Heavy metals in the surroundings of mining and metallurgical sites in the Lori region in Armenia

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This report was prepared and published as a part of the project "Involvement of Civil Society in Decision making Process on Mining in Armenia", 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 IPEN, and the Global Greengrants Fund.
The Project was implemented by Arnika – Toxics and Waste Programme, based in Prague, Czech Republic, Armenian Women for Health and Healthy Environment (AWHHE), based in Yerevan, Armenia, and Ecolur, based in Yerevan, Armenia.

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ARNIKA ECOLUR NEW INFORMATIONAL POLICY IN ECOLOGY Armenian Women for Health and Healthy Environment NGO TRANSITION GLOBAL GREENGRANTS FUND

Summary

The study was focused on the monitoring and evaluation of pollution by heavy metals in the industrial region of Alaverdi in the north-east of Armenia.

A comprehensive sampling of soil, sediments, sand from children's playgrounds, and human hair was carried out to monitor the distribution of contamination with respect to potentially hazardous effects on human health. The sampling area covers the close surroundings of industrial facilities in Alaverdi (the Alaverdi metallurgical plant), Akhtala, and Teghut (copper and molybdenum mines and tailing ponds). These are found at or near the River Debed. All of these can be potential sources of heavy metal contamination, not only for their close surroundings but, via the River Debed, also for more distant regions. Considering industrial activities in the region, the main pollutant is copper, followed by other heavy metals such as arsenic, molybdenum, zinc, and lead.

Higher concentrations of copper and other heavy metals in river sediments, garden soils, and even the soils and sands of children's playgrounds indicate anthropogenic pollution with potential hazardous effects on the health of the local population. To minimize the risk, proper technological steps should be taken to reduce emissions from sources of pollution.

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 "Involvement of Civil Society in the Decision-making Process on Mining in Armenia", implemented by Arnika – Toxic and Waste Programme, Ecolur, and AWHHE (Armenian Women for Health and a Healthy Environment) under the Transformation Cooperation Programme. The production of this publication was also made possible thanks to the Global Greengrants Fund.

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1. Introduction

This study is focused on the presentation and discussion of data related to contamination by heavy metals in selected locations in the Lori region in Armenia. A comprehensive set of environmental and biological samples was taken and analysed. The environmental samples were sediments, soil (mostly from vegetable gardens or other agricultural fields), and sand or soil from children's playgrounds. Biological samples included human hair and free-range hens' eggs. The environmental samples and human hair samples were analysed for their heavy metal content and the results of the analysis are reported in this study. The investigation of hens' eggs is reported in a separate study.

The sampling of the environment in and around the municipalities of Alaverdi, Akhtala, and Teghut in the Lori region in Armenia took place in July 2018. 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 the samples that had been collected, with a focus on heavy metals. The analyses of the environmental samples took place at the University of Chemistry and Technology in Prague, Czech Republic, and biological samples of human hair were analysed by the National Institute of Public Health in the Czech Republic.

The evaluation of the influence of the copper-processing industry in the Alaverdi region on the local inhabitants and the environment is part of the study. The potential sources of pollution that were discussed are the Alaverdi copper and molybdenum smelter, the copper and molybdenum mines in Akhtala and 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 sediments and some areas which were not monitored.

The authors would like to acknowledge the NGOs participating in the sampling campaigns:

Armenian Women for Health and a Healthy Environment (AWHHE), based in Yerevan, Armenia

Ecolur, based in Yerevan, Armenia

Centre for Community Mobilization and Support, based in Alaverdi, Lori, Armenia

1.1. Potential sources of contamination

The area that was sampled covers the region of the municipalities of Alaverdi, Akhtala, Shnogh, and Teghut and their surroundings. There are mines, a smelting factory, and associated tailing ponds in the region. All of 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 watercourse on purpose.

All the emissions from these sources can be lowered using proper cleaning techniques or even the best available technologies (BAT) for waste management and wastewater treatment. Flue-gas cleaning will reduce atmospheric emissions. A variety of techniques can be implemented in the process, including particulate matter separators or scrubbers for the reduction of SO_x, NO_x, and other gases.

In previous studies [1,3-7,12-17,20,22-25] heavy metal pollution was found in the region. Most of the works concentrated on soil pollution (specifically, the concentration of heavy metals in soil) or the concentration of heavy metals (copper, lead, nickel, zinc) in river water and their effect on aquatic life. The results of the previous studies can be summarized in the following statements: "Investigations showed that as a result of mining and the activities of the metallurgical industry and the inadequate management of industrial waste and wastewater, the river ecosystems in these territories were exposed to heavy metal pollution." [15] and "According to the determined concentrations of the studied trace elements in fruits and vegetables, it can be stressed 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." [23]

Metallurgical plant, Alaverdi

Armenian Copper Programme, CJSC, is a metallurgical plant from the union of the Vallex group. It is located in the town of Alaverdi, which is in the Lori region in the north-east of Armenia. The town is situated at the bottom of the Debed river gorge. The town has an approximate population of 11,000 (2016). Since the end of the 18th century, the town 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. The company has more than 500 employees. [36]

A dominant feature of the factory is a chimney that smokes non-stop on the hill above the factory. The smoke from the smokestack 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 ACP copper smelter has been suspended since October 2018 because of unsatisfactory fulfilment of the rules concerning emissions.

Several studies [3,5,17,20,26] have shown higher concentrations of lead, arsenic, copper, and zinc in the soil and water in Alaverdi.

Copper mines and tailing dams, Akhtala

Akhtala is a historical town situated 15 km north-east of the town of Alaverdi, downstream from it along the River Debed. The population of Akhtala is around 1300 (2016). The town is located along the River Shamlugh, which enters the Debed.

Near Akhtala there are mines where copper and molybdenum ore is found and extracted. The ore is processed in the Akhtala Mountain Enrichment Combine, owned by Metal Prince Ltd. This company also uses an open tailing dam at Nahatak, near Mets Ayrum, approximately 8 km from Akhtala. Two other closed tailing dams can be found near Akhtala.

Mines and closed and open tailing dams are all potential sources of contamination of the environment by heavy metals. A high concentration of heavy metals (up to 250 mg/kg As and more than 180 mg/kg Pb, and more than 300 mg/kg Cu) was found by [3, 4], respectively. Excessive concentrations were also found by [18,25,27]. Water and mud of different colours (yellow, blue) have been reported and local inhabitants claim to suffer from illness such as nausea, headaches, or cancer.

Mine and tailing dam, Teghut

Teghut lies in the valley of the River Shnogh, which flows into the River Debed approximately 20 km from Alaverdi. In the vicinity of Teghut there is a newly built (opened 2015, temporarily closed in 2018) copper and molybdenum mine, one of the largest in Armenia. The production capacities of "Teghut" CJSC allow annual production of more than 100,000 tons of copper and over 1,000 tons of molybdenum concentrate. The mine was built by the Vallex group company, which used a loan from a Danish pension fund, but the loan was withdrawn after an environmental regulation had been breached.

Environmental problems still remain, and local people accuse the mine of leaking and discharging leachate into the environment. They also claim to have lower crop yields. There are some uncertainties concerning the outflow from the tailing dam. [1,6-8,21,29]

1.2. Effects of exposure to heavy metals on human health

Copper, zinc, and molybdenum, which are present in excessive concentrations, are at the same time essential elements and their presence in the human body is required. While they are effectively received exclusively through diet, the presence of these elements in higher concentrations can cause some undesirable effects. On the other hand, lead and arsenic, found in some samples, are highly toxic and their intake must be avoided.

The literature [2,17,23] confirms that there are high concentrations of heavy metals (copper, zinc, molybdenum, and lead) in regions with mining and smelting activities. These studies also claim that heavy metals have harmful effects on the health of local populations. The World Health Organization (WHO) and US Environmental Protection Agency (EPA) have specified limits for the safe daily intake in food or drinking water of individual toxic agents.

Copper

Copper is an essential biogenic element and is found in the human body as part of several enzymes. The daily dose of copper in a diet should be around 1 mg. The only way to accept copper effectively is through the intake of nutrition.

The average concentration of copper in the earth’s crust is between 25 and 75 mg/kg (ppm), and soil generally contains between 2 and 250 ppm copper, although concentrations close to 17,000 ppm have been found near copper mines, smelters, and brass production facilities. High concentrations of copper may be found in soil because dust from these industries settles out of the air, or wastes from mining and other copper industries are disposed of on the land. Copper generally stays firmly attached to the surface layer of soil. Copper has a tendency to be absorbed by solid organic matter, clay minerals, and oxyhydroxides, i.e. compounds with a large surface.

One may be exposed to this copper by skin contact. Children may also be exposed to this copper by hand-to-mouth contact and eating contaminated dirt and dust.

Humans and other mammals have efficient mechanisms to regulate copper levels in the body in such a way that they are generally protected from excess dietary copper levels. However, at high enough levels, chronic overexposure to copper can damage the liver and kidneys. Copper, as well as other heavy metals, may contribute to the development of neurological diseases such as Alzheimer's or Parkinson's disease. The EPA does not classify copper as a human carcinogen. An excess of copper ions can cause oxidative stress to plants.

Molybdenum

Molybdenum often accompanies copper in its ores and it has a strong connection to the copper system in living organisms too. Molybdenum is an element that is present in various enzymes. An imbalance in one's copper-molybdenum-sulphur intake can lead to anaemia, gastrointestinal disturbances, bone disorders, and growth retardation.

The level of molybdenum in normal soil varies between 0.25 and 5 ppm (mg/kg). In mining areas and near molybdenum-emitting industries, considerably higher values have been reported. Several cases of workers exposed to high doses of molybdenum have been reported around the world.

Both acute and prolonged exposure to excessive molybdenum may give rise to morphological changes in the liver, kidneys, and spleen. Proteinuria and functional disturbances of the liver have been reported. Other symptoms after prolonged exposure are anaemia, diarrhoea, and deformities of the joints and long bones, as well as the mandibular exostoses.

Arsenic

Arsenic is a naturally occurring element and is found throughout the environment; for most people, food is the major source of exposure. Acute (short-term) high-level inhalation exposure to arsenic dust or fumes results in gastrointestinal effects (nausea, diarrhoea, abdominal pain); disorders of the central and peripheral nervous system have occurred in workers acutely exposed to inorganic arsenic. Chronic (long-term) inhalation exposure to inorganic arsenic by humans is associated with irritation of the skin and mucous membranes and effects on the brain and nervous system.

The daily need for arsenic as a trace element ranges from 12-15 µg. Excessive levels of arsenic in the body can lead to serious health problems. Characteristic effects of As ingestion include generalized hyperkeratosis, warts or corns on the palms and soles, and areas of hyperpigmentation interspersed with small areas of hypopigmentation on the face, neck, and back.

Arsenic is classified as a human carcinogen. Epidermoid carcinoma of the skin, and to some extent lung cancer, may also be induced by long-term ingestion of arsenic-polluted water. Arsenic exposure may be assessed by analysing the As content in hair and nails, as arsenic tends to accumulate in these tissues over time as a result of the high sulphhydryl content of keratin, and is slowly excreted in this manner.

The toxicity of arsenic is dependent on its speciation; As^{III+} compounds are more toxic than AS^{V+} compounds.

