THE PRICE OF GOLD

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THE PRICE OF GOLD

How gold mining affects pollution with heavy metals in Armenia

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View on Ararat village and town. PHOTO: Viktoriya Mayakotskaya

Content

SUMMARY

Mining and ore processing activities have long been an integral part of Armenia's economy, providing valuable resources and employment opportunities. However, the lack of effective regulations and mitigation measures has resulted in the release of toxic heavy metals into the environment.

In 2022 and 2023 we conducted a study in four regions of Armenia, where gold is mined or processed. The regions of interest were Lori Province (including Karaberd village and nearby areas) and Kotayk Province (including Meghradzor village and nearby areas); Ararat Province (including Ararat and Surenavan villages) and Aragatsotn Province (including Melikgyugh village and nearby areas).

In total, we collected and analyzed 55 environmental samples including 29 soil samples, 22 sediment samples, 3 samples of mining residue, and 1 fish sample. Furthermore, we collected 83 biological samples comprising 55 urine samples and 28 hair samples from residents in the communities impacted and examined them for concentrations of heavy metals.
The main findings of the study are presented below:

Ararat, Surenavan:

- Our results indicate that the environment in the area of Ararat could be classified as moderately to strongly polluted by arsenic, and moderately polluted by chromium and nickel. Elevated concentrations of arsenic, cadmium, chromium and nickel in the soil were found in close proximity to the gold processing plant. The soil in some of the private gardens used for growing crops contain elevated levels of arsenic, lead, and zinc.

- Urinary arsenic in the Ararat, Surenavan cohort measured higher than the mean in the U.S. population or among European adolescents, however, hair arsenic did not exceed the maximum level suggested by the U.S. CDC. Urinary copper may warrant caution, and urinary nickel was measured higher than reference values in the literature and elsewhere in Armenia. Several individuals with higher values of urinary cadmium, hair cadmium, and hair lead should be counselled individually.

Karaberd:

- The pattern of occurrence of heavy metals in sediments in the Karaberd area raises the suspicion that the following heavy metals are being released into the river basin from the gold mine: arsenic, cadmium, copper, iron, mercury, molybdenum, nickel, lead, and zinc. Our results also indicate that the environment in the area could be classified as moderately to heavily polluted by arsenic and cadmium, and moderately polluted by lead and zinc. Soils in some private gardens used for growing crops contain elevated levels of arsenic, cadmium, lead, and zinc.

- Cadmium, copper, and nickel urinary levels in both men and women cohorts were measured considerably higher than reference values in other studies and warrant further examination of possible sources and clinical symptoms. Urinary arsenic in the Karaberd cohort indicates a moderate concern compared to reference values in the literature.

Meghradzor:

- The pattern of occurrence of heavy metals in sediments in the Meghradzor area raises suspicion that the following heavy metals are being released into the river basin from the gold mine: arsenic, cadmium, copper, iron, mercury, molybdenum, nickel, lead, and zinc. Our results also indicate that the environment in the area could be classified as moderately polluted by arsenic. Soils in some private gardens used for growing crops contain elevated levels of arsenic, chromium, and lead.

- In the female cohort in Meghradzor, urinary cadmium and nickel represent compounds of moderate to high level of concern. One female sample specifically was tested for moderate to high level of copper in urine. In the male cohort, urinary copper and cadmium are the main compounds of concern in one of the tested individuals. Abnormally elevated levels of urinary arsenic were detected in the samples of a senior women (75 µg/g creatinine) and 5-year-old boy (37 µg/g creatinine).

Melikgyugh:

- The pattern of heavy metals in sediments in the Melikgyugh area raises suspicions that arsenic and cadmium are being released into the river basin from the gold mine. Our results also indicate that the environment in the area could be classified as moderately to strongly polluted by arsenic, cadmium, and chromium. Soils in some private gardens used for growing crops contain elevated levels of chromium and zinc.

- Out of the four women tested for urine heavy metals, one tested particularly high for arsenic and nickel, and her hair tests deepen concerns about cadmium, copper, and mercury long-term exposures. The singular study participant should be examined for clinical symptoms related to heavy metals and counselled on preventive measures of exposure.

Through comprehensive data collection, analysis, and consultation with relevant stakeholders, this report highlights the gravity of heavy metals pollution and its impact on the health of residents in selected Armenian communities.

1 INTRODUCTION

The mining sector plays a crucial role both in the Armenian industry and economy. In 2022, over 900 mines were registered in Armenia, with 45 dedicated to metal extraction. Most of these mines - 26 as of 2023 - specialize in gold mining. Moreover, seven Armenian mines extract mainly copper and molybdenum, and four are exclusively copper mines. Other mines extract iron, molybdenum, magnesium, and secondary metals. The number and variety of local mines illustrate the rich and diverse mineral resources of this Transcaucasian country.

Looking at the data for 2020 and 2021, the production of copper ore and copper concentrate accounts for the bulk of mining activity, with 55 to 56 per cent of the market share in this period. Precious metals like gold and silver are also significant, accounting for approximately 22% of the overall picture during the comparative years. The long-term trend of rising gold prices on international exchanges significantly impacts investment decisions in this valuable metal's mining. This trend may explain the high demand for opening new mining deposits throughout Armenia. In 2021, gold exports constituted more than seven percent of the overall exports of the country, highlighting the substantial economic impact of this metal on the Armenian economy (EITI, 2022).

While the mining industry can bring potential societal advantages, it also poses notable hazards to the nearby ecosystems and local inhabitants. As with other extractive industries, mining requires careful planning before the project begins and ongoing monitoring until the ecosystem is fully restored to its pre-mining state. Along with the mining facility, additional structures such as tailings ponds, landfills, solid waste heaps, warehouses for operating chemicals and extraction technology are part of the infrastructure. Poor planning and inadequate maintenance of any of these operations can result in environmental pollution (Swedish Geological AB, 2016).

Environmental pollution derives from gradual dust and regular noise emissions, while accidents can release hazardous substances, such as mercury or cyanide, and contaminate water and soil. There is also a risk from accompanying elements in the mined rock that can impact the safety of the environment. People living near these activities, particularly vulnerable groups such as children, pregnant women, women at reproductive age and elderly, may be at severe health risk from exposure to these chemicals.

Long-term exposure to heavy metals such as lead, mercury, cadmium, and arsenic can increase the risk of migraines and decreased bone density, reduced immunity and kidney function, infertility, and cancer along with developmental and cardiovascular diseases. Heavy metals pose a serious health risk to humans exposed through contaminated water, air, or soil and foods.

Our study focused on gathering information on the presence of heavy metals in the surrounding environment of areas where gold is mined or processed. Specifically, we collected environmental samples including soil and sediment, to indicate the extent of contamination in soil and water. In 2022 and 2023 the study was conducted in four regions: Ararat province, near a gold processing plant; Lori province, in the village of Karaberd and near an active gold mine; Kotayk province, in the village of Meghradzor, where ore mining and processing take place; and Aragatsotn province, in the village of Melikgyugh, the site of a former gold mine. Human biomonitoring data complemented the environmental data. We collected urine and hair samples at the same sites in the vicinity of the operations of interest as indicators of long- and short-term exposure. These were used to monitor the heavy metal burden of the rural populations.

Water channel in the village of Ararat. PHOTO: Viktoriya Mayakotskaya

2 LOCATION DESCRIPTION

This study presents the results of research on the heavy metals presence in environmental and biological matrices in four regions, see Figure 2.1. Sample collection was carried out sequentially and divided into two phases. In 2022, sampling was conducted in the village of Karaberd, part of the enlarged community of Pambak, Lori region, and the village of Meghradzor, part of the enlarged community of Tsaghkadzor, Kotayk region. In 2023, sampling was carried out in the villages of Ararat and Surenavan, which are part of the enlarged community of Ararat, Ararat region, and in the village of Melikgyugh, which is part of the enlarged community of Aparan, Aragatsotn region. All these sites are strongly associated with mining and processing of gold-bearing ores. The object of the research was to determine the level of impact of the mining and ore-processing industry and its infrastructure on the environmental condition of the area and the level of burden on the health of the inhabitants of the affected communities. A more detailed presentation of each site will be discussed in the following chapters.

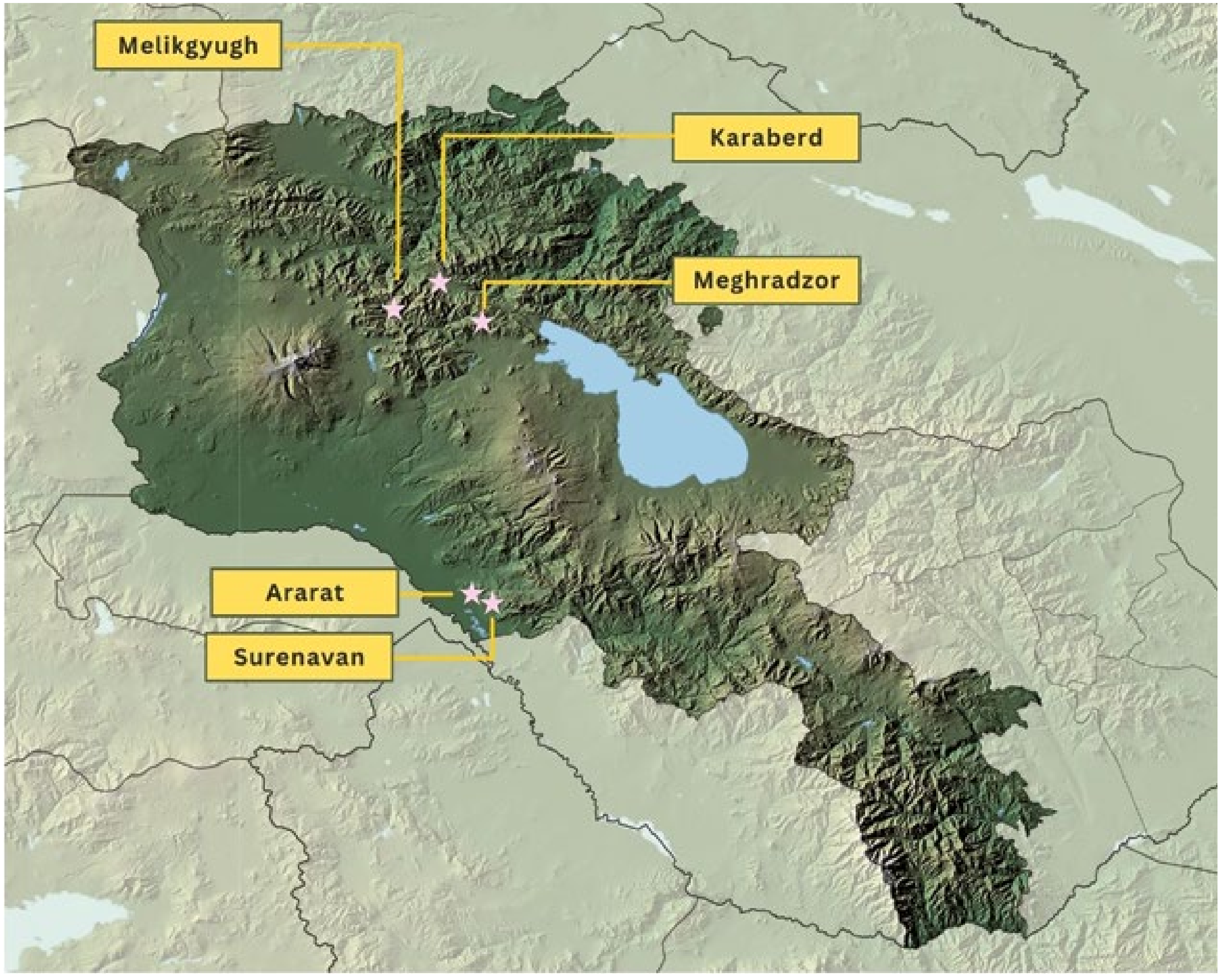

Figure 2.1 Map of sampled areas in 2022-2023

2.1 Ararat, Surenavan

The Ararat gold processing plant is located 40 km south of Armenia's capital, Yerevan. The nearest communities to the plant are the municipalities of Ararat and the village of Surenavan. In 2017, the population of the Ararat enlarged community was estimated at 20,300, of which 7,609 lived in Ararat village and 2,434 in Surenavan village. The Ararat Valley is one of Armenia's most fertile regions and is extensively cultivated. The province is known for producing various crops, including grains, fruits and vegetables.

The Ararat gold processing plant has been in operation since the 1990s and is currently on hold due to limited ore supply from the Sotq mine. The Ararat Gold Processing Plant is expected to process approximately 1 million tons of ore per year. Apart from the plant itself, the company's infrastructure includes a 165-ha tailings pond 5.8 km from the Ararat gold processing plant, which is close to the Kachan channel, a major source of fresh water for the region.

One of Armenia's two cement manufacturing plants, the Ararat Cement Plant is located between Ararat (approx. 3 km) and the village of Surenavan (approx. 7 km) and has a production capacity of 1.2 million tons of cement per year, see Figure 2.2.

Figure 2.2 Map of the town and village of Ararat, Surenavan village and potential industrial polluting spots (Ararat gold processing plant, Ararat cement plant, tailings pond)

2.2 Karaberd

The Karaberd gold mine is situated in northern Armenia's Lori Region, on the territory of Karaberd village, part of the enlarged community of Pambak, just three kilometres northeast of the regional city of Vanadzor, see Figure 2.3. The central section of the mine is found near the watershed, at absolute heights varying from 1,500 to 1,750 metres above sea level. The Karaberd village is located 1.4 kilometres away, the Pambak village is located 2.4 kilometres away, and the Gugark village is located 2.2 kilometres away. Karaberd village has a population of 146 individuals. Residents are engaged in agriculture, mainly growing potatoes, cabbage and other vegetables. The important Pambak River, a tributary of the transboundary Debed River, flows through the area, but the community often complains about the lack of irrigation water and its poor quality.

The Karaberd gold mine has been in operation since 2013, with an approved ore extraction period of 11 years until 2024. The primary minerals extracted from the mine are gold and silver deposits. The yearly extraction for the initial three years of operation was 11.55 thousand tonnes of ore, while for the following years it rose to 29.7 thousand tones. In 2021 the extraction capacity was 33,447 tons of gold containing ore.

Figure 2.3 Map of the Karaberd, Pambak villages, Vanadzor and Karaberd gold mine

2.3 Meghradzor

The Meghradzor gold mine is located on the territory of Meghradzor village, part of the enlarged community of Tsaghkadzor of Kotayk province with a total population of 5,741, of which 2,884 live in Meghradzor. The Meghradzor mine has been in operation since 2012. The local residents are involved in agricultural activities, livestock breeding, apiculture, tourism, and mining.

The owner organization Meghradzor Gold Ltd. is licensed to mine 120,000 tons of ore per year until 2023 and has applied to renew the license for an extension until 2030. According to the records, 67,555 tons of gold-bearing ore was extracted from the Meghradzor mine in 2020 and 62,660 tons in 2021. In the Meghradzor gold mine, the ore is not only mined, but it is also crushed into a final enriched concentrate with a high fraction of gold and silver.

Figure 2.4 Map of Meghradzor village and Meghradzor gold mine

Meghradzor is located in an area of frequent seismic activity. It is crossed by several faults. The area is traversed by the Marmarik, Meghradzor and other rivers along with their tributaries. The Marmarik River is affected by the operation of the Meghradzor mine and is regularly polluted by effluent from the Meghradzor gold processing plant. Harmful emissions are generated during mine operations, releasing approximately 5 tons of harmful substances into the air annually, including 1.33 tons during blasting activities and 3,246 tons during normal operations.

The municipality of Hrazdan, where both the Hrazdan thermal power station and the Hrazdan cement factory are located, is about 8 km south-east of Meghradzor. These facilities have the potential to cause significant pollution in the region.

2.4 Melikgyugh

The Tukhmanuk gold mine is located on the territory of village of Melikgyugh, part of the enlarged community of Aparan of Aragatsotn province, in the basin of the Kasakh and Meghradzor rivers, at an altitude of 2,300-2,800 metres above sea level. Melikgyugh has a population of 1,165 inhabitants, many of whom engaged in agriculture activities.

The Tukhmanuk gold deposit is a former mine that was in operation from 2004 to 2015. The owner organization “Mego Gold” LLC was due to be the operator of the gold mine’s central site from 2012 to 2040, but there has been no work at the mine since 2015. There are 3 unreclaimed tailings ponds containing waste from the ore enrichment plant in the area in addition to the former mine. The total area under the tailings is 6-7 ha.

The production plan for the deposit was to mine 300,000 tons of ore per year (500 kg Au) and in the second phase to increase the concentrator capacity to 1.5 million tons per year (2.4 tons Au).

Figure 2.5 Map of Melikgyugh village and the facilities of the Melikgyugh gold mine

3 METHODS

3.1 Samples collection and analytical methods

3.1.1 Environmental samples

The sampling was conducted according to a sampling plan covering areas near the potential contamination hotspots, combining results from previous studies, Google Earth ("Google Earth," 2023) and reports from local activists. Samples were taken from public places and private gardens. At each site, soil and sediment samples were taken as pooled samples consisting of several partial samples. The collected samples were stored at low temperatures for transport.

In this study, the results of heavy metals in soil and sediment samples are presented in mg/kg dry matter for the soil and sediment samples and mg/kg fresh matter for the fish sample. All analyses were performed in the laboratories of the State Veterinary Institute in Prague (Czech Republic) and the Institute of Public Health in Ústí nad Labem (Czech Republic).

An overview of the sampling and analytical techniques for environmental samples is given below:

Table 3.1 Sampling methods and analytical techniques used for heavy metal detection in the environmental samples.

