintain the anonymity of the people who cooperated during the sampling campaign.

3. Methodology

3.1 Sampling procedures

The sampling was conducted according to a sampling plan covering nine sampling sites close to potential sources of contamination using a combination of results from previous studies, the Google Earth system, and reports from local activists. The samples of soils and foodstuffs were taken from private vegetable and fruit gardens in July 2019. One sample of soil and two to five samples of fruits and vegetables were taken in vegetable gardens or other agricultural fields of each of the nine farms that were investigated. One to three hair samples of people consuming vegetable products from the gardens were taken at the farms. Additionally, two samples of honey were collected from two different bee-keepers that have colonies around the farms.

In total, nine soil samples, 30 fruit and vegetable samples, two honey samples, and 13 hair samples were taken at the sampling sites that were investigated. Four samples of fruit and vegetables were not analysed for the reason of limited financial resources. Detailed lists of the samples that were analysed are presented in Tables 17, 18, and 19 in Annex I.

Samples of soils were taken as mixed samples formed of five partial subsamples taken from points forming a square shape at each sampling site. The samples were taken with a steel trowel from the surface layer of the soil from which potential vegetal cover was removed. The samples were homogenized in a steel bowl and transferred into 250-ml polyethylene containers with screwed-on lids. The mixed samples were homogenized in a steel bowl, and some of them were quartered after homogenization. After each sampling, all the sampling equipment was cleaned with tap water. The samples were initially stored in a dry place at normal temperature and then, after being transported to the laboratory, in a refrigerator, where they were kept until the analysis.

A total of 15 plant species, including eight species of fruits, one species of pods, one species of bulb vegetable, three species of root and tuber vegetables, and two species of fresh herbs or leaf vegetables were sampled. Additional details on the fruits and vegetables that were sampled are given in Table 18 in Annex I. These plant species were cultivated in private gardens and orchards on the farms that were investigated. Several subsamples of the same plant species were randomly taken from all the selected home gardens and farmlands to form composite samples and ensure their representativeness. The samples were initially stored in a dry place in a refrigerator. While being transported to the laboratory, they were placed in a cooling box and then again in a refrigerator, where they were kept until the analysis.

Human hair was taken from persons living on the farms that were investigated and consuming fruit and vegetables produced there. All the relevant information is recorded in the questionnaire which is part of each sampling protocol. The information provided is confidential unless the giver agrees with its presentation, and therefore the samples were analysed anonymously, with only the information necessary for good evaluation of the results. These include whether and how often the giver eats fish, if the person smokes or lives in the presence of a smoker, and if the person dyes his or her hair. Selected information is shown in Table 19 Annex I. Strands of hair were cut from the occipital region of the head, as close to the scalp as possible.

3.2 Analytical methods

Chemical analyses for the determination of the heavy metal (As, Cd, Cu, Mo, Ni, Pb, Cr) concentration in soil were conducted using atomic absorption spectrometry in mineralized samples. Prior to the analysis, the environmental samples underwent several operations. The samples were homogenized and a representative part (20 g) was used for the determination of dry matter by a gravimetric method. Another representative part was taken for the analysis of heavy metals by means of a mineralization procedure. The analytical procedure used for the mineralization as follows: 15 g of the sample was placed into a beaker together with 100 ml of distilled water, 30 ml of concentrated nitric acid, and 10 ml of concentrated hydrochloric acid. The mixture was boiled for two hours. Then, after cooling, it was filtered through a fluted filter paper. The filtered solutions were used for the determination of heavy metals by means of Atomic Absorption Spectrometry (AAS) using a Microwave Plasma Atomic Emission Spectrometer (Agilent Technologies). The analyses were conducted at the University of Chemistry and Technology in Prague.

Heavy metals (Hg, As, Cd, Cu, Mo, Ni, Pb) in the samples of foodstuffs (vegetables, fruits, and honey) and hair were analysed by the National Institute of Public Health of the Czech Republic in Prague using inductively coupled plasma mass spectroscopy (ICP-MS) and the mercury levels were determined with an AMA-254 Single-Purpose Atomic Absorption Spectrometer.

3.3 Health risk assessment of soils

The health risk assessment is based on the assumption that under certain specified conditions there is a risk of damage to human health, while the risk rate from zero to maximum is determined by the type of activity, length of stay in the location, and the environmental conditions. A zero health risk is not really possible; however, the risk of damage must be minimized to an acceptable level in terms of health and environmental risks. To determine the risk, it is necessary to clarify the most important transport routes and then specify exposure scenarios for potentially threatened recipients. There are two approaches to the evaluation of the dose effects – for substances with a threshold (non-carcinogenic) and non-threshold (carcinogenic) effect.

For substances with a non-carcinogenic effect it is anticipated that the body repair processes are able to cope successfully with exposure to a toxic substance, but only up to a certain dose, and then the effect is already apparent. The threshold, known as NOAEL (No Observed Adverse

Effect Level), is the exposure level at which no adverse effects are observed. Alternatively, LOAEL (Lowest Observed Adverse Effect Level) values can be used. They correspond to the lowest dose levels at which negative health effects are observed. ADI (Acceptable Daily Intake) and RfD (Reference Dose) are derived using NOAEL or LOAEL values and the relevant UF (Uncertainty Factors) or MF (Modifying Factors). These factors have to compensate for all the uncertainty and variability in determining the NOAEL or LOAEL values. The results of the calculation (ADI or RfD) are usually much lower than NOAEL or LOAEL and represent the estimation of the daily exposure of the human population (including sensitive population groups) which is very likely to pose no risk of adverse effects to human health, even if it lasts throughout a lifetime. In the case of carcinogenic substances, it is assumed that there is no such thing as a dose that would not cause modifications at the molecular level and subsequently lead to the development of malignant disease. Evaluation of the dose-effect relation uses the SF (Slope Factor) parameter, which indicates the possible top edge of the probability of malignant disease per unit of average daily dose received throughout a lifetime.[xviii]

For the calculation of risk exposure to substances with a non-carcinogenic effect a received and absorbed dose with an acceptable toxicological intake of the substance is compared (i.e. RfD – Reference Dose). The risk level then represents the Hazard Quotient (HQ). The calculation is performed according to the equation:

$$HQ = \frac{E}{RfD}$$

E – Parameter Average Daily Dose (ADD) or Lifetime Average Daily Dose (LADD), or Chronic Daily Intake (CDI) (mg/kg.day);
RfD – Reference Dose (mg/kg.day).

The calculation method for substances with a carcinogenic effect uses the ELCR – Excess Lifetime Cancer Risk – parameter (a dimensionless indicator corresponding to the probability of developing cancer with lifetime exposure, which can be described by the following equation):

$$ELCR = CDI \cdot SF \quad ELCR = LADD \cdot SF$$

CDI – parameter Chronic Daily Intake, or Lifetime Average Daily Dose (LADD) relative to lifetime exposure over 70 years (mg/kg.day);
SF – Slope Factor (mg/kg.day).

Risk-Integrated Software for Cleanups (RISC) is a software package developed to assess human health risks in contaminated areas. It can integrate up to fourteen possible exposure pathways, and calculates the risks associated with them, both carcinogenic and non-carcinogenic.

Table 1: Agents classified by the International Agency for Research on Cancer (IARC).[xix]

Group 1	Carcinogenic to humans	arsenic and inorganic arsenic compounds
Group 2A	Probably carcinogenic to humans	inorganic compounds of lead
Group 2B	Possibly carcinogenic to humans	lead
Group 3	Not classifiable regarding its carcinogenicity to humans	organic compounds of lead
Group 4	Probably not carcinogenic to humans	

3.4 Health risk assessment of foodstuffs

The estimated daily intake (EDI) and target hazard quotient (THQ) were calculated in a similar way to a study investigating heavy metal loads in the same area in recent years.[xx] The estimated daily intake (EDI) of the heavy metals that were assessed by human subjects was calculated using the following equation, which is recommended by the US EPA[xxi]:

$$EDI = \frac{(C \cdot IR \cdot EF \cdot ED)}{(BW \cdot AT)}$$

where EDI is the average daily intake or dose through ingestion (mg/kg of body weight/ day), C is the trace element concentration in the exposure medium (mg/kg), IR is the ingestion rate (kg/day), and EF is the exposure frequency (day/year); the values of IR and EF that were used for each foodstuff are shown in Table 2; ED is the duration of the exposure (it was set to 63.6 years for males and 69.7 years for females on the basis of the average life expectancy, starting from eight years of age); BW is the body weight (kg). 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 days multiplied by the number of exposure years). Cumulative daily intakes were calculated as the sum of the individual EDI values for each trace element.

Table 2: Values of ingestion rate and exposure frequency used for the calculation of EDI.

Foodstuff	IR [kg/day]	EF [day/year]
Hazelnuts	0.1	24
Beans	0.2	100
Potatoes	0.2	100
Malva	0.02	30
Onions	0.1	100
Nectarines	0.2	60
Figs	0.1	60
Plums	0.2	60
Basil	0.005	100
Cornelian cherries	0.1	30
Pears	0.2	60
Beetroot	0.2	100
Carrots	0.2	100
Apples	0.2	60
Honey	0.01	100

The human health risk caused by exposure to trace elements can be expressed in terms of THQ. THQ, based on the 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.

$$THQ = \frac{EDI}{RfD}$$

The RfDs applied for nickel, molybdenum, arsenic, and cadmium were 0.02, 0.005, 0.0003, and 0.001 mg/kg BW/d, respectively[xxii xxiii xxiv xxv]. Taking into consideration the provisional tolerable weekly intake, the oral RfD for lead was 0.0035 mg/kg/BW/d.[xxvi] For inorganic mercury, the tolerable weekly intake (0.004 mg/kg/BW/d) was considered.[xxvii] The dietary reference intake (0.01 mg/kg/BW/d) was used as an RfD for copper.[xxviii] If the value of THQ is less than 1, the risk of non-carcinogenic 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 hazard index (HI) to estimate the risk of a mixture of contaminants. The HI refers to the sum of more than one THQ for multiple substances.[xxix]

4. Results

Summary results of heavy metals in soils, foodstuffs, and hair are shown in Tables 3, 4, and 5, respectively. All the results of the analytical measurements for each sample are shown in Tables 20, 21, and 22 in Annex II.

Table 3: Summary of heavy metal concentrations in soil samples.

	Arsenic [mg/kg DW]	Cadmium [mg/kg DW]	Copper [mg/kg DW]	Molybdenum [mg/kg DW]	Nickel [mg/kg DW]	Lead [mg/kg DW]	Chromium [mg/kg DW]
min	27.85	0.29	98.80	0.33	11.36	10.34	12.88
max	146.80	12.90	7737.32	5.87	58.42	173.74	67.63
mean	52.47	2.51	1289.91	2.14	40.84	77.53	43.24
SD	37.28	4.05	2476.96	1.81	13.65	55.10	14.09

Table 4: Summary of heavy metal concentrations in foodstuff samples.

	Mercury [mg/kg FM]	Arsenic [mg/kg FM]	Cadmium [mg/kg FM]	Copper [mg/kg FM]	Molybdenum [mg/kg FM]	Nickel [mg/kg FM]	Lead [mg/kg FM]
min	<0.001	<0.01	<0.005	0.15	<0.005	<0.05	<0.05
max	0.001	0.07	0.03	6.81	8.85	0.61	0.22
mean	0.0001	0.02	0.00	1.22	1.06	0.10	0.01
SD	0.0003	0.03	0.01	1.31	2.27	0.13	0.04

Table 5: Summary of heavy metal concentrations in hair samples.

	Mercury [mg/kg]	Arsenic [mg/kg]	Cadmium [mg/kg]	Copper [mg/kg]	Molybdenum [mg/kg]	Nickel [mg/kg]	Lead [mg/kg]
min	0.021	<0.1	0.01	7.8	<0.5	<1	0.21
max	0.65	0.14	0.07	16.3	<0.5	45.1	1.58
mean	0.113	0.14	0.03	10.58	<0.5	16.31	0.76
SD	0.166	0.04	0.02	4.54	0.00	15.73	0.50

5. Discussion

First, various legal standards and auxiliary evaluation criteria of heavy metals in soils and foodstuffs are presented in this chapter. Then the concentrations of heavy metals determined in the soil samples from the sampling sites are compared to the respective legal standards and commonly occurring levels. Additionally, the carcinogenic and non-carcinogenic risks associated with heavy metals were calculated for the soil samples. Furthermore, the concentrations of heavy metals determined in the samples of foodstuffs are compared to the respective legal standards and levels that were measured in previous studies. Finally, the heavy metal levels in the hair samples are evaluated.

5.1 Legal standards

While the presence of some elements in different inorganic and organic matrices in various concentrations is natural, there may not be a clear way to identify a threshold of pollution. Different regions have their own geochemical background. The main differences in distinguishing polluted and clean areas come out from medical studies evaluating changes in human health. However, it is the regional legislation which is binding. Therefore, several threshold and limit concentrations from different approaches were used for comparison with the results of the samples to gain a view of local pollution levels.