Lead

Lead has been incriminated in a wide spectrum of toxic effects and it is considered to be one of the persistent heavy metals and is one of the global environmental pollutants. Its presence in blood is unfavourable at all concentrations as it is a xenobiotic for all life forms. Lead can cause effects on the blood, as well as the nervous, immune, renal, and cardiovascular systems. Early childhood and prenatal exposure is associated with slowed cognitive development, learning deficits, and other effects. Exposure to high amounts of lead can cause gastrointestinal symptoms and severe damage to the brain and kidneys, and may have effects on reproduction. There is no safe trashold for lead exposure.

Once taken into the body, lead becomes distributed throughout the body in the blood and is accumulated in the bones. Lead is responsible for the induction of oxidative stress by the elevation of reactive oxygen species and inhibits the reactions of enzymes.

Zinc

Zinc is an essential trace element. It is considered to be relatively non-toxic, particularly if taken orally. The daily need for an adult healthy person is 9 to 11 mg of zinc, children from 2 to 8 mg, women during pregnancy and lactation from 11 to 13 mg. Rather than zinc toxicity, zinc deficiency is observed. However, manifestations of toxicity symptoms (nausea, vomiting, epigastric pain, lethargy and fatigue) will occur with extremely high zinc intakes, over 300 mg/d, which is about 20 times above the Recommended Dietary Allowance (RDA) of 15 mg(d. Excessive zinc concentrations may lead to the deterioration of copper or iron metabolism.

The free zinc ion in solution is highly toxic to aquatic life: bacteria, plants, invertebrates, and even vertebrate fish. Humans may be exposed to Zn compounds such as ZnO fumes during moulding or welding, which can result in a nervous malady called metal fume fever.

1.3. Heavy metals in human hair

Study on mercury

The sampling of human hair is part of a more extensive study investigating the effects of exposure to mercury on people living close to mercury sources such as coal-fired power plants, waste incinerators, gold mines, non-ferrous smelters, and others. Mercury sources are listed in the Minamata Convention. An IPEN-governed study [37] collected samples of women of childbearing age across a high number of localities. The goal of the study was to inform the local populations of such areas about the possible danger and to monitor the spread of mercury around the globe.

Exposure to mercury – even small amounts – may cause serious health problems and is a threat to the development of a child in utero and early in life. Mercury may have toxic effects on the nervous, digestive, and immune systems, and on the lungs, kidneys, skin, and eyes. Mercury is considered by the WHO to be one of the top ten chemicals or groups of chemicals of major public health concern. People are mainly exposed to mercury in the form of methylmercury when they eat fish and shellfish. Methylmercury is an organic compound arising as a metabolic by-product of aquatic animals exposed to inorganic mercury. Once methylmercury is in the environment, it becomes part of the food chain and accumulates up the food chain, polluting marine mammals, birds, and other animals that consume fish. Generally, higher concentrations are found in larger and older animals. Methylmercury pollution also harms the health of people who eat fish regularly. Testing fish and human hair for mercury is a good indicator of mercury pollution levels in various geographic regions and communities.

The analysis of the above-mentioned study, conducted by the Biodiversity Research Institute, found that 42% of the women sampled had average mercury levels above the US EPA health advisory level of 1 ppm, above which brain damage, IQ loss, and kidney and cardiovascular damage may occur. The study additionally found that 53% of the global sample of women measured more than 0.58ppm of mercury, a level associated with the onset of foetal neurological damage.

Hair sampling is not an invasive technique and can provide information about exposure to mercury over time, making it preferable to blood analysis. Hair is particularly relevant in assessing exposure to methylmercury in the diet. In 1990, the WHO decided that a total level of mercury in hair of less than 10,000 µg/kg of hair is unlikely to be associated with adverse health effects. Levels of mercury above this limit for a pregnant woman correspond to a risk of harm to the nervous system of the foetus: "*Women who might become pregnant, women who are pregnant, or women who are breastfeeding should not eat more than one small portion (<100g) per week of large predatory fish, such as swordfish, shark, marlin, and pike. If they eat this portion, they should not eat any other fish during this period. Also, they should not eat tuna more than twice per week. The advice also applies to young children.*"

Copper, zinc, arsenic, and lead in human hair

Hair can accumulate not only toxic metals such as lead and cadmium, but also essential metals such as zinc, manganese and iron, which can be taken into consideration when evaluating metal pollution in the environment.

Copper occurs at approximately 15 mg/kg (10-30 mg/kg), zinc at 200 mg/kg (150-220 mg/kg) [22,24,32,41]. Sex does not influence Cu and Zn, while age influences Cu and Zn concentrations, but only significantly in females; Cu levels decrease above 60 years of age, whereas Zn levels increase significantly with age. Hair colour influences Cu concentrations in both males and females. In males, white hair contains less Cu than black hair; in females, white hair's Cu levels are significantly lower than those of dark blond, red, light brown, and brown hair. There are no significant differences in Zn concentrations with respect to different hair colours in either males or females.[9] Lead was found in the hair of humans exposed to pollution in concentrations from 5 to 20 or, sporadically, 50 mg/kg. [24,27] Arsenic, if present in human hair, was found in concentrations up to 0.5 mg/kg in a study [11]. Another study [7] focused on arsenic-polluted water found concentrations from 0 to 20 mg/kg with an average of 9.22 mg/kg of As in hair, which corresponds with the findings of [40], with 0.7 and 6.1 mg/kg in clean and polluted areas, respectively.

The metal content in hair is not affected only by diet or environmental pollution, but an important role is also played by cosmetics used for hair care. Hair dyes may contain metals (e.g. lead). It has also been found that peroxide bleaches and permanents altered the levels of S, Ca, Fe, and Ni in hair, peroxide altered Zn, and perms increased Cu and As concentrations. [33]

2. Sampling procedures and analytical methods

2.1. Environmental sampling

In total, 60 environmental samples of soil and sediments were taken for chemical analyses. The area that was sampled covered the surroundings of the municipalities of Alaverdi, Akhtala, and Shnogh in the Lori region and also four background samples were taken near the Dilijan National Park. Background samples serve for the evaluation of concentrations of contaminants in comparison with the natural occurrence of these elements at a site which is not affected by anthropogenic pollution. The sampling was conducted according to a sampling plan covering areas both close to and distant from potential contamination hot-spots using a combination of results from previous studies, the Google Earth system, and reports from local activists. The samples were taken from public sites, kindergarten- or schoolyards, and private gardens. The exact GPS coordinates are listed in Annex 1 of this publication, "Sampling sites and identification of samples".

The samples were taken as mixed samples formed of several partial subsamples (the exact number of subsamples for each sample is given in the specific sampling protocol). Soil samples were taken with a steel trowel; sediment samples were taken either with a steel trowel or a plexi-glass core sampler. The samples were taken from the surface layer of soil/sediment from which potential vegetal cover was removed. The samples were homogenized in a steel bowl and transferred into 250-ml polyethylene containers. After each sampling all the sampling equipment was cleaned with tap or with river water if available. The samples were initially stored in a dry place at normal temperature and then, after transport to the laboratory, in a refrigerator, where they were kept until the analysis.

2.2. Sampling of biological samples

Human hair was taken from women living or working in Alaverdi. 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 she smokes or lives in the presence of a smoker, and if she dyes her hair. Selected information is shown in Annex 5: Hair sampling. Approximately 30 strands of hair were cut from the occipital region of the head, as close to the scalp as possible.

2.3. Analytical techniques

Chemical analyses for determination of the heavy metal concentration in soil and sediments 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 (15 g) was used for the determination of dry matter by a gravimetric method. Another representative part was taken for analysis of heavy metals by means of a mineralization procedure. The analytical procedure used for the mineralization was as follows: 15 g of the sample was placed into a beaker together with 10 ml of distilled water, 30 ml of concentrated nitric acid, and 10 ml of concentrated hydrochloric acid. The mixture was boiled for 2 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 (As, Cu, Pb) in the biological samples 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.

2.4. RISC analysis

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. Children are more threatened by soil pollution, with hand-to-mouth ingestion of soil being the main route of exposure. Other common exposure pathways are dermal contact with soil or ingestion of vegetables growing in contaminated soil.

If the value of carcinogenic risk 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. If there is a hazard quotient (HQ) <1 it is considered that there are no significant adverse health effects, whereas a HQ >1 implies that potential adverse health effects exist. More research must be done in order to determine any toxic threats.

3. Limits and regulations for heavy metal concentrations in soil

While the presence of some elements in different types of soil 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, shown below in Table 1, were used for comparison with the results of the samples to gain a view of local pollution levels.

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. Concentrations of pollutants in 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, agriculture...).

The concentrations of pollutants in the samples from playgrounds were compared with the hygienic limits set by Decree no. 238/2011 for playgrounds in the Czech Republic (MZD 2011).

*Table 1 Limits and standards for heavy metal pollution in soil: Armenian maximum allowable concentration; French and Dutch soil standards, US EPA (United States Environmental Protection Agency) screening level, which, when exceeded, leads to the classification of soil as polluted for industrial and other areas; pollution concentration of which an excess can threaten the health of humans and animals; background level in normal Czech soil, *6-valent Cr All concentrations in mg/kg of dry matter.*

	As	**Cd**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Zn**
Armenian soil standards	2	NA	6.0	3	NA	4.0	32	NA
French soil standards	37	20	NA	190	NA	NA	400	NA
Dutch soil standards	34	1.6	100	40	254	38	140	160
US EPA –	2.4	800	5.6*	41,000	5100	20,000	800	310,000

industrial areas								
US EPA – other areas	0.61	70	0.29*	3100	390	1500	400	23,000
Czech pollution indication	40	20	NA	300	NA	200	400	400
Czech background concentration	20	0.5	90	60	NA	50	60	120
Czech playgrounds	10	0.3	85	45	0.8	60	50	90

The values of Czech pollution indicators shown in Table 1 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, Zn). The same decree was also used to list background levels found in non-polluted soils.

The content of metals can be compared with other auxiliary criteria (Table 2) – soil pollution criteria according to the methodological guidelines of the Czech Ministry of the Environment of 31 July 1996. These criteria are not legally binding; however, they are often applied in the Czech Republic on a voluntary basis.

Table 2 Auxiliary criteria for soils. The concentration of elements is given in mg/kg of dry matter. Description below.

Criterion (mg/kg)	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Mo**	**Ni**	**Pb**	**Zn**
A	30	0.5	130	70	0.4	0.8	60	80	150
B	65	10	450	500	2.5	50	180	250	1500
C – residential area	70	20	500	600	10	100	250	400	2500
C – recreational area	100	25	800	1000	15	160	300	400	3000
C – industrial area	140	30	1000	1500	20	240	500	600	5000

Criterion A approximately corresponds with the natural concentration level of the chemical substance in the environment. The exceeding of criterion A is considered as contamination of the particular environmental compartment except in areas with a naturally higher abundance of the chemical substance. If criterion B is not exceeded, the contamination is not considered sufficiently significant to justify the need for more detailed information on the contamination. e.g. to start an investigation or monitoring of the contamination.

Criterion B is considered a contamination level that may have negative impacts on human health and individual environmental compartments. It is necessary to gather additional information to find out whether the site represents a significant environmental burden and what risks it poses. Criterion B is therefore designed as an intervention level which, when exceeded, justifies the demand for further investigation of the contamination. The exceeding of criterion B requires a preliminary assessment of the risks posed by the contamination, the identification of its source and reasons, and – depending on the results of the investigation – a decision on further investigation and starting a monitoring campaign.