Sample type	Year	Sampling method	Mineralization	Analytical technique
Soil	**2022**	sampling soil spoon and a bulb planting tool (several subsamples)	HNO_3, HF, H_2O_2	ICP-OES
	2023	sampling soil spoon and a bulb planting tool (several subsamples)	HNO_3, H_2O_2	HNO_3, H_2O_2 ICP-MS AAS-AMA
Sediment	**2022**	sampling with a soil spoon or a plexiglass core sampler from the shore (several subsamples)	HNO_3, HF, H_2O_2	ICP-OES
	2023	sampling with a soil spoon or a plexiglass core sampler from the shore (several subsamples)	HNO_3, H_2O_2	ICP-MS AAS-AMA
Fish	**2023**	fish catch	HNO_3, H_2O_2	ICP-MS AAS-AMA

3.1.2 Biological samples

Biological samples (urine and hair samples) were collected from the residents of the four areas of interest, where environmental samples were also taken. A questionnaire including questions about age, occupation, health care, diet, health problems, etc. was carried out during the sampling to obtain information about the participants. The following table provides an overview of the sampling and analysis methods used for biological samples.

Table 3.2 Sampling methods and analytical techniques used for heavy metal detection in biological samples.

Sample type	Year	Sampling method	Mineralization	Analytical technique
Hair	**2022-2023**	sample of a strand of hair taken from the occipital region of the head of the participant, as close as possible to the scalp.	Acids mix+ microwave digestion	ICP-MS
Urine	**2022-2023**	15 ml of a morning urine sample is collected in a sterile container with a screw cap.	-	ICP-MS

3.2 Legislation and reference levels

3.2.1 Environmental samples

Finding appropriate benchmarks to assess the level of environmental pollution by heavy metals is not a simple question, and approaches to solving it may vary. There have been numerous guidelines developed in dealing with contaminated soils and sediments (Burton, Jr., 2002). The presence of some elements in different inorganic and organic matrices is natural, because different regions have their own geochemical background. From this fact comes the traditional older approach in which contamination was determined by assessing the bulk chemical concentrations of individual elements and comparing them with background or reference values. Since the 1980s, guidelines have attempted to incorporate biological effects evaluating changes in human health. However, it is the regional legislation which is binding. Therefore, several reference concentrations from different approaches were used for comparison with the results of the samples to gain a view of local pollution levels. Reference values for soils, sediments, and fish are shown in Table 3.3, Table 3.4 and Table 3.5, respectively.

Table 3.3 Reference levels of heavy metals in soils. Concentrations of heavy metals are expressed in mg/kg of dry weight (mg/kg DW).

	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
Armenian soil standard[1]	2.0	-	6.0	3.0	-	-	-	4.0	32	-	-
Czech pollution indication[2]	40	20	-	-	-	20	-	-	400	-	-
Czech background indication[2]	20	0.5	90	60	-	0.3	-	50	60	130	120
Levels of pollution limits – industrial soil (US EPA)[3]	3	10	-	4700	82,000	4.6	580	1,200	800	580	35,000
Levels of pollution limits – resident soil (US EPA)[3]	0.68	0.71	-	310	5,500	1.1	39	84	400	39	2,300

Table 3.4 Reference levels of heavy metals in sediments. Concentrations of heavy metals are expressed in mg/kg of dry weight (mg/kg DW).

	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
Czech Limit Values[4]	30	1	200	100	-	0.8	-	80	100	180	300
Canadian Threshold Effect Level[5]	5.9	0.6	37.3	37.7	-	0.17	-	-	35	-	123
Canadian Probable Effect Level[5]	17	3.5	90	197	-	0.486	-	-	91.3	-	315

Table 3.5 Maximum levels of heavy metals in muscle meat of fish placed on the market in the European Union.
Concentrations of heavy metals are expressed in mg/kg of fresh matter (mg/kg FM).

As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
-	0.05	-	-	-	0.5	-	-	0.3	-	-

1 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"
2 Czech Decree No. 153/2016 issued by the Ministry of Agriculture. Available on: https://www.zakonyprolidi.cz/cs/2016-153
3 US EPA. Regional Screening Levels of November 2023. https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables
4 Czech Decree No. 257/2009 issued by the Ministry of Agriculture. Available on: https://www.zakonyprolidi.cz/cs/2009-257
5 Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Available on: https://ccme.ca/en/current-activities/canadian-environmental-quality-guidelines

The first reference values with which we compare measured concentrations in the soil samples are the Armenian soil standards (The Minister of Health of the Republic of Armenia, 2010). Armenia has one of the strictest limits (along with Russia) on soil pollution. Another benchmark for us are the Czech pollution indicators and the Czech background indicators (The Ministry of Agriculture of the Czech Republic, 2016), which describes the quality and protection of agricultural soil. The Czech pollution indicators show levels whose exceeding may present a threat to human and animal health. The Czech background indicators are values that, if exceeded, may put in risk the health safety of food or feed. The concentrations of heavy metals in soil samples were also compared with the US EPA Regional Screening Levels (RSL). Regional screening levels were derived by the United States Environmental Protection Agency (US EPA) for some compounds that have a CAS registration number. RSLs are concentrations of chemical compounds in the environment (soils, 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. There are two RSL categories – land used for industrial purposes and land used for residential purposes.

As reference values for heavy metals in sediments, we use Czech Limit Values and Sediment Quality Guidelines for the Protection of Aquatic Life. Czech Limit Values (The Ministry of Agriculture of the Czech Republic, 2009) are used to determine the concentration of heavy metals in sediments, which, if exceeded, prohibits the application of sediment to fertilize agricultural land. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life were developed by the Canadian Council of Ministers of the Environment as broadly protective tools to support the functioning of healthy aquatic ecosystems. Comparison of measured concentrations of various contaminants within the sediments with these guideline values provide a basic indication on the degree of contamination and likely impact on ecology. The guidelines consist of Threshold Effect Levels (TELs) and Probable Effect Levels (PELs). A value below the PEL and above the TEL means the possible effect range within which adverse effects occasionally occur. A value above the PEL means the probable effect range within which adverse effects frequently occur.

As reference values for heavy metals in fish we use maximum permissible levels in muscles of fish placed on the market in the European Union (The European Commission, 2023).

3.2.2 Biological samples

Regulatory standards are typically well established for heavy metals in drinking water or ambient air, and for metals as dietary contaminants. However, reference values in human samples vary by laboratory and region. It is important to note that a level of heavy metals in a sample considered as “normal” does not always imply an absence of health consequences and vice versa, “abnormal” test results do not necessarily involve toxicity. Instead, higher than average concentration of a heavy metal in a biological sample warrants further investigation on the possible sources of exposure and careful clinical examination of present or plausible symptoms.

Urine heavy metals typically reveal a recent exposure to the substance as most heavy metals get eliminated from the body via kidney and the urinary system. The efficiency of renal excretion varies, and the variability is based on factors such as the specific metal, exposure levels, acids and bases states of the organism, capacity of the kidney, and general individual health and hydration status. On the other hand, a spot urine examination may not accurately demonstrate long-term exposure to the metal, especially for substances with short half-life in the body or in low concentrations. Despite the possible deficiencies, we use the method of spot urine sampling for its convenience for participants, sufficient reliability, and consistency compared to our previous reports.

Hair analysis is commonly used to assess exposures to heavy metals over an extended period. Hair can accumulate heavy metals from the blood stream over time, providing a historical view of exposure, and it is used ordinarily for assessing chronic exposure to metals of no biological role in the organism such as arsenic, lead, cadmium, or mercury. Here, we also tested the hair samples for chromium, copper, molybdenum, and nickel.

Contrary to the more invasive, complex and time-consuming methods, spot urine and hair sampling provide a significant advantage in remote communities for their general acceptability and convenience. The two methods together reveal both recent and chronic exposure to selected heavy metals. Moreover, the methods are suitable for general monitoring of exposures to heavy metals and preventing adverse health effects in the long term. Our assessment of biological samples from small groups and individuals across several locations in Armenia empowers the residents to seek medical advice, professional assessment of heavy metals and provides guidance on potential interventions or preventive measures if needed.

Arsenic (As)

Albeit a naturally occurring element in many forms, either as inorganic compounds or as organic compounds, and accompanies some ore deposits, arsenic is a potent poison in both acute and chronic exposures. Mining and metallurgical industries, along with coal burning, represent significant anthropogenic sources of arsenic (Bencko and Cikrt, 1995). Contaminated water and soil via crops such as rice, and airborne particles contain inorganic arsenic whereas organic arsenic is typically found in seafood and is considered less harmful to human health. The International Agency for Research on Cancer (IARC) considers arsenic and arsenic compounds a human 1 carcinogen namely with reference to lung, bladder, prostate and kidney cancer (IARC, 2023). Non-carcinogenic health risks of arsenic exposure include impaired neurobehavioral development of children, and adverse cardiovascular health (Rasheed et al., 2016). The U.S. Center for Disease Control (CDC) provides a reference value for total urinary arsenic: the geometric mean for the U.S. population is 6.94 µg/g of creatinine (CDC, 2022) or (CDC, 2017). The normal human level in unexposed individuals is set to less than 100 µg/l of urine (must be corrected per gram of creatinine), and less than 1 mg/kg (ppm) in hair (ATSDR, 2007). Measurement of urinary arsenic levels is recognized as a reliable indicator of recent arsenic exposure.

Lead (Pb)

The most constant indicator of human lead contamination is the blood level. However, for our report's purpose we examined lead in urine and hair samples as a sufficient proxy of blood lead (Gulson et al., 1998). Additionally, hair samples taken from below the scalp were found as significantly correlating with blood lead levels as well (Christensen et al., 2023). There is no safety threshold level of lead in any of the biological matrices, yet higher levels are associated with severe effect: e.g., increase in blood lead from 10 to 20 µg/dl was found associated with an IQ decrease by 2.6 points (Schwartz, 1994). Still U.S. CDC set the reference value for elevated blood lead level in children to 5 µg/l and suggests the normal range of urine lead between 16 and 60 µg/g creatinine (CDC, 1984). A recent study from Poland revealed the mean lead level in hair of 2.01 mg/kg (10^{th} and 90^{th} percentile 0.634 and 3.94 mg/kg) (Michalak et al., 2014). Environmental and dietary exposure to lead has decreased over time, among others due to limitation in the use of lead in gasoline, a fact that was also reflected in a decrease of lead content in children hair in the 1990s (Wilhelm et al., 2002). However, to this day, hair lead remains a predictor of neurological diagnosis, e.g., hair lead of a median of 5.793 mg/kg was significantly higher in the group of children with autism spectrum disorder compared to controls (Fiłon et al., 2020).

Cadmium (Cd)

Cadmium levels in drinking water and ambient air are expected to be low, except in the vicinity of cadmium-emitting industries. The general population may be exposed to cadmium in foods (typically in leafy vegetables, potatoes, grains, and organ meats such as liver or kidney) and cigarette smoke. Absorbed cadmium gets widely distributed in the body, with the highest levels found in the liver and kidneys; and excreted slowly – through urine and feces equally. The half time for cadmium in the organism is estimated to be greater than 26 years (ATSDR, 2012a). The geometric mean urine level of cadmium in the U.S. general population over 20 years of age is 0.189 µg/g of creatinine (CDC, 2022). On the other side of the Atlantic, the European Human Biomonitoring Initiative (HBM4EU) measured urine cadmium corrected to creatinine in nine European countries between 0.094 and 0.389 µg/g of creatinine (Snoj Tratnik et al., 2022). Hair samples must be clean from ambient contamination prior to collection otherwise cadmium hair levels cannot be considered a reliable predictor of cadmium body burden (ATSDR, 2008). The mean hair concentration of Cd was found 0.062 mg / kg in adult population in part of China, lower concentrations are found in children (up to 0.054 mg/kg) – in Ohio, US, and in female participants (Jursa et al., 2018; Zhou et al., 2016).

Mercury (Hg)

Mercury occurs naturally in many chemical and physical forms at different temperatures. One of the concerting forms of the metal is methylmercury, a highly toxic compound that accumulates in living tissues such as fish and seafood and becomes a source of exposure to humans. The anthropogenic sources of mercury include combustion processes, burning of coal or municipal waste, and mining (Sundseth et al., 2017).

Hence, general populations are primarily exposed to mercury through food and ambient air. Mercury in the gastrointestinal tract is absorbed almost completely, and absorption via inhalation is considered high, as well. The major route of elimination depends on the type of mercury – elemental mercury is excreted predominantly via exhaled air, inorganic mercury via urine and feces, while methylmercury that enters the body from foods, gets expelled through hair.

The most recent geometric mean for urine mercury in the general U.S. population over 20 years of age was reported on 0.318 µg/g creatinine (CDC, 2022). Hair mercury for women in the childbearing age in the U.S. is recommended to be kept below 1 mg/kg. The geometric mean was found 0.2 µg/g in a cohort of women; and reached to about 0.38 µg/g if the participant consumed fish frequently (McDowell et al., 2004). The WHO sets the "level of concern" above 2 µg/g in the hair for the general population (UNEP, 2008). Among 17 European countries, the mean hair mercury concentration was 0.14 µg/g (Katsonouri, 2020). Among the highest hair mercury concentrations were recently measured in gold mining regions in Philippines (Drasch et al., 2001) and Bolivia (Barbieri et al., 2009), the mean of 2.7 and 3.8 µg/g respectively and maxima of 34.7 and 37.8 respectively; and other mercury contaminated areas such as Huancavelica, Peru where residents ranged between 0.1 to 3.6 µg/g of hair (Hagan et al., 2015).

Copper (Cu)

Although copper is an essential trace element required for various physiological processes, excessive exposure can lead to copper-related toxicity. Exposure in the general population originates from ingestion of food that may be affected by application of Cu-containing fertilizers and fungicidal sprays to the crops. Upon absorption, copper gets distributed to the liver, lungs, kidneys, and excreted in the bile through feces. Minor routes of excretion include urine, breastmilk, sweat, menstrual flow, nails, and hair.

Urine copper is typically collected over 24 hours for a pre-symptomatic screening of hereditary Wilson's disease with the normal range for urine copper 20-50 µg/24 hours. A morning urine spot copper was measured anywhere from 5.72 to 7.26 µg/l in multiple European studies (Ougier, 2022). Our previous study in Armenia however reported on the mean of 9.3 µg Cu/g creatinine (Grechko, 2021). Copper content in the hair correlates to its serum concentration with about 10 – 100 times higher values, ranging from 7 to 95 µg/g (Bost et al., 2016). In a set of studies among the general population in Slovenia, hair copper was measured at its' upper limits of 15.725 µg/g in children, the arithmetic mean in a cohort of mothers was 12.485 µg/g (Ougier, 2022). In a Chinese study that contrasted toxic trace elements in the mining and reference areas, hair copper ranged from 11.136 to 78.197 mg/kg (in the age group from 2 – 9 years old) in the hair samples from polluted areas; and 8.69 to 10.07 mg/kg in the reference regions (Yang et al., 2021). A good biomarker of excessive copper exposure as an early warning for protection of vulnerable populations is yet to be found. Here, however, we measured hair and urinary copper as a proxy in the selected areas.

Nickel (Ni)

Nickel is a versatile metal used mainly as a key component in stainless steel production. Low levels of nickel are present in many common foods, but except occupational exposure, the daily intake of nickel in the general population is estimated under 0.5 mg/day. However, people living near oil refineries or coal-fired power plants, and tobacco smokers may have elevated intake of nickel.

The mean urinary nickel in the U.S. general population over 20 years of age is 1.11 µg/g of creatinine (CDC, 2022). Nickel was measured in hair of residents of sulphide-rich areas in Finland at a mean of 0.71 mg/kg, and slightly higher in the reference population, at 0.83 mg/kg for nickel in hair (Kousa et al., 2022). In our previous study, the mean hair nickel concentration was detected at 13.96 mg/kg (Grechko, 2021). In a Pakistani study, nickel was measured in the scalp hair of nonsmokers and smokers at 6.1 and 74.85 µg/g respectively (Afridi et al., 2010).

Chromium (Cr)

Chromium is a natural component of many minerals. As for industrial uses, chromium is invaluable in textile and papermaking industries, in glassmaking and medicine, as a component of dyes, catalysts, wood conserving solutions, and fertilizers (Jin et al., 2014).

Exposure to hexavalent chromium poses severe health consequences to the skin and the internal organs and systems such as respiratory system, kidney and liver, and immunity (Guertin et al., 2004). Chromium (VI) is classified by the IARC in group 1 (National Toxicology Program (NTP), 2021).

The general population may be exposed to chromium through food, drinking water and air, particularly near the industrial sites that produce chromate, stainless steel, or chrome pigment, or run welding, plating, or alloy operations. The mean levels of chromium in urine are 0.22 µg/l (ATSDR, 2012b). Hair chromium is a standardized measure of chronic exposure (EFSA, 2014). In literature, a large variation in "normal" hair concentration can be found – from 0.001 to 4.56 (Mikulewicz et al., 2013) or 0.03 to 1.26 with median of 0.22 µg/g (Sazakli et al., 2014) while the mean hair cadmium in tannery workers was found as high as 17.4 µg/g (Saner et al., 1984).

Molybdenum (Mo)

Molybdenum is naturally present in many foods, including legumes, grains, nuts, leafy vegetables, and meats. In general, dietary intake provides an adequate but not excessive amount of molybdenum for most individuals. Certain regions may have soils with elevated molybdenum levels, which can lead to higher concentrations in locally grown crops.

Acute molybdenum toxicity is rare and typically associated with industrial exposure rather than dietary intake while chronic toxicity from dietary sources is uncommon. However, certain individuals may be at risk if they consume excessive amounts of molybdenum supplements or if they work in environments with high occupational exposure to molybdenum compounds such as mining, metal processing, and welding.

Hair molybdenum is measured as a proxy of possible excessive exposure. In one study, a reference population had a mean of 0.3029 mg/kg hair while the highest hair concentrations in polluted areas had the mean of 17.682 mg/kg hair (Ray et al., 2012). In our previous study in Armenia, molybdenum was tested below LOQ in all samples and areas (Grechko, 2021).

4 RESULTS

4.1 Ararat, Surenavan

4.1.1 Environmental samples

An overview of the heavy metal concentrations that were measured in the soil, sediment, and fish samples collected in the Ararat and Surenavan area are shown in Table 4.1, Table 4.2, Table 4.3, respectively. In the tables for soil and sediment samples, numbers of samples exceeding the limit of quantification, concentration ranges, arithmetic means, and medians for each of the metals are shown. Concentrations of heavy metals in soils and sediments are converted to mg/kg dry weight (mg/kg DW). For the fish sample, the single concentration of each heavy metal in the sample is shown because only one mixed sample of two fish was analyzed. The concentration of heavy metals in the fish sample is given in mg/kg fresh matter (mg/kg FM). A detailed overview of the measured concentrations of heavy metals for each individual sample can be found in Annex (Tables V-VIII).