The concentrations of heavy metals in the soil and sediment samples were compared to the Armenian soil standards (Order No. 01-N of 25 January 2010 of the Minister of Health of the Republic of Armenia “On Approving Sanitary Rules and Norms N 2.1.7.003-10 for Sanitary Requirements for Land Quality”). Armenia has one of the strictest limits (along with Russia) on soil pollution. For comparison, the French and Dutch soil standards according to the literature are shown. The values of the Czech pollution indicators shown in Table 6 are taken from Czech Decree No. 153/2016 issued by the Ministry of Agriculture, which describes the quality and protection of agricultural soil. These indicators show levels whose exceeding may present a threat to human and animal health (As, Cd, Hg, Pb) or plant growth or production (Cu, Ni).

Concentrations of pollutants in soil samples were also compared with the US EPA Regional Screening Levels (RSL). Regional screening levels were derived by the US EPA (United States Environmental Protection Agency) for some compounds that have a CAS registration number. RSLs are concentrations of chemical compounds in the environment (soils, sediments, water, and air). These levels were derived using exposure parameters and factors representing the maximum justifiable chronic exposure. This exposure is based on direct contact with target compounds. If the RSLs are exceeded, further exploration or removal of the contamination should be carried out. Some specific features should be taken into account when RSLs are used, such as the content of some substances as a result of geological conditions. There are two RSL categories – land used for industrial purposes and land used for other purposes (living, relaxation, or agriculture).

For the evaluation of fruits and vegetables, the maximum levels of heavy metals were used. The regulation of European Commission No 1881/2006 setting maximum levels of certain contaminants in foodstuffs regulates the maximum limit of heavy metals in various food products on the European market. However, this regulation only sets a maximum level for cadmium and lead; for other heavy metals maximum levels are not defined for vegetables and fruits. Similarly, *Codex Alimentarius: General standard for contaminants and toxins in food and feed* by the FAO/WHO sets maximum levels in various vegetables and fruits only for the same two heavy metals. The national legislation in Armenia includes maximum permissible levels for more heavy metals and is listed in the Order of the Minister of Healthcare of Armenia approving Food Safety Requirements (Table 9).

The concentrations of heavy metals determined in the soil and foodstuff samples were compared to the maximum allowed or reference concentrations as defined in decrees, norms, or laws. Various legal criteria or reference levels of heavy metals for soils are presented in Table 6. The maximum levels of heavy metals in foodstuffs defined for the market in the European Union, by the FAO/WHO in the Codex Alimentarius, and in Armenia are presented in Tables 7, 8, and 9, respectively.

Table 6: Legal standards for heavy metals in soils

Legal standard	**Arsenic [mg/kg DW]**	**Cadmium [mg/kg DW]**	**Copper [mg/kg DW]**	**Molybdenum [mg/kg DW]**	**Nickel [mg/kg DW]**	**Lead [mg/kg DW]**	**Chromium [mg/kg DW]**
Armenian soil standards[xxx]	2	NA	3	NA	4	32	6
French soil standards	37	20	190	NA	NA	400	NA
Dutch soil standards	34	1.6	40	254	38	140	100
Czech soil pollution indication[xxxi]	40	20	300	NA	200	400	NA
Levels of pollution limits – industrial areas (US EPA)[xxxii]	2.4	800	41,000	5,100	20,000	800	NA
Levels of pollution limits – other areas (US EPA)[xxxiii]	0.61	70	31,000	390	1,500	400	NA

Table 7: Maximum levels of heavy metals used for foodstuffs placed on the market in the European Union. Concentrations of heavy metals are expressed in mg/kg of fresh matter [mg/kg FM].[xxxiv]

Foodstuffs	**Mercury [mg/kg FM]**	**Arsenic [mg/kg FM]**	**Cadmium [mg/kg FM]**	**Copper [mg/kg FM]**	**Molybdenum [mg/kg FM]**	**Nickel [mg/kg FM]**	**Lead [mg/kg FM]**
Vegetables and fruits, excluding root and tuber vegetables, leaf vegetables, fresh herbs, leafy brassica, stem vegetables.	**-**	**-**	**0.05**	**-**	**-**	**-**	
Root and tuber vegetables (excluding celeriac, parsnips, salsify, and horseradish), stem vegetables (excluding celery). For potatoes the maximum level applies to peeled potatoes.	**-**	**-**	**0.1**	**-**	**-**	**-**	
Leaf vegetables, fresh herbs, leafy brassica, celery, celeriac, parsnips, salsify, horseradish, and some fungi.	**-**	**-**	**0.2**	**-**	**-**	**-**	
Legume vegetables, cereals, and pulses.	**-**	**-**		**-**	**-**	**-**	**0.2**
Vegetables, excluding brassica vegetables, leaf vegetables and fresh herbs. For potatoes the maximum level applies to peeled potatoes.	**-**	**-**		**-**	**-**	**-**	**0.1**
Brassica vegetables, leaf vegetables, and some fungi.	**-**	**-**		**-**	**-**	**-**	**0.3**

Fruit, excluding berries and small fruit.	-	-		-	-	-	**0.1**
Berries and small fruit	-	-		-	-	-	**0.2**

Table 8: Maximum levels of heavy metals in foodstuffs defined by the FAO/WHO in the Codex Alimentarius: General standard for contaminants and toxins in food and feed. Concentrations of heavy metals are expressed in mg/kg of fresh matter [mg/kg FM][xxxv]

Foodstuffs	**Mercury [mg/kg FM]**	**Arsenic [mg/kg FM]**	**Cadmium [mg/kg FM]**	**Copper [mg/kg FM]**	**Molybdenum [mg/kg FM]**	**Nickel [mg/kg FM]**	**Lead [mg/kg FM]**
Brassica vegetables	-	-	0.05	-	-	-	0.1
Bulb vegetables	-	-	0.05	-	-	-	0.1
Fruiting vegetables	-	-	0.05	-	-	-	0.05
Leaf vegetables	-	-	0.2	-	-	-	0.3
Legume vegetables	-	-	0.1	-	-	-	0.1
Pulses	-	-	0.1	-	-	-	0.2
Root and tuber vegetables	-	-	0.1	-	-	-	0.1
Stalk and stem vegetables	-	-	0.1	-	-	-	-
Fruits with the exception of berries and other small fruits	-	-	-	-	-	-	0.1

Table 9: Maximum permissible levels of heavy metals in foodstuffs defined for Armenia.[xxxvi] Concentrations of heavy metals are expressed in mg/kg of fresh matter [mg/kg FM].

Foodstuffs	**Mercury [mg/kg FM]**	**Arsenic [mg/kg FM]**	**Cadmium [mg/kg FM]**	**Copper [mg/kg FM]**	**Molybdenum [mg/kg FM]**	**Nickel [mg/kg FM]**	**Lead [mg/kg FM]**
Nuts	0.005	0.3	0.1	-	-	-	0.5
Vegetables and fruits	0.02	0.2	0.03	-	-	-	0.5

5.2 Evaluation of heavy metal levels in soil

One of the objectives of the research was to determine the concentration of heavy metals in various soil samples taken from private agricultural allotments in the mining area in Armenia and compare the measured data with legal standards and with concentrations mentioned in other studies. Since the Armenian soil standards for heavy metals are very strict, a high number of samples (in fact almost all of them) do not meet the limits of Order No. 01-N of 25 January 2010 of the Minister of Health of the Republic of Armenia “On Approving Sanitary Rules and Norms N 2.1.7.003-10 for Sanitary Requirements for Land Quality”. Therefore, another comparison was made with the US EPA recommendation for non-industrial areas and French, Dutch, and Czech soil standards, which describe the protection of the quality of agricultural soil. As the US EPA recommendation is based on health risks, it could be considered as the most useful of these reference values.

The overall mean value of the total **arsenic** for different soils is estimated as 6.83 mg/kg. The background contents of various soil groups range from <0.1 to 67 mg/kg. The range of arsenic in soils in the United States is broad, from <0.1 to 93 mg/kg, and the geometric mean for arsenic in topsoil in the United States is reported to be 5.8 mg/kg. An arsenic content of 9.7 mg/kg is reported for surficial materials in Alaska and an arsenic range of 4–15 mg/kg in uncontaminated soils in Canada. The background value in Slovakia is given as 7.2 mg/kg. The range of arsenic in soils in Poland is 0.9–3.4 mg/kg. Western Siberian soil has an arsenic content from 18 to 32 mg/kg.[xxxvii] The mean concentration of arsenic in the soil samples (52.47 mg/kg DW) is several times higher than the worldwide average and other averages in the countries mentioned above. Moreover, the mean concentration of arsenic in the soil is more than three times higher than the mean concentration of arsenic in the soil and sediment samples reported by Arnika Association one year earlier.[xxxviii] The levels of arsenic in all the soil samples exceeded the Armenian soil standard and US EPA levels of pollution limits for non-industrial areas and most of them (67%) exceeded the French, Dutch, and Czech soil standards (Table 10). The high arsenic levels indicate widespread arsenic pollution of the soil of private gardens. This fact is most probably not caused by the release of arsenic from the bedrock, but as a result of industrial pollution. For the proper evaluation of arsenic pollution, the data about the natural background is necessary, as it could vary significantly.

Our results are consistent with the previous research of arsenic soil contamination that classified Alaverdi and Akhtala as moderately to strongly polluted. This research[xxxix] found that 75.5% of the soil samples exceeded the Clean-up Level for arsenic in the town of Alaverdi and so did 3.2% of the soil samples in the town of Akhtala. In Alaverdi the results suggested the influence of emissions from the copper smelter on contamination. In Akhtala anthropogenic influence was related to the operation of industrial activities.

The world average soil **cadmium** concentration is estimated as 0.41 mg/kg. The main factor determining the cadmium contents of soils is parent material. The average contents of cadmium in soils lie between 0.2 and 1.1 mg/kg. Surface soils from the major agricultural production areas of the United States contain cadmium within the range of <0.01 to 2.0 mg/kg (geometric mean 0.175 mg/kg). The cadmium content in reference soils from different countries ranges from 0.06 to 4.3 mg/kg. Soils from Sichote-Alin (a remote region of Russia) contain cadmium from 0.2 to 1.14 mg/kg, with the greatest concentration in flooded soils. Relatively high cadmium contents, up to 8.9 mg/kg (on average 0.3 mg/kg), are reported for some topsoils in the Slovak Republic.[xl] The mean concentration of cadmium in our soil samples (2.51 mg/kg DW) is several times higher than the worldwide average and the worldwide ranges mentioned above. This fact is mainly due to one soil sample (AKH1-S-1) with an outstanding value (12.9 mg/kg DW), but three other soil samples have cadmium concentrations so high that they lie outside the worldwide range. All the soil samples comply with the US EPA levels of pollution limits for non-industrial areas, and the French and Czech soil standards, but two samples (CHT1-S-1 and AKT1-S-1) exceed the Dutch soil standard (Table 10). The Armenian soil standards do not mention the maximum cadmium level in soil at all.

The general values for the average total **copper** contents in soils of different groups all over the world range between 14 and 109 mg/kg. The contents of copper are closely associated with soil texture and are usually lowest in light sandy soils and highest in loamy soils.[xli] The mean concentration of copper in the soil samples (1289.91 mg/kg DW) is nearly twelve times higher than the highest value of the averages of different soil groups mentioned above. This fact indicates that there is a very high level of copper that could not be caused only by its high content in the bedrock. All the soil samples exceed the Armenian, Dutch, and French soil standards and five samples exceed the Czech soil standards, but none of the soil samples exceed the US EPA levels of pollution limits for non-industrial areas (Table 10).

The world-soil average content of **molybdenum** in soils has been established as 1.1 mg/kg (range 0.9–1.8 mg/kg) and is fairly similar to its crustal abundance.[xlii] The mean concentration of molybdenum in the soil samples (2.14 mg/kg DW) is more than twice as high as the worldwide average content mentioned above. The molybdenum levels in our four soil samples lie outside the range of the worldwide natural content in soil mentioned above. This fact could be explained by a higher molybdenum background and its releasing from the bedrock as a result of mining activities. None of the soil samples exceed the Dutch soil standard and US EPA levels of pollution limits for non-industrial areas (Table 10).

Soils throughout the world contain **nickel** in a very broad range. This means that the concentrations as reported for various countries are within the range of 13–37 mg/kg.[xliii] The mean concentration of nickel in the soil samples (40.84 mg/kg DW) is higher than the worldwide range of nickel levels in soils mentioned above. This fact indicates that there are elevated nickel levels in the soil of the gardens that were investigated. The levels of nickel in all the soil samples exceeded the Armenian soil standard and five of them (56%) exceeded the Dutch soil standard as well. All the soil samples comply with the US EPA levels of pollution limits for non-industrial areas and the Czech soil standard for nickel (Table 10).