The exceeding of criterion C represents contamination which may pose a significant risk to human health and environmental compartments. The risk level can be determined only by a risk analysis. The recommended levels of remediation target parameters resulting from the risk analysis can be higher than criterion C. In addition to the risk analysis, assessments of technical and economic aspects of the problem solution are necessary documents for the decision on the type of remedial measures.

4. Results

Summary results are shown in Table 3 below; all the results for each sampling site are shown in Table 9 in Annex 2, "Heavy metal content in environmental samples". The set of sample results for focused elements has a wide range, from low values with no pollution to high concentrations of pollutants.

A higher concentration of copper is found in most samples. Copper is often accompanied by molybdenum and zinc or, in fewer cases, by lead and arsenic. Nickel and cadmium were not found in excessive concentrations.

Table 3 Summary of heavy metal concentrations in soil and sediment samples. The results are shown in mg/kg of dry matter. Minimum, maximum, and mean values for each element are shown along with the standard deviation. High values of standard deviations indicate high disparity of the data set, ranging from clean to highly polluted sites.
**The standard deviation for copper is calculated from the set without the five most outlying values.*

	As	Cd	Cr	Cu	Mo	Ni	Pb	Zn
min	< 3.00	< 0.20	4.00	22.9	< 0.70	2.25	0.75	33.5
max	143	5.05	233	59150	1667	33.9	206	4320
median	*15.9*	*0.57*	*23.4*	*439*	*5.70*	*16.8*	*33.0*	*258*
STD	31.4	1.00	36.5	980*	300	9.81	49.0	702

The highest concentrations of heavy metals were found in samples suspected of causing pollution – samples of slag (more than 9000 mg/kg Cu; 1300 mg/kg Mo; 200 mg/kg Cr), sediment from the water puddles in front of a closed shaft (up to 60000 mg/kg Cu), and sediments from the River Shamlugh close to active mines (>7000 mg/kg Cu). However, these samples were followed by children's playgrounds (>1000 mg/kg Cu; 200 mg/kg Pb; 140 mg/kg As) in Alaverdi and sediments of the Debed downstream from the Alaverdi smelter (2,200 mg/kg Cu, 350 mg/kg Mo). The lowest concentrations of heavy metals (<30 mg/kg Cu; <1 mg/kg Mo; <20 mg/kg Pb) were found in the four background samples from the Dilijan National Park, which were sampled as reference material.

Other samples vary in terms of their concentrations of pollutants according to their location, orientation to exposure to pollution (sites sheltered from the wind show lower pollution), or land use (soil from gardens watered with polluted river water is more polluted than soil from gardens which use clean water from different sources). The results of the sampling provide evidence on the spread of the pollution from hot-spots to the surroundings. The distribution of pollution takes place both by water and by wind.

There are at least three contributors to the pollution of the River Debed. The presence of heavy metals in sediments from the River Debed grows as the river goes downstream. While upstream, before the river enters the town of Alaverdi, the concentration of copper in the sediment is 73 mg/kg and that of zinc 256 mg/kg and molybdenum is below the detection limit, in the town centre, below the smelter, the concentrations rise to 2260 mg/kg Cu; 359 mg/kg Zn, and 603 mg/kg Mo. These concentrations then decrease and stabilize their values to 800-900 mg/kg Cu; 300 mg/kg Zn, and 200 mg/kg Mo. However, Debed sediments are then again more polluted after receiving water from the Rivers Shamlugh and Snogh in Akhtala and Shnogh, respectively. These two rivers gain heavy metals from mines and tailing dams in their upstream parts. Again, the Shnogh sediment upstream from sources of pollution is cleaner (100 mg/kg Cu) than sediments from the downstream part (from 400 to 800 mg/kg Cu). The upstream part of the River Shamlugh was not sampled because of the location of the mine, with a restricted area. However, sediments from the Shamlugh are among the most polluted samples of the study. The concentration of copper exceeds 1200 mg/kg and reaches up to 9500 mg/kg. Copper is here accompanied by zinc in a concentration over 1200 mg/kg. The water of the Shamlugh can be described (not only at the time of sampling but also from local reports) as yellow-coloured, with a large amount of fine colloidal particles. Another observed phenomenon is the presence of a blue layer, presumably of copper sulphate, on rocks in the creek.

All three rivers (the Debed, Shamlugh, and Shnogh) serve as water sources for watering gardens in the area. This means further spread of the contamination, which now directly affects human health through the contamination of the current vegetable crop. Along the rivers gardens can be found with copper concentrations in the soil ranging from 600 to 2000 mg/kg. One of the exceptions is a garden where clean water which is not from the river is used for watering and the soil contains 142 mg/kg Cu.

Another way in which pollution is distributed is by atmospheric emissions through the wind. Smoke from the Alaverdi smelter reaches all the settlements around and above Alaverdi – Sanahin, Haghpat, Akori, and Madan. Soils from children's playgrounds, gardens, orchards, and fields show the presence of heavy metals, not only copper. Copper is present in concentrations from 400 and often over 600 mg/kg and zinc from 100 mg/kg, and in some cases lead and arsenic are present at around 150 or 100 mg/kg, respectively. The samples from these localities show high variations in pollution, which may be caused by different exposure to pollution-bearing winds. Several sites with copper concentrations less than 300 mg/kg are found. More distant areas, such as Odzun, with an even lower copper concentration (<150 mg/kg), do not show pollution.

Pollution found in garden soils may confirm reports from locals about lower crop production and plant damage caused by polluted air. Plants in some gardens show visible damage resulting from oxidative stress.

Another source of pollution is slag piles found along the roads. Slag is a material containing high concentrations of heavy metals (>5000 mg/kg Cu; >1300 mg/kg Mo; >170 mg/kg Cr) but also a potential source of carcinogenic polychlorinated dibenzodioxins (PCDD/F). Slag, probably serving as winter road cover, was found at several locations along the roads each 2 m in piles of approx. 15 kg. The piles were open to the atmosphere and therefore it was possible for contaminants to be leaked into the environment.

Results show that pollution in the area is present and spread. To minimize the risk on human health some actions regarding the waste management (wastewater, air emissions, slag) should be taken to consideration.

4.1. Comparison of heavy metal levels in environmental samples with legislative thresholds

Since the Armenian soil standards for heavy metals are very strict, a high number of samples (in fact almost all of them) did 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 other areas and two Czech accesses – 1) pollution indication from Czech Decree No. 153/2016, issued by the Ministry of Agriculture, which describes the protection of the quality of agricultural soil, and 2) soil pollution criterion B according to the methodological guidelines of the Czech Ministry of the Environment, which are not legally binding but are considered as a contamination level that may have negative impacts on human health and individual environmental compartments. Soil or sand from children's playgrounds was compared with the hygienic limits set by Decree No. 238/2011 for playgrounds in the Czech Republic (MZD 2011). Selected limits are shown below in Table 4.

A total of 58 samples of soil and sediments was analysed. The numbers of samples exceeding the selected standard for each parameter are shown in Table 5. The Armenian soil standards were exceeded in the majority of cases. In comparison with other standards, the pollution is not so vast. According to this evaluation, the pollution is caused mainly by As, Cu, and Zn. Out of six samples from playgrounds, none would pass comparison with the Czech limits for playgrounds, as the Cu, Mo, and Zn levels were high in all the samples, As, Cd, and Pb were found in excessive concentrations in four or three (Pb) samples out of six. The best results are shown by the samples ALVD-2-PLAY-2 and SANAH-1-SAND-1.

Table 4 Standards used for comparison of soil pollution in mg/kg of dry matter

	As	Cd	Cr	Cu	Mo	Ni	Pb	Zn
Armenian soil standards	2	NA	6	3	NA	4	32	NA
US EPA – other areas	0.61	70	0.29*	3100	390	1500	400	23,000
Czech pollution indication	40	20	NA	300	NA	200	400	400
Czech auxiliary criterion B	65	10	450	500	50	180	250	1500
Czech playgrounds	10	0.3	85	45	0.8	60	50	90

Table 5 Number of samples with an excessive concentration; a total of 58 samples was compared with soil standards. Among others, six samples of soil from children's playgrounds were analysed.

	As	Cd	Cr	Cu	Mo	Ni	Pb	Zn
Armenian soil standards	57	NA	56	58	NA	53	29	NA
US EPA – other areas	57	0	NA	7	4	0	0	0
Czech pollution indication	14	0	NA	38	NA	0	0	20
Czech auxiliary criterion B	7	0	0	27	12	0	0	3
Czech playgrounds	4	4	0	6	5	0	3	6

4.2. Evaluation of pollution using RISC model

The RISC model was calculated for As and Pb; other elements (Cd, Cr, Ni) were not present in a relevant concentration or are not applicable for the model (Cu, Mo). Lead did not show any direct adverse effect in the model; however, arsenic occurred in some samples in such a high concentration as to have an adverse effect on children. Moreover, two of these samples were soils from children's playgrounds (ALA-3-PLAY-4 and ALA-3-PLAY-5). Other dangerous samples come from private gardens, where is also a potential of children being exposed to the contaminated soil. All the sediments from the River Shamlugh in Akhtala are at, or just above, the limit for the hazard quotient (HQ). The calculation of non-carcinogenic HQ and carcinogenic risks is shown in Annex 4: "Results of the calculation of human health risks associated with heavy metals – hazard quotients (HQ)" in Tables 12, 13, and 14. Table 6 below shows the HQ associated with As for the playground samples.

Table 6 Non-carcinogenic risk associated with arsenic in soil from children's playgrounds with computed hazard quotients (HQ). If there is a hazard quotient (HQ) <1 it is considered that there are no significant adverse health effects, whereas an HQ >1 implies that potential adverse health effects exist.

Sample	Concentration in soil As, mg/kg	Exposition pathway			
		Ingestion of soil	Dermal contact with soil	Ingestion of vegetables	Total HQ
ALA-3-PLAY-1	<5.0	0.0E+00	0.0E+00	0.0E+00	0.0E+00
ALVD-2-SAND-2-PLAY	31.3	2.2E-01	1.3E-02	4.1E-01	6.4E-01
ALA-3-PLAY-3	32.3	2.3E-01	1.4E-02	4.2E-01	6.6E-01
ALA-3-PLAY-4	143	1.0E+00	6.0E-02	1.9E+00	2.9E+00
ALA-3-PLAY-5	141	1.0E+00	5.9E-02	1.8E+00	2.9E+00
SANAH-1-SAND-1	8.09	5,7E-02	3,4E-03	1,1E-01	1,7E-01

4.3. Results of hair sampling

A total of 14 hair samples was analysed for heavy metals (Annex 6: "Hair analysis protocol with results"), specifically As, Cu, Hg, and Pb. The results for mercury were compared with the US EPA recommendation [15] of a 1000 µg/kg reference dose not to be exceeded in women of childbearing age and a level of 10,000 µg/kg, which can be associated with adverse health effects. As there are no recommendations or standards for other elements (As, Cu, Pb) in hair, the results were compared with several studies [7,11,40] dealing with concentrations of heavy metals or trace elements in the hair of healthy humans or humans exposed to pollution: copper occurs at approximately 15 mg/kg (10-30 mg/kg), zinc at 200 mg/kg (150-220 mg/kg), lead from 5 to 20 mg/kg. Arsenic, if present in human hair, can be found in concentrations from 0.5 up to 10 mg/kg.