Taking soil sample. PHOTO: Viktoriya Mayakotskaya

Table 4.1 Heavy metal concentrations in the soil samples from the area of Ararat and Surenavan (mg/kg DW). The total number of samples (n) is 8; LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
n >LOQ (% of all samples)	8 (100%)	8 (100%)	8 (100%)	8 (100%)	8 (100%)	8 (100%)	8 (100%)	8 (100%)
Range of samples > LOQ	6.8-241.2	0.2-0.8	44.9-97.6	39-280	0.0122-0.0983	31-152	9-84	67-499
Mean of samples >LOQ	39.0	0.4	68.2	115.7	0.0341	67.5	31.1	180.9
Median	9.9	0.3	65.3	101.0	0.0210	62.3	22.0	113.1

Table 4.2 Heavy metal concentrations in the sediment samples from the area of Ararat and Surenavan (mg/kg DW). The total number of samples (n) is 3; LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
n >LOQ (% of all samples)	3 (100%)	3 (100%)	3 (100%)	3 (100%)	3 (100%)	3 (100%)	3 (100%)	3 (100%)
Range of samples >LOQ	12.8-14.9	0.1-0.2	56.1-74.5	22-35	0.0148-0.0321	43-68	10-12	58-72
Mean of samples >LOQ	14.8	0.2	65.6	29.3	0.0219	57.5	11.7	64.4
Median	14.9	0.2	66.3	31.2	0.0188	60.8	12.3	62.3

Table 4.3 Heavy metal concentrations in the fish sample from the area of Ararat (mg/kg FM). Only one fish sample was analyzed, LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Concentration	0.09	<LOQ	<LOQ	0.41	0.052	<LOQ	<LOQ	29.8

4.1.2 Biological samples

Heavy metals in urine, women's cohort

Number of Participants (n): 18
Age of participants: 17 – 47 years (mean 32.3)

Table 4.4 Urinary concentrations of the five heavy metals tested in women in the areas of Ararat and Surenavan (µg/g creatinine). Range, geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification.

	As	Cd	Cu	Ni	Pb
n >LOQ (% of all samples)	18 (100%)	4 (22.2%)	7 (38.9%)	14 (77.8%)	7 (38.9%)
Range of samples > LOQ	6-34	0.4-1.3	7-96	3-47	2-32
Mean of samples > LOQ	14.28	0.59	44.62	6.78	4.29
Median	13.5	0	0	5	0
95th Percentile	34	0.71	74.75	17.25	16.7

Heavy metals in hair, women's cohort

Number of Participants (n): 13
Age of participants: 18 – 47 years (mean 35)

Table 4.5 Heavy metal concentrations in the hair of women tested in Ararat and Surenavan regions (mg/kg). Range and geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification. NA - no samples above LOQ.

	As	Cd	Cr	Cu	Hg	Mo	Ni	Pb
n > LOQ (% of all samples)	4 (30.1%)	8 (61.5%)	0	13 (100%)	13 (100%	2 (15.4%)	10 (76.9%)	12 (92.3%)
Range > LOQ	0.04	0.009-0.445	NA	3.3-44.3	0.022-0.162	0.05-0.06	0.23-3.36	0.06-6.19
Mean > LOQ	0.04	0.034	NA	12.79	0.656	0.055	0.61	0.34
Median	0	0.011	NA	12.6	0.07	0	0.3	0.37
95th percentile	0.04	0.26	NA	38	0.162	0.054	2.1	3.5

4.2 Karaberd

4.2.1 Environmental samples

An overview of the heavy metal concentrations that were measured in the collected samples of soil, sediment, and mining waste in the Karaberd area are shown in Table 4.6, Table 4.7, Table 4.8, respectively. In the tables for soil and sediment samples, numbers of samples exceeding the limit of quantification, concentration ranges, arithmetic means, and medians for each of the metals are shown. For mining waste, the single concentration of each heavy metal is shown because only one sample of mining waste from a heap near the gold mine was analyzed. The concentrations of heavy metals in soil, sediment, and mining waste samples are converted to mg/kg dry weight (mg/kg DW). A detailed overview of the measured concentrations of heavy metals for each individual sample can be found in Annex (Tables V-VII).

Table 4.6 Heavy metal concentrations in the soil samples from the area of Karaberd (mg/kg DW). The total number of samples (n) is 7; LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mo**	**Ni**	**Pb**	**V**	**Zn**
n >LOQ (% of all samples)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)
Range of samples >LOQ	5.6-19	0.4-2.2	19.8-51.9	20-90	14,400-33,400	1.1-4	14-38	13-110	44.2-113	71-394
Mean of samples >LOQ	11.9	0.9	30.3	45.9	22,400	2.5	20.6	38.9	75.0	175.0
Median	12.1	0.6	25.9	41.0	18,000	2.3	18.0	18.0	67.5	155.0

Table 4.7 Heavy metal concentrations in the sediment samples from the area of Karaberd (mg/kg DW). The total number of samples (n) is 7; LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Mo**	**Ni**	**Pb**	**V**	**Zn**
n >LOQ (% of all samples)	7 (100%)	2 (29%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)
Range of samples >LOQ	3.2-172	0.2-30.2	5.2-24.6	27-129	20,700-11,4000	0.0015-0.809	1.5-77.5	5.8-33	6-93	21.1-150	36-17,600
Mean of samples >LOQ	28.3	15.2	14.5	78.4	40,414	0.1187	13.0	16.1	22.3	111.6	2,579.9
Median	4.4	0	12.7	99.0	29,300	0.0028	2.2	16.0	11.0	128.0	84.0

Table 4.8 Heavy metal concentrations in the sample of waste from the area of Karaberd (mg/kg DW). Only one sample of waste was analyzed, LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mo**	**Ni**	**Pb**	**V**	**Zn**
Concentration	10.7	1.9	2.9	402	24,900	5.3	3.0	15.0	81.2	220

4.2.2 Biological samples

Heavy metals in urine, women's cohort

Number of Participants (n): 9
Age of participants: 46 – 83 years (mean 62)

Table 4.9 Urinary concentrations of the five heavy metals tested in women in the area of Karaberd (µg/g creatinine). Range, geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification.

	As	Cd	Cu	Ni	Pb
n >LOQ (% of all samples)	9 (100%)	9 (100%)	4 (44.4%)	9 (100%)	9 (100%)
Range of samples > LOQ	7-16	0.3-0.7	29-116	1-17	1-7
Mean of samples > LOQ	12.63	0.45	60.4	3.66	2
Median	12	0.4	0	4	2
95th Percentile	16	0.66	104	12.6	5.4

Heavy metals in urine, men's cohort

Number of Participants (n): 5
Age of participants: 49-83 years (mean 68.8)

Table 4.10 Urinary concentrations of the five heavy metals tested in men in the Karaberd area (µg/g creatinine). Range, geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification.

	As	Cd	Cu	Ni	Pb
n >LOQ (% of all samples)	5 (100%)	4 (80%)	3 (60%)	5 (100%)	5 (100%)
Range of samples > LOQ	9-42	0.3-3	15-23	2-5	1-2
Mean of samples > LOQ	12.51	0.65	17.3	3.47	1.15
Median	9	0.4	15	5	1
95th Percentile	35.6	2.5	21.4	5	1.8

Heavy metals in hair, women's cohort

Number of Participants (n): 4
Age of participants: 59 – 83 years (mean 65.5)

Table 4.11 Heavy metal concentrations in the hair of women tested in Karaberd (mg/kg). Range and geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification. NA – not applicable. Chromium not tested.

	As	Cd	Cr	Cu	Hg	Mo	Ni	Pb
n > LOQ (% of all samples)	3 (75%)	4 (100%)	.	4 (100%)	4 (100%)	1 (25%)	0	4 (100%)
Range > LOQ	0.03-0.07	0.08-0.039	.	7.6-13.7	0.021-0.147	0.05	NA	0.1-0.56
Mean > LOQ	0.047	0.019	.	9.41	0.059	0.05	NA	0.28
Median	0.04	0.022	.	8.7	0.074	0	NA	0.38
95th percentile	0.067	0.038	.	13.04	0.142	0.04	NA	0.56

Gold mine in Karaberd (view of Vanadzor). PHOTO: Monika Yeritsyan

Sediment sampling in Pambak River. PHOTO: Monika Yeritsyan

4.3 Meghradzor

4.3.1 Environmental samples

An overview of the heavy metal concentrations that were measured in the collected samples of soil, sediments, and mining waste in the Meghradzor area are shown in Table 4.12, Table 4.13, Table 4.14, respectively. The tables show numbers of samples exceeding the limit of quantification, concentration ranges, arithmetic means, and medians for each of the heavy metals. The concentrations of heavy metals in soil, sediment, and mining waste samples are converted to mg/kg dry weight (mg/kg DW). A detailed overview of the measured concentrations of heavy metals for each individual sample can be found in Annex (Tables V-VII).

Table 4.12 Heavy metal concentrations in the soil samples from the area of Meghradzor (mg/kg dry weight). The total number of samples (n) is 7; LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mo**	**Ni**	**Pb**	**Zn**
n >LOQ (% of all samples)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	6 (86%)	7 (100%)	7 (100%)	7 (100%)
Range of samples >LOQ	3.1-20	0.2-0.6	14.7-64.4	40-130	24,300-48,500	1.4-3.2	10-49	12-42	86-220
Mean of samples >LOQ	8.5	0.4	34.2	58.3	31,029	2.4	22.4	24.1	148.6
Median	5.6	0.4	39.3	45.0	27,100	2.3	22.0	22.0	130.0

Table 4.13 Heavy metal concentrations in the sediment samples from area of Meghradzor (mg/kg dry weight). The total number of samples (n) is 5; LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Mo**	**Ni**	**Pb**	**Zn**
n >LOQ (% of all samples)	5 (100%)	4 (80%)	5 (100%)	5 (100%)	5 (100%)	5 (100%)	5 (100%)	5 (100%)	5 (100%)	5 (100%)
Range of samples >LOQ	3.4-116	0.4-20.3	2.4-59.3	18-191	11,300-45,300	0.003-0.729	1-3.5	6-42	14-96	45-342
Mean of samples >LOQ	33.1	5.8	26.9	60.2	27,600	0.1492	2.0	18.6	33.0	152.0
Median	9.5	1.2	29.2	20.0	28,400	0.0048	1.6	17.0	19.0	107.0

Table 4.14 Heavy metal concentrations in the samples of waste from the area of Meghradzor (mg/kg dry weight). The total number of samples (n) is 2; LOQ – limit of quantification.

	As	Cd	Cr	Cu	Fe	Mo	Ni	Pb	Zn
n >LOQ (% of all samples)	2 (100%)	2 (100%)	2 (100%)	2 (100%)	2 (100%)	2 (100%)	2 (100%)	2 (100%)	2 (100%)
Range of samples >LOQ	36.1-39.7	0.6-0.9	4.1-7.7	88-158	23,500-31,000	1.4-1.8	4-6	27-40	123-203
Mean of samples >LOQ	37.9	0.75	5.9	123	27,250	1.6	5	33.5	163
Median	37.9	0.75	5.9	123	27,250	1.6	5	33.5	163

4.3.2 Biological samples

Heavy metals in urine, women's cohort

Number of participants: 14
Age of participants: 7-70 years (mean 43.3)

Table 4.15 Urinary concentrations of the five heavy metals tested in women in Meghradzor (µg/g creatinine). Range, geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification.

	As	Cd	Cu	Ni	Pb
n >LOQ (% of all samples)	14 (100%)	9 (64.3%)	1 (7.14%)	13 (92.8%)	13 (92.8%)
Range of samples > LOQ	10-75	0.2-1	12	1-11	1-6
Mean of samples > LOQ	17.96	0.52	12	3.26	2
Median	15	0.35	0	2.5	1.5
95th Percentile	49	0.94	4.2	9.7	6

Heavy metals in urine, men's cohort

Number of participants: 5
Age of participants: 5-67 years (5-, 9,10-, 58- and 67-year-old)

Table 4.16 Urinary concentrations of the five heavy metals tested in men in the area of Meghradzor (µg/g creatinine). Range, geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification.

	As	Cd	Cu	Ni	Pb
n >LOQ (% of all samples)	5 (100%)	1 (20%)	1 (20%)	3 (60%)	5 (100%)
Range of samples > LOQ	10-37	0.6	20	1-2	1-4
Mean of samples > LOQ	21.85	0.6	20	1.26	1.89
Median	22	0	0	1	2
95th Percentile	36.8	0.48	16	1.8	3.8

Heavy metals in hair

Number of Participants (n): 5
Age of participants: 31 – 65 years (mean 48.4)

Table 4.17 Heavy metal concentrations in the hair of women tested in Meghradzor (mg/kg). Range and geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification. NA – not applicable. Chromium not tested.

	As	Cd	Cr	Cu	Hg	Mo	Ni	Pb
n > LOQ (% of all samples)	3 (60%)	5 (100%)	-	5 (100%)	5 (100%)	2 (40%)	2 (40%)	5 (100%)
Range > LOQ	0.02-0.05	0.003-0.058	-	8.5-68.6	0.04-0.293	0.05-0.06	0.24-0.88	0.26-0.73
Mean > LOQ	0.031	0.011	-	15.26	0.079	0.055	0.46	0.5
Median	0.02	0.007	-	11.5	0.063	0	0	0.56
95th percentile	0.046	0.05	-	57.28	0.248	0.058	0.75	0.7

Beside the Meghradzor cohort of women, we examined a hair sample of a 14-year-old male. It showed no accumulation of nickel or arsenic, had 9 µg/kg of cadmium, 8 mg/kg of copper, 72 mg/kg of mercury, 0.12 mg/kg of molybdenum, and 0.14 mg/kg of lead.

4.4 Melikgyugh

4.4.1 Environmental samples

An overview of the heavy metal concentrations that were measured in the collected soil and sediment samples in the Melikgyugh area are shown in Table 4.18 and Table 4.19, respectively. The tables show numbers of samples exceeding the limit of quantification, concentration ranges, arithmetic means, and medians for each of the heavy metals. The concentrations of heavy metals in both soil and sediment samples are converted to mg/kg dry weight (mg/kg DW). A detailed overview of the measured concentrations of heavy metals for each individual sample can be found in Annex (Tables V-VII).

Table 4.18 Heavy metal concentrations in the soil samples from the area of Melikgyugh (mg/kg DW). The total number of samples (n) is 7; LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
n >LOQ (% of all samples)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)
Range of samples > LOQ	5.2-119	0.3-2.8	55.9-117.5	41-57	0.0167-0.0711	37-63	15-212	71-254
Mean of samples >LOQ	24.4	0.8	83.2	48.1	0.0307	49.4	45.7	165.8
Median	7.7	0.4	77.3	49	0.0238	49.1	17.2	153.7

Table 4.19 Heavy metal concentrations in the sediment samples from the area of Melikgyugh (mg/kg DW). The total number of samples (n) is 7; LOQ – limit of quantification.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
n >LOQ (% of all samples)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)	7 (100%)
Range of samples >LOQ	5.4-38.1	0.3-0.5	62.6-102.1	32-42	0.0096-0.0275	34-69	14-30	65-101
Mean of samples >LOQ	26.0	0.4	77.0	36.9	0.0182	49.6	19.2	84.8
Median	28.8	0.4	73.7	37.2	0.0209	47.9	17.4	91.9

4.4.2 Biological samples

Heavy metals in urine, women's cohort

Number of Participants (n): 4
Age of participants: 20 – 33 years (mean 25.5)

Table 4.20 Urinary concentrations of the five heavy metals tested in women in Melikgyugh (µg/g creatinine). Range, geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification. NA – not applicable.

	As	Cd	Cu	Ni	Pb
n >LOQ (% of all samples)	4 (100%)	0	0	4 (100%)	0
Range of samples above > LOQ	10-120	NA	NA	2-4	NA
Geometric Mean of samples > LOQ	20.73	NA	NA	2.63	NA
Median (entire set of samples)	12.5	NA	NA	2.5	NA
95th Percentile	104.1	NA	NA	3.85	NA

Heavy metals in hair, women's cohort

Number of Participants (n): 5
Age: 20 – 70 years (mean 43.8)

Table 4.21 Heavy metal concentrations in the hair of women tested in Melikgyugh (mg/kg). Range and geometric mean calculated for samples above LOQ, Median and 95th percentile calculated for the full set of samples. Number of samples (n); LOQ – limit of quantification. NA – not applicable.

	As	Cd	Cr	Cu	Hg	Mo	Ni	Pb
n > LOQ (% of all samples)	4 (80%)	3 (60%)	0	5 (100%)	5 (100%)	0	5 (100%)	5 (100%)
Range > LOQ	0.02-0.05	0.007-0.183	NA	7.6-13.3	0.045-0.156	NA	0.24-0.77	0.15-0.5
Mean > LOQ	0.028	0.05	NA	9.13	0.094	NA	0.37	0.23
Median	0.02	0.007	NA	7.9	0.111	NA	0.33	0.19
95th Percentile	0.046	0.166	NA	12.68	0.156	NA	0.69	0.46

Surenavan is a village of storks. PHOTO: Viktoriya Mayakotskaya

5 DISCUSSION

5.1 Ararat, Surenavan

5.1.1 Environmental samples

Because of its industrial past, the area of Ararat has been a location of interest for research into the heavy metal occurrence in the environment. In the area, three potential sources of heavy metal pollution are located – the Ararat Cement Factory, the gold processing plant of Ararat Gold Company and the tailings pond of the plant. The Ararat Gold Company and the Ararat Cement Plant were among the nine largest air polluters in Armenia, responsible for up to 93% of air emissions in 2004 (OECD, 2004). Ararat is one of the important agrarian regions and main providers of fruits and vegetables in the country. For that reason, a risk assessment of heavy metals in fruit and vegetables grown in the area has been carried out by (Beglaryan, 2021). The outcome of the study indicated that the local adult population's health risk assessment results showed some concerns associated with arsenic and lead from locally produced fruit and vegetables. As part of our investigation, we took eight soil samples, three sediment samples and one mixed fish sample in the area.