The overall mean value of total **lead** for different soils is estimated as 27 mg/kg. The background average contents given for soils in different countries vary from 18 mg/kg in Sweden to 27 mg/kg in China.[xliv] The mean concentration of lead in the soil samples (77.53 mg/kg DW) is more than twice as high as the averages mentioned above. This fact indicates that there are elevated lead levels in the soils of the gardens that were investigated. Six soil samples exceed the level of lead in the Armenian soil standard and one soil sample the Dutch soil standard. All the soil samples comply with the US EPA levels of pollution limits for non-industrial areas and the Czech and French soil standards for lead (Table 10). Previous research[xlv] on soil contamination in Alaverdi and Akhtala found even higher levels of pollution and stated that the Clean-up Level for lead was exceeded by 24.0% of the soil samples in Alaverdi and 27.1% in Akhtala. The analysis in that study showed that in the town of Alaverdi the amount of lead is significantly associated with proximity to the smelter and the anthropogenic origin of lead in the residential soil of Alaverdi and Akhtala.

The world average content of **chromium** in soils has been established as 60 mg/kg.[xlvi] The mean concentration of chromium in the soil samples (43.24 mg/kg DW) is lower than the worldwide average mentioned above. All the soil samples comply with the Armenian soil standard, but at the same time do not comply with the Dutch soil standard (Table 10).

Table 10: Number of soil samples that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the number of sediment or sand samples from each hotspot area are expressed in brackets.

Legal standard	**Arsenic**	**Cadmium**	**Copper**	**Molybdenum**	**Nickel**	**Lead**	**Chromium**
Armenian soil standards	9 (100%)	-	9 (100%)	-	9 (100%)	6 (67%)	0 (0%)
French soil standards	6 (67%)	0 (0%)	9 (100%)	-	-	0 (0%)	-
Dutch soil standards	6 (67%)	2 (22%)	9 (100%)	0 (0%)	5 (56%)	1 (11%)	9 (100%)
Czech soil standards	6 (67%)	0 (0%)	5 (56%)	-	0 (0%)	0 (0%)	-
Levels of pollution limits – industrial areas (US EPA)	9 (100%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	-
Levels of pollution limits – other areas (US EPA)	9 (100%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	-

5.3 Evaluation of soil pollution using the RISC model

The samples collected in the hot spot areas were used to perform a human health risk assessment. On the basis of the toxicological data, a risk assessment using the RISC software was performed for five heavy metals: arsenic, mercury, cadmium, nickel, and lead. Samples with results of the calculation of human health risks which exceeded 10^{-6} for ELCR and 1 for HQ for children or adults are presented in Tables 11, 12, and 13. A full list of the results of the calculation of human health risks (ELCR and HQ) for children or adults are presented in Tables 23, 24, 25, and 26 in Annex III.

If the carcinogenic risk (ELCR) is $<10^{-6}$, it is considered that there are no significant adverse health effects. If it is between 10^{-6} and 10^{-4}, adverse effects may occur in the future, and thus factors need to be taken into consideration. Finally, if it is $>10^{-4}$, the risk is unacceptable and serious measures must be taken immediately. A hazard quotient (HQ) <1 considers that there are no significant adverse health effects, whereas an HQ >1 implies that potential adverse health effects exist. More research must be done in order to determine any toxic threats. The results are based on the standard calculation coefficients defined in Risk-Integrated Software for Cleanups (RISC). The results are related to the average population.

The carcinogenic and non-carcinogenic risks of arsenic for local residents via several exposure pathways were evaluated for all the sampling sites. This evaluation included assessing exposure to arsenic by ingestion of soil (including dust ingestion), dermal contact, and the consumption of crops grown on the soil. The total Excess Lifetime Cancer Risk values for arsenic are between 10^{-6} and 10^{-4} for children in all nine soil samples and in eight soil samples for adults. In these cases, adverse effects may occur in the future, and thus factors need to be taken into consideration. For all the soil samples the problematic exposure pathway of carcinogenic risk for arsenic is the ingestion of crops grown on the soil that was examined, but the ingestion of soil is a potentially risky pathway for children in most of the soil samples as well (Table 11). Hazard quotients (HQ) which represent the non-carcinogenic risks posed by arsenic exceed a value of 1 for children in two (CHT1-S-1 and AKH1-S-1) of the soil samples (Table 12). According to the RISC evaluation of our soil samples, arsenic is the most problematic heavy metal for human health in the hot-spot area.

The non-carcinogenic risks posed by cadmium, nickel, and lead to local residents via several exposure pathways were also evaluated for soil samples collected at the sampling sites. Unacceptable risks (HQ >1) to children posed by cadmium were identified in one soil sample (AKH1-S-1). The problematic exposure pathway for cadmium is the ingestion of crops grown on the soil that was sampled. This result makes cadmium the second most risky heavy metal for human health in the hot-spot area. The hazard quotients for nickel and lead do not exceed the value of one in any of the soil samples, and therefore these metals do not represent unacceptable non-carcinogenic risks.

Table 11: Results of the calculation of carcinogenic human health risks (ELCR) associated with arsenic in soil samples taken in Armenia. ELCR values exceeding 10^{-6} are in bold.

Site	**Sample ID**	**Concentration [mg/kg DW]**	**ELCR for adults**				**ELCR for children**			
			Exposure pathway				**Exposure pathway**			
			Ingestion of soil	**Dermal contact with soil**	**Ingestion of vegetable**	**Total**	**Ingestion of soil**	**Dermal contact with soil**	**Ingestion of vegetable**	**Total**
1	AKR1-S-1	43.36	5.2E-07	1.6E-07	**1.5E-05**	**1.5E-05**	**1.2E-05**	6.9E-07	**2.2E-05**	**3.5E-05**
2	SAN1-S-1	41.29	5.0E-07	1.5E-07	**1.4E-05**	**1.5E-05**	**1.1E-05**	6.6E-07	**2.1E-05**	**3.3E-05**
3	ALA1-S-1	44.99	5.4E-07	1.7E-07	**1.5E-05**	**1.6E-05**	**1.2E-05**	7.2E-07	**2.3E-05**	**3.6E-05**
4	CHT1-S-1	146.80	1.8E-06	5.4E-07	**5.0E-05**	**5.2E-05**	**4.0E-05**	2.3E-06	**7.5E-05**	**1.2E-04**
5	AKH1-S-1	66.95	8.0E-07	2.5E-07	**2.3E-05**	**2.4E-05**	**1.8E-05**	1.1E-06	**3.4E-05**	**5.3E-05**
6	MTA1-S-1	29.52	3.5E-07	1.1E-07	**1.0E-05**	**1.0E-05**	8.0E-06	4.7E-07	**1.5E-05**	**2.3E-05**
7	HAG1-S-1	27.85	3.3E-07	1.0E-07	9.5E-06	9.9E-06	7.5E-06	4.5E-07	**1.4E-05**	**2.2E-05**
8	SHA1-S-1	40.95	4.9E-07	1.5E-07	**1.4E-05**	**1.5E-05**	**1.1E-05**	6.6E-07	**2.1E-05**	**3.3E-05**
9	MTA2-S-1	30.51	3.7E-07	1.1E-07	**1.0E-05**	**1.1E-05**	8.2E-06	4.9E-07	**1.6E-05**	**2.4E-05**

Table 12: Results of the calculation of non-carcinogenic human health risks (HQ) associated with arsenic in soil samples taken in Armenia. HQ values exceeding 1 are in bold. Only samples with HQ values exceeding 1 are listed in the table.

Site	**Sample ID**	**Concentration [mg/kg DW]**	**HQ for adults**				**HQ for children**			
			Exposure pathway				**Exposure pathway**			
			Ingestion of soil	**Dermal contact with soil**	**Ingestion of vegetable**	**Total**	**Ingestion of soil**	**Dermal contact with soil**	**Ingestion of vegetable**	**Total**
4	CHT1-S-1	146.80	3.1E-02	9.2E-03	8.7E-01	9.1E-01	**1.0E+00**	6.2E-02	**1.9E+00**	**3.0E+00**
5	AKH1-S-1	66.95	1.4E-02	4.2E-03	4.0E-01	4.1E-01	4.8E-01	2.8E-02	8.7E-01	**1.4E+00**

Table 13: Results of the calculation of non-carcinogenic human health risks (HQ) associated with cadmium in soil samples taken in Armenia. HQ values exceeding 1 are in bold. Only samples with HQ values exceeding 1 are listed in the table.

Site	**Sample ID**	**Concentration [mg/kg DW]**	**HQ for adults**				**HQ for children**			
			Exposure pathway				**Exposure pathway**			
			Ingestion of soil	**Dermal contact with soil**	**Ingestion of vegetable**	**Total**	**Ingestion of soil**	**Dermal contact with soil**	**Ingestion of vegetable**	**Total**
5	AKH1-S-1	12.90	1.7E-03	1.7E-05	5.9E-01	5.9E-01	5.5E-02	8.3E-05	**1.4E+00**	**1.5E+00**

5.4 Evaluation of heavy metal levels in foodstuffs

Metal contaminants in garden and allotment soils could possibly affect human health through a variety of pathways. This study focused on the potential pathway of the consumption of fruits and vegetables grown on contaminated soil. There are reports indicating that some plant species may accumulate specific heavy metals. Vegetables, particularly leaf ones, accumulate higher amounts of heavy metals. Generally, the roots and leaves of the plants accumulate higher concentrations of heavy metal than their stems and fruits.[xlvii] Distinctive differences were identified when comparing one vegetable to another, legumes tending to be low accumulators, root vegetables tending to be moderate accumulators, and leaf vegetables being high accumulators.[xlviii] The ability of leaf vegetables to uptake and accumulate heavy metals was the highest, and that of melon vegetables was the lowest. This indicated that the low accumulators (melon vegetables) were suitable for being planted on contaminated soil, while the high accumulators (leaf vegetables) were unsuitable.[xlix] These conclusions are in line with our results, in which two leaf vegetable samples (Basil and Malva) contained higher concentrations of some risky heavy metals (mercury and lead).

When our results are compared with the legislative values, the maximum levels were only exceeded in one case (Table 14). The maximum levels of cadmium and lead in foodstuffs set by the FAO/WHO and European Union were met. In the case of the food safety requirements set by the Order of the Minister of Healthcare of Armenia, one sample of leaf vegetable (Malva) exceeds the maximum permissible level of cadmium. The maximum values in the legislative acts do not indicate the possible health risks posed by the consumption of these foods, but only the characteristics of the foods in terms of marketing.

We compared the levels of heavy metals in foodstuffs (Table 15) with a recent study[l] from the same mining area that performed these calculations. Generally, we found lower levels of mercury, copper, nickel, and lead in different species of vegetables and fruits, except one sample of leafy vegetable (Malva), where we found 0.22 mg of lead per kg of fresh matter. On the other hand, in some samples we found slightly higher values of arsenic levels in different species of fruits and vegetables.

To assess the health risks associated with the ingestion of heavy metals from vegetables, the appropriate methods are calculating the Estimated Daily Intake (EDI) of heavy metals, the Target Hazard Quotient (THQ), and the Hazard Index (HI). The data set that was collected was not sufficiently comprehensive for accurate calculations of these indicators, so we at least modelled the assumed information with the consumption of foodstuffs to get an estimate of the potential impact on human health. Full lists of the calculated EDI of the heavy metals that were assessed for each foodstuff and their sum by males and females are presented in Tables 27 and 28 in Annex IV,. The sums of the THQ of the heavy metals that were assessed for all foodstuffs and hazard indices for all the heavy metals that were assessed by males and females are presented in Table 16. The calculations show that none of the heavy metals exceed the reference value of THQ when a mix of the foodstuffs that were investigated is consumed. Therefore, the risk of a non-carcinogenic toxic effect of each heavy metal separately is assumed to be low. The HI value expresses the combined non-carcinogenic effects of multiple elements and exceeds the reference value of 1 for both males and females.

Table 14: Number of foodstuff samples that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the number of sediment or sand samples from each hotspot area are expressed in brackets.

Legal standard	Mercury	Arsenic	Cadmium	Copper	Molybdenum	Nickel	Lead
Maximum permissible levels of heavy metals in foodstuffs (Armenia)	0 (0%)	0 (0%)	1 (3.6%)	-	-	-	0 (0%)
Maximum levels of heavy metals in foodstuffs (European Union)	-	-	0 (0%)	-	-	-	0 (0%)
Maximum levels of heavy metals in foodstuffs (FAO/WHO)	-	-	0 (0%)	-	-	-	0 (0%)

Table 15: Heavy metal concentrations in fruits and vegetables that were found in a previous study[li] in the vicinity of the town of Alaverdi in 2018.