From 14 hair samples taken in Alaverdi, 11 show good or normal results comparable with other studies from around the world. 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. The few fish-eaters consume fish from the supermarket, without using local sources of fish from Alaverdi. One sample (HGPT-2-HAIR-3) contained significantly higher concentrations of Cu, Pb, and Hg (1460; 23,2 and 0,192 mg/kg, respectively). These results may relate to the fact that the hair was bleached 1.5

months prior to sampling; however, as the part of the hair closest to the scalp was used for the analysis, hair bleaching does not seem to be the most important factor in there being a high concentration of heavy metals. The remaining two samples (HGPT-2-HAIR-2 and ALVD-2-HAIR-9) contain higher concentrations of copper (53 and 40 mg/kg, respectively) than the average. All three samples with elevated and high levels of heavy metals were taken from the only women from the group that was sampled who eat local fish. This factor contributes to the assumption that a human diet based on the consumption of local fish is the exposure pathway of heavy metals into the bodies of the women who were sampled.

All the samples met the US EPA limit for mercury (1.0 mg/kg) and contained only low or moderate concentrations of arsenic.

Table 7 Summary table of concentrations in mg/kg of heavy metals in hair. The copper data is computed with the sample HGPT-2-HAIR-3 excluded.

mg/kg	As	Cu*	Hg	Pb
min	<0.04	5	<0.012	0.13
max	0.480	53.4	0.246	23.2
mean	0.090	14.9	0.046	0.919
STD	0.175	13.6	0.071	6.032

5. Conclusion

The concentrations of heavy metals in the samples show pollution caused by copper processing plants. Contamination by copper, zinc, molybdenum, lead, or arsenic is found in both sediments and soils. Most of the sites that were sampled can be considered as polluted; in fact, only randomly distributed samples in the main area or the most distant sites did not show pollution.

According to the results, all the presumed potential sources (the Alaverdi copper smelter, the Akhtala and Teghut mines, and the tailing dams) seem to be a real threat to human health and the environment.

One area that is affected is the River Debed. It is an important river for the region and at the same time it is the main way in which pollution spreads to a larger area.

A high heavy metal content is also shown by three out of the six children's playgrounds that were sampled. Children are the most sensitive and most vulnerable group of the population and therefore affected more by pollution. It is also confirmed by the RICS model, which shows that at two playgrounds there is a direct adverse effect present.

All the hair samples met the US EPA limit for mercury (1.0 mg/kg, maximum concentration found 0.246 mg/kg of Hg). 11 out of 14 hair samples did not show high concentrations of other heavy metals (As, Cu, Pb), two samples contained a higher concentration of copper, and one sample contained a high concentration of heavy metals. All three samples with elevated or high concentrations of heavy metals are associated with the consumption of local fish, which probably represent the exposure pathway of heavy metals into the human body.

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7. Annexes

7.1. Annex 1 Sampling sites and identification of samples

Table 8 Information on sampling sites from sampling protocols

Sample ID	Sampling site	GPS	Material and preparation	Comment
AKH-3-SOIL-1	Akhtala, schoolyard	N 41°8’57.329” E 44°46’17.188”	clay-sandy soil, 8 subsamples, depth 0-10 cm, homogenization	
AKHT-1-SED-1A	Mets Ayrum, tailing pond	N 41°10’30.108” E 44°49’7.216”	sediment, 1 point sample, depth from 20 to 30 cm	green and blue colour
AKHT-3-KAL-1	Akhtala, road	N 41°9’19.692” E 44°47’7.476”	sludge, 15 homogenized subsamples from an area of 1 m2	Piles of dried sludge from tailing pond stored along the road
AKHT-3-SED-1	Akhtala, channel	N 41°8’57.444” E 44°46’54.732”	sandy grey sediment, 5 subsamples 2 m from each another, homog.	
AKHT-3-SED-2	Akhtala, shallow	N 41°9’36.288” E 44°43’55.056”	fine brown clay, 5 subsamples 1 m from each other, homog.	copper sulphate present on the rocks around shallow part
AKHT-3-SED-3	Akhtala, brook in forest	N 41°9’7.945” E 44°44’45.236”	sandy sediment on the brook banks, 5 subsamples, 1 m distance, homog. + quartation	brook with ochre-brown water flowing from mining shafts
AKHT-3-SED-4	Akhtala, brook in forest	N 41°9’7.945” E 44°44’45.236”	ochre-brown sediment, 15 subsamples taken along 100 distance, homog.	same site as AKHT-3-SED-3
AKHT-3-SED-5	Chochkan, brook in gardens	N 41°9’54.468” E 41°9’54.468”	sediment, 5 subsamples, 2 m from one another, homogenization	Brook flowing from the site of operating tailing pond
AKHT-3-SED-6	Chochkan, pipe in gardens	N 41°9’54.684” E 44°50’22.956”	clayish sediment, 1 point sample under the pipe end	Small pipe ending next to the garden fences bringing material from operating tailing pond
AKHT-3-SED-LJL	Karkop, River Debed	N 41 ° 10’ 48.8’’ E 44°51’’45,5’’	sediment, 5 samples along 10 m, by core sampler, homogenized	right bank under the bridge, municipal waste pollution

ALA-3-PLAY-1	Alaverdi, town centre playground	N 41°5'32.294" E 44°38'37.478"	playground soil under swings, 5 subsamples, homogenized	
ALVD-2-SAND-2-PLAY	Sanahin, schoolyard	N 41°4'18.408" E 44°37'6.866"	school playground, 5 subsamples, homogenization	ALA-3-PLAY-2
ALA-3-PLAY-3	Sanahin, kindergarten	N 41°5'34.84" E 44°39'18.212"	grassy kindergarten playground, 5 subsamples, homogenized	
ALA-3-PLAY-4	Alaverdi, kindergarten	N 41°5'30.466" E 44°39'17.467"	grassy kindergarten playground, 5 subsamples, homogenized	site of swimming pool
ALA-3-PLAY-5	Alaverdi, playground	N 41°5'52.616" E 44°39'18.482"	playground at a café, 5 subsamples, homogenization	
ALVD-1-SED-1	Tumanyan, River Debed	N 41°0'13.716" E 44°38'25.577"	sandy sediment, 5 subsamples, 10-m-long transect, homogenization	Debed upstream from Alaverdi, left bank
ALVD-1-SED-2	Alaverdi, town centre, River Debed	N 41°5'51.716" E 44°40'8.447"	sandy sediment, 3 subsamples, homogenization	under metallurgical plant, municipal waste pollution
ALVD-1-SED-3	Alaverdi, River Debed	N 41°6'2.448" E 44°41'47.465"	sandy sediment, 5 subsamples, from 30 m transect, homogenization	right bank on the road to Alaverdi, municipal waste pollution
ALVD-1-SED-4	Neghots, River Debed	N 41°7'59.34" E 44°45'50.404"	7 subsamples, distance 3 to 5 m, homogenization	left bank, greenery along river, municipal waste pollution
ALVD-1-SED-5	Alaverdi, shaft "Adit 5"	N 41°6'22.219" E 44°39'21.308"	orange clay, point sample	puddle next to shaft close to abandoned mine
ALVD-1-SLAG-1	Alaverdi, road to Akori	N 41°5'43.307" E 44°8'20.591"	brown inner layer of the slag pile, mixed sample from one pile	several slag piles along the road
ALVD-1-SLAG-1A	Alaverdi, road to Akori	N 41°5'43.307" E 44°8'20.591"	black surface layer of the slag pile, mixed sample from one pile	

ALVD-1-SOIL-1	Odzun, crop field	N 41°2′18.287″ E 44°37′24.182″	agricultural brown soil, 5 subsamples, homogenized	
ALVD-1-SOIL-2	Odzun, football pitch	N 41°3′44.384″ E 44°36′50.123″	dry soil, 5 subsamples, homogenized	
ALVD-1-SOIL-3	Odzun, corn field	N 41°3′54.151″ E 44°36′44.19″	agricultural brown soil, 5 subsamples, homogenized	
ALVD-1-SOIL-4	Madan, vegetable garden	N 41°7′29.222″ E 44°39′11.002″	dark brown soil, 5 subsamples, quartation, homogenization	leaves damaged by oxidation
ALVD-1-SOIL-5	Madan, meadow	N 41°7′24.208″ E 44°39′6.203″	5 subsamples, homogenization, content of organic matter	directly opposite the chimney
ALVD-1-SOIL-6	Akori, gardens and orchard	N 41°5′31.56″ E 44°36′44.863″	brown soil, 5 subsamples, homogenization	
ALVD-1-SOIL-7	Akori, vegetable garden	N 41°5′22.02″ E 44°37′14.754″	dark brown soil, 5 subsamples, homogenization	
ALVD-1-SOIL-8	Akori, orchard	N 41°5′41.233″ E 44°38′2.468″	dark brown soil, 5 subsamples, homogenization	
ALVD-1-SOIL-9	Sanahin, orchard	N 41°5′28.727″ E 44°39′58.432″	brown garden soil with roots, 5 subsamples, homogenization	
ALVD-1-SOIL-10	Sanahin, residential area	N 41°5′36.172″ E 44°39′45.266″	clay, 5 subsamples, homogenized	grassland with cows and municipal waste
ALVD-2-SOIL-1	Alaverdi, Andranik St.	N 41°5′57.444″ E 44°39′6.876″	flowerbed in school garden, 6 subsamples, homogenization	
ALVD2-SOIL-5	Alaverdi	N 41°5′54.708″ E 44°38′54.024″	brown soil from vegetable garden, 6 subsamples, homogenization	
ALVD-2-SOIL-6	Alaverdi	N 41°5′48.444″ E 44°40′12.972″	brown soil from vegetable garden, 6 subsamples, homogenization	
DIL-SED-1	Dilijan National Park	N 40°45′8.672″ E 44°57′56.678″	forest brook, brown sand, 5 subsamples,	background sample

			homogenization	
DIL-SED-2	Haghartzin, River Agstev	N 40°46’3.684” E 45°0’20.088”	pasture and rest site along river, dark grey sediment, 6 subsamples, homogenization	background sample
DIL-SOIL-1	Dilijan National Park, meadow	N 40°44’31.164” E 44°59’0.222”	brown soil, 3 subsamples, homogenization	background sample
DIL-SOIL-2	Dilijan National Park, Gosh	N 40°43’51.377” E 44°59’28.763”	orchard soil, 3 subsamples, homogenization	background sample, orchard above village of Gosh
HGPT2-SOIL-2	Haghpat	N 41°5’46.212” E 44°42’42.228”	brown vegetable garden soil, 6 subsamples, homogenization	
HGPT2-SOIL-3	Haghpat	N 41°5’45.744” E 44°42’44.28”	brown vegetable garden soil, 6 subsamples, homogenization	
HGPT2-SOIL-4	Haghpat	N 41°5’45.924” E 44°42’42.804”	brown vegetable garden soil, 6 subsamples, homogenization	
SANAH-1-SAND-1	Sanahin, children’s playground	N 41°5’31.394” E 44°39’9.104”	sand with dust and soil, point sample	children’s playground
SANAH-1-SOIL-1	Sanahin	N 41°5’24.277” E 44°39’22.55”	brown garden soil, 5 subsamples, homogenization	
SANAH-1-SOIL-2	Sanahin	N 41°5’22.639” E 44°39’19.681”	brown garden soil, 5 subsamples, homogenization	
TEG-1-SED-1	Teghut	N 41°7’24.402” E 44°50’31.97”	sandy sediment, 5 subsamples, homogenization	brook, drainage at tailing pond
TEG-1-SED-2	Teghut	N 41°10’11.802” E 44°50’44.175”		Debed, orchard
TEG-1-SED-3	Teghut	N 41°9’7.063” E 44°49’53.292”	eroded and sedimented sandy material, 5 subsamples,	Shnogh, at the confluence with the Debed