Our results indicate that the environment in the Ararat area could be classified as moderately to strongly polluted by arsenic. The overall mean value of total **arsenic** for various soil types is estimated at 6.83 mg/kg, but the background contents of various soil groups range from <0.1 to 67 mg/kg (Kabata-Penditas, 2011). Arsenic concentrations in the soil samples that we collected are within this range, except for one sample from the vicinity of the gold processing plant (ARARAT-SOIL-05/23) with concentration of 241.2 mg/kg DW. All samples show concentrations equal to or higher than the world average. The levels of arsenic in all soil samples exceed Armenian soil standard and US EPA levels of pollution limits for industrial areas. All three sediment samples collected exceed the Canadian Threshold Effect Level, but do not exceed the Canadian Probable Effect Level. Arsenic levels in the samples point out arsenic pollution of soil of private gardens. This could be caused by arsenic release from the bedrock, but also as a result of industrial pollution. For the proper evaluation of arsenic pollution, data about natural background are necessary as these could vary significantly.

According to our results, cadmium does not pose a significant risk in the Ararat area. The world average soil **cadmium** concentration is estimated as 0.41 mg/kg and cadmium content in reference soils from different countries ranges from 0.06 to 4.3 mg/kg (Kabata-Penditas, 2011). The mean concentration of cadmium in the soil samples collected (0.4 mg/kg DW) is at comparable level to the worldwide average. The highest concentration of 0.8 mg/kg was in the soil sample taken near the gold processing plant (ARARAT-SOIL-05/23), it is also the only sample that does not comply with the US EPA level of pollution limits for residential areas. All sediment samples are lower than the selected reference values.

The world average content of **chromium** in soils has been established as 60 mg/kg (Kabata-Penditas, 2011). The mean and median concentrations of chromium in the soil samples (68.2 and 65.3 mg/kg DW) are a little higher than the worldwide average mentioned above and any of the samples does not meet the Armenian soil standard for chromium. All three sediment samples collected exceed the Canadian Threshold Effect Level, but do not exceed the Canadian Probable Effect Level.

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 (Kabata-Penditas, 2011). The mean concentration of copper in the soil samples (115.7 mg/kg DW) is slightly higher than the highest value of averages of different soil groups mentioned above. All eight soil samples exceed the Armenian soil standard for copper, but any of the soil samples does not exceed the US EPA pollution limit for residential areas. All three sediment samples collected comply with the Canadian Sediment Quality Guidelines.

The average content of **mercury** in soils all over Europe is estimated as 0.0383 mg/kg (ESDAC, 2021). The mean concentration of mercury in our soil samples (0.0341 mg/kg DW) is slightly lower than the European average. Two soil samples from private gardens exceed the average European mercury concentration - ARARAT-SOIL-01/23 with 0.0524 mg/kg DW and SRNV-SOIL-03/23 with 0.0983 mg/kg DW, but all eight soil samples comply with the US EPA pollution limit for residential areas. All three sediment samples collected comply with the Canadian Sediment Quality Guidelines.

Soils throughout the world contain **nickel** within the range of 13–37 mg/kg (Kabata-Penditas, 2011). The mean concentration of nickel in the soil samples (57.8 mg/kg DW) is considerably higher than the worldwide range of nickel in soils. This fact points out elevated nickel levels in the soils of the area. The levels of nickel in all eight soil samples exceed the Armenian soil standard, but only one soil sample also exceed the US EPA pollution limit for residential areas. This is again the soil sample that was collected close to the gold processing plant (ARARAT-SOIL-05/23) with nickel concentration of 152 mg/kg DW.

The overall mean value of total **lead** for different soils is estimated at 27 mg/kg (Kabata-Penditas, 2011). The mean concentration of lead in the soil samples (31.1 mg/kg DW) is higher than the mean estimated for soils. Concentrations of lead in two soil samples exceed the Armenian soil standard, but all the soil samples comply the US EPA pollution limit for residential areas. High lead concentrations were found in two soil samples from Surenavan with concentrations of 84 mg/kg DW and 62 mg/kg DW. These two soil samples come from land that is not cultivated agriculturally. All three sediment samples collected comply with the Canadian Sediment Quality Guidelines for lead.

The general values for the average total **zinc** content in soils of various groups globally range between 60 and 89 mg/kg DW (Kabata-Penditas, 2011). The mean concentration of zinc in the soil samples collected (180.9 mg/kg DW) is more than two times higher than the higher value of the range mentioned above. Concentrations of zinc in all the soil samples comply with the US EPA pollution limit for residential areas. High concentrations of zinc were found in three Surenavan soil samples, especially in sample SRNV-SOIL-1/23 containing 499 mg/kg DW of zinc. This sample was taken from a plot of land used for growing vegetables. All three sediment samples collected comply with the Canadian Sediment Quality Guidelines for zinc.

Table 5.1 Number of soil samples from the Ararat area that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the total number of soil samples are expressed in brackets.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Mo**	**Ni**	**Pb**	**V**	**Zn**
Armenian soil standard	8 (100%)	-	8 (100%)	8 (100%)	-	-	-	8 (100%)	2 (25%)	-	-
Czech pollution indication	1 (13%)	0 (0%)	-	-	-	0 (0%)	-	-	0 (0%)	-	-
Czech background indication	1 (13%)	3 (38%)	1 (13%)	6 (75%)	-	0 (0%)	-	6 (75%)	2 (25%)	NA	4 (50%)
Levels of pollution limits – industrial areas (US EPA)	8 (100%)	0 (0%)	-	0 (0%)	NA	0 (0%)	NA	0 (0%)	0 (0%)	NA	0 (0%)
Levels of pollution limits – other areas (US EPA)	8 (100%)	1 (13%)	-	0 (0%)	NA	0 (0%)	NA	1 (13%)	0 (0%)	NA	0 (0%)

Table 5.2 Number of sediment samples from the Ararat area that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the total number of sediment samples are expressed in brackets.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Mo**	**Ni**	**Pb**	**V**	**Zn**
Czech Limit Values	0 (0%)	0 (0%)	0 (0%)	0 (0%)	NA	0 (0%)	NA	0 (0%)	0 (0%)	NA	0 (0%)
Canadian Threshold Effect Level	3 (100%)	0 (0%)	3 (100%)	0 (0%)	NA	0 (0%)	NA	-	0 (0%)	NA	0 (0%)
Canadian Probable Effect Level	0 (0%)	0 (0%)	0 (0%)	0 (0%)	NA	0 (0%)	NA	-	0 (0%)	NA	0 (0%)

Fig. 5.1 Concentrations of As, Pb, and Zn in soil samples from Ararat and Surenavan; mg/kg DW

The sample of **fish** collected from a pond in the Ararat area does not pose a risk due to heavy metal content. The concentrations of four metals (Cd, Cr, Ni, and Pb) were below the limit of quantification, while only low concentrations of four metals (As, Cu, Hg, and Zn) were measured. The fish sample complies with the criteria for cadmium, mercury, and lead concentrations for fish placed on the market in the European Union.

5.1.2 Biological samples

Participants of our study contributed 14 urine and 12 hair samples, and 4 urine and 1 hair samples in Ararat and Surenavan respectively (2 participants in Ararat and 3 in Surenavan provided urine only). All participants identified as women, their age ranging from 17 to 47 years (mean of 32.3 years) indicative of their reproductive age.

Contamination with **arsenic** was present in all urine samples with the geometrical mean of **14.28 µg/g of creatinine** and 95th percentile of 34 µg/g creatinine; and in 4 hair specimens, each at a concentration of **0.04 mg/kg**. The urinary concentrations measured in samples in Ararat and Surenavan do not indicate as high exposures to arsenic as e.g. in general adult populations across several Asian countries (mean of 84.6 µg/g creatinine, (Mizuno et al., 2021)cadmium, lead, and selenium, however indicate higher exposure than e.g., among adolescents in three European countries (geometrical mean of 4.37 µg/g creatinine, (Govarts, 2023) or any age group in the US (geometrical mean of 6.94 µg/g creatinine for the total population in 2017-2018); although the 95th percentile in the US population reaches 51.9 µg/g creatinine (CDC, 2022). While there are no regulatory limits for arsenic in urine, both EU in its Drinking Water Directive (Directive 2020/2184/EU) and the US EPA set the maximum contaminant level in drinking water for arsenic at 10 µg/l. Also, the normal hair arsenic concentration, according to CDC, should not exceed 1 mg/kg (ATSDR, 2007). Therefore, the 0.04 mg/kg measured in the four hair samples in Ararat and Surenavan, while the remaining 70 % of samples revealed no arsenic above LOQ, does not suggest a critical chronic exposure in the measured individuals.

However, environmental sampling in the area raises caution on the regional arsenic pollution, particularly because the sample size obtained for biological samples in the region was small and data from various European studies show that possible health concerns may not be excluded even at low levels, particularly during the reproductive period (Buekers et al., 2023). Higher acute, urinary, and lower cumulative exposures in the hair, along with moderate to severe environmental pollution with arsenic poses risks to the youngest population due to oral exposure via ingested soil and dust.

Our sampling in the Ararat and Surenavan regions revealed urine **lead** in nearly 40 % of samples with the mean of **4.29 µg/g creatinine** and 95th percentile at 16.7 µg/g creatinine (including two outliers of 14 and 32 µg/g creatinine); and the hair mean concentration of **0.34 mg/kg** (95th percentile 3.5mg/kg) including an outlier of 6.19 mg/kg hair. Considering the border findings from environmental sampling, the lead concentration we detected in several biological samples cautions towards practices reducing lead exposure, particularly in local children.

The primary route of exposure to **cadmium** is via ingestion of contaminated food and water and inhalation of polluted air or cigarette smoke. In Ararat and Surenavan, four out of 18 women (over 20%) tested positive for cadmium in the urine and over 60 % (8 participants) had cadmium level higher than LOQ detected in their hair. Among the four positive urine samples, one stood out with **1.3 µg/g creatinine** while the remaining three read either **0.04 or 0.06 µg/g creatinine**. The mean urine level in the general US population is 0.193 µg/g creatinine (ATSDR, 2012a), and the mean cadmium urine levels were most recently measured at 0.146 µg/g creatinine, 95th percentile 0.534 µg/g creatinine in the European countries (Govarts, 2023). Although cadmium gets distributed widely in the body and excreted slowly, urinary cadmium levels primarily reflect total body burden. Here, we identified individuals rather than entire cohorts or areas contaminated with cadmium beyond the levels of concern. The mean hair cadmium in the Ararat-Surenavan cohort was 0.034 mg/kg, 95th percentile of 0.26 mg/kg in eight out of 13 samples. Likewise in urine cadmium, one sample (a different one) of 0.445 (and yet another of 0.136 mg/kg) stood out and should be consulted separately with the study subjects.

All thirteen women tested above LOQ for mercury and copper in the hair. While **mercury** represents a toxic heavy metal that have adverse, namely developmental, and neurological, effects whose exposure should minimized and/or prevented, **copper** is an essential element required for various physiological processes in the human body, but excessive copper exposure may lead to gastrointestinal, neurological, hepatic, or hematological symptoms. In the Ararat and Surenavan, the range of hair mercury was measured from **0.022 to 0.167 mg/kg**, mean of 0.066 and 95th percentile of

0.162 mg/kg, that is at levels that represent a moderate to low concern. Just like for hair mercury, copper was detected in all thirteen hair samples in this cohort. The mean concentration was calculated at **12.79 mg/kg**, the 95th percentile of 39 mg/kg, i.e. within the normal range suggested by (Bost et al., 2016) and at levels comparable elsewhere in Armenia (Grechko, 2021). Urinary copper was tested above LOQ in nearly 40% of the samples, at a mean of **44.62 µg/g of creatinine**, at levels that reach higher than indicated for the reference European studies and higher than our previous studies in Armenia. Further investigation into urinary copper in the area is warranted.

Chromium was not detected in either of the 13 hair samples. **Nickel** was revealed in ten hair samples (nearly 80%) at the mean of **0.61 mg/kg** and the 95th percentile of 2.1 mg/kg. However, the results are difficult to assess in the context as few studies were published on the significance of hair nickel. Urinary nickel of mean **6.78 µg/g creatinine** indicated higher concentration than in our previous reports and certainly higher than in the U.S. general populations. **Molybdenum**, a trace element that was detected in two hair samples in the Ararat-Surenavan cohort at **0.05 and 0.06 mg/kg hair**, that is higher than in our previous reports from Armenia yet within the reference values of other studies (see above).

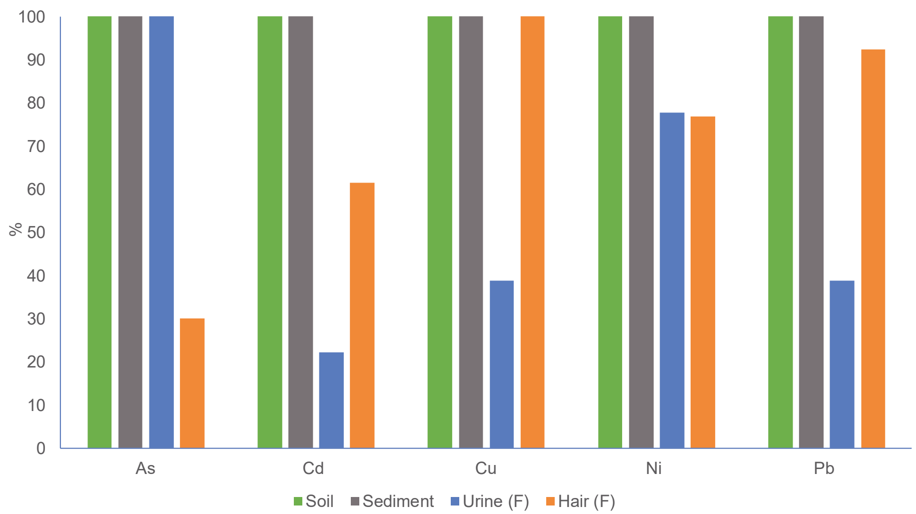

Figure 5.2 Summary of the occurrence (%) of positive findings for selected heavy metals (>LOQ) in samples from Ararat and Surenavan: soil (n=8), sediment (n=3), female urine(n=18), female hair (n=13).

Hair sampling. PHOTO: Viktoriya Mayakotskaya

5.2 Karaberd

5.2.1 Environmental samples

The Karaberd gold mine is known as a potential source of heavy metal pollution. Due to suspected pollution, the occurrence of heavy metals in the Pambak River, which flows through the area, was investigated in the past. The investigation found that the water of the Pambak River exceeded the maximal permissible levels of iron and copper for culture-municipal water use in 2005. Moreover, the water of the river exceeded the maximal permissible levels for manganese, aluminum, lead, zinc and cadmium in 2006. Remarkable increases of heavy metals' concentrations were observed in waters of the Pambak River in 2006 compared with 2005 (Suvaryan et al., 2011). As part of our investigation, we collected seven soil samples, seven sediment samples and one sample of mining waste in the area.

Our results indicate that the environment in the Karaberd area could be classified as moderately to strongly polluted by arsenic. The overall mean value of the total **arsenic** for different soil is estimated as 6.83 mg/kg, but the background contents of various soil groups range from <0.1 to 67 mg/kg (Kabata-Penditas, 2011). Arsenic concentrations in the soil samples were within this range, but most of the samples showed concentrations noticeably higher than the world average. The levels of arsenic in all the soil samples exceed the Armenian soil standard and the US EPA pollution limit for industrial areas. Arsenic concentrations in the sediment samples comply with the Canadian Threshold Effect Level except for one sample (KARAB-SED-02/22) with concentration of 172 mg/kg DW, which does not comply with the Canadian Probable Effect Level either.

The world average soil **cadmium** concentration is estimated at 0.41 mg/kg and cadmium content in reference soils from different countries ranges from 0.06 to 4.3 mg/kg(Kabata-Penditas, 2011). The concentrations of cadmium in the soil samples are in the range of concentrations found in other countries but are equal to or higher than the world average. The concentrations of cadmium in three soil samples exceed the US EPA pollution limit for industrial areas, with the highest concentration of 2.2 mg/kg DW found in the soil sample KARAB-SOIL-01/22 that was collected close to the gold mine. Cadmium concentrations in sediment samples were below the limit of quantification except for the sample KARAB-SED-02/22 that was collected from a flooded former gold-mine tunnel. This sample with concentration of 30.2 mg/kg DW exceeds the Canadian Probable Effect Level for cadmium.

The world average content of **chromium** in soils has been established as 60 mg/kg (Kabata-Penditas, 2011). The mean concentration of chromium in the soil samples (30.3 mg/kg DW) are lower than the worldwide average mentioned above, but any of the samples does not meet the Armenian soil standard for chromium. All the sediment samples comply with the Canadian Threshold Effect Level for chromium.

The general values for the average total **copper** content in soils of different groups all over the world range between 14 and 109 mg/kg (Kabata-Penditas, 2011). The mean concentration of copper in the soil samples (78.4 mg/kg DW) is in the range of different soil groups. All seven soil samples exceed the Armenian soil standard, but any of the soil samples does not exceed the US EPA pollution limit for residential areas. Copper concentrations in four of the seven sediment samples exceed the Canadian Threshold Effect Level. High concentrations of copper are present in sediment samples from drainage of the gold mine and from the Pambak River downstream of the mine, while the copper concentrations in sediment samples collected upstream of the goldmine are lower. In addition, a high concentration of copper (402 mg/kg DW) was also found in the mining waste sample. These findings indicate that the gold mine could be a source of copper pollution to the drainage water.

The abundance of **iron** in soils averages about 35,000 mg/kg and is likely to be increased in heavy loamy soils and some organic soils (Kabata-Penditas, 2011). Iron concentrations in all soil samples are lower than the global average iron content in soil, but they exceed the US EPA pollution limit for residential areas. The sediment sample KARAB-SED-02/22 collected from a flooded former gold-mine tunnel contains a high iron concentration of 114,000 mg/kg DW.