	Mercury [mg/kg FM]	Arsenic [mg/kg FM]	Cadmium [mg/kg FM]	Copper [mg/kg FM]	Nickel [mg/kg FM]	Lead [mg/kg FM]
Apples	0.0015	0.003	0.0013	0.725	1.46	0.082
Pears	0.002	0.0017	0.003	0.64	0.117	0.001
Plums	0.0015	0.0005	0.0013	0.635	0.156	0.005
Cornelian cherries	0.0013	0.0027	ND	0.29	0.08	0.013
Figs	0.094	0.0017	ND	7.8	2.01	0.18
Beans	0.0015	0.004	0.0013	10.7	1.7	0.129
Potatoes	0.0012	0.005	0.001	12.43	0.68	0.12
Greens	0.003	0.1	ND	20.78	1.43	0.068

Table 16: Sum of target hazard quotients of the heavy metals that were assessed for all foodstuffs and hazard indices for all the heavy metals that were assessed by males and females.

Sex	Mercury	Arsenic	Cadmium	Copper	Molybdenum	Nickel	Lead	Hazard index
Male	0.0000 107632	0.2211 350294	0.0198 082192	0.5410 684932	0.6080 602740	0.0142 035225	0.0014 760973	1.40
Female	0.0000 125571	0.2579 908676	0.0231 095890	0.6312 465753	0.7094 036530	0.0165 707763	0.0017 221135	1.64

5.5 Evaluation of heavy metal levels in hair

Among many human tissues, human hair can be used as a biomarker of the environmental burden of toxic metals.[lii] [liii] [liv] The bioaccumulation of heavy metals in human hair is rather a complex process. The factors that influence bioaccumulation include nourishment, the chemical forms of the metal and their binding sites, age, sex, genetic inheritance, and environmental quality.[lv] A total of 13 hair samples was analysed for heavy metals, specifically mercury, arsenic, cadmium, copper, molybdenum, nickel, and lead. The US EPA made a recommendation[lvi] of a 1 mg/kg reference that should not be exceeded in women of childbearing age and a level of 10 mg/kg which can be associated with adverse health effects. As there are no recommendations or standards for other elements (As, Cd, Cu, Mo, Ni, Pb) in hair, the results were compared with several studies dealing with concentrations of heavy metals or trace elements in the hair of healthy humans or humans exposed to pollution. Humans may be contaminated by heavy metals associated with aquatic ecosystems by the consumption of contaminated fish and other aquatic food. This fact is due to the capacity of some aquatic organisms to concentrate heavy metals much more than the concentration present in water.[lvii]

Levels of **mercury** have been intensively studied because of their effects on human health, especially on people living close to sources of mercury such as coal-fired power plants, waste incinerators, gold mines, non-ferrous smelters, and others. Testing human hair for mercury is a good indicator of mercury pollution levels in various geographic regions and communities. The results for mercury were compared with the US EPA recommendation[lviii] of a 1.0 mg/kg reference dose not to be exceeded in women of childbearing age and a level of 10 mg/kg which can be associated with adverse health effects. All the samples met the US EPA limit for mercury. The hair samples contained mostly low concentrations of mercury. Only one sample (AKR1-H-2) had a higher mercury level (0.65 mg/kg) compared to the other samples. This hair sample was provided by a 53-year-old woman who could have accumulated for a long time compared to other family members who had lower concentrations, although their diet is probably the same. Because only low mercury concentrations (0.001 mg/kg FM or lower) have been found in vegetables and fruits, the presence of mercury in the samples of hair is likely to be associated with intake from another source. Possible sources of mercury intake by food such as fish might need to be examined.

Various **arsenic** levels have been reported in human hair. In areas that are not significantly polluted, arsenic levels were found in concentrations up to 0.5 mg/kg[lix]. Another study[lx] states that regular levels of arsenic in hair are between 0.3 and 1.75 mg/kg. The results of a study[lxi] conducted within two villages in the Atacama Desert (Chile), of which one has a population chronically exposed to arsenic, showed levels of 0.7 mg/kg and 6.1 mg/kg in clean and polluted areas, respectively. These findings correspond with a study[lxii] focused on arsenic-polluted water that found concentrations from 0 to 20 mg/kg, with an average of 9.22 mg/kg, of arsenic in hair. Even higher arsenic levels in hair were found for the human population living in a village next to an abandoned cupric pyrite mine in south-east Alentejo (Portugal). The mean concentrations of arsenic were found to be 10.83 mg/kg and 27.19 mg/kg for children and adults, respectively.[lxiii] On the other hand, arsenic levels are not significantly elevated in some areas with high exposure to arsenic. The mean level of arsenic in hair samples collected in electronic waste recycling areas was 0.423 mg/kg (with a range from 0.0879 to 2.21 mg/kg).[lxiv] All the hair samples that we collected on farms contained only very low concentrations of arsenic. Only one sample has a higher value than the level of quantification (<0.1). The findings of our research have not found that arsenic is significantly deposited in the hair, although it is present in the soil and foodstuffs. Therefore, the occurrence of arsenic and its effect on human health in the local population should be investigated further, especially the concentration in blood or other body tissues.

Levels of **cadmium** in human hair have been studied at various contaminated sites. Hair samples collected in an electronic waste recycling area showed the mean level of cadmium as 0.94 mg/kg and a broad range of 0.01–13.7.[lxv] A study of lead levels in hair samples performed in the village of Zwardofi situated on the south-western border of Poland found the mean level of cadmium to be 0.3 mg/kg.[lxvi] Similar cadmium levels in human hair were found in a village next to an abandoned cupric pyrite mine in south-east Alentejo (Portugal), where the mean cadmium concentrations were found to be 0.25 mg/kg and 0.83 mg/kg for children and adults, respectively.[lxvii] The mean cadmium concentration (0.03 mg/kg) that we found in the hair samples of people living in the mining area was at the lower end of the range found in other studies. Rather, these results point to a lower cadmium pollution burden for local residents.

Levels of **copper** in human hair occur at approximately 15 mg/kg (10-30 mg/kg).[lxviii] [lxix] [lxx] Similar levels of copper concentration were found in human hair in polluted areas. Copper levels in hair samples in a small mountain resort village situated in the south-western border of Poland were 12.9 mg/kg and 4.5 mg/kg for males and females, respectively.[lxxi] The copper levels in the hair of people living in a village next to an abandoned cupric pyrite mine in south-east Alentejo (Portugal) were 10.83 mg/kg and 27.19 mg/kg for children and adults, respectively.[lxxii] Much higher copper levels in human hair could occur at some polluted sites. Hair samples collected at an electronic waste recycling area in China showed the mean level of copper to be 53.0 mg/kg and a range of 10.85 to 537 mg/kg.[lxxiii] The mean copper concentration (10.58 mg/kg) that we found in the hair samples of people living in the mining area was in the range found in other studies, but the same values were found in some of the polluted areas as well. The copper content in the hair of people in the locality is in line with the values that are commonly found and is much lower than at highly polluted sites.

There is not enough available data in expert sources about **molybdenum** levels in human hair. All the hair samples that were collected during our sampling campaign contained molybdenum concentrations below the limit of quantification (0.5 mg/kg). From the available information it is not possible to evaluate the potential burden on the residents in terms of molybdenum pollution.

The levels of **nickel** in human hair have been studied at various contaminated sites. Hair samples collected at an electronic waste recycling area showed the mean level of nickel to be 1.77 mg/kg and the range to be 0.007-9.44 mg/kg.[lxxiv] A study of nickel levels in hair samples performed in the village of Zwardofi, situated on the south-western border of Poland, found that the mean levels of nickel were 4.6 mg/kg and 5.5 mg/kg for males and females, respectively.[lxxv] The mean nickel concentration (16.31 mg/kg) that we found in the hair samples of people living in the mining area was higher than what was found in other studies of potentially polluted areas. There was a wide range in the concentrations that we found. Such a high mean zinc concentration in the hair is mainly due to the high levels in the hair of three residents living on farm number one in Akori.

A broad range of **lead** concentration was found in the hair of humans exposed to pollution in concentrations from 5 to 50 mg/kg.[lxxvi] [lxxvii] A study of lead levels in hair samples performed in the small mountain resort village of Zwardofi, which is situated on the south-western border of Poland, found values of 18.3 mg/kg and 3.4 mg/kg for males and females, respectively.[lxxviii] Much higher lead levels in hair were found in an electronic waste recycling area, with a mean of 85.3 mg/kg and a range of 1.93–730 mg/kg.[lxxix] The mean lead concentration (0.76 mg/kg) that we found in the hair samples from people living in the mining area was at the lower end of the range found in other studies. Rather, our results point to a lower lead pollution burden for local residents. Contrary to our findings, a study that investigated lead levels in the blood of children born and living in the communities of Alaverdi and Akhtala stated that the children in these communities were exposed to lead.[lxxx] The occurrence of lead in the blood or other body tissues of the local population should be investigated further.

6. Conclusions

This study focused on the monitoring and evaluation of concentrations of heavy metals in soils, foodstuffs, and human hair in the industrial region of Alaverdi and Akhtala in the north-east of Armenia. A series of samples was taken in the area and compared with the legal pollution criteria with the objective of examining the extent to which the pollution affects segments of the environment, and how serious it might be for human health.

Increased levels of arsenic, cadmium, copper, molybdenum, nickel, and lead were found in the soils of the area that was investigated. Most of the sites that were sampled can be considered as polluted.

The levels of these pollutants could represent a threat to the environment and, in some cases, human health. The most widespread heavy metal in the areas is arsenic, followed by cadmium. The concentrations of heavy metals in multiple soil samples exceed various legal standards, most frequently the Armenian soil standard, but in many cases also the Dutch soil standard, French soil standard, Czech soil standard, and the US EPA level of the pollution limit for non-industrial areas. The concentrations of heavy metals in the samples show pollution caused by copper processing plants. According to the results, all the presumed potential sources (the Alaverdi copper smelter, the Akhtala mines, and the tailing dams) seem to be threats to the environment.

Analysis using the Risk-Integrated Software for Cleanups (RISC) indicated the following results. The most risky heavy metal in the hot-spot areas was arsenic, followed by cadmium. All the soil samples were polluted with arsenic, showing that adverse carcinogenic effects associated with the consumption of vegetables may occur in the long term. Moreover, two samples exceeded the hazard quotient (HQ) associated with cadmium, which indicates a non-carcinogenic risk for human health. Potential adverse health effects exist associated with arsenic and cadmium exist in these cases, which was not confirmed by the arsenic and cadmium levels in the hair samples. More research should be done in order to determine this toxic threat at the sites that were studied; in particular, it will be necessary to determine the possible accumulation of cadmium and arsenic in other tissues of the human body.

As the consumption of fruits and vegetables grown on contaminated soil represents a potential pathway to human bodies with accumulative effect, we compared our results with the legislative maximum levels. The maximum levels of cadmium and lead in foodstuffs set by the FAO/WHO and European Union were met. In the case of the food safety requirements set by the Order of the Minister of Healthcare of Armenia, one sample of leaf vegetable (Malva) exceeds the maximum permissible level of cadmium. We did not find significantly higher levels of heavy metals in vegetables and fruits than another study from the same mining area, except one sample of leaf vegetable (Malva). The calculations show that none of the heavy metals exceed the reference value of the target hazard quotient when a mix of the foodstuffs that were investigated is consumed. Therefore, the risk of non-carcinogenic toxic effects of each heavy metal separately is assumed to be low.

From thirteen hair samples taken in the mining area, most of them show good or normal results that are comparable with other studies from around the world that investigate pollution with heavy metals . Those people who were sampled who had normal results eat fish, the main source of heavy metals in the human diet, either not at all or only rarely. One sample (AKR1-H-2) contains a significantly higher concentration of mercury (0.65 mg/kg), but this value is safely below the US EPA recommendation of a 1.0 mg/kg reference dose not to be exceeded in women of childbearing age. Three hair samples from one farm located in Akori contained elevated levels of nickel in comparison with other hair samples and with levels found in other studies.

Unfortunately, our sampling possibilities did not cover the required extension of the necessary monitoring of heavy metals. We collected only a limited number of soil, foodstuff, and hair samples from the huge mining region; therefore, this study cannot give comprehensive evidence about the heavy metal pollution situation. Therefore, continuous environmental monitoring should be performed to monitor the level of heavy metals and help with implementing strategies to reduce the impact of contamination on the inhabitants. Detailed investigations need to be conducted for the overall assessment of the health risks posed by heavy metals, taking into consideration not only the adverse health effects posed by the ingestion of vegetables but also through other exposure pathways. Moreover, it would be useful to monitor the presence of heavy metals in other human tissues in addition to hair. To mitigate health risks, community members' awareness on the issue, their training in risk mitigation, and involvement in problem solving should be prioritized. In the event that the BAT/BEP standards are not yet in place in mining operations, we can recommend their implementation, which could reduce the additional burden of heavy metal exposure for local residents.