			homogenization	
TEG-1-SED-4	Teghut	N 41°7’31.804” E 44°50’29.63”	sandy light brown sediment, 7 subsamples, homogenization	Shnogh, river passing through green belt of gardens
TEG-1-SED-5	Teghut	N 41°7’31.746” E 44°50’29.519”	sandy light brown sediment, 7 subsamples, homogenization	Shnogh, upstream from tailing pond
TEG-1-SED-6	Teghut	N 41°8’39.167” E 44°49’57.594”	sandy light brown sediment, 5 subsamples, homogenization	Shnogh, meadow
TEG-1-SOIL-1	Teghut	N 41°8′40.266” E 44°50′1.729”	brown garden soil, 5 subsamples, homogenization	
TEG-1-SOIL-2	Teghut	N 41°8’40.266” E 44°50’1.729”	brown eroded organic soil, point sample	garden and orchard
TEG-1-SOIL-3	Teghut	N 41°10’8.62” E 44°50’47.169”	brown garden soil, 5 subsamples, homogenization	garden and orchard
TEG-1-SOIL-4	Teghut	N 41°7’32.912” E 44°50’24.59”	brown wet sandy soil with old spring, 5 subsamples, homogenization	ńext to residential area
TEG-1-SOIL-5	Teghut	N 41°7’31.804” E 44°50’29.63”	brown garden soil, 4 subsamples, homogenization	potentially clean sample, garden watering with clean water
TGPT-1-SOIL-6	Teghut, Archis	N 41°10’2.582” E 44°51’27.558”	brown garden soil, 5 subsamples, homogenization	orchard watered from River Debed

7.2. Annex 2 Heavy metal content in environmental samples

Table 9 Concentration of heavy metals in samples in mg/kg of dry matter.

sample	As, mg/kg	Cd, mg/kg	Cr, mg/kg	Cu, mg/kg	Mo, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
AKH-3-SOIL-1	26.0	0.72	29.2	262	2.06	29.4	61.7	260
AKHT-1-SED-1A	15.8	0.53	36.9	255	3.49	30.8	28.4	166
AKHT-3-KAL-1	54.5	1.26	6.28	545	8.51	2.25	37.2	473
AKHT-3-SED-1	54.4	2.70	6.17	1199	13.9	3.31	46.1	1212
AKHT-3-SED-2	55.8	2.88	4.00	9467	8.01	9.04	117	4322
AKHT-3-SED-3	50.5	1.07	33.9	2179	349	3.82	53.0	1359
AKHT-3-SED-4	53.0	5.05	17.1	7299	88.8	11.1	79.7	2725
AKHT-3-SED-5	74.7	1.54	8.43	816	14.1	3.58	56.7	586
AKHT-3-SED-6	52.4	0.87	7.40	533	19.0	2.80	37.5	312
AKHT-3-SED-LJL	15.6	0.88	36.5	1505	236	8.81	24.8	409
ALA-3-PLAY-1	<5.0	2.13	24.0	1091	<0.95	27.5	155	466
ALA-3-PLAY-3	32.3	0.82	25.5	218	3.23	21.9	48.5	249
ALA-3-PLAY-4	143	1.09	81.6	1007	72.7	32.9	206	1240
ALA-3-PLAY-5	141	3.69	55.8	5223	53.0	22.3	190	889
ALVD-1-SED-1	8.42	0.48	19.2	73.0	0.84	16.3	16.6	256
ALVD-1-SED-1	10.4	0.18	7.59	293	7.86	8.52	15.1	74.4
ALVD-1-SED-2	13.0	0.58	40.3	2260	603	11.9	13.8	359
ALVD-1-SED-3	10.9	0.50	23.3	819	184	9.37	36.7	271
ALVD-1-SED-4	10.1	0.57	26.6	954	218	9.31	16.3	338
ALVD-1-SED-5	108	0.49	18.2	59,148	14.5	4.48	22.5	759
ALVD-1-SLAG-1	24.2	0.17	175	5859	1307	4.67	3.39	757
ALVD-1-SLAG-1A	37.5	0.19	233	9379	1668	5.06	14.1	921
ALVD-1-SOIL-1	14.2	0.32	34.1	119	<0.9	33.9	21.0	120
ALVD-1-SOIL-10	13.0	0.26	22.5	76.9	1.14	27.1	24.2	107
ALVD-1-SOIL-2	15.9	0.27	23.0	94.4	0.93	24.9	29.3	108
ALVD-1-SOIL-3	9.82	0.39	23.1	153	<0.8	32.7	26.4	110
ALVD-1-SOIL-4	67.7	2.25	12.0	1038	2.27	10.7	122	425
ALVD-1-SOIL-5	68.6	1.73	8.43	710	2.36	5.72	133	257
ALVD-1-SOIL-6	17.1	0.89	39.1	284	1.79	24.0	64.1	187
ALVD-1-SOIL-7	19.5	1.35	38.6	599	1.66	28.4	88.6	325
ALVD-1-SOIL-8	14.8	0.79	23.8	389	<0.9	25.2	48.3	132
ALVD-1-SOIL-9	23.9	1.23	29.9	423	2.72	25.9	62.4	228
ALVD-2-SAND-2-PLAY	31.3	0.19	11.4	121	4.96	12.5	14.5	158
ALVD-2-SOIL-1	76.4	2.00	36.8	1713	5.70	25.9	156	612
ALVD2-SOIL-5	40.0	1.95	50.0	1273	2.63	31.6	132	1823
ALVD-2-SOIL-6	52.8	2.06	40.5	1931	2.26	29.0	104	442

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sample	**As, mg/kg**	**Cd, mg/kg**	**Cr, mg/kg**	**Cu, mg/kg**	**Mo, mg/kg**	**Ni, mg/kg**	**Pb, mg/kg**	**Zn, mg/kg**
DIL-SED-1	5.40	0.07	8.54	22.9	0.70	9.28	8.36	53.9
DIL-SED-2	8.19	<0.05	13.0	28.6	<0.8	9.67	10.1	55.6
DIL-SOIL-1	5.04	0.07	31.2	27.6	<0.8	19.6	7.51	61.4
DIL-SOIL-2	6.33	0.06	23.1	31.0	<0.9	15.6	11.9	78.7
HGPT2-SOIL-2	16.1	1.00	32.3	379	1.27	22.5	66.8	499
HGPT2-SOIL-3	15.3	0.88	37.2	432	1.63	26.9	65.8	477
HGPT2-SOIL-4	21.5	0.79	42.0	421	1.65	32.7	59.4	333
SANAH-1-SAND-1	8.09	0.13	9.84	319	64.4	16.9	11.5	149
SANAH-1-SOIL-2	15.4	0.27	23.2	145	1.38	21.6	40.9	202
TEG-1-SED-1	7.79	0.02	21.2	432	33.4	13.1	4.58	103
TEG-1-SED-2	16.0	0.45	47.6	4160	719	5.93	23.0	663
TEG-1-SED-3	5.19	0.12	7.96	645	26.5	7.00	2.18	43.6
TEG-1-SED-4	6.41	0.11	12.7	772	40.0	8.20	2.02	49.9
TEG-1-SED-5	4.96	<0.05	9.50	99.2	1.77	8.51	0.75	33.8
TEG-1-SED-6	4.91	0.11	5.35	481	23.5	5.68	1.36	33.5
TEG-1-SOIL-1	6.55	0.10	33.1	148	2.59	26.4	15.4	77.4
TEG-1-SOIL-1	11.0	0.26	21.6	153	1.61	22.6	38.2	181
TEG-1-SOIL-2	6.57	0.23	13.8	1900	14.8	16.7	6.82	85.5
TEG-1-SOIL-3	23.4	1.47	23.5	388	2.23	24.5	42.0	303
TEG-1-SOIL-4	8.46	0.08	16.3	445	45.5	16.8	8.63	144
TEG-1-SOIL-5	11.3	0.15	26.7	142	2.40	16.9	17.2	144
TGPT-1-SOIL-6	29.3	0.80	31.1	431	4.64	25.9	39.2	285

7.3. Annex 3: Legal standards for heavy metals in soil

Table 10 Limits and standards for heavy metal pollution in soil: Armenian maximum allowable concentration; French and Dutch soil standards, US EPA (United States Environmental Protection Agency) screening level which, when exceeded, means soil is classified as polluted for industrial and other areas; pollution concentration which, when exceeded, can threaten human and animal health; background level in normal soil, limits for playgrounds in the Czech Republic (MZD 2011).
**6-valent Cr*

	As	Cd	Cr	Cu	Mo	Ni	Pb	Zn
Armenian soil standard	2	NA	6.0	3	NA	4.0	32	NA
French soil standard	37	20	NA	190	NA	NA	400	NA
Dutch soil standard	34	1.6	100	40	254	38	140	160
US EPA – industrial areas	2.4	800	5.6*	41,000	5100	20,000	800	310,000
US EPA – other areas	0.61	70	0.29*	3,100	390	1500	400	23,000
Czech pollution indication	40	20	NA	300	NA	200	400	400
Czech background concentration	20	0.5	90	60	NA	50	60	120
Czech playground	10	0.3	85	45	0.8	60	50	90

7.4. Annex 4: Results of the calculation of human health risks associated with heavy metals – hazard quotients (HQ)

Table 11 Hazard quotients for carcinogenic risk associated with As. If the carcinogenic risk 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, 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.