The sediment samples contain low concentrations of **mercury**, except for one sediment sample with a concentration of 0.802 mg/kg DW. This sediment sample (KARAB-SED-02/22) was collected from a road flooded by gold mine drainage, which could indicate that mining is a source of mercury.

The world average content of **molybdenum** in soils has been established as 1.1 mg/kg and is fairly similar to its crustal abundance (Kabata-Penditas, 2011). The concentrations of molybdenum in the soil samples are several times higher than or equal to the world average content in soils, however, the concentrations in the samples comply with the US EPA pollution limit for residential areas. The sediment sample (KARAB-SED-02/22) collected from a road flooded by gold mine drainage contains very high molybdenum concentration of 77.5 mg/kg DW.

Soils throughout the world contain **nickel** within the range 13–37 mg/kg (Kabata-Penditas, 2011). The concentrations of nickel in the soil samples vary within the range of worldwide concentrations. The levels of nickel in all eight soil samples exceed the Armenian soil standard, but any of them does not exceeds the US EPA pollution limit for residential areas. The sediment sample KARAB-SED-02/22 collected from a flooded former gold-mine tunnel contains a high nickel concentration of 33 mg/kg DW.

The overall mean value of total **lead** for different soils is estimated as 27 mg/kg DW (Kabata-Penditas, 2011). Three soil samples have lead concentrations higher than the world average, although these samples comply with the US EPA pollution limit for residential areas. High lead concentrations are found in two soil samples that were collected close to the gold mine (KARAB-SOIL-01/22 a KARAB-SOIL-02/22) and in one sample from a private garden (KARAB-SOIL-05/22). The concentration of lead in the sediment sample KARAB-SED-02/22 collected from a former flooded gold-mine tunnel exceeds the Canadian Probable Effect Level.

Levels of **vanadium** in soils are closely related to the parent rock types. Its worldwide soil average is estimated as 129 mg/kg, with the range of 69–320 mg/kg (Kabata-Penditas, 2011). While vanadium concentrations in all soil samples were lower than the world average, the detected limits all exceed the US EPA pollution limit for residential areas.

The general values for the average total **zinc** content in soils of various groups, all over the world, range between 60 and 89 mg/kg DW (Kabata-Penditas, 2011). Zinc concentrations in four soil samples exceed the range of averages found worldwide. In two cases, they are soil samples collected in proximity to the gold mine, but in two cases they are soil samples from private gardens intended for growing crops. Concentration of zinc in any of the soil samples does not exceed the US EPA pollution limit for residential areas. High concentration of zinc is found in the sediment sample KARAB-SED-02/22 that was collected from a flooded former gold-mine tunnel. This sediment sample with concentration of 17,600 mg/kg DW does not comply with Canadian Probable Effect Level.

Table 5.3 Number of soil samples from the Karaberd area that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the total number of soil samples are expressed in brackets.

	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
Armenian soil standard	7 (100%)	-	7 (100%)	7 (100%)	-	-	-	7 (100%)	3 (43%)	-	-
Czech pollution indication	0 (0%)	0 (0%)	-	-	-	NA	-	-	0 (0%)	-	-
Czech background indication	0 (0%)	5 (71%)	0 (0%)	2 (29%)	-	NA	-	0 (0%)	1 (14%)	0 (0%)	4 (57%)
Levels of pollution limits – industrial areas (US EPA)	7 (100%)	0 (0%)	-	0 (0%)	0 (0%)	NA	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)
Levels of pollution limits – other areas (US EPA)	7 (100%)	3 (43 %)	-	0 (0%)	7 (100%)	NA	0 (0%)	0 (0%)	0 (0%)	7 (100%)	0 (0%)

Table 5.4 Number of sediment samples from the Karaberd area that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the total number of sediment samples are expressed in brackets.

	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
Czech Limit Values	1 (14%)	1 (14%)	0 (0%)	3 (43%)	NA	1 (14%)	NA	0 (0%)	0 (0%)	NA	1 (14%)
Canadian Threshold Effect Level	1 (14%)	1 (14%)	0 (0%)	4 (57%)	NA	1 (14%)	NA	-	1 (14%)	NA	1 (14%)
Canadian Probable Effect Level	1 (14%)	1 (14%)	0 (0%)	0 (0%)	NA	1 (14%)	NA	-	1 (14%)	NA	1 (14%)

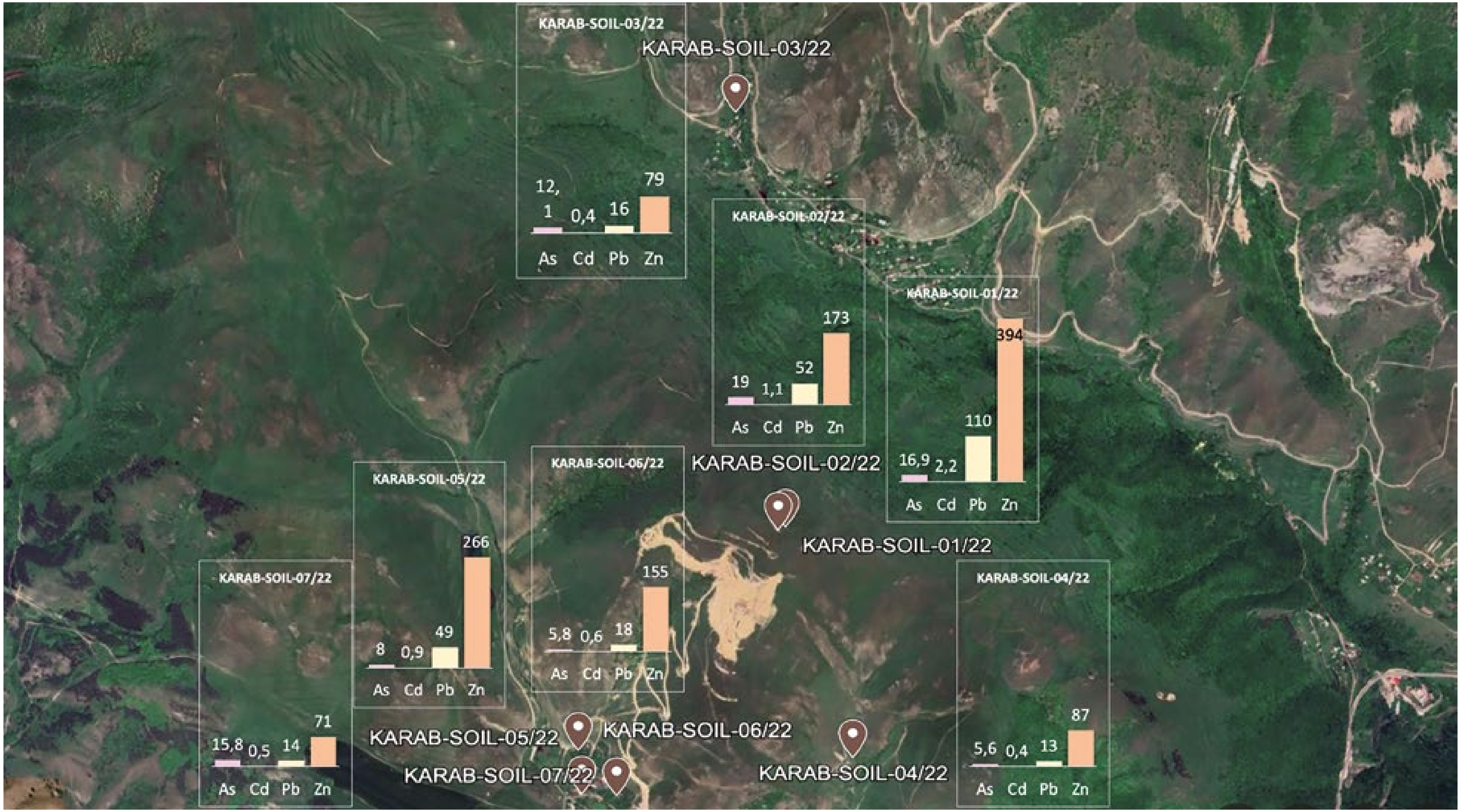

Figure 5.3 Concentrations of As, Cd, Pb, and Zn in soil samples from Karaberd; mg/kg DW.

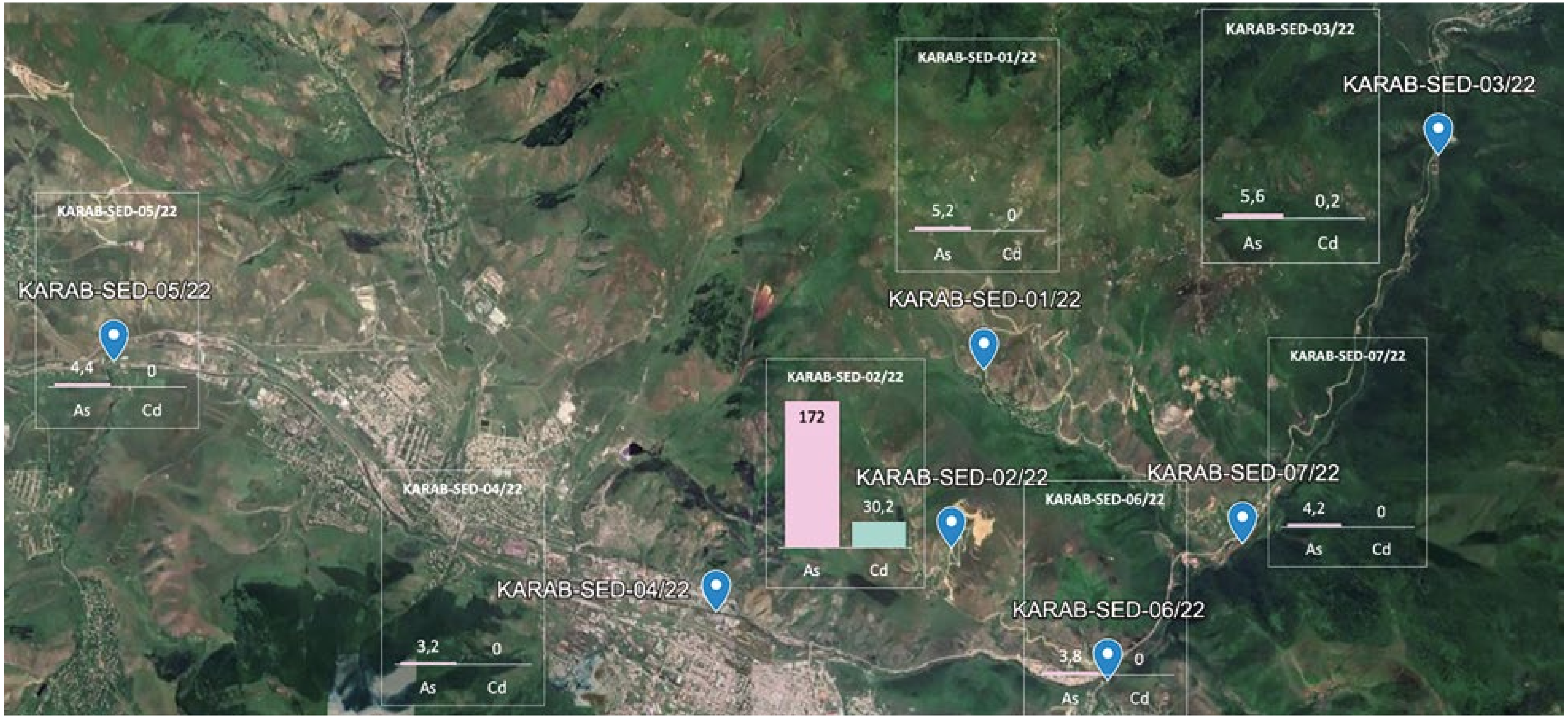

Figure 5.4 Concentrations of As and Cd in sediment samples from Karaberd; mg/kg DW. Direction of river flow from KARAB-SED-05/22 to KARAB-SED-03/22.

5.2.2 Biological samples

In Karaberd, we collected urine samples from nine women aged 46 to 83 years old, and five men of age 49 – 83 years; and four hair samples from women between 59 and 83 years old.

As for **arsenic** contamination, all urine samples measured recent exposure above LOQ, and their mean concentration was comparable among the female and male samples (**12 and 12.51 µg/g creatinine** resp.) however, the 95th percentile in the male was twice as high as in women (35.6 vs 16 µg/g creatinine). In three out of four hair samples (all sampled were women), arsenic measured between **0.03 and 0.07 mg/kg**. Urine but not hair arsenic concentrations indicate higher than normal but moderate exposures to arsenic in the senior population tested in the area.

Our sampling in the Karaberd cohort revealed urine lead above LOQ in all tested samples, higher levels of lead in urine was found in the female cohort compared to the group of four men tested (mean of **2 and 1.15 µg/g creatinine**; 95th percentile 5.4 vs 1.8 µg/g creatinine). The mean hair lead concentration among the four tested women was **0.28 mg/kg** (95th percentile 0.56 mg/kg) which ranges below the level of concern among lead-unexposed communities (Michalak et al., 2014; Strumylaite et al., 2004).

The primary route of exposure to **cadmium** is via ingestion of contaminated food and water and inhalation of polluted air or cigarette smoke. In Karaberd, all urine and hair female samples and 80% of male urine samples tested for cadmium above LOQ. With the geometrical mean of **0.65 µg/g creatinine** and 95th percentile of 2.5 µg/g creatinine, the male cadmium urine levels ranked higher than all the other cohort tested in this or previous reports from Armenia (Suta, 2019). The mean urine level in the general US population is 0.193 µg/g creatinine (ATSDR, 2012a), and the mean cadmium urine levels was most recently measured at 0.146 µg/g creatinine, 95th percentile 0.534 µg/g creatinine in the European countries (Govarts, 2023). The female cohort in Karaberd tested at the mean of **0.45 µg/g creatinine** (95th percentile 0.66 µg/g creatinine) in urine. In the female hair, the mean for cadmium was **0.189 mg/kg** and 95th percentile of 0.038 mg/kg; levels that roughly resemble the results from the Tumanyan and

Hair sampling. PHOTO: Viktoriya Mayakotskaya

Stepanavan Regions (Grechko, 2021). Although cadmium gets distributed widely in the body and excreted slowly, urinary cadmium levels primarily reflect total body burden. In Karaberd, cadmium urinary concentrations in both genders warrant further investigation into the possible source or sources of pollution and clinical symptoms.

Hair **mercury** in the Karaberd cohort was detected in all four samples, and ranged from 0.02 to 0.147 mg/kg, mean of **0.059 mg/kg** and 95th percentile of 0.142 mg/kg, i.e., at levels that that represent a moderate concern. **Copper** was also detected in all four hair samples, the mean concentration was calculated at **9.41 mg/kg**, the 95th percentile of 13.04 mg/kg, i.e. within the normal range suggested by (Bost et al., 2016) and below the levels detected elsewhere in Armenia (Grechko, 2021). Urinary copper levels in the cohort of women were considerably higher than in the male (mean of **60.4 vs 17.3 µg/g creatinine**); still both levels indicate a considerable concern that warrants further assessment.

Although no nickel above LOQ was detected in any of the four hair samples, urinary n**ickel** was measure in all nine female samples at the mean of **3.66 µg/g creatinine** and all male urine samples at the mean of **3.47 µg/g creatinine**, that is at levels that represent a higher concern compared to the general U.S. population and our previous studies in Armenia.

Molybdenum was detected in a single sample in the Karaberd cohort at **0.05 mg/kg hair**, the trace metal therefore portends low concern in this area. **Chromium** was not tested in the Karaberd hair samples.

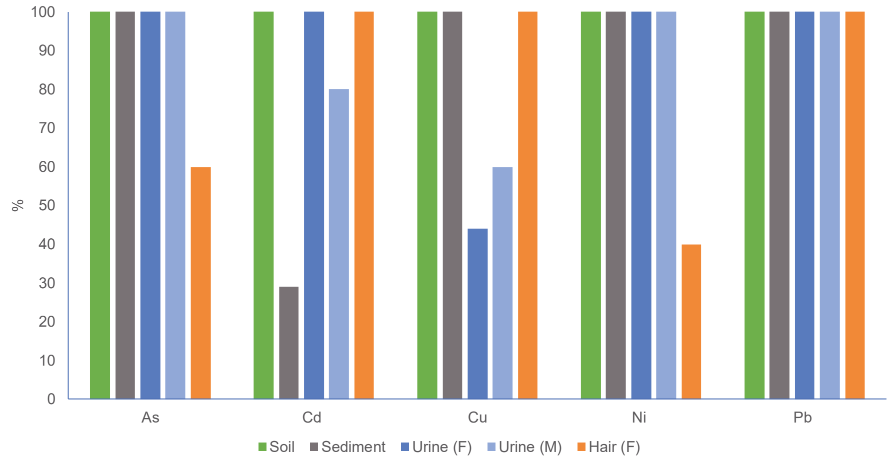

Figure 5.5 Summary of the occurrence (%) of positive findings for selected heavy metals (>LOQ) in samples from Karaberd: soil (n=7), sediment (n=7), female urine (n=9), male urine (n=5), female hair (n=4).

5.3 Meghradzor

5.3.1 Environmental samples

In the area of Meghradzor where potential sources of heavy metal pollution are the Meghradzor gold mine, a gold processing plant and two tailing ponds, we collected seven soil samples, five sediment samples and two samples of mining waste.