7. References

i

Li Z., Ma Z., der Kuijp T.J., Yuan Z., Huang L. (2014): A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. *Science of the Total Environment*, 468-469, 843-853.

ii

Pacyna E.G., Pacyna J.P., Fudala J., Strzelecka-Jastrzab E., Hlawiczka S., Panasiuk D., Nitter S., Pregger T., Pfeiffer H., Friedrich R. (2007): Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. *Atmospheric Environment*, 41,(38), 8557-8566.

iii

Jaishankar M., Tseten T., Anbalagan N., Mathew B.B., Beeregowda K.N. (2014): Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*, 7(2), 60-72.

iv

Akopyan K., Petrosyan V., Grigoryan R., Melkomian D.M. (2018): Assessment of residential soil contamination with arsenic and lead in mining and smelting towns of northern Armenia. *Journal of Geochemical Exploration*, 184, 97-109.

v

American University in Armenia Center for Responsible Mining (2016): Results of Soil & Drinking-Water Testing in Kindergartens & Schools, Akhtala City, Republic of Armenia.

vi

American University in Armenia Center for Responsible Mining (2016): Results of Soil and Drinking-Water Testing in Kindergartens and Schools of Alaverdi City, Lori Marz, Republic of Armenia.

vii

Gevorgyan G.A., Mamyan A.S., Hambaryan L.R., Khudaverdyan S.K., Vaseashta A. (2016): Environmental Risk Assessment of Heavy Metal Pollution in Armenian River Ecosystems: Case Study of Lake Sevan and Debed River Catchment Basins. *Polish Journal of Environmental Studies*, 25 (6), 2387-2399.

viii

Mamyan A.S., Gevorgyan G.A. (2017): Comparative investigation of the river phytoplankton of the Debed river catchment basin's mining and non-mining areas. *Biolog. Journal of Armenia*, 4 (69).

ix

Grigoryan K.V. (1989): The effect of irrigation water contaminated by industrial sewage on the content of heavy metals in the soil and some crops. *Soil Science*, 9, 97-103.

x

Pipoyan D., Beglaryan M., Merendino N. (2018): Dietary Exposure Assessment of Potentially Toxic Trace Elements in Fruits and Vegetables Grown in Akhtala, Armenia. *International Journal of Nutrition and Food Engineering*, 12 (8), ICFSN 2018: 20th International Conference on Food Science and Nutrition 2018.

xi

Grboyan, S. (2014): Lead exposure and measure of IQ level among children in Alaverdi, Akhtala and Yerevan. American University of Armenia School of Public Health.

xii

Grigoryan R. (2015): Case of Akhtala Community, Armenia: Environmental and Health Consequences of Mining Industry. American University in Armenia Center for Responsible Mining.

[xiii] Grigoryan R., Petrosyan V., Melkom Melkomian D., Khachadourian V., McCartor A., Crape B. (2016): Risk factors for children's blood lead levels in metal mining and smelting communities in Armenia: a cross-sectional study. *BMC Public Health*, 16(1), 945.

[xiv] Gevorgyan G.A., Mamyan A.S., Hambaryan L.R., Khudaverdyan S.K., Vaseashta A. (2016): Environmental Risk Assessment of Heavy Metal Pollution in Armenian River Ecosystems: Case Study of Lake Sevan and Debed River Catchment Basins. *Polish Journal of Environmental Studies*, 25 (6), 2387-2399.

[xv] Pipoyan D., Beglaryan M., Merendino N. (2018): Dietary Exposure Assessment of Potentially Toxic Trace Elements in Fruits and Vegetables Grown in Akhtala, Armenia. *International Journal of Nutrition and Food Engineering,* 12 (8), ICFSN 2018: 20th International Conference on Food Science and Nutrition 2018.

[xvi] Vallex Group. [online] [cit. 2019-09-24]. Available at: http://vallexgroup.am

[xvii] Bystrianský M., Šír M., Straková J., Krejčová N. (2018): Heavy metals in the surroundings of mining and metallurgical sites in the Lori region in Armenia. Arnika – Toxics and Waste Programme.

[xviii] US EPA. Human Health: Exposure Assessment [online] [cit. 2019-09-24]. Available at: https://www.epa.gov/risk/human-health-risk-assessment

[xix] International Agency for Research on Cancer. IARC Monographs on Evaluation of Carcinogenic Risks to Humans. [online] [cit. 2019-09-24]. Available at: http://monographs.iarc.fr/ENG/Classification/

[xx] Pipoyan D., Beglaryan M., Sireyan L., Merendino N. (2018): Exposure assessment of potentially toxic trace elements via consumption of fruits and vegetables grown under the impact of Alaverdi's mining complex. *Human and Ecological Risk Assessment: An International Journal*, DOI: 10.1080/10807039.2018.1452604

[xxi] US EPA (1997): Exposure Factors Handbook. EPA/600/P-95/002F. Washington, DC, USA. Available online at: https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deidD12464

[xxii] US EPA (1989): Cadmium. CASRN 7440-43-9. Washington, DC, USA. Available online at https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbrD141

[xxiii] US EPA (1991): Arsenic, Inorganic; CASRN 7440-38-2. Washington, DC, USA. Available online at https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbrD278

[xxiv] US EPA (1991): Nickel, Soluble Salts; CASRN Various. Washington, DC, USA. Available online at https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbrD27

[xxv] US EPA (1992): Molybdenum; CASRN 7439-98-7. Washington, DC, USA. Available online at https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=425

[xxvi] EFSA Panel on Contaminants in the Food Chain (2010): Scientific opinion on lead in food. EFSA J 8(4):1570. Available online at http://www.efsa.europa.eu/en/efsajournal/pub/1570

[xxvii] EFSA Panel on Contaminants in the Food Chain (2012): Scientific opinion on the risk for public health related to the presence of mercury and methylmercury in food. EFSA J 10(12):2985.

[xxviii] Agency for Toxic Substances and Diseases Registry (2004): Toxicological Profile for Copper. Update. Agency for Toxic Substances and Diseases Registry, Centers for Disease Control, Atlanta, GA, USA. Available online at https://www.atsdr.cdc.gov/toxprofiles/tp.asp?idD206&tidD37

[xxix] Zuang P., Lu H., Li Z. (2014): Multiple exposure and effects assessment of heavy metals in the population near mining area in South China. PLoS One 9(4):e9448.

[xxx] Order No. 01-N of 25 January 2010 of the Minister of Health of the Republic of Armenia “On Approving Sanitary Rules and Norms N 2.1.7.003-10 for Sanitary Requirements for Land Quality”

[xxxi] Czech Decree No. 153/2016 issued by the Ministry of Agriculture.

[xxxii] US EPA. Regional Screening Levels. [online] [cit. 2019-09-24]. Available at: http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/docs/params_sl_table_run_JAN2015.pdf

[xxxiii] US EPA. Regional Screening Levels. [online] [cit. 2019-09-24]. Available at: http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/docs/params_sl_table_run_JAN2015.pdf

[xxxiv] Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

[xxxv] FAO/WHO (2015): Codex Alimentarius: General standard for contaminants and toxins in food and feed. Codex Stan 193-1995.

[xxxvi] Order of the Minister of Healthcare of Armenia approving Food Safety Requirements

[xxxvii] Kabata-Pendias A. (2011): Trace Elements in Soil and Plants, *CRC Press, Taylor & Francis Group*, 2011.

[xxxviii] Bystrianský M., Šír M., Straková J., Krejčová N. (2018): Heavy metals in the surroundings of mining and metallurgical sites in the Lori region in Armenia. Arnika – Toxics and Waste Programme.

[xxxix] Akopyan K., Petrosyan V., Grigoryan R., Melkomian D.M. (2018): Assessment of residential soil contamination with arsenic and lead in mining and smelting towns of northern Armenia. *Journal of Geochemical Exploration*, 184, 97-109.

[xl] Kabata-Pendias A. (2011): Trace Elements in Soil and Plants, *CRC Press, Taylor & Francis Group*, 2011.

[xli] Kabata-Pendias A. (2011): Trace Elements in Soil and Plants, *CRC Press, Taylor & Francis Group*, 2011.

[xlii] Kabata-Pendias A. (2011): Trace Elements in Soil and Plants, *CRC Press, Taylor & Francis Group*, 2011.

[xliii] Kabata-Pendias A. (2011): Trace Elements in Soil and Plants, *CRC Press, Taylor & Francis Group*, 2011.

[xliv] Kabata-Pendias A. (2011): Trace Elements in Soil and Plants, *CRC Press, Taylor & Francis Group*, 2011.

[xlv]

Akopyan K., Petrosyan V., Grigoryan R., Melkomian D.M. (2018): Assessment of residential soil contamination with arsenic and lead in mining and smelting towns of northern Armenia. *Journal of Geochemical Exploration*, 184, 97-109.

xlvi

Kabata-Pendias A. (2011): Trace Elements in Soil and Plants, *CRC Press, Taylor & Francis Group*, 2011.

xlvii

Pipoyan D. (2017): Health risk assessment of environmental contaminants for population via consumption of vegetables and fruits grown in mining areas. A case study: Armenia. [online] [cit. 2019-09-24]. Available at: http://dspace.unitus.it/bitstream/2067/3012/1/dpipoyan_tesid.pdf

xlviii

Alexander P.D., Alloway B.J., Dourado A.M. (2006): Genotypic variations in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables. *Environmental Pollution*, 144 (3), 736-745.

xlix

Zhou H., Yang W.T., Zhou X., Liu L., Gu J.F., Wang W.L., Zou J.L., Tian T., Peng P.Q., Liao B.H. (2016): Accumulation of Heavy Metals in Vegetable Species Planted in Contaminated Soils and the Health Risk Assessment. *International Journal of Environmental Research of Public Health*, 13 (3): 289.

l

Pipoyan D., Beglaryan M., Sireyan L., Merendino N. (2018): Exposure assessment of potentially toxic trace elements via consumption of fruits and vegetables grown under the impact of Alaverdi's mining complex. *Human and Ecological Risk Assessment: An International Journal*, DOI: 10.1080/10807039.2018.1452604

li

Pipoyan D., Beglaryan M., Sireyan L., Merendino N. (2018): Exposure assessment of potentially toxic trace elements via consumption of fruits and vegetables grown under the impact of Alaverdi's mining complex. *Human and Ecological Risk Assessment: An International Journal*, DOI: 10.1080/10807039.2018.1452604

lii

Yoshinaga J., Imai H., Nazakawa M., Suzuki T. (1990): Lack of significantly positive concentrations in hair. *Sci. Total Environ*, 99, 125-135.

liii

Nowak B. (1996): Occurrence of heavy metals and Na, Ca, K in human hair, teeth and nails. *Biol. Trace Element Res*, 51, 11-22.

liv

Bergonmi M., Borella P., Fantuzzi G. (1989): Blood, teeth and hair: 3 different materials used to evaluate exposure to lead and cadmium in children living in an industrial zone. *Ann.-Iq. Italy*, 1(5), 1185-98.

lv

Schegel-Zawadzka M. (1992): Chromium content in the hair of children and students in southern Poland. *Biol. Trace Element Res*, 32, 79-84.

lvi

U.S. Environmental Protection Agency: Chemicals and Toxics Topics [online] [cit. 2019-09-27]. Available at: https://www.epa.gov/environmental-topics/chemicals-and-toxics-topics

lvii

Olgunoglu M.P., Olgunoglu I.A., Bayhan Y.K. (2015): Heavy metal concentrations (Cd, Pb, Cu, Zn, Fe) in Giant Red Shrimp (*Aristaeomorpha foliacea Risso 1827*) from the Mediterranean Sea, *Polish Journal of Environmental Studies*, 24 (2), 631.

lviii

U.S. Environmental Protection Agency: Chemicals and Toxics Topics [online] [cit. 2019-09-27]. Available at: https://www.epa.gov/environmental-topics/chemicals-and-toxics-topics

[lix] Crommentuijn T., Sijm D., de Bruijn J., van den Hoop M., van Leeuwen K., van de Plassche E. (2000): Maximum permissible and negligible concentrations for metals and metalloids in the Netherlands, taking into account background concentrations. *Journal of Environmental Management* 60 (2), 121-143.

[lx] Galvao L.A.C., Corey G. (1987): Serie Vigilancia 3. Arsénico. *Centro Panamericano de Ecología Humana y Salud, Organización Panamericana de la Salud, Organización Mundial de la Salud, Metepec.*

[lxi] Yáñez J., Fierro V., Mansilla H., Figueroa L., Cornejo L., Barnes R.M. (2005): Arsenic speciation in human hair: a new perspective for epidemiological assessment in chronic arsenicism. *Journal of Environmental Monitoring*, 12.

[lxii] Armienta M.A., Rodríguez R., Cruz O. (1997): Arsenic Content in Hair of People Exposed to Natural Arsenic Polluted Groundwater at Zimapán, México. *Bulletin of Environmental Contamination and Toxicology*, 59, 583-589.

[lxiii] Pereira R., Ribeiro R., Goncalves F. (2004): Scalp hair analysis as a tool in assessing human exposure to heavy metals (S. Domingos mine, Portugal). *Science of the Total Environment* 327, 81-92.

[lxiv] Wang T., Fu J., Wang Y., Liao C., Tao Y., Jiang G. (2009): Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area. *Environmental Pollution* 157, 2445-2451.