Sample ID	Concentration As, mg/kg	Soil ingestion	Dermal contact	Vegetable consumption	Total CR
AKH-3-SOIL-1	26.01	7,0E-06	4,2E-07	1,3E-05	2,1E-05
AKHT-1-SED-1A	15.77	4,3E-06	2,5E-07	8,0E-06	1,3E-05
AKHT-3-KAL-1	54.52	1,5E-05	8,7E-07	2,8E-05	4,3E-05
AKHT-3-SED-1	54.45	1,5E-05	8,7E-07	2,8E-05	4,3E-05
AKHT-3-SED-2	55.76	1,5E-05	8,9E-07	2,8E-05	4,4E-05
AKHT-3-SED-3	50.49	1,4E-05	8,1E-07	2,6E-05	4,0E-05
AKHT-3-SED-4	52.99	1,4E-05	8,5E-07	2,7E-05	4,2E-05
AKHT-3-SED-5	74.68	2,0E-05	1,2E-06	3,8E-05	5,9E-05
AKHT-3-SED-6	52.43	1,4E-05	8,4E-07	2,7E-05	4,2E-05
AKHT-3-SED-LJL	15.60	4,2E-06	2,5E-07	8,0E-06	1,2E-05
ALA-3-PLAY-1	<5.0	NA	NA	NA	NA
ALA-3-PLAY-3	32.26	8,7E-06	5,2E-07	1,6E-05	2,6E-05
ALA-3-PLAY-4	143.24	3,9E-05	2,3E-06	7,3E-05	1,1E-04
ALA-3-PLAY-5	140.61	3,8E-05	2,2E-06	7,2E-05	1,1E-04
ALVD-1-SED-1	8.42	2,3E-06	1,3E-07	4,3E-06	6,7E-06
ALVD-1-SED-1	10.44	2,8E-06	1,7E-07	5,3E-06	8,3E-06
ALVD-1-SED-2	12.95	3,5E-06	2,1E-07	6,6E-06	1,0E-05
ALVD-1-SED-3	10.91	2,9E-06	1,7E-07	5,6E-06	8,7E-06
ALVD-1-SED-4	10.12	2,7E-06	1,6E-07	5,2E-06	8,1E-06
ALVD-1-SED-5	108.28	2,9E-05	1,7E-06	5,5E-05	8,6E-05
ALVD-1-SLAG-1	24.24	6,5E-06	3,9E-07	1,2E-05	1,9E-05
ALVD-1-SLAG-1A	37.54	1,0E-05	6,0E-07	1,9E-05	3,0E-05
ALVD-1-SOIL-1	14.23	3,8E-06	2,3E-07	7,3E-06	1,1E-05
ALVD-1-SOIL-10	13.00	3,5E-06	2,1E-07	6,6E-06	1,0E-05
ALVD-1-SOIL-2	15.94	4,3E-06	2,6E-07	8,1E-06	1,3E-05
ALVD-1-SOIL-3	9.82	2,7E-06	1,6E-07	5,0E-06	7,8E-06
ALVD-1-SOIL-4	67.66	1,8E-05	1,1E-06	3,5E-05	5,4E-05
ALVD-1-SOIL-5	68.62	1,9E-05	1,1E-06	3,5E-05	5,5E-05
ALVD-1-SOIL-6	17.14	4,6E-06	2,7E-07	8,7E-06	1,4E-05
ALVD-1-SOIL-7	19.53	5,3E-06	3,1E-07	1,0E-05	1,6E-05
ALVD-1-SOIL-8	14.83	4,0E-06	2,4E-07	7,6E-06	1,2E-05
ALVD-1-SOIL-9	23.93	6,5E-06	3,8E-07	1,2E-05	1,9E-05
ALVD-2-SAND-2-PLAY	31.28	8,4E-06	5,0E-07	1,6E-05	2,5E-05
ALVD-2-SOIL-1	76.36	2,1E-05	1,2E-06	3,9E-05	6,1E-05
ALVD2-SOIL-5	40.00	1,1E-05	6,4E-07	2,0E-05	3,2E-05
ALVD-2-SOIL-6	52.78	1,4E-05	8,4E-07	2,7E-05	4,2E-05
DIL-SED-1	5.40	1,5E-06	8,6E-08	2,8E-06	4,3E-06
DIL-SED-2	8.19	2,2E-06	1,3E-07	4,2E-06	6,5E-06
DIL-SOIL-1	5.04	1,4E-06	8,1E-08	2,6E-06	4,0E-06
DIL-SOIL-2	6.33	1,7E-06	1,0E-07	3,2E-06	5,0E-06
HGPT2-SOIL-2	16.08	4,3E-06	2,6E-07	8,2E-06	1,3E-05
HGPT2-SOIL-3	15.35	4,1E-06	2,5E-07	7,8E-06	1,2E-05
HGPT2-SOIL-4	21.54	5,8E-06	3,4E-07	1,1E-05	1,7E-05
SANAH-1-SAND-1	8.09	2,2E-06	1,3E-07	4,1E-06	6,4E-06
SANAH-1-SOIL-2	15.36	4,1E-06	2,5E-07	7,8E-06	1,2E-05
TEG-1-SED-1	7.79	2,1E-06	1,2E-07	4,0E-06	6,2E-06

TEG-1-SED-2	15.96	4,3E-06	2,6E-07	8,1E-06	1,3E-05
TEG-1-SED-3	5.19	1,4E-06	8,3E-08	2,6E-06	4,1E-06
TEG-1-SED-4	6.41	1,7E-06	1,0E-07	3,3E-06	5,1E-06
TEG-1-SED-5	4.96	1,3E-06	7,9E-08	2,5E-06	3,9E-06
TEG-1-SED-6	4.91	1,3E-06	7,9E-08	2,5E-06	3,9E-06
TEG-1-SOIL-1	6.55	1,8E-06	1,0E-07	3,3E-06	5,2E-06
TEG-1-SOIL-1	11.02	3,0E-06	1,8E-07	5,6E-06	8,8E-06
TEG-1-SOIL-2	6.57	1,8E-06	1,1E-07	3,4E-06	5,2E-06
TEG-1-SOIL-3	23.44	6,3E-06	3,7E-07	1,2E-05	1,9E-05
TEG-1-SOIL-4	8.46	2,3E-06	1,4E-07	4,3E-06	6,7E-06
TEG-1-SOIL-5	11.27	3,0E-06	1,8E-07	5,7E-06	9,0E-06
TGPT-1-SOIL-6	29.34	7,9E-06	4,7E-07	1,5E-05	2,3E-05

Table 12 Hazard quotients for non-carcinogenic risk for children associated with As. A hazard quotient (HQ) > 1.0 means that a risk is present, Q < 1.0 means that there are no significant direct adverse health effects.

Sample ID	Concentration As, mg/kg	Soil ingestion	Dermal contact	Vegetable consumption	Total HQ
AKH-3-SOIL-1	26.01	1,8E-01	1,1E-02	3,4E-01	5,3E-01
AKHT-1-SED-1A	15.77	1,1E-01	6,6E-03	2,0E-01	3,2E-01
AKHT-3-KAL-1	54.52	3,9E-01	2,3E-02	7,1E-01	1,1E+00
AKHT-3-SED-1	54.45	3,9E-01	2,3E-02	7,1E-01	1,1E+00
AKHT-3-SED-2	55.76	4,0E-01	2,3E-02	7,2E-01	1,1E+00
AKHT-3-SED-3	50.49	3,6E-01	2,1E-02	6,6E-01	1,0E+00
AKHT-3-SED-4	52.99	3,8E-01	2,2E-02	6,9E-01	1,1E+00
AKHT-3-SED-5	74.68	5,3E-01	3,1E-02	9,7E-01	1,5E+00
AKHT-3-SED-6	52.43	3,7E-01	2,2E-02	6,8E-01	1,1E+00
AKHT-3-SED-LJL	15.60	1,1E-01	6,6E-03	2,0E-01	3,2E-01
ALA-3-PLAY-1		0,0E+00	0,0E+00	0,0E+00	0,0E+00
ALA-3-PLAY-3	32.26	2,3E-01	1,4E-02	4,2E-01	6,6E-01
ALA-3-PLAY-4	143.24	1,0E+00	6,0E-02	1,9E+00	2,9E+00
ALA-3-PLAY-5	140.61	1,0E+00	5,9E-02	1,8E+00	2,9E+00
ALVD-1-SED-1	8.42	6,0E-02	3,5E-03	1,1E-01	1,7E-01
ALVD-1-SED-1	10.44	7,4E-02	4,4E-03	1,4E-01	2,1E-01
ALVD-1-SED-2	12.95	9,2E-02	5,4E-03	1,7E-01	2,7E-01
ALVD-1-SED-3	10.91	7,7E-02	4,6E-03	1,4E-01	2,2E-01
ALVD-1-SED-4	10.12	7,2E-02	4,3E-03	1,3E-01	2,1E-01
ALVD-1-SED-5	108.28	7,7E-01	4,5E-02	1,4E+00	2,2E+00
ALVD-1-SLAG-1	24.24	1,7E-01	1,0E-02	3,2E-01	5,0E-01
ALVD-1-SLAG-1A	37.54	2,7E-01	1,6E-02	4,9E-01	7,7E-01
ALVD-1-SOIL-1	14.23	1,0E-01	6,0E-03	1,8E-01	2,9E-01
ALVD-1-SOIL-10	13.00	9,2E-02	5,5E-03	1,7E-01	2,7E-01
ALVD-1-SOIL-2	15.94	1,1E-01	6,7E-03	2,1E-01	3,3E-01
ALVD-1-SOIL-3	9.82	7,0E-02	4,1E-03	1,3E-01	2,0E-01
ALVD-1-SOIL-4	67.66	4,8E-01	2,8E-02	8,8E-01	1,4E+00
ALVD-1-SOIL-5	68.62	4,9E-01	2,9E-02	8,9E-01	1,4E+00
ALVD-1-SOIL-6	17.14	1,2E-01	7,2E-03	2,2E-01	3,5E-01
ALVD-1-SOIL-7	19.53	1,4E-01	8,2E-03	2,5E-01	4,0E-01
ALVD-1-SOIL-8	14.83	1,1E-01	6,2E-03	1,9E-01	3,0E-01
ALVD-1-SOIL-9	23.93	1,7E-01	1,0E-02	3,1E-01	4,9E-01
ALVD-2-SAND-2-PLAY	31.28	2,2E-01	1,3E-02	4,1E-01	6,4E-01
ALVD-2-SOIL-1	76.36	5,4E-01	3,2E-02	9,9E-01	1,6E+00
ALVD2-SOIL-5	40.00	2,8E-01	1,7E-02	5,2E-01	8,2E-01

ALVD-2-SOIL-6	52.78	3,7E-01	2,2E-02	6,9E-01	1,1E+00
DIL-SED-1	5.40	3,8E-02	2,3E-03	7,0E-02	1,1E-01
DIL-SED-2	8.19	5,8E-02	3,4E-03	1,1E-01	1,7E-01
DIL-SOIL-1	5.04	3,6E-02	2,1E-03	6,6E-02	1,0E-01
DIL-SOIL-2	6.33	4,5E-02	2,7E-03	8,2E-02	1,3E-01
HGPT2-SOIL-2	16.08	1,1E-01	6,8E-03	2,1E-01	3,3E-01
HGPT2-SOIL-3	15.35	1,1E-01	6,4E-03	2,0E-01	3,1E-01
HGPT2-SOIL-4	21.54	1,5E-01	9,0E-03	2,8E-01	4,4E-01
SANAH-1-SAND-1	8.09	5,7E-02	3,4E-03	1,1E-01	1,7E-01
SANAH-1-SOIL-2	15.36	1,1E-01	6,5E-03	2,0E-01	3,2E-01
TEG-1-SED-1	7.79	5,5E-02	3,3E-03	1,0E-01	1,6E-01
TEG-1-SED-2	15.96	1,1E-01	6,7E-03	2,1E-01	3,3E-01
TEG-1-SED-3	5.19	3,7E-02	2,2E-03	6,7E-02	1,1E-01
TEG-1-SED-4	6.41	4,6E-02	2,7E-03	8,3E-02	1,3E-01
TEG-1-SED-5	4.96	3,5E-02	2,1E-03	6,4E-02	1,0E-01
TEG-1-SED-6	4.91	3,5E-02	2,1E-03	6,4E-02	1,0E-01
TEG-1-SOIL-1	6.55	4,6E-02	2,7E-03	8,5E-02	1,3E-01
TEG-1-SOIL-1	11.02	7,8E-02	4,6E-03	1,4E-01	2,3E-01
TEG-1-SOIL-2	6.57	4,7E-02	2,8E-03	8,5E-02	1,3E-01
TEG-1-SOIL-3	23.44	1,7E-01	9,8E-03	3,0E-01	4,8E-01
TEG-1-SOIL-4	8.46	6,0E-02	3,6E-03	1,1E-01	1,7E-01
TEG-1-SOIL-5	11.27	8,0E-02	4,7E-03	1,5E-01	2,3E-01
TGPT-1-SOIL-6	29.34	2,1E-01	1,2E-02	3,8E-01	6,0E-01

Table 13 Hazard quotients for non-carcinogenic risk for children associated with Pb. A hazard quotient (HQ) > 1.0 means that risk is present, Q < 1.0 means that there are no significant direct adverse health effects.