The overall mean value of the total **arsenic** for different soil is estimated as 6.83 mg/kg, but the background contents of various soil groups range from <0.1 to 67 mg/kg (Kabata-Penditas, 2011). Specifically, there were high concentrations of arsenic detected in three soil samples. The first one is the soil sample MGHR-SOIL-03/22 that comes from a place where mining likely took place in the past and its concentration of arsenic reaches 20 mg/kg DW. The other two soil samples with high concentrations of arsenic come from private gardens. The levels of arsenic in all soil samples exceed the Armenian soil standard and the US EPA pollution limit for industrial areas. Arsenic concentrations in four sediment samples exceed the Canadian Threshold Effect Level and two of them also exceed the Canadian Probable Effect Level. The first of two sediment samples with the highest arsenic concentration was collected from a water stream flowing from the direction of the gold mine with an arsenic concentration of 29.6 mg/kg DW, and the second was collected from a water stream flowing to the Marmarik Reservoir upstream the gold mine with a concentration of 116 mg/kg DW. The reservoir is located on the Marmarik River upstream from Meghradzor. This finding of a high concentration of arsenic could indicate that there is some other source of pollution somewhere in the area above the dam. However, we are not aware of any mining or industrial activities in the catchment of the water stream that flows into the reservoir. An indicator that the gold mine could be a source of arsenic pollution is the fact that samples of mining waste contain high arsenic concentrations of 36.1 mg/kg DW and 39.7 mg/kg DW.

The world average soil **cadmium** concentration is estimated as 0.41 mg/kg and cadmium content in reference soils from different countries ranges from 0.06 to 4.3 mg/kg (Kabata-Penditas, 2011). The concentrations of cadmium in the collected soil samples are in the range of concentrations found in other countries. The concentrations of cadmium in all soil samples comply with the US EPA pollution limit for residential areas. The situation is different for cadmium concentrations in sediments. The situation is different for sediments where the cadmium concentrations are higher. The sediment sample MGHR-SED-02/22 that was collected in the Marmarik River reaches 20.3 mg/kg DW of cadmium and exceeds the Canadian Probable Effect Level for cadmium.

The world average content of **chromium** in soils has been established as 60 mg/kg (Kabata-Penditas, 2011). Chromium concentrations in the soil samples are lower than the worldwide average except in one soil sample MGHR-SOIL-07/22 that was collected in a private garden in the village of Meghradzor. Any of the soil sample does not comply with the Armenian soil standard for chromium. The sediment sample MGHR-SED-05/22 that was collected from a water stream flowing to the Marmarik Reservoir exceeds the Canadian Threshold Effect Level for chromium.

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 (Kabata-Penditas, 2011). Copper concentrations in the soil samples were in the range of different soil groups all over the world except in one soil sample. All seven soil samples exceed the Armenian soil standard, but any of the soil samples does not exceed the US EPA pollution limit for residence areas. Copper concentrations in two of the five sediment samples exceed the Canadian Threshold Effect Level. Especially high copper concentration is found in the sediment sample MGHR- SED- 01/22 collected in a water stream flowing from the direction of the gold mine, in which the copper concentration is measured at 191 mg/kg DW. High concentrations of copper were also found in the mining waste samples. These two findings indicate that the gold mine may be a source of copper pollution.

The abundance of **iron** in soils averages about 35 000 mg/kg and is likely to be increased in heavy loamy soils and some organic soils (Kabata-Penditas, 2011). Iron concentrations in two soil samples exceed the world average values, but all soil samples show higher concentrations than the US EPA pollution level for residential areas. One sediment sample MGHR-SED-01/22 collected from a water stream flowing from the direction of the gold mine contains a high iron concentration of 45,300 mg/kg DW.

The sediment samples contain low concentrations of **mercury**, except for one sediment sample with a concentration of 0.729 mg/kg DW. This sediment sample MGHR-SED-01/22 was collected from a water stream flowing from the direction of the gold mine.

The world 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 (Kabata-Penditas, 2011). The concentrations of molybdenum in the soil samples are several times higher than the world average content in soils, however, the concentrations in the samples comply with the US EPA pollution limit for residential areas.

Soils throughout the world contain **nickel** within the range 13–37 mg/kg (Kabata-Penditas, 2011). The concentrations of nickel in soil samples vary within the range of worldwide concentrations except one sample with a concentration of 49 mg/kg DW. The concentrations of nickel in all seven soil samples exceed the Armenian soil standard, but any of them exceeds the US EPA pollution limit for residential areas.

The overall mean value of total **lead** for different soils is estimated as 27 mg/kg DW (Kabata-Penditas, 2011). Three soil samples show lead concentrations higher than the world average and one soil sample exceeds the Armenian soil standard. Concentrations of lead in all soil samples comply with the US EPA pollution limit for residential areas. The highest lead concentration of 42 mg/kg DW has been found in the soil sample MGHR-SOIL-04/22 collected in a private garden. The concentration of lead in the sediment sample MGHR-SED-01/22, collected from a water stream flowing from the direction of the gold mine, reaches 96 mg/kg DW and exceeds the Canadian Probable Effect Level.

The general values for the average total **zinc** content in soils of various types globally range between 60 and 89 mg/kg DW (Kabata-Penditas, 2011). Concentrations of zinc in six soil samples (over 25 %) exceed the range of averages found worldwide, but zinc concentrations in any of the soil samples do not exceed the US EPA pollution limit for residential areas. High zinc concentration was found in the sediment sample MGHR-SED-01/22 collected from a water stream flowing from the direction of the gold mine. This sediment sample with concentration of 342 mg/kg DW does not comply with the Canadian Probable Effect Level.

Table 5.5 Number of soil samples from the Meghradzor area that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the total number of soil samples are expressed in brackets.

	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
Armenian soil standard	7 (100%)	-	7 (100%)	7 (100%)	-	-	-	7 (100%)	1 (14%)	-	-
Czech pollution indication	0 (0%)	0 (0%)	-	-	-	NA	-	-	0 (0%)	-	-
Czech background indication	1 (14%)	3 (43%)	0 (0%)	2 (29%)	-	NA	-	0 (0%)	0 (0%)	NA	4 (57%)
Levels of pollution limits – industrial areas (US EPA)	7 (100%)	0 (0%)	-	0 (0%)	0 (0%)	NA	0 (0%)	0 (0%)	0 (0%)	NA	0 (0%)
Levels of pollution limits – other areas (US EPA)	7 (100%)	0 (0%)	-	0 (0%)	7 (100%)	NA	0 (0%)	0 (0%)	0 (0%)	NA	0 (0%)

Table 5.6 Number of sediment samples from the Meghradzor area that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the total number of sediment samples are expressed in brackets.

	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
Czech Limit Values	1 (20%)	3 (60%)	0 (0%)	1 (20%)	NA	0 (0%)	NA	0 (0%)	0 (0%)	NA	1 (20%)
Canadian Threshold Effect Level	4 (80%)	3 (60%)	1 (20%)	2 (40%)	NA	1 (20%)	NA	-	1 (20%)	NA	2 (40%)
Canadian Probable Effect Level	2 (40%)	1 (20%)	0 (0%)	0 (0%)	NA	1 (20%)	NA	-	1 (20%)	NA	2 (40%)

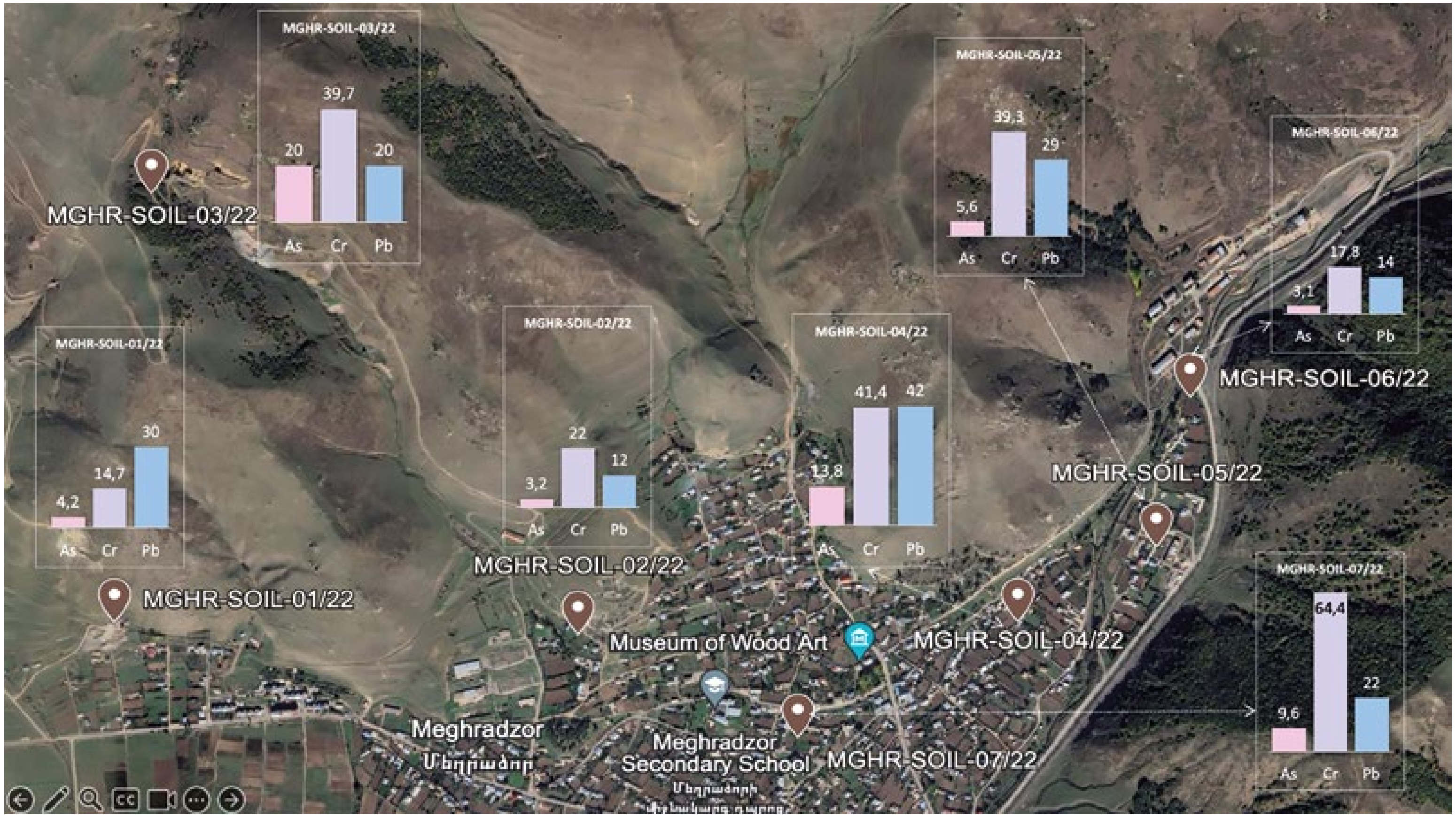

Figure 5.6 Concentrations of As, Cr and Pb in soil samples from Meghradzor; mg/kg DW.

Figure 5.7 Concentrations of As in sediment samples from Meghradzor; mg/kg DW. Direction of river flow from MGHR-SED-05/22 to MGHR-SED-03/22.

5.3.2 Biological samples

In Meghradzor, we collected 14 urine and 5 hair samples from local women, urine samples from five men: three boys aged 5, 9, and 10 years and two men 58 and 67 years of age, and a single hair sample from a 14-year-old young man.

Arsenic in urine was determined in all samples, with the mean and median higher in the female samples but 95th percentile lower than the male cohort. Apart from a 75 µg/g creatinine in a urine sample of a 60-year-old woman, particularly concerning is the highest measured urine arsenic in the sample of a 5-year-old boy (37 µg/g creatinine). Children chronically exposed to high levels of arsenic exhibit a range of symptoms including increased risk of infections, impaired respiratory and hepatic functions, and neurodevelopment, lessened cognitive functions (e.g., impaired attention, memory, verbal comprehension and reasoning) and skin changes, along with an increased chance of skin, bladder, and lung cancer (ATSDR, 2007), and the trend for cognitive functions in the young age seems evident even at moderate exposures (Vaidya, 2023)a contaminant of groundwater and irrigated crops, is a global public health hazard. Exposure to low levels of arsenic through food extends well beyond the areas with high arsenic content in water.\n \n \n Objective\n To identify cognitive impairments following commonly prevalent low-level arsenic exposure and characterize their underlying brain mechanisms.\n \n \n Design, Setting, and Participants\n This multicenter population-based cohort study analyzed cross-sectional data of the Indian Consortium on Vulnerability to Externalizing Disorders and Addictions (cVEDA.

Our sampling in the Meghradzor cohort revealed urine **lead** above LOQ in nearly all tested samples (over 90%), lead in urine was found slightly higher in the female cohort compared to the group of five men tested (mean of **2 and 1.89 µg/g creatinine**; 95th percentile 6 vs 3.8 µg/g creatinine). The mean hair lead concentration among the five tested women and in the one tested male were **0.5 mg/kg** and 0.14 mg/kg respectively (95th percentile was 0.7 mg/kg in the female cohort), values that range below the level of concern in the general populations (Michalak et al., 2014; Strumylaite et al., 2004).

Tailings pond in Meghradzor. PHOTO: Martin Marek

Nine out of fourteen female urine (over 60%) and all five hair samples tested above LOQ for **cadmium**, along with one of five male urine and the single male hair sample we collected in the area. With the mean of **0.52 µg/g creatinine** (and 95th percentile of 0.94 µg/g creatinine) in women and **0.6 µg/g creatinine** in the male sample; and the mean of **0.011 mg/kg** (95th percentile 0.05 mg/kg) for cadmium in hair. Our cohort in Meghradzor tested higher than previous reports from Armenia (Suta, 2019), and additionally above the mean urine level in the general US population that was measured at 0.189 µg/g creatinine (ATSDR, 2012a). The mean cadmium urine levels were most recently measured at 0.146 µg/g of creatinine (95th percentile 0.534 µg/g creatinine) in adults in the European countries (Govarts, 2023). Meghradzor residents should be counselled on exposure to cadmium, its associated health risks and on the possible sources of pollution. Cadmium is a human carcinogen (IARC), and the health implication of exposure to the toxic compound can be effectively prevented.

Hair **mercury** in the Meghradzor cohort ranged from 0.04 to 0.293 mg/kg with the mean of **0.079 mg/kg** and 95th percentile 0.247 mg/kg. The measured hair mercury levels of four women and one male represent a moderate to low concern. While the mercury test result of one of the woman samples (0.293 mg/kg) warrants possible preventive measures even this highest measured value is within the recommended range for hair mercury (see above).

Copper was detected in one female and one male urine sample at moderate levels, and in all hair samples at levels that raise concern (see the previous two areas). **Nickel** was detected in nearly all female and 60 % male urine samples at levels exceeding the U.S. general population mean, particularly in the female (**3.26 µg/g creatinine**). Two samples tested positive for hair nickel at a level that is of low concern. **Molybdenum** tested above LOQ in two out of five female hair samples and the one male hair sample, at levels of very low concern. Hair samples were not tested for **chromium** in this area.

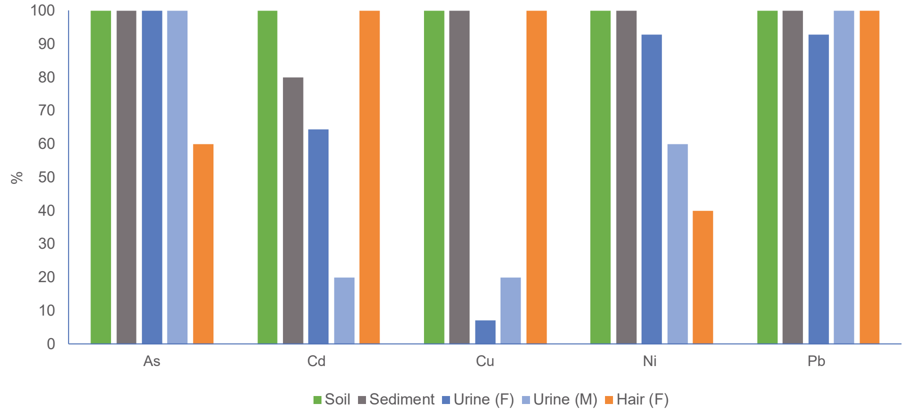

Figure 5.8 Summary of the occurrence (%) of positive findings for selected heavy metals (>LOQ) in samples from Meghradzor: soil (n=7), sediment (n=5), female urine (n=14), male urine(n=5), female hair (n=5).

Closed mine tunnel in Meghradzor. PHOTO: Monika Yeritsyan

5.4 Melikgyugh

5.4.1 Environmental samples

In the area of Melikgyugh where potential sources of heavy metal pollution are the Tukhmanuk gold mine, a gold processing plant and three tailing ponds, we collected seven soil samples and seven sediment samples.

The overall mean value of the total **arsenic** for different soils is estimated as 6.83 mg/kg, but the background contents of various soil groups range from <0.1 to 67 mg/kg (Kabata-Penditas, 2011). Arsenic concentrations in the soil samples vary within the range of values reported worldwide, except for one soil sample with a very high arsenic concentration of 119 mg/kg DW. This soil sample MLGH-SOIL-04/23 was collected close to the gold mine and tailings ponds in the direction of the water outflow from the gold mine. Another soil sample MLGH- SOIL-05/23 also collected close to the gold mine shows a high arsenic concentration of 19 mg/kg DW. In contrast, five soil samples collected from private gardens intended for growing crops show several times lower arsenic concentrations. However, the levels of arsenic in all soil samples exceed the Armenian soil standard and the US EPA pollution limit for industrial areas. Arsenic concentrations in six of the seven sediment samples exceed the Canadian Probable Effect Level. The six sediment samples with high arsenic concentrations were found in watercourses that drain the former gold mine and its related mining infrastructure. The sediment sample with a several times lower arsenic concentration, on the other hand, was collected from a watercourse that drains an area where no mining is taking place. These findings could indicate that the gold mine may contaminate watercourse sediments with arsenic.

The world average soil **cadmium** concentration is estimated as 0.41 mg/kg and cadmium content in reference soils from different countries ranges from 0.06 to 4.3 mg/kg (Kabata-Penditas, 2011). The concentration of cadmium in three soil samples out of seven is higher than the range reported for different countries. The soil sample MLGH-SOIL-04/23 exceeds the US EPA pollution limit for residential areas. This is again the soil sample that was collected close to the gold mine and its related mining infrastructure, and the cadmium concentration in it reaches 2.7 mg/kg DW. In contrast, cadmium concentrations in sediment samples were relatively low and comply with the Canadian Probable Effect Level.