[lxv] Wang T., Fu J., Wang Y., Liao C., Tao Y., Jiang G. (2009): Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area. *Environmental Pollution* 157, 2445-2451.

[lxvi] Nowak B., Kozlowski H. (1998): Heavy Metals in Human Hair and Teeth – The Correlation with Metal Concentration in the Environment. *Biological Trace Element Research*, 62, 213-228.

[lxvii] Pereira R., Ribeiro R., Goncalves F. (2004): Scalp hair analysis as a tool in assessing human exposure to heavy metals (S. Domingos mine, Portugal). *Science of the Total Environment* 327, 81-92.

[lxviii] Hilderbrand D.C., White D.H. (1974): Trace-element analysis in hair: an evaluation. *Clinical Chemistry*, 20(2), 148-151.

[lxix] Krejpcio Z., Olejnik D., Wojciak R.W., Gawecki J. (1999): Comparison of trace elements in the hair of children inhabiting areas of different environmental pollution types. *Polish Journal of Environmental Studies*, 4 (08).

[lxx] Salnikova E.V., Burtseva T.I., Skalnaya M.G., Skalny A.V., Tinkov A.A. (2018): Copper and zinc levels in soil, water, wheat, and hair of inhabitants of three areas of the Orenburg region, Russia. *Environmental Research*, 166, 158-166.

[lxxi] Nowak B., Kozlowski H. (1998): Heavy Metals in Human Hair and Teeth – The Correlation with Metal Concentration in the Environment. *Biological Trace Element Research*, 62, 213-228.

[lxxii]

Pereira R., Ribeiro R., Goncalves F. (2004): Scalp hair analysis as a tool in assessing human exposure to heavy metals (S. Domingos mine, Portugal). *Science of the Total Environment* 327, 81-92.

lxxiii Wang T., Fu J., Wang Y., Liao C., Tao Y., Jiang G. (2009): Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area. *Environmental Pollution* 157, 2445-2451.

lxxiv Wang T., Fu J., Wang Y., Liao C., Tao Y., Jiang G. (2009): Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area. *Environmental Pollution* 157, 2445-2451.

lxxv Nowak B., Kozlowski H. (1998): Heavy Metals in Human Hair and Teeth – The Correlation with Metal Concentration in the Environment. *Biological Trace Element Research*, 62, 213-228.

lxxvi Krejpcio Z., Olejnik D., Wojciak R.W., Gawecki J. (1999): Comparison of trace elements in the hair of children inhabiting areas of different environmental pollution types. *Polish Journal of Environmental Studies*, 4 (08).

lxxvii Mehra R., Thakur A.S. (2016): Relationship between lead, cadmium, zinc, manganese and iron in hair of environmentally exposed subjects. *Arabian Journal of Chemistry*, 9, 1214-1217.

lxxviii Nowak B., Kozlowski H. (1998): Heavy Metals in Human Hair and Teeth – The Correlation with Metal Concentration in the Environment. *Biological Trace Element Research*, 62, 213-228.

lxxix Wang T., Fu J., Wang Y., Liao C., Tao Y., Jiang G. (2009): Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area. *Environmental Pollution* 157, 2445-2451.

lxxx Grigoryan R., Petrosyan V., Melkomian D.M., Khachadourian V., McCartor A., Crape B. (2016): Risk factors for children’s blood lead levels in metal mining and smelting communities in Armenia: a cross-sectional study. *BMC Public Health*, 16: 945.

Annex I: Lists of samples

Table 17: List of soil samples taken at sampling sites

Site	Sample ID	Date of sampling	Matrix	Sampling site	Sampling and sample preparation	Possible source of pollution and its distance [m]	Comments
1	AKR1-S-1	21 July 2019	soil	private garden in Alaverdi (potato field)	5 sub-samples, homogenization	Alaverdi copper smelting factory, 2500	
2	SAN1-S-1	21 July 2019	soil	private garden in Sanahin (onion field)	5 sub-samples, homogenization	Alaverdi copper smelting factory, 1700	loose brown soil with visible particles of plastic, aluminium wire, asbestos
3	ALA1-S-1	21 July 2019	soil	private garden in Alaverdi (bean field)	5 sub-samples, homogenization	Alaverdi copper smelting factory, 1000	loose brown soil without particles of plastic and other materials
4	CHT1-S-1	22 July 2019	soil	private garden in Chochkan (bean field)	5 sub-samples, homogenization	Mets Ayrum tailing pond, 700	soil without visible particles of plastic, textiles, etc.; field is irrigated with water from the River Debet
5	AKH1-S-1	22 July 2019	soil	private garden in Akhtala (bean field)	5 sub-samples, homogenization	Akhtala mine	sample without visible particles of plastic or other materials; field is irrigated with water from the River Akhtala
6	MTA1-S-1	22 July 2019	soil	private garden in Mets Ayrum (potato field)	5 sub-samples, homogenization	Mets Ayrum tailing pond, 150	brown soil with visible particles of plastic and nails
7	HAG1-S-1	23 July 2019	soil	private garden in Hakhpat	5 sub-samples, homogenization	Alaverdi copper smelting factory	brown soil with visible particles of aluminium wire
8	SHA1-S-1	23 July 2019	soil	private garden in Shamlug (potato field)	5 sub-samples, homogenization	Akhtala mine, 500	brown soil
9	MTA2-S-1	23 July 2019	soil	private garden in Mets Ayrum (potato field)	5 sub-samples, homogenization	Mets Ayrum tailing pond, 20	dry brown soil without plastic particles

Table 18: List of food samples taken at sampling sites

Site	Sample ID	Date of sampling	Food product	Latin name	Count of pieces or volume	Sampling site description	Potential source of pollution and it distance	Comments
1	AKR1-V-1	21 July 2019	Hazelnut	*Corylus avellana*	33	private vegetable and fruit garden in Akori	Alaverdi copper smelting factory, 2500	ash from burning wood is used as fertilizer; communal waste is burned once in 2-3 months; ash from burning waste is not used as fertilizer
1	AKR1-V-2	21 July 2019	Green bean	*Phaseolus*	22			
1	AKR1-V-4	21 July 2019	Potato	*Solanum tuberosum*	15			
2	SAN1-V-2	21 July 2019	Coloured bean	*Phaseolus*	20	private vegetable and fruit garden in Sanahin	Alaverdi copper smelting factory, 1700	ash from burning wood is not used as fertilizer; non-drinking water from the mountains is used for irrigation
2	SAN1-V-4	21 July 2019	Malva	*Malva*	20			
2	SAN1-V-5	21 July 2019	White onion	*Allium cepa*	3			
3	ALA1-V-1	21 July 2019	Nectarine	*Prunus persica*	7	private vegetable and fruit garden in Alaverdi	Alaverdi copper smelting factory, 1000	ash from burning wood is not used as fertilizer; drinking water is used for irrigation
3	ALA1-V-2	21 July 2019	Fig	*Ficus carica*	3			
3	ALA1-V-3	21 July 2019	Green bean	*Phaseolus*	13			
4	CHT1-V-1	22 July 2019	Violet plum	*Prunus*	27	private vegetable and fruit garden in Chochkan	Mets Ayrum tailing pond, 700	ash from burning wood is not used as fertilizer; water from the River Debet is used for irrigation
4	CHT1-V-2	22 July 2019	Bean	*Phaseolus*	17			
4	CHT1-V-3	22 July 2019	Basil	*Ocimum basilicum*	25			
5	AKH1-V-1	22 July 2019	Fig	*Ficus carica*	2	private vegetable and fruit garden in Akhtala	Akhtala mine	ash from burning wood is used as fertilizer; water from the River Akhtala is used for irrigation
5	AKH1-V-2	22 July 2019	Cornelian cherry	*Cornus mas*	100			
5	AKH1-V-3	22 July 2019	Coloured bean	*Phaseolus*	17			
6	MTA1-V-1	22 July 2019	Pear	*Pyrus*	3	private vegetable and fruit garden in Mets Ayrum	Mets Ayrum tailing pond, 50	ash from burning wood is not used as fertilizer; water from the River Debet is used for irrigation
6	MTA1-V-2	22 July 2019	Coloured bean	*Phaseolus*	17			
6	MTA1-V-3	22 July 2019	Potato	*Solanum tuberosum*	14			
7	HAG1-V-1	23 July 2019	Green bean	*Phaseolus*	17	private vegetable and fruit garden in Hakhpat	Alaverdi copper smelting factory	ash from burning wood is not used as fertilizer; non-drinking water from the mountains is used for irrigation; burning of waste 3-4 times in summer
7	HAG1-V-2	23 July 2019	Beetroot	*Beta vulgaris*	1			
7	HAG1-V-3	23 July 2019	Carrot	*Daucus carota*	6			
8	SHA1-V-1	23 July 2019	Green bean	*Phaseolus*	25	private vegetable	Akhtala mine, 500	ash from burning wood is used as

8	SHA1-V-2	23 July 2019	Potato	*Solanum tuberosum*	13	garden in Shamlug		fertilizer; drinking water from the mountains is used for irrigation
9	MTA2-V-1	23 July 2019	Pear	*Pyrus*	4	private vegetable and fruit garden in Mets Ayrum	Mets Ayrum tailing pond, 20	ash from burning wood is used as fertilizer; drinking water from close to the tailing pond is used for irrigation
9	MTA2-V-2	23 July 2019	Apple	*Malus*	6			
9	MTA2-V-3	23 July 2019	Potato	*Solanum tuberosum*	23			
-	AKH1-MED-1	22 July 2019	Honey		200 ml glass	honey producer in Akhtala		
-	HAG1-MED-1	25 July 2019	Honey		200 ml glass	honey producer in Hagvi		

Table 19: List of hair samples taken at sampling sites.

Site	Sample ID	Date of sampling	Gender	Age [years]	Fish eaters	Smoker home	Comments
1	AKR1-H-1	21 July 2019	female	6	Yes	No	
1	AKR1-H-2	21 July 2019	female	53	Yes	No	dyed hair
1	AKR1-H-3	21 July 2019	male	17	Yes	No	
2	SAN1-H-1	21 July 2019	female	69	Yes	Yes	
2	SAN1-H-2	21 July 2019	female	28	Yes	Yes	
2	SAN1-H-3	21 July 2019	male	2	Yes	Yes	
3	ALA1-H-1	21 July 2019	female	10	Yes	Yes	
5	AKH1-H-1	22 July 2019	female	28	Yes	No	
6	MTA1-H-2	22 July 2019	female	29	Yes	No	dyed hair
7	HAG1-H-1	23 July 2019	female	9	Yes	Yes	
8	SHA1-H-1	23 July 2019	female	27	Yes	Yes	dyed hair
9	MTA2-H-1	23 July 2019	male	12	No	Yes	
9	MTA2-H-2	23 July 2019	female	34	No	Yes	

Annex II: Results

Table 20: Concentrations of heavy metals in soil samples.

Site	Sample ID	Arsenic [mg/kg DW]	Cadmium [mg/kg DW]	Copper [mg/kg DW]	Molybdenum [mg/kg DW]	Nickel [mg/kg DW]	Lead [mg/kg DW]	Chromium[1] [mg/kg DW]
1	AKR1-S-1	43.36	1.38	401.92	0.50	41.70	71.15	42.51
2	SAN1-S-1	41.29	0.29	105.44	3.98	36.36	20.50	42.02
3	ALA1-S-1	44.99	1.52	7737.32	1.44	50.86	77.03	45.71
4	CHT1-S-1	146.80	3.89	785.55	5.87	52.48	122.08	39.21
5	AKH1-S-1	66.95	12.90	1779.64	2.72	35.20	173.74	47.70
6	MTA1-S-1	29.52	0.89	150.55	0.85	11.36	91.35	12.88
7	HAG1-S-1	27.85	0.37	115.19	0.33	37.15	16.94	43.06
8	SHA1-S-1	40.95	0.92	434.83	2.03	58.42	114.65	67.63
9	MTA2-S-1	30.51	0.38	98.80	1.55	44.01	10.34	48.44

1) Total concentration of chromium.

Table 21: Concentrations of heavy metals in foodstuff samples. Concentrations of heavy metals are expressed in mg/kg of fresh matter [mg/kg FM].