Sample ID	Concentration Pb, mg/kg	Soil ingestion	Dermal contact	Vegetable consumption	Total HQ
AKH-3-SOIL-1	61.72	3,6E-02	7,4E-04	0,0E+00	3,7E-02
AKHT-1-SED-1A	28.42	1,7E-02	3,4E-04	0,0E+00	1,7E-02
AKHT-3-KAL-1	37.17	2,2E-02	4,5E-04	0,0E+00	2,2E-02
AKHT-3-SED-1	46.14	2,7E-02	5,5E-04	0,0E+00	2,8E-02
AKHT-3-SED-2	116.53	6,9E-02	1,4E-03	0,0E+00	7,0E-02
AKHT-3-SED-3	53.01	3,1E-02	6,4E-04	0,0E+00	3,2E-02
AKHT-3-SED-4	79.72	4,7E-02	9,6E-04	0,0E+00	4,8E-02
AKHT-3-SED-5	56.74	3,3E-02	6,8E-04	0,0E+00	3,4E-02
AKHT-3-SED-6	37.47	2,2E-02	4,5E-04	0,0E+00	2,3E-02
AKHT-3-SED-LJL	24.80	1,5E-02	3,0E-04	0,0E+00	1,5E-02
ALA-3-PLAY-1	155.05	9,1E-02	1,9E-03	0,0E+00	9,3E-02
ALA-3-PLAY-3	48.48	2,9E-02	5,8E-04	0,0E+00	2,9E-02
ALA-3-PLAY-4	206.42	1,2E-01	2,5E-03	0,0E+00	1,2E-01
ALA-3-PLAY-5	189.75	1,1E-01	2,3E-03	0,0E+00	1,1E-01
ALVD-1-SED-1	16.65	9,8E-03	2,0E-04	0,0E+00	1,0E-02
ALVD-1-SED-1	15.12	8,9E-03	1,8E-04	0,0E+00	9,1E-03
ALVD-1-SED-2	13.78	8,1E-03	1,7E-04	0,0E+00	8,3E-03
ALVD-1-SED-3	36.70	2,2E-02	4,4E-04	0,0E+00	2,2E-02
ALVD-1-SED-4	16.35	9,6E-03	2,0E-04	0,0E+00	9,8E-03
ALVD-1-SED-5	22.46	1,3E-02	2,7E-04	0,0E+00	1,4E-02
ALVD-1-SLAG-1	3.39	2,0E-03	4,1E-05	0,0E+00	2,0E-03
ALVD-1-SLAG-1A	14.05	8,3E-03	1,7E-04	0,0E+00	8,5E-03
ALVD-1-SOIL-1	21.02	1,2E-02	2,5E-04	0,0E+00	1,3E-02

ALVD-1-SOIL-10	24.17	1,4E-02	2,9E-04	0,0E+00	1,5E-02
ALVD-1-SOIL-2	29.33	1,7E-02	3,5E-04	0,0E+00	1,8E-02
ALVD-1-SOIL-3	26.35	1,6E-02	3,2E-04	0,0E+00	1,6E-02
ALVD-1-SOIL-4	122.01	7,2E-02	1,5E-03	0,0E+00	7,3E-02
ALVD-1-SOIL-5	132.95	7,8E-02	1,6E-03	0,0E+00	8,0E-02
ALVD-1-SOIL-6	64.10	3,8E-02	7,7E-04	0,0E+00	3,9E-02
ALVD-1-SOIL-7	88.61	5,2E-02	1,1E-03	0,0E+00	5,3E-02
ALVD-1-SOIL-8	48.28	2,8E-02	5,8E-04	0,0E+00	2,9E-02
ALVD-1-SOIL-9	62.37	3,7E-02	7,5E-04	0,0E+00	3,8E-02
ALVD-2-SAND-2-PLAY	14.51	8,6E-03	1,7E-04	0,0E+00	8,7E-03
ALVD-2-SOIL-1	156.33	9,2E-02	1,9E-03	0,0E+00	9,4E-02
ALVD2-SOIL-5	132.00	7,8E-02	1,6E-03	0,0E+00	7,9E-02
ALVD-2-SOIL-6	104.38	6,2E-02	1,3E-03	0,0E+00	6,3E-02
DIL-SED-1	8.36	4,9E-03	1,0E-04	0,0E+00	5,0E-03
DIL-SED-2	10.07	5,9E-03	1,2E-04	0,0E+00	6,1E-03
DIL-SOIL-1	7.51	4,4E-03	9,0E-05	0,0E+00	4,5E-03
DIL-SOIL-2	11.89	7,0E-03	1,4E-04	0,0E+00	7,2E-03
HGPT2-SOIL-2	66.82	3,9E-02	8,0E-04	0,0E+00	4,0E-02
HGPT2-SOIL-3	65.83	3,9E-02	7,9E-04	0,0E+00	4,0E-02
HGPT2-SOIL-4	59.38	3,5E-02	7,1E-04	0,0E+00	3,6E-02
SANAH-1-SAND-1	11.45	6,8E-03	1,4E-04	0,0E+00	6,9E-03
SANAH-1-SOIL-2	40.88	2,4E-02	4,9E-04	0,0E+00	2,5E-02
TEG-1-SED-1	4.58	2,7E-03	5,5E-05	0,0E+00	2,8E-03
TEG-1-SED-2	22.99	1,4E-02	2,8E-04	0,0E+00	1,4E-02
TEG-1-SED-3	2.18	1,3E-03	2,6E-05	0,0E+00	1,3E-03
TEG-1-SED-4	2.02	1,2E-03	2,4E-05	0,0E+00	1,2E-03
TEG-1-SED-5	0.75	4,4E-04	9,0E-06	0,0E+00	4,5E-04
TEG-1-SED-6	1.36	8,0E-04	1,6E-05	0,0E+00	8,2E-04
TEG-1-SOIL-1	15.43	9,1E-03	1,9E-04	0,0E+00	9,3E-03
TEG-1-SOIL-1	38.17	2,3E-02	4,6E-04	0,0E+00	2,3E-02
TEG-1-SOIL-2	6.82	4,0E-03	8,2E-05	0,0E+00	4,1E-03
TEG-1-SOIL-3	42.01	2,5E-02	5,0E-04	0,0E+00	2,5E-02
TEG-1-SOIL-4	8.63	5,1E-03	1,0E-04	0,0E+00	5,2E-03
TEG-1-SOIL-5	17.23	1,0E-02	2,1E-04	0,0E+00	1,0E-02
TGPT-1-SOIL-6	39.22	2,3E-02	4,7E-04	0,0E+00	2,4E-02

7.5. Annex 5: Hair sampling

Table 14 Origin of hair samples with giver's identification and selected conditions influencing hair quality. All givers were non-smoking women living or working in Alaverdi or Haghpat.

Sample	Age	Fish species	Fish Source	Fish/ week	Fish in 2 weeks	Smoker home	Comments
HGPT2-HAIR-1	55	0		0	No	No	dyed hair 1 month ago
HGPT2-HAIR-2	85	trout	Local fisherman	1-2	Yes	Yes	
HGPT2-HAIR-3	37	trout	Supermarket (Armenian fish), local fish market	7	Yes	No	bleached hair 1.5 months ago
ALVD2-HAIR-4	22	0		0	No	Yes	
ALVD2-HAIR-5	22	trout	Supermarket (Armenian fish)	0-1	No	Yes	
ALVD2-HAIR-6	30	0		0	No	Yes	
ALVD2-HAIR-7	25	trout	Supermarket (Armenian fish)	0	No	No	dyed hair
ALVD2-HAIR-8	24	0	Supermarket (Armenian fish)	0	No	Yes	dyed hair
ALVD2-HAIR-9	22	trout	Local fish market	0-1	No	Yes	dyed hair 1 year ago
ALVD2-HAIR-10	83	trout	Supermarket (Armenian fish)	0-1	No	No	
ALVD2-HAIR-11	34	trout	Supermarket (Armenian fish)	1	Yes	Yes	dyed hair
ALVD2-HAIR-12	61	trout	Supermarket (Armenian fish)	7	Yes	Yes	
ALVD2-HAIR-13	34	mackerel, trout	Supermarket (Armenian fish)	0	No	No	dyed hair 6 weeks ago
ALVD2-HAIR-14	59	trout	Supermarket (Armenian fish)	1	No	No	dyed hair 2 weeks ago

7.6. Annex 6: Hair analysis protocol with results

Státní zdravotní ústav Centrum laboratorních činností Laboratoř pro analýzu stopových prvků Zkušební laboratoř č 1206, akreditovaná ČIA podle normy ČSN EN ISO/IEC 17025	ilac-MRA L 1206

Protokol o výsledku laboratorních zkoušek
č.: 1.4/18/327

Název zkoušky: Stanovení mědi, arsenu, olova a rtuti ve vlasech

Zadavatel:	**ARNIKA - Program toxické látky a odpady**		
Adresa:	Dělnická 13, 170 00 Praha 7		
Kontaktní osoba:	Kristína Žulkovská	Tel.: 735 762 035	e-mail: kristina.zulkovska@arnika.org

Číslo expertizy:	EX181439 3652/2018		
Vzorky předal:	Kristína Žulkovská (Arnika)		
Vzorky přijal:	RNDr. L. Kašparová	Datum:	18. 9. 2018

Typ vzorků:	Biologický materiál - vlasy		
Označení vzorků:	HGPT2-HAIR-1 HGPT2-HAIR-2 HGPT2-HAIR-3 ALVD2-HAIR-4 ALVD2-HAIR-5	ALVD2-HAIR-6 ALVD2-HAIR-7 ALVD2-HAIR-8 ALVD2-HAIR-9 ALVD2-HAIR-10	ALVD2-HAIR-11 ALVD2-HAIR-12 ALVD2-HAIR-13 ALVD2-HAIR-14
Čísla vzorků:	1.4C/18/01036 - 1.4C/18/01049	Počet vzorků:	14
Zkoušky provedl:	Mgr. K. Žádná ICP-MS; Ing. M. Čejchanová AMA (Hg)		

Výsledky zkoušky:

číslo vzorku	označení vzorku	*měď*	*arsen*	*olovo*	*rtuť*
		mg/kg	*mg/kg*	*mg/kg*	*mg/kg*
1.4C/18/1036	**HGPT2-HAIR-1**	**18,3**	**NQ**	**0,30**	**0,024**
1.4C/18/1037	**HGPT2-HAIR-2**	**53,4**	**0,48**	**5,34**	**0,086**
1.4C/18/1038	**HGPT2-HAIR-3**	**1460**	**0,40**	**23,2**	**0,192**
1.4C/18/1039	**ALVD2-HAIR-4**	**12,3**	**0,04**	**2,23**	**0,036**
1.4C/18/1040	**ALVD2-HAIR-5**	**18,0**	**0,04**	**0,29**	**0,027**
1.4C/18/1041	**ALVD2-HAIR-6**	**16,6**	**0,05**	**1,00**	**0,038**
1.4C/18/1042	**ALVD2-HAIR-7**	**14,5**	**0,05**	**0,95**	**0,025**
1.4C/18/1043	**ALVD2-HAIR-8**	**15,5**	**NQ**	**0,57**	**0,028**
1.4C/18/1044	**ALVD2-HAIR-9**	**40,0**	**0,04**	**1,75**	**0,033**
1.4C/18/1045	**ALVD2-HAIR-10**	**11,1**	**0,24**	**3,91**	**0,022**
1.4C/18/1046	**ALVD2-HAIR-11**	**11,5**	**NQ**	**0,16**	**0,246**
1.4C/18/1047	**ALVD2-HAIR-12**	**10,2**	**NQ**	**0,13**	**0,032**

SZÚ	Státní zdravotní ústav Šrobárova 48, 100 42 Praha 10 Tel. 267082670, E-mail: lucie.kasparova@szu.cz	Číslo protokolu: 1.4/18/327 Strana č. 1 (celkem 2) Počet příloh: 0

Státní zdravotní ústav
Centrum laboratorních činností
Laboratoř pro analýzu stopových prvků
Zkušební laboratoř č 1206,
akreditovaná ČIA podle normy ČSN EN ISO/IEC 17025

ilac-MRA L 1206

číslo vzorku	označení vzorku	*měď*	*arsen*	*olovo*	*rtuť*
		mg/kg	*mg/kg*	*mg/kg*	*mg/kg*
1.4C/18/1048	**ALVD2-HAIR-13**	**5,0**	**0,05**	**1,18**	**NQ**
1.4C/18/1049	**ALVD2-HAIR-14**	**8,1**	**NQ**	**0,14**	**0,062**
	mez detekce	0,15	0,01	0,01	0,004
	mez stanovitelnosti	0,50	0,04	0,05	0,012
	nejistota	± 15 %	± 15 %	± 15 %	± 15 %
	poznámka	N b)	N b)	N b)	a)

Vysvětlivky: ND – výsledek pod mezí detekce
NQ – výsledek pod mezí stanovitelnosti
N – neakreditovaná zkouška
Nejistota měření je stanovena jako rozšířená nejistota s koeficientem rozšíření k = 2 pro 95% interval spolehlivosti.

Použité metody: a) Použitá metoda: stanovení rtuti analyzátorem AMA 254 (SOP 4B/1.4)
b) podle SOP stanovení prvků metodou ICP-MS po mineralizaci vzorku

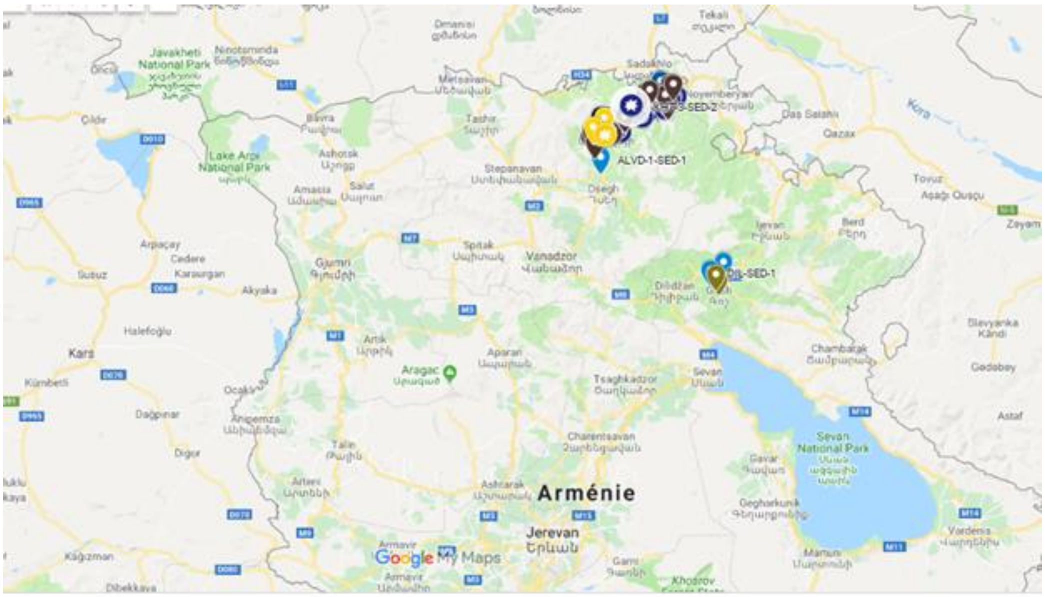
Laboratoř prohlašuje, že veškeré výsledky se týkají jen předmětu zkoušky.
Tento protokol může být reprodukován jedině celý, jeho část pouze s písemným souhlasem vedoucího laboratoře.

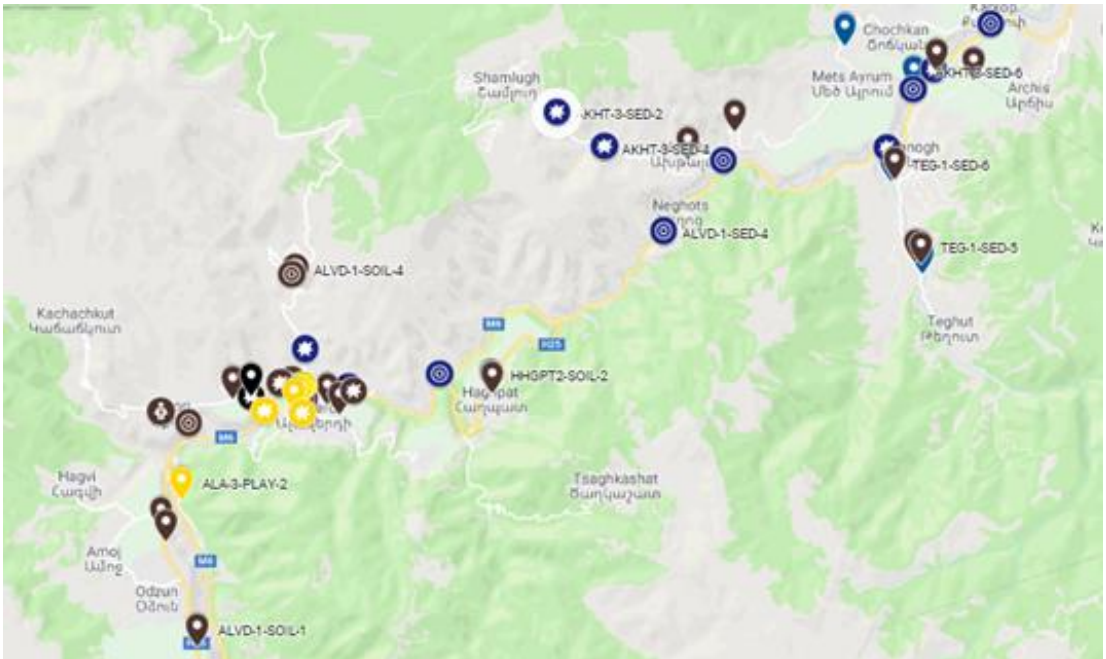
Datum: 4. 10. 2018

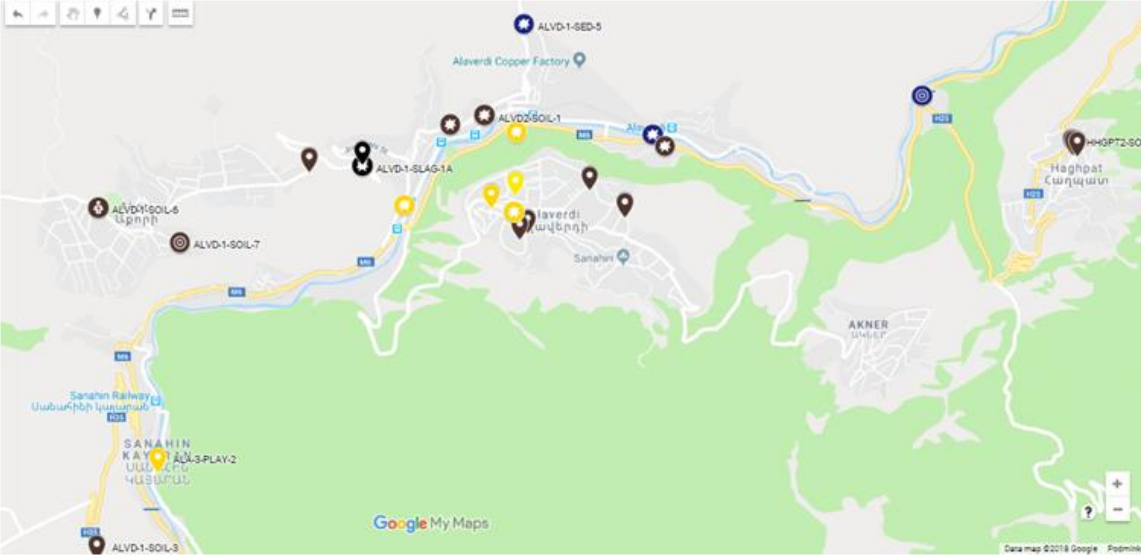
STÁTNÍ ZDRAVOTNÍ ÚSTAV Centrum laboratorních činností SZÚ -4- Zkušební laboratoř č. 1206, akreditovaná ČIA

RNDr. Lucie Kašparová
technický vedoucí

7.7. Annex 7 Maps of sampling sites







7.8. Annex 8: Pictures

Covered tailing pond in Akhtala leaking.

Sampling the creek running from the Akhtala tailing dam.

Sanahin: Smoking Alaverdi smelter in the background.

Sampling the kindergarden in Alaverdi. Soils from children playgrounds, gardens, orchards and fields show presence of heavy metals, not only copper.

Hair Samplin in Haghpat. Samples with elevated and high levels of heavy metals come from only women from the sampled group who eat local fish. This factor contributes to the assumption that the human diet based on local fish consumption is the exposure pathway of heavy metals to the body of sampled women.

Sampling from Mets Ayrum tailing dam near Akhtala and from creek running from Akhtala mining area. The cyan color of the water is likely caused by copper sulphate. Polluted water from the river and creeks is used for wattering gardens.

Sampling Debed river close to Teghut.

This publication has been produced with the financial assistance of the Ministry of Foreign Affairs of the Czech Republic under Transformation Cooperation Programme. Production of this publication was possible also thanks to Global Greengrants Fund.

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