The world average content of **chromium** in soils has been established as 60 mg/kg (Kabata-Penditas, 2011). Chromium concentrations in the soil samples are higher or equal than the worldwide average. Any of the soil samples does not comply with the Armenian soil standard for chromium. All the sediment samples exceed the Canadian Threshold Effect Level for chromium and one sediment sample also exceeds the Canadian Probable Effect Level.

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 (Kabata-Penditas, 2011). The copper concentrations in the soil samples were in the range of different soil groups worldwide. All seven soil samples exceed the Armenian soil standard, but any of the soil samples does not exceed the US EPA pollution limit for residential areas. Copper concentrations in two of the seven sediment (almost 30%) samples slightly exceed the Canadian Threshold Effect Level.

In the Melikgyugh area, we have not detected mercury pollution of soils and sediments. The average content of **mercury** in soils of different groups in Europe is estimated as 0.0383 mg/kg (ESDAC, 2021). The concentrations of mercury in all sediment samples are both lower than the average European concentration and comply with the US EPA pollution limit for residential areas. The sediment samples contain low concentrations of mercury, and all the samples comply with the Canadian Threshold Effect Level for mercury.

Soils throughout the world contain **nickel** within the range 13–37 mg/kg (Kabata-Penditas, 2011). Nickel concentrations in the soil samples are equal or exceed concentrations in the range reported worldwide. The concentrations of nickel in all seven soil samples exceed the Armenian soil standard, but any of them exceeds the US EPA pollution limit for residential areas.

The overall mean value of total **lead** for different soils is estimated as 27 mg/kg DW (Kabata-Penditas, 2011). The concentrations of lead in the soil samples were below the overall mean value, except for the sample MLGH-SOIL-04/23 that was collected close to the gold mine and tailing ponds in the direction of the water outflow from the gold mine. Lead concentration of this sample reaches 212 mg/kg DW and exceeds the Armenian soil standard. Concentrations of lead in all soil samples comply with the US EPA pollution limit for residential areas. The concentrations of lead in the sediment samples comply with the Canadian Probable Effect Level.

The general values for the average total **zinc** content in soils of different types globally range between 60 and 89 mg/kg DW (Kabata-Penditas, 2011). Concentrations of zinc in six soil samples exceed the range of averages found worldwide, but concentration of zinc in any of the soil samples does not exceed the US EPA pollution limit for residential areas. The concentrations of zinc in the sediment samples comply with the Canadian Probable Effect Level.

Table 5.8 Number of soil samples from the Melikgyugh area that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the total number of soil samples are expressed in brackets.

	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
Armenian soil standard	7 (100%)	-	7 (100%)	7 (100%)	-	-	-	7 (100%)	1 (14%)	-	-
Czech pollution indication	1 (14%)	0 (0%)	-	-	-	0 (0%)	-	-	0 (0%)	-	-
Czech background indication	1 (14%)	3 (43%)	3 (43%)	0 (0%)	-	0 (0%)	-	3 (43%)	1 (14%)	NA	5 (71%)
Levels of pollution limits – industrial areas (US EPA)	7 (100%)	0 (0%)	-	0 (0%)	NA	0 (0%)	NA	0 (0%)	0 (0%)	NA	0 (0%)
Levels of pollution limits – other areas (US EPA)	7 (100%)	1 (14%)	-	0 (0%)	NA	0 (0%)	NA	0 (0%)	0 (0%)	NA	0 (0%)

Table 5.9 Number of sediment samples from the Melikgyugh area that exceed any of the mentioned legal standards for each heavy metal. The proportions of these samples from the total number of sediment samples are expressed in brackets.

	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
Czech Limit Values	3 (43%)	0 (0%)	0 (0%)	0 (0%)	NA	0 (0%)	NA	0 (0%)	0 (0%)	NA	0 (0%)
Canadian Threshold Effect Level	6 (86%)	0 (0%)	7 (100%)	2 (29%)	NA	0 (0%)	NA	-	0 (0%)	NA	0 (0%)
Canadian Probable Effect Level	6 (86%)	0 (0%)	1 (14%)	0 (0%)	NA	0 (0%)	NA	-	0 (0%)	NA	0 (0%)

Figure 5.9 Concentrations of Cr and Zn in soil samples from Melikgyugh; mg/kg DW.

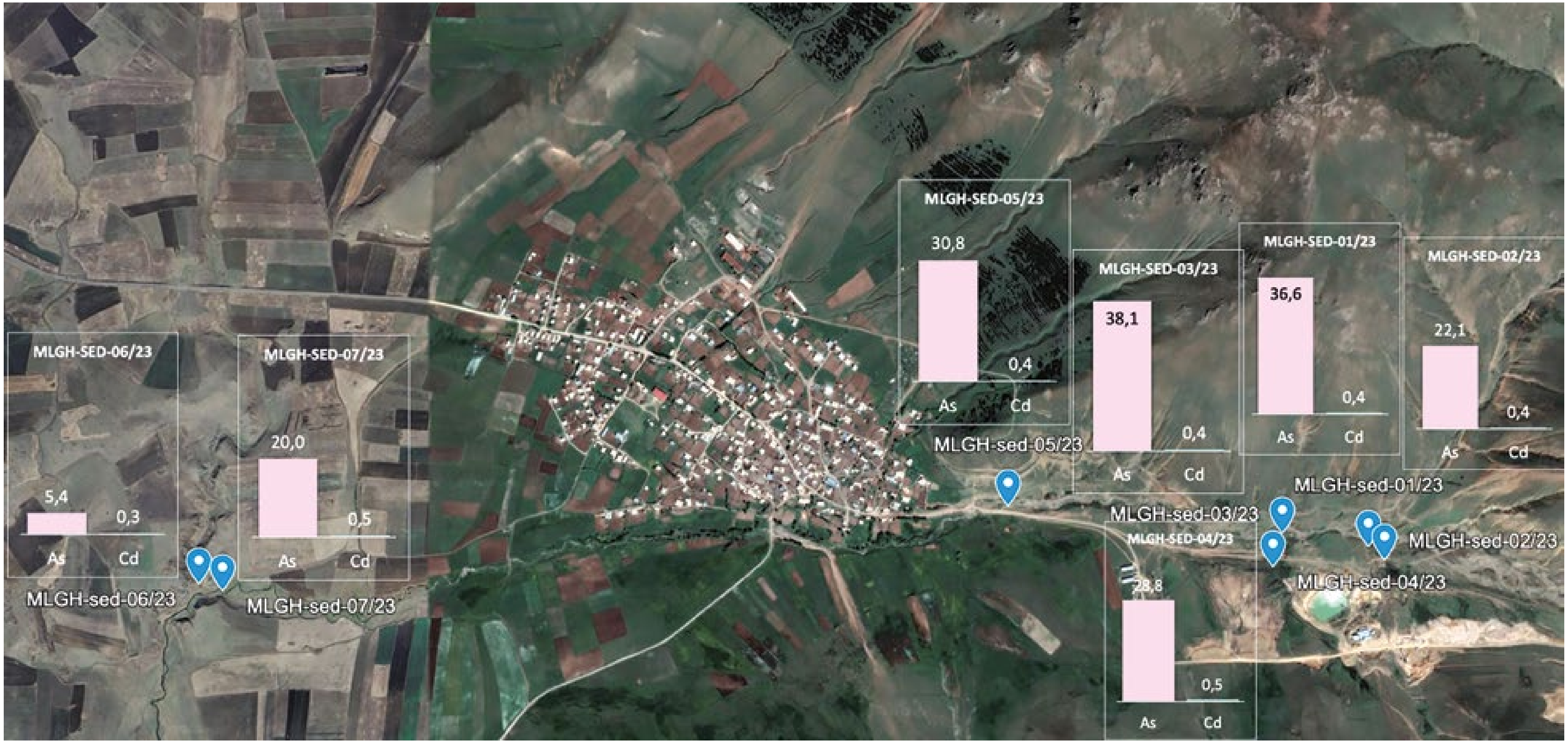

Figure 5.10 Concentrations of As and Cd in sediment samples from Melikgyugh; mg/kg DW. Direction of river flow from MLGH-sed-02/23 to MLGH-sed-06/23.

5.4.2 Biological samples

Four and five women in Melikgyugh were examined for heavy metals in their urine and hair samples, respectively. The four urine samples were contributed from young women aged between 20 and 33 years, three of them measured **arsenic** between 10 and 14 µg/g creatinine while a 26-year-old measured as high as 120 µg/g creatinine. The singular sample also measured cadmium, lead, and nickel in the hair at concentrations beyond 95th percentile for the cohort.

Lead was not detected in either of the four urine samples in the Melikgyugh cohort but in all hair samples we collected. Concentrations of lead in hair ranged from 0.15 to 0.5 mg/kg i.e., on the lower spectrum of the cohorts included in this report and below the level of concern and general lead-unexposed populations (Michalak et al., 2014; Strumylaite et al., 2004).

Cadmium was detected in three out of five hair samples tested at the mean of 0.05 mg/kg and the 95th percentile of 0.166 mg/kg. The measured value is lower than our previous report from Armenia (Grechko, 2021). Cadmium was not detected in any of the urine samples.

All five hair samples in Melikgyugh tested for **mercury** above LOQ. The cohort ranged from 0.045 to 0.156 mg/kg, mean of **0.094 mg/kg** and 95th percentile of 0.156 mg/kg. The levels represent a moderate to low concern.

Copper was detected in all hair samples, the mean concentration was calculated at **9.13 mg/kg** and 95th percentile 12.68 mg/kg, i.e. at levels within the normal range suggested by (Bost et al., 2016) and below the levels detected elsewhere in Armenia (Grechko, 2021). Urine copper was not detected.

Nickel was found in every hair and urinary sample in the Melikgyugh cohort. The mean of urine nickel (**2.63 µg/g creatinine**) exceeded the U.S. general population levels, yet hair nickel seems to remain at a level for low concern. Two samples tested positive for hair nickel at a level that is of low concern. **Chromium** nor **molybdenum** were not detected in any of the hair samples.

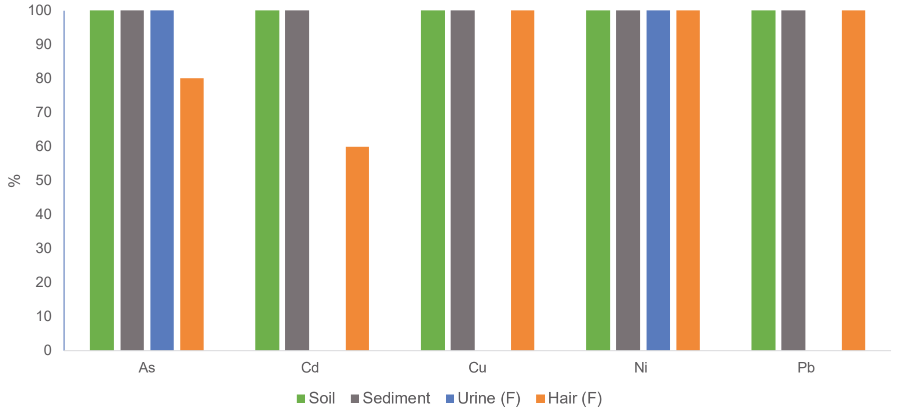

Figure 5.11 Summary of the occurrence (%) of positive findings for selected heavy metals (>LOQ) in samples from Melikgyugh: soil (n=7), sediment (n=7), female urine (n=4), female hair (n=5).

Tailings pond in Melikgyugh. PHOTO: Aleksandr Grebeshkov

View of Melikgyugh village: PHOTO: Aleksandr Grebeshkov

6 CONCLUSION AND RECOMMENDATIONS

Our study has revealed concerning levels of heavy metals pollution in the environment, posing significant health risks to the residents of the studied communities in four Armenian regions. The key findings from our investigation underscore the urgent need for regulatory intervention and environmental management strategies to mitigate the adverse effects of mining and ore processing activities.

The levels of heavy metals such as arsenic, cadmium, chromium, nickel, lead, and zinc measured in the environmental samples we collected in Ararat, Surenavan, Karaberd, Meghradzor, and Melikgyugh highlight the widespread contamination of soil and sediments. Health implications associated with contaminated environment are profound. Long term exposures of the residents to heavy metals may not manifest immediately but the bioaccumulating potential of the compounds pose a real risk to both individual and public health. Specifically, mercury measured high particularly in Melikgyugh can lead to neurological impairment, cognitive and behavioral deficits, especially in children, affecting memory, attention, and coordination. Further, cardiovascular effects such as high blood pressure and heart and vessel disease, and cardiovascular mortality are associated with chronic exposure to lead, mercury, and arsenic. Along with arsenic, cadmium that we detected in all tested areas is known to impair kidney function and lead to renal insufficiency and kidney damage. Cadmium accumulates in the bones, leading to bone demineralization which is especially detrimental in post-menopausal women. Arsenic exposure not only causes skin changes including hyperpigmentation and keratosis, consequences of chronic arsenic extent to increased risk of various cancers such as lung, bladder, skin and liver. Prolonged copper exposure indicated in two areas can lead to liver damage caused by the metal buildup in the liver. Chronic exposure nickel detected in Melikgyugh, Meghradzor and Karaberd may cause gastrointestinal issues and immune system impairments.

It is important to note that health-related consequences of heavy metal exposure can vary based on individual susceptibility, concentration and duration of exposure, and overall health. However, elevated levels of heavy metals in urine and hair samples typically indicate an increased level of environmental exposure of the tested individual or communities. Values of heavy metals that surpass reference values warrant immediate attention of healthcare professional, counseling, and secondary prevention of further damage in the exposed individual or community, followed by an investigation of the source of exposure and primary preventive measures. Vulnerable population such as children, pregnant women and elderly are of particular attention of public health and healthcare professional due to their specific needs and conditions. Long-term monitoring of exposure levels and implementing preventive measures are crucial to minimizing the health risks associated with chronic heavy metal exposure.

Recommendations for Individual Action:

Reducing individual impact of industrial pollution with heavy metals involves adopting measures to minimize contact with contaminated air, water, and soil. Below we recommend a few strategies to help reduce personal burden of heavy metals and protect health of the individual their family:

Stay informed

Monitor environmental announcements and assessments related to potential heavy metal emissions and contaminations. This information will be available through local environmental agencies or community organizations.

Limit Consumption of Contaminated Food and Water

Monitor Fish Consumption:

» Be aware of fish advisories in your area, especially if you consume fish from local water bodies. Some fish may contain elevated levels of mercury or other heavy metals.

Filter Drinking Water:

» Use reputable or certified water purification systems to mitigate the risk of consuming contaminated water or consider obtaining information about the quality of your tap water from local authorities.

Personal Hygiene

Practice rigorous personal hygiene such as hand washing, especially when working in or around mining areas.

Utilize appropriate personal protective equipment, including gloves and masks, when handling soil or water with potential heavy metal contamination.

Practice Safe Gardening

Test Soil Quality: If you have a garden, test the soil for heavy metal contamination. Follow guidelines to reduce exposure, such as adding clean soil or using raised beds.

Wash Produce Thoroughly: Wash fruits and vegetables thoroughly to remove any contaminants from the surface.

Diversify Diets:

Consume a varied diet to minimize the risk of accumulating elevated levels of specific heavy metals from singular food sources.

Incorporate foods rich in vitamins and minerals to potentially mitigate the effects of heavy metal exposure.

Limit Direct Contact:

Refrain from direct contact with soil, dust, or water in mining areas, particularly where visible contamination is evident.

Educate children on potential risks and discourage engagement in recreational activities in known contaminated areas.

Health Check-ups:

Participants in this study with high heavy metal content require secondary analysis and more detailed investigation.

Populations affected by mining should seek preventive health screenings and check-ups.

Community Advocacy:

Participate actively in community groups or environmental organizations advocating for responsible mining practices.

Attend community meetings to articulate concerns and elevate awareness regarding environmental issues.

Advocate for sustainable development initiatives and diversified job prospects within the local community.

Recommendation for local public health authorities:

Public health authorities play a vital role in minimizing exposure to heavy metals from industrial sites to protect the health of communities. Their efforts typically focus on monitoring, assessment, education, and intervention. Here are several ways in which public health authorities work to reduce exposure to heavy metals:

Health Risk Assessment:

Conduct Exposure Assessments: Public health authorities assess the levels of heavy metals in the air, water, soil, and food to determine potential exposure risks for the local population.

Identify Vulnerable Populations: Identify vulnerable populations, such as children, pregnant women, and the elderly, who may be at higher risk of adverse health effects.

Health Education and Outreach:

Community Awareness Programs: Develop and implement community awareness programs to educate residents about the sources and risks of heavy metal exposure.

Distribution of Information: Distribute educational materials explaining how individuals can minimize exposure, such as reducing fish consumption from contaminated water bodies.

Monitoring and Surveillance:

Health Surveillance: Establish health surveillance systems to monitor the health status of communities exposed to heavy metals, enabling the early detection of potential health impacts.

Biological Monitoring: Conduct biomonitoring programs to measure heavy metal levels in the bodies of individuals, providing valuable data on exposure.

Regulatory Advocacy:

Recommend Policy Changes: Advocate for and recommend changes in regulations and policies to reduce heavy metal emissions from industrial sources.

Collaborate with Regulatory Agencies: Work closely with environmental and occupational health regulatory agencies to ensure compliance with established standards.

Emergency Response Planning:

Develop Emergency Response Plans: Collaborate with local emergency management agencies to develop plans for responding to accidental releases of heavy metals, ensuring rapid and effective response and communication with the community.

Clinical Care and Intervention:

Medical Guidance: Provide medical guidance to healthcare professionals on the diagnosis and management of heavy metal exposure-related health issues.

Intervention Programs: Develop intervention programs for individuals with elevated heavy metal levels, including medical treatment and counseling.

Occupational Health Monitoring:

Worker Health Protection: Collaborate with occupational health authorities to monitor and protect the health of workers in industries that handle heavy metals.

Occupational Exposure Limits: Advocate for and enforce occupational exposure limits to protect workers from excessive exposure.

Collaboration with Environmental Agencies:

Interagency Collaboration: Work collaboratively with environmental protection agencies to integrate public health considerations into environmental policies and regulations.