Site	Sample ID	Species	Mercury [mg/kg FM]	Arsenic [mg/kg FM]	Cadmium [mg/kg FM]	Copper [mg/kg FM]	Molybdenum [mg/kg FM]	Nickel [mg/kg FM]	Lead [mg/kg FM]
1	AKR1-V-1	Hazelnut	NA	0.07	<0.005	6.81	0.204	0.61	<0.05
1	AKR1-V-2	Green bean	<0.001	0.07	<0.005	0.99	3.069	0.25	<0.05
1	AKR1-V-4	Potato	<0.001	0.02	0.014	2.33	0.37	0.07	<0.05
2	SAN1-V-2	Coloured bean	<0.001	<0.01	<0.005	0.55	0.965	0.11	<0.05
2	SAN1-V-4	Malva	0.001	0.07	0.031	1.84	0.536	0.19	0.22
2	SAN1-V-5	White onion	<0.001	0.01	0.005	0.86	0.185	<0.05	<0.05
3	ALA1-V-1	Nectarine	NA	0.04	<0.005	0.27	0.019	<0.05	<0.05
3	ALA1-V-2	Fig	NA	0.02	<0.005	0.95	0.07	0.17	<0.05
3	ALA1-V-3	Green bean	<0.001	0.03	<0.005	0.62	2.38	0.14	<0.05
4	CHT1-V-1	Violet plum	NA	<0.01	<0.005	0.76	<0.005	<0.05	<0.05
4	CHT1-V-2	Bean	<0.001	0.06	0.011	2.41	8.853	0.31	<0.05
4	CHT1-V-3	Basil	0.001	0.07	<0.005	1.78	0.476	0.09	<0.05
5	AKH1-V-1	Fig	NA	<0.01	<0.005	0.54	0.043	<0.05	<0.05
5	AKH1-V-2	Cornelian cherry	NA	0.02	<0.005	0.32	0.017	<0.05	<0.05
5	AKH1-V-3	Coloured bean	<0.001	0.01	0.006	2.24	8.319	<0.05	<0.05
6	MTA1-V-1	Pear	NA	<0.01	<0.005	0.74	0.01	0.05	<0.05
6	MTA1-V-2	Coloured bean	<0.001	<0.01	<0.005	1.07	2.189	0.17	<0.05
6	MTA1-V-3	Potato	<0.001	<0.01	<0.005	1.98	0.197	0.16	<0.05
7	HAG1-V-1	Green bean	<0.001	<0.01	<0.005	0.6	0.462	0.17	<0.05
7	HAG1-V-2	Beetroot	<0.001	<0.01	0.01	0.66	0.025	<0.05	<0.05
7	HAG1-V-3	Carrot	<0.001	0.01	<0.005	0.34	0.057	<0.05	<0.05
8	SHA1-V-1	Green bean	<0.001	0.01	<0.005	0.49	0.803	0.05	<0.05
8	SHA1-V-2	Potato	<0.001	<0.01	0.013	2.02	0.183	0.05	<0.05
9	MTA2-V-1	Pear	NA	<0.01	<0.005	0.77	0.019	<0.05	<0.05
9	MTA2-V-2	Apple	NA	<0.01	<0.005	0.15	0.028	<0.05	<0.05
9	MTA2-V-3	Potato	<0.001	<0.01	0.012	1.67	0.131	0.08	<0.05
-	AKH1-MED-1	Honey	NA	<0.01	<0.005	0.15	0.009	<0.05	<0.05
-	HAG1-MED-1	Honey	NA	<0.01	<0.005	0.31	0.006	0.05	<0.05

Table 22: Concentrations of heavy metals in hair samples

Site	Sample ID	Mercury [mg/kg]	Arsenic [mg/kg]	Cadmium [mg/kg]	Copper [mg/kg]	Molybdenum [mg/kg]	Nickel [mg/kg]	Lead [mg/kg]
1	AKR1-H-1	0.045	<0.1	0.011	7.8	<0.5	28.6	1.58
1	AKR1-H-2	0.65	<0.1	0.05	8.7	<0.5	45.1	0.99
1	AKR1-H-3	0.07	0.14	0.06	8.2	<0.5	33.4	0.59
2	SAN1-H-1	0.092	NA	NA	NA	NA	NA	NA
2	SAN1-H-2	0.108	<0.1	0.02	9.6	<0.5	2.3	0.57
2	SAN1-H-3	0.121	NA	NA	NA	NA	NA	NA
3	ALA1-H-1	0.021	<0.1	0.04	11.9	<0.5	27	1.51
5	AKH1-H-1	0.119	<0.1	0.02	16.3	<0.5	<1	0.4
6	MTA1-H-2	0.05	<0.1	0.01	10.9	<0.5	1.7	0.66
7	HAG1-H-1	0.035	<0.1	0.02	9.2	<0.5	5.2	0.38
8	SHA1-H-1	0.111	<0.1	0.07	11.7	<0.5	1.8	0.88
9	MTA2-H-1	0.021	<0.1	0.04	12	<0.5	16.7	0.64
9	MTA2-H-2	0.024	<0.1	0.02	10.1	<0.5	1.3	0.21

Annex III: Non-carcinogenic human health risks associated with heavy metals

Table 23: Results of the calculation of non-carcinogenic human health risks (HQ) associated with arsenic in soil samples taken in Armenia. HQ values exceeding 1 are in bold.

Site	Sample ID	Concentration [mg/kg DW]	HQ for adults				HQ for children			
			Exposure pathway				Exposure pathway			
			Ingestion of soil	Dermal contact with soil	Ingestion of vegetable	Total	Ingestion of soil	Dermal contact with soil	Ingestion of vegetable	Total
1	AKR1-S-1	43.36	9.1E-03	2.7E-03	2.6E-01	2.7E-01	3.1E-01	1.8E-02	5.6E-01	8.9E-01
2	SAN1-S-1	41.29	8.7E-03	2.6E-03	2.4E-01	2.5E-01	2.9E-01	1.7E-02	5.4E-01	8.5E-01
3	ALA1-S-1	44.99	9.4E-03	2.8E-03	2.7E-01	2.8E-01	3.2E-01	1.9E-02	5.8E-01	9.2E-01
4	CHT1-S-1	146.80	3.1E-02	9.2E-03	8.7E-01	9.1E-01	**1.0E+00**	6.2E-02	**1.9E+00**	**3.0E+00**
5	AKH1-S-1	66.95	1.4E-02	4.2E-03	4.0E-01	4.1E-01	4.8E-01	2.8E-02	8.7E-01	**1.4E+00**
6	MTA1-S-1	29.52	6.2E-03	1.9E-03	1.7E-01	1.8E-01	2.1E-01	1.2E-02	3.8E-01	6.1E-01
7	HAG1-S-1	27.85	5.8E-03	1.8E-03	1.6E-01	1.7E-01	2.0E-01	1.2E-02	3.6E-01	5.7E-01
8	SHA1-S-1	40.95	8.6E-03	2.6E-03	2.4E-01	2.5E-01	2.9E-01	1.7E-02	5.3E-01	8.4E-01
9	MTA2-S-1	30.51	6.4E-03	1.9E-03	1.8E-01	1.9E-01	2.2E-01	1.3E-02	4.0E-01	6.3E-01

Table 24: Results of the calculation of non-carcinogenic human health risks (HQ) associated with cadmium in soil samples taken in Armenia. HQ values exceeding 1 are in bold.

Site	Sample ID	Concentration [mg/kg DW]	HQ for adults – Exposure pathway: Ingestion of soil	HQ for adults – Exposure pathway: Dermal contact with soil	HQ for adults – Exposure pathway: Ingestion of vegetable	HQ for adults – Exposure pathway: Total	HQ for children – Exposure pathway: Ingestion of soil	HQ for children – Exposure pathway: Dermal contact with soil	HQ for children – Exposure pathway: Ingestion of vegetable	HQ for children – Exposure pathway: Total
1	AKR1-S-1	1.38	1.8E-04	1.8E-06	6.3E-02	6.4E-02	5.9E-03	8.8E-06	1.5E-01	1.6E-01
2	SAN1-S-1	0.29	3.8E-05	3.8E-07	1.3E-02	1.3E-02	1.3E-03	1.9E-06	3.2E-02	3.3E-02
3	ALA1-S-1	1.52	2.0E-04	2.0E-06	7.0E-02	7.0E-02	6.6E-03	9.8E-06	1.7E-01	1.7E-01
4	CHT1-S-1	3.89	5.1E-04	5.1E-06	1.8E-01	1.8E-01	1.7E-02	2.5E-05	4.3E-01	4.4E-01
5	AKH1-S-1	12.90	1.7E-03	1.7E-05	5.9E-01	5.9E-01	5.5E-02	8.3E-05	**1.4E+00**	**1.5E+00**
6	MTA1-S-1	0.89	1.2E-04	1.2E-06	4.1E-02	4.1E-02	3.8E-03	5.7E-06	9.8E-02	1.0E-01
7	HAG1-S-1	0.37	4.8E-05	4.8E-07	1.7E-02	1.7E-02	1.6E-03	2.4E-06	4.1E-02	4.3E-02
8	SHA1-S-1	0.92	1.2E-04	1.2E-06	4.2E-02	4.2E-02	4.0E-03	5.9E-06	1.0E-01	1.1E-01
9	MTA2-S-1	0.38	5.0E-05	5.0E-07	1.8E-02	1.8E-02	1.7E-03	2.5E-06	4.2E-02	4.4E-02

Table 25: Results of the calculation of non-carcinogenic human health risks (HQ) associated with nickel in soil samples taken in Armenia.

Site	Sample ID	Concentration [mg/kg DW]	HQ for adults – Exposure pathway: Ingestion of soil	HQ for adults – Exposure pathway: Dermal contact with soil	HQ for adults – Exposure pathway: Ingestion of vegetable	HQ for adults – Exposure pathway: Total	HQ for children – Exposure pathway: Ingestion of soil	HQ for children – Exposure pathway: Dermal contact with soil	HQ for children – Exposure pathway: Ingestion of vegetable	HQ for children – Exposure pathway: Total
1	AKR1-S-1	41.70	1.6E-04	4.0E-06	5.0E-03	5.2E-03	3.1E-03	9.2E-05	8.8E-03	1.2E-02
2	SAN1-S-1	36.36	1.4E-04	3.5E-06	4.4E-03	4.5E-03	2.7E-03	8.0E-05	7.6E-03	1.0E-02
3	ALA1-S-1	50.86	1.9E-04	4.9E-06	6.1E-03	6.3E-03	3.8E-03	1.1E-04	1.1E-02	1.5E-02
4	CHT1-S-1	52.48	2.0E-04	5.1E-06	6.3E-03	6.5E-03	3.9E-03	1.2E-04	1.1E-02	1.5E-02
5	AKH1-S-1	35.20	1.3E-04	3.4E-06	4.2E-03	4.4E-03	2.6E-03	7.7E-05	7.4E-03	1.0E-02
6	MTA1-S-1	11.36	4.3E-05	1.1E-06	1.4E-03	1.4E-03	8.5E-04	2.5E-05	2.4E-03	3.3E-03
7	HAG1-S-1	37.15	1.4E-04	3.6E-06	4.5E-03	4.6E-03	2.8E-03	8.2E-05	7.8E-03	1.1E-02
8	SHA1-S-1	58.42	2.2E-04	5.7E-06	7.0E-03	7.2E-03	4.4E-03	1.3E-04	1.2E-02	1.7E-02
9	MTA2-S-1	44.01	1.7E-04	4.3E-06	5.3E-03	5.5E-03	3.3E-03	9.7E-05	9.2E-03	1.3E-02

Table 26: Results of the calculation of non-carcinogenic human health risks (HQ) associated with lead in soil samples taken in Armenia.

Site	Sample ID	Concentration [mg/kg DW]	HQ for adults Exposure pathway				HQ for children Exposure pathway			
			Ingestion of soil	Dermal contact with soil	Ingestion of vegetable	Total	Ingestion of soil	Dermal contact with soil	Ingestion of vegetable	Total
1	AKR1-S-1	71.15	1.2E-03	1.1E-04	0.0E+00	1.3E-03	4.2E-02	8.5E-04	0.0E+00	4.3E-02
2	SAN1-S-1	20.50	3.5E-04	3.3E-05	0.0E+00	3.8E-04	1.2E-02	2.5E-04	0.0E+00	1.2E-02
3	ALA1-S-1	77.03	1.3E-03	1.2E-04	0.0E+00	1.4E-03	4.5E-02	9.2E-04	0.0E+00	4.6E-02
4	CHT1-S-1	122.08	2.1E-03	2.0E-04	0.0E+00	2.3E-03	7.2E-02	1.5E-03	0.0E+00	7.3E-02
5	AKH1-S-1	173.74	3.0E-03	2.8E-04	0.0E+00	3.2E-03	1.0E-01	2.1E-03	0.0E+00	1.0E-01
6	MTA1-S-1	91.35	1.6E-03	1.5E-04	0.0E+00	1.7E-03	5.4E-02	1.1E-03	0.0E+00	5.5E-02
7	HAG1-S-1	16.94	2.9E-04	2.7E-05	0.0E+00	3.2E-04	1.0E-02	2.0E-04	0.0E+00	1.0E-02
8	SHA1-S-1	114.65	1.9E-03	1.8E-04	0.0E+00	2.1E-03	6.8E-02	1.4E-03	0.0E+00	6.9E-02
9	MTA2-S-1	10.34	1.8E-04	1.7E-05	0.0E+00	1.9E-04	6.1E-03	1.2E-04	0.0E+00	6.2E-03

Annex IV: Estimated daily intake of the heavy metals that were assessed via the consumption of foodstuffs

Table 27: Estimated daily intake of the heavy metals that were assessed by males for each foodstuff and their sum.

Food product	Mercury [mg/kg BW/day]	Arsenic [mg/kg BW/day]	Cadmium [mg/kg BW/day]	Copper [mg/kg BW/day]	Molybdenum [mg/kg BW/day]	Nickel [mg/kg BW/day]	Lead [mg/kg BW/day]
Hazelnut	0.0000000000	0.0000065753	0.0000000000	0.0006396869	0.0000191624	0.0000572994	0.0000000000
Bean	0.0000000000	0.0000176125	0.0000016634	0.0008776908	0.0026457926	0.0001174168	0.0000000000
Potato	0.0000000000	0.0000039139	0.0000076321	0.0015655577	0.0001724070	0.0000704501	0.0000000000
Malva	0.0000000235	0.0000016438	0.0000007280	0.0000432094	0.0000125871	0.0000044618	0.0000051663
Onion	0.0000000000	0.0000039139	0.0000019569	0.0003365949	0.0000724070	0.0000000000	0.0000000000
Nectarine	0.0000000000	0.0000187867	0.0000000000	0.0001268102	0.0000089237	0.0000000000	0.0000000000
Fig	0.0000000000	0.0000023483	0.0000000000	0.0001749511	0.0000132681	0.0000199609	0.0000000000
Plum	0.0000000000	0.0000000000	0.0000000000	0.0003569472	0.0000000000	0.0000000000	0.0000000000

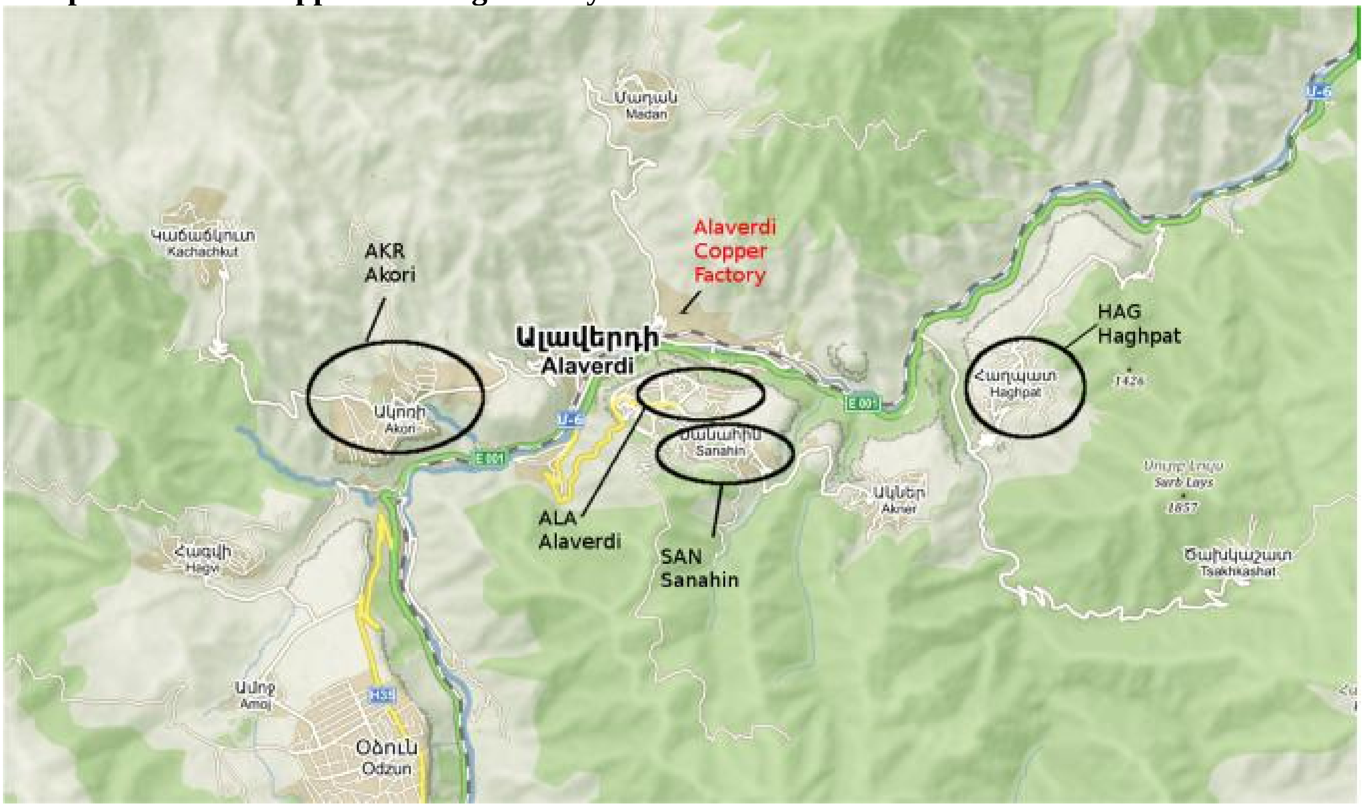
Basil	0.0000000196	0.0000013699	0.0000000000	0.0000348337	0.0000093151	0.0000017613	0.0000000000
Cornelian cherry	0.0000000000	0.0000023483	0.0000000000	0.0000375734	0.0000019961	0.0000000000	0.0000000000
Pear	0.0000000000	0.0000000000	0.0000000000	0.0003545988	0.0000068102	0.0000117417	0.0000000000
Beetroot	0.0000000000	0.0000000000	0.0000078278	0.0005166341	0.0000195695	0.0000000000	0.0000000000
Carrot	0.0000000000	0.0000078278	0.0000000000	0.0002661448	0.0000446184	0.0000000000	0.0000000000
Apple	0.0000000000	0.0000000000	0.0000000000	0.0000704501	0.0000131507	0.0000000000	0.0000000000
Honey	0.0000000000	0.0000000000	0.0000000000	0.0000090020	0.0000002935	0.0000009785	0.0000000000
Sum of all foodstuffs	**0.0000000431**	**0.0000663405**	**0.0000198082**	**0.0054106849**	**0.0030403014**	**0.0002840705**	**0.0000051663**

Table 28: Estimated daily intake of the heavy metals that were assessed by females for each foodstuff and their sum.

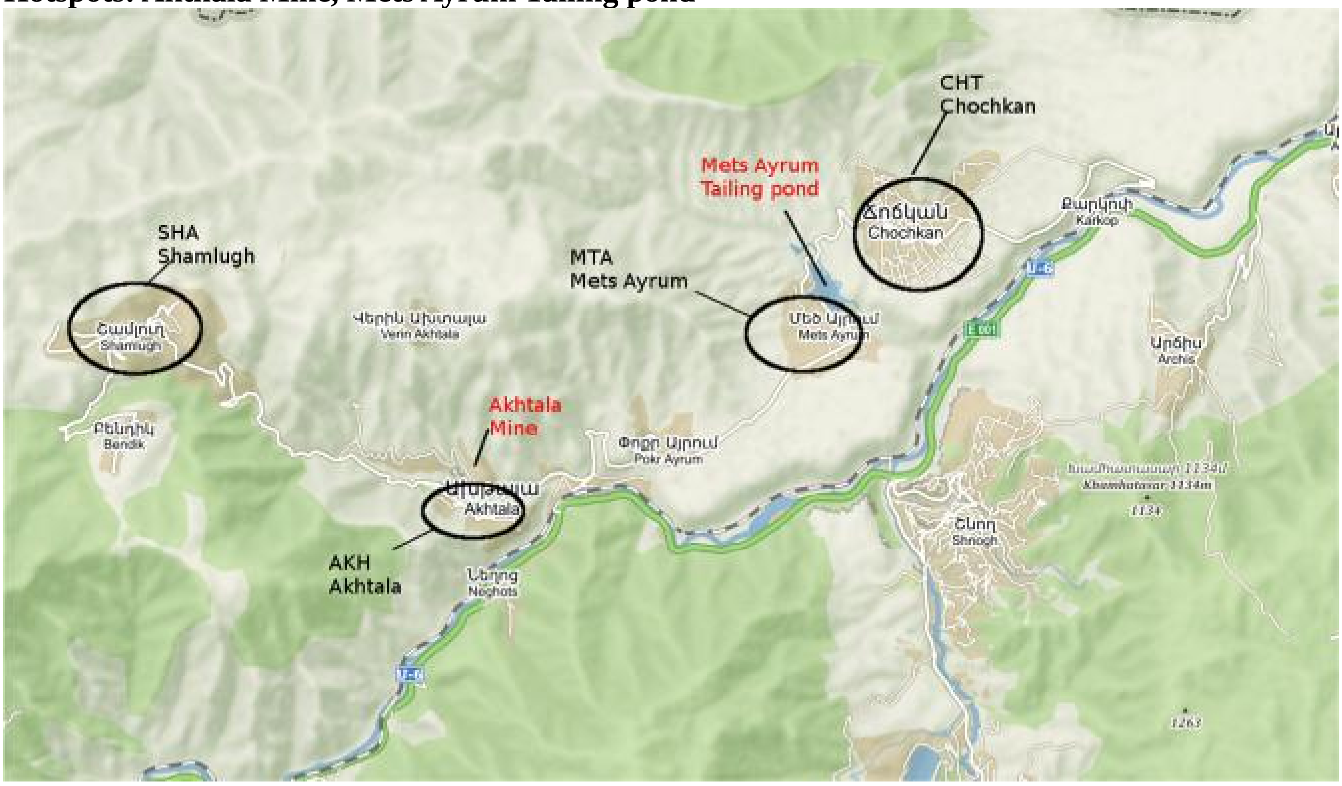
Food product	Mercury [mg/kg BW/day]	Arsenic [mg/kg BW/day]	Cadmium [mg/kg BW/day]	Copper [mg/kg BW/day]	Molybdenum [mg/kg BW/day]	Nickel [mg/kg BW/day]	Lead [mg/kg BW/day]
Hazelnut	0.0000000000	0.0000076712	0.0000000000	0.0007463014	0.0000223562	0.0000668493	0.0000000000
Bean	0.0000000000	0.0000205479	0.0000019406	0.0010239726	0.0030867580	0.0001369863	0.0000000000
Potato	0.0000000000	0.0000045662	0.0000089041	0.0018264840	0.0002011416	0.0000821918	0.0000000000
Malva	0.0000000274	0.0000019178	0.0000008493	0.0000504110	0.0000146849	0.0000052055	0.0000060274
Onion	0.0000000000	0.0000045662	0.0000022831	0.0003926941	0.0000844749	0.0000000000	0.0000000000
Nectarine	0.0000000000	0.0000219178	0.0000000000	0.0001479452	0.0000104110	0.0000000000	0.0000000000
Fig	0.0000000000	0.0000027397	0.0000000000	0.0002041096	0.0000154795	0.0000232877	0.0000000000
Plum	0.0000000000	0.0000000000	0.0000000000	0.0004164384	0.0000000000	0.0000000000	0.0000000000
Basil	0.0000000228	0.0000015982	0.0000000000	0.0000406393	0.0000108676	0.0000020548	0.0000000000
Cornelian cherry	0.0000000000	0.0000027397	0.0000000000	0.0000438356	0.0000023288	0.0000000000	0.0000000000
Pear	0.0000000000	0.0000000000	0.0000000000	0.0004136986	0.0000079452	0.0000136986	0.0000000000
Beetroot	0.0000000000	0.0000000000	0.0000091324	0.0006027397	0.0000228311	0.0000000000	0.0000000000
Carrot	0.0000000000	0.0000091324	0.0000000000	0.0003105023	0.0000520548	0.0000000000	0.0000000000
Apple	0.0000000000	0.0000000000	0.0000000000	0.0000821918	0.0000153425	0.0000000000	0.0000000000
Honey	0.0000000000	0.0000000000	0.0000000000	0.0000105023	0.0000003425	0.0000011416	0.0000000000
Sum of all foodstuffs	**0.0000000502**	**0.0000773973**	**0.0000231096**	**0.0063124658**	**0.0035470183**	**0.0003314155**	**0.0000060274**

Annex V: Maps of sampling areas

Hotspot: Alaverdi Copper Smelting Factory



Hotspots: Akthala Mine, Mets Ayrum Tailing pond



Annex VI: Pictures

Sampling sites close to tailing pond

Malva – sample with high level of cadmium

Land after irrigation in Akhtala garden. People very often use water from Shamlugh river and Debed river, where also waste waters from mines and copper factory flows.

This document has been produced with the financial assistance of the Ministry of Foreign Affairs of the Czech Republic under the Transformation Cooperation Programme. This work is part of the project "Empowering civil society in Alaverdi and Akhtala in addressing problems with industrial pollution", implemented by Arnika – Toxic and Waste Programme, Center for Community Mobilization and Support (CCMS), and Ecolur, under the Transformation Cooperation Programme. The production of this publication was also made possible thanks to the Global Greengrants Fund.