Data Sharing: Share data on heavy metal exposure and health outcomes with environmental agencies for a comprehensive understanding of the issue.

Research and Surveillance Programs:
Support Research Initiatives: Support research studies investigating the health effects of heavy metal exposure, contributing to the scientific understanding of the issue.

Long-Term Surveillance: Establish long-term surveillance programs to monitor health trends and assess the effectiveness of interventions.

Public Health Interventions:
Community Interventions: Implement targeted interventions, such as providing access to clean water sources, conducting soil remediation projects, and promoting community-based initiatives to reduce exposure.

Public health authorities work collaboratively with various stakeholders, including local governments, healthcare professionals, community organizations, and industries, to create comprehensive strategies aimed at reducing exposure to heavy metals from industrial sites and safeguarding public health.

Hospital in the village of Ararat. PHOTO: Viktoriya Mayakotskaya

Recommendation for local governance

Local governments are seminal in protecting the health of communities and reducing exposure to heavy metals from industrial sites through the implementation of regulations, monitoring, and enforcement of environmental standards. Here, we suggest several ways in which local governments and public health authorities can work to minimize heavy metal exposure in their communities:

Environmental Regulations:
Emission Standards: Enforce strict emission standards for industrial facilities to limit the release of heavy metals into the air.

Effluent Standards: Set and enforce effluent standards to control the discharge of heavy metals into water bodies from industrial processes.

Zoning and Land Use Planning:
Industrial Zoning: Implement zoning regulations to control the location and density of industrial activities, preventing heavy metal emissions in residential or sensitive areas.

Buffer Zones: Establish buffer zones between industrial sites and residential areas to minimize potential exposure to pollutants.

Environmental Impact Assessments (EIAs):
Require EIAs: Mandate comprehensive EIAs for new industrial projects to assess potential environmental impacts, including heavy metal emissions.

Mitigation Measures: Ensure that mitigation measures are implemented based on the findings of EIAs to minimize the environmental impact of industrial activities.

Monitoring and Surveillance:
Air and Water Quality Monitoring: Implement regular monitoring programs to measure heavy metal concentrations in air and water. Use the data to identify sources of pollution and enforce compliance.

Soil Monitoring: Conduct soil quality assessments to identify contaminated areas and take remedial actions.

Waste Management:
Hazardous Waste Regulations: Enforce regulations on the proper handling, storage, and disposal of hazardous waste, including heavy metal-containing waste generated by industries.

Promote Recycling: Encourage industries to adopt recycling practices to reduce the generation of hazardous waste.

Public Awareness and Education:
Community Outreach: Engage with local communities to raise awareness about the risks associated with heavy metal exposure and inform residents about protective measures.

Public Information: Provide accessible information about environmental regulations, monitoring results, and government actions to ensure transparency and public understanding.

Incentives for Cleaner Technologies:
Financial Incentives: Offer financial incentives or tax breaks for industries that adopt cleaner technologies, reducing heavy metal emissions.

Research and Development Support: Invest in research and development initiatives to promote the development and adoption of cleaner and more environmentally friendly industrial processes.

Enforcement and Penalties:
Strict Enforcement: Enforce environmental regulations through inspections and penalties for non-compliance, ensuring that industries adhere to established standards.

Legal Action: Take legal action against industries that consistently violate environmental regulations, including heavy metal emission limits.

Collaboration with Industries:
Industry Partnerships: Collaborate with industries to find solutions for reducing heavy metal emissions and encourage the adoption of best practices.

Technology Transfer: Facilitate the transfer of cleaner technologies to industries, promoting sustainable and environmentally friendly practices.

Emergency Response Planning:
Emergency Preparedness: Develop and implement emergency response plans to address accidental releases of heavy metals, ensuring prompt and effective containment and cleanup.

By implementing these measures, local governments can effectively reduce exposure to heavy metals from industrial sites, protecting the health and well-being of their communities and the environment. Collaboration with regulatory agencies, community stakeholders, and industries is essential for the success of these initiatives.

Sediment sampling. PHOTO: Aleksandr Grebeshkov

View of the tailings pond near the village of Ararat.
PHOTO: Viktoriya Mayakotskaya

7 ANNEX

Table I: List of soil samples collected in areas of interest.

Area	**ID**	**Date of sampling**	**Hot spot**	**Distance from hot spot [m]**	**Sampling site description**
Meghradzor	MGHR-SOIL-01/22	17.09.2022	Meghradzor gold mine	1,000	a private garden close to a significant pile of mining waste and brook flowing from the mine
Meghradzor	MGHR-SOIL-02/22	17.09.2022	Meghradzor gold mine	1,000	a private garden, sampling spot was next to the fence
Meghradzor	MGHR-SOIL-03/22	17.09.2022	Meghradzor gold mine	200	a mine tunnel
Meghradzor	MGHR-SOIL-04/22	17.09.2022	Meghradzor gold mine	3,000	a private garden
Meghradzor	MGHR-SOIL-05/22	17.09.2022	Meghradzor gold mine	2,700	a private garden with dense vegetation
Meghradzor	MGHR-SOIL-06/22	17.12.2022	Meghradzor gold mine	2,500	a private garden, soil irrigated with water from the Marmarik water stream
Meghradzor	MGHR-SOIL-07/22	17.09.2022	Meghradzor gold mine	2,000	a private garden, untreated land with dense vegetation
Karaberd	KARAB-SOIL-01/22	18.09.2022	Karaberd gold-molyb. mine	100	untreated soil 10 m close to a waste pile
Karaberd	KARAB-SOIL-02/22	18.09.2022	Karaberd gold-molyb. mine	100	a meadow above the mine
Karaberd	KARAB-SOIL-03/22	18.09.2022	Karaberd gold-molyb. mine	500	a private garden with apple trees
Karaberd	KARAB-SOIL-04/22	18.09.2022	Karaberd gold-molyb. mine	700	a private backyard with bee houses
Karaberd	KARAB-SOIL-05/22	18.09.2022	Karaberd gold-molyb. mine	800	a private garden
Karaberd	KARAB-SOIL-06/22	18.09.2022	Karaberd gold-molybd. mine	500	an untreated private garden, close to the mine
Karaberd	KARAB-SOIL-07/22	18.09.2022	Karaberd gold-molybd. mine	600	a private garden, untended, dense vegetation
Melikgyugh	MLGH-SOIL-01/23	17.06.2023	Melikgyugh gold mine + tailing pond	1,900	a field close to a house
Melikgyugh	MLGH-SOIL-02/23	17.06.2023	Melikgyugh gold mine + tailing pond	1,600	agricultural soil, potato field
Melikgyugh	MLGH-SOIL-03/23	17.06.2023	Melikgyugh gold mine + tailing pond	1,800	agricultural soil, potato field
Melikgyugh	MLGH-SOIL-04/23	17.06.2023	Melikgyugh gold mine + tailing pond	250	untreated soil close to the tailing pond

Melikgyugh	MLGH-SOIL-05/23	17.06.2023	Melikgyugh gold mine + tailing pond	250	untreated soil close to the tailing pond
Melikgyugh	MLGH-SOIL-06/23	17.06.2023	Melikgyugh gold mine + tailing pond	1,700	untreated soil
Melikgyugh	MLGH-SOIL-07/23	17.06.2023	Melikgyugh gold mine + tailing pond	2,000	agricultural soil, tree garden and potato field
Ararat	ARARAT-SOIL-01/23	13.06.2023	Ararat gold plant	3,500	vegetables garden, irrigation by the water from Kachan Channel
Ararat	ARARAT-SOIL-02/23	13.06.2023	Ararat gold plant	3,600	backyard highly covered with grass and weed, tree garden
Ararat	ARARAT-SOIL-03/23	13.06.2023	Ararat gold plant	3,700	agricultural soil, potato field
Ararat	ARARAT-SOIL-04/23	13.06.2023	Ararat tailing pond	4,000	a private garden (fruit trees, grapes, wheat)
Ararat	ARARAT-SOIL-05/23	13.06.2023	Ararat gold plant	300	untreated soil close to the Ararat gold plant
Ararat	SRNV-SOIL-01/23	13.06.2023	Ararat tailing pond	600	a private garden with vegetables and trees
Ararat	SRNV-SOIL-02/23	13.06.2023	Ararat tailing pond	6,500	untreated land
Ararat	SRNV-SOIL-03/23	13.06.2023	Ararat tailing pond	5,000	untreated land next to local brook and road

Table II: List of sediment samples collected in areas of interest.

Area	ID	Date of sampling	Hot spot	Distance from hot spot [m]	Sampling site description
Meghradzor	MGHR-SED-01/22	17.09.2022	Meghradzor gold mine	200	a brook flowing from the Meghradzor mine
Meghradzor	MGHR-SED-02/22	17.09.2022	Meghradzor gold mine	1,500	the section of the Marmarik River below the mouth of a stream flowing from the mine
Meghradzor	MGHR-SED-03/22	17.09.2022	Meghradzor gold mine	2,000	the Marmarik river next to the bridge
Meghradzor	MGHR-SED-04/22	17.09.2022	Meghradzor gold mine	2,000	a brook flowing to the Marmarik river
Meghradzor	MGHR-SED-05/22	17.09.2022	Meghradzor gold mine	8,000	a brook flowing to the Marmarik Reservoir, recreation area
Karaberd	KARAB-SED-01/22	18.09.2022	Karaberd gold-molyb. mine	500	a brook from the stone mine
Karaberd	KARAB-SED-02/22	18.09.2022	Karaberd gold-molyb. mine	200	a water reservoir (flooded former mine corridor)
Karaberd	KARAB-SED-03/22	18.09.2022	Karaberd gold-molyb. mine	10,000	the Pambak river
Karaberd	KARAB-SED-04/22	23.09.2022	Karaberd gold-molyb. mine	4,000	the Pambak river in the municipal area
Karaberd	KARAB-SED-05/22	23.09.2022	Karaberd gold-molyb. mine	15,000	the Pambak river sample site is close to the bridge
Karaberd	KARAB-SED-06/22	18.09.2022	Karaberd gold-molyb. mine	1,000	the Pambak river, a lot of municipal waste around
Karaberd	KARAB-SED-07/22	18.09.2022	Karaberd gold-molyb. mine	2,000	the Pambak river near the Pambak train station
Melikgyugh	MLGH-SED-01/23	17.06.2023	Melikgyugh gold mine + tailing pond	250	a brook upstream the heap and tailing pond
Melikgyugh	MLGH-SED-02/23	17.06.2023	Melikgyugh gold mine + tailing pond	250	a brook flowing from the direction of the mining waste heap
Melikgyugh	MLGH-SED-03/23	17.06.2023	Melikgyugh gold mine + tailing pond	250	a brook under the tailing pond
Melikgyugh	MLGH-SED-04/23	17.06.2023	Melikgyugh gold mine + tailing pond	250	a brook flowing out from the tailing pond
Melikgyugh	MLGH-SED-05/23	17.06.2023	Melikgyugh gold mine + tailing pond	500	a brook close to the Melikgyugh village
Melikgyugh	MLGH-SED-06/23	17.06.2023	Melikgyugh gold mine + tailing pond	3,500	a brook flowing from the Mijnatun village

Melikgyugh	MLGH-SED-07/23	17.06.2023	Melikgyugh gold mine + tailing pond	3,500	a brook flowing from the Melikgyugh village
Ararat	ARARAT-SED-01/23	13.06.2023	Ararat tailing pond	300	the Kachan channel upstream of the tailing pond
Ararat	ARARAT-SED-02/23	13.06.2023	Ararat tailing pond	2,500	the Kachan channel downstream of the tailing pond
Ararat	SRNVN-SED-03/23	13.06.2023	Ararat tailing pond	1,000	a fish pond

Table III: Samples of waste collected in areas of interest.

Area	**ID**	**Date of sampling**	**Hot spot**	**Distance hot spot [m]**	**Description of sample site**
Meghradzor	MGHR-WASTE-02/22	17.09.2022	Meghradzor gold mine	2,000	mining waste dump
Meghradzor	MGHR-WASTE-01/22	17.09.2022	Meghradzor gold mine	2,000	mining waste dump, sampled from waste heap
Karaberd	KARAB-WASTE-01/22	19.09.2022	Karaberd gold mine	50	mining waste dump, sampled from waste heap, orange colour

Table IV: Basic characteristic of the fish sample.

Area	**ID**	**Date of sampling**	**Hot spot**	**Distance from hot spot [m]**	**Sampling site description**	**Description of sample**
Ararat	SRNVN-FISH-01/23	13.06.2023	Ararat tailing pond	1,000	a fish pond fed by the Kachan channel	two units of *Cyprinus carpio* (females, 2 years old)

Table V: Heavy metals concentrations in soil samples (mg/kg DW).

ID	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
MGHR-SOIL-01/22	4.2	0.3	14.7	40	27,100	NA	2.9	10	30	NA	86
MGHR-SOIL-02/22	3.2	0.3	22	45	38,000	NA	2.5	14	12	NA	107
MGHR-SOIL-03/22	20	0.6	39.7	130	48,500	NA	2.3	23	20	NA	191
MGHR-SOIL-04/22	13.8	0.6	41.4	63	24,600	NA	3.2	27	42	NA	193
MGHR-SOIL-05/22	5.6	0.6	39.3	47	24,300	NA	1.4	22	29	NA	220
MGHR-SOIL-06/22	3.1	0.2	17.8	42	28,900	NA	<LOQ	12	14	NA	130
MGHR-SOIL-07/22	9.6	0.4	64.4	41	25,800	NA	2.2	49	22	NA	113
KARAB-SOIL-01/22	16.9	2.2	37.5	90	31,600	NA	4	22	110	99.3	394
KARAB-SOIL-02/22	19	1.1	31.3	61	33,400	NA	3.5	19	52	102	173
KARAB-SOIL-03/22	12.1	0.4	51.9	41	26,200	NA	2.3	38	16	113	79
KARAB-SOIL-04/22	5.6	0.4	20.8	34.5	17,800	NA	2.4	17	13	67.5	87
KARAB-SOIL-05/22	8	0.9	25.9	45	18,000	NA	1.1	18	49	48.1	266
KARAB-SOIL-06/22	5.8	0.6	19.8	30	15,400	NA	2.1	14	18	51	155
KARAB-SOIL-07/22	15.8	0.5	24.7	20	14,400	NA	2.3	16	14	44.2	71
MLGH-SOIL-01/23	7.7	0.4	97.8	45	NA	0.0711	NA	61	23	NA	140
MLGH-SOIL-02/23	5.2	0.6	74.3	50	NA	0.0282	NA	44	15	NA	213
MLGH-SOIL-03/23	5.2	0.7	77.3	57	NA	0.0314	NA	49	22	NA	254
MLGH-SOIL-04/23	119.0	2.8	55.9	49	NA	0.0210	NA	37	212	NA	237
MLGH-SOIL-05/23	19.0	0.4	117.4	41	NA	0.0167	NA	53	17	NA	71
MLGH-SOIL-06/23	8.4	0.3	58.9	51	NA	0.0238	NA	37	16	NA	154
MLGH-SOIL-07/23	6.2	0.3	100.8	43	NA	0.0228	NA	63	15	NA	92
ARARAT-SOIL-01/23	8.5	0.2	57.1	68	NA	0.0529	NA	51	17	NA	103
ARARAT-SOIL-02/23	6.8	0.2	73.7	142	NA	0.0195	NA	73	12	NA	88
ARARAT-SOIL-03/23	6.8	0.2	68.6	39	NA	0.0164	NA	67	10	NA	78
ARARAT-SOIL-04/23	7.6	0.2	62.1	59	NA	0.0154	NA	65	9	NA	67
ARARAT-SOIL-05/23	241.2	0.8	97.6	136	NA	0.0375	NA	152	27	NA	124
SRNV-SOIL-01/23	16.6	0.3	60.1	280	NA	0.0207	NA	41	28	NA	499
SRNV-SOIL-02/23	11.4	0.5	44.9	70	NA	0.0122	NA	31	84	NA	242
SRNV-SOIL-03/23	12.8	0.6	81.6	132	NA	0.0983	NA	59	62	NA	246

Table VI: Heavy metals concentrations in sediment samples (mg/kg DW).

ID	As	Cd	Cr	Cu	Fe	Hg	Mo	Ni	Pb	V	Zn
MGHR-SED-01/22	29.6	1.4	10.4	191	45,300	0.729	3.5	9	96	NA	342
MGHR-SED-02/22	9.5	20.3	33.4	20	35,000	0.0034	1.4	17	14	NA	167
MGHR-SED-03/22	7.1	<LOQ	29.2	19	18,000	0.003	1.6	19	15	NA	45
MGHR-SED-04/22	3.4	0.4	2.4	18	11,300	0.0048	1	6	19	NA	99
MGHR-SED-05/22	116	1.2	59.3	53	28,400	0.0057	2.7	42	21	NA	107
KARAB-SED-01/22	5.2	<LOQ	6.6	27	20,700	0.0015	1.9	5.8	6	86.1	36
KARAB-SED-02/22	172	30.2	5.2	99	114,000	0.809	77.5	33	93	21.1	17,600
KARAB-SED-03/22	5.6	0.2	18	129	29,300	0.0094	2.7	16	13	129	106
KARAB-SED-04/22	3.2	<LOQ	24.6	34	31,700	0.0028	1.5	16	18	128	84
KARAB-SED-05/22	4.4	<LOQ	22.9	35	27,700	0.0018	2.3	16	7	128	75
KARAB-SED-06/22	3.8	<LOQ	11.6	100	30,300	0.0022	2.5	12	8	150	68.5
KARAB-SED-07/22	4.2	<LOQ	12.7	125	29,200	0.0043	2.5	14	11	139	90
MLGH-SED-01/23	36.6	0.4	62.6	32	NA	0.0120	NA	34	17	NA	65
MLGH-SED-02/23	22.1	0.4	102.1	42	NA	0.0212	NA	69	23	NA	101
MLGH-SED-03/23	38.1	0.4	70.8	32	NA	0.0096	NA	38	14	NA	69
MLGH-SED-04/23	28.8	0.5	89.5	35	NA	0.0209	NA	65	30	NA	95
MLGH-SED-05/23	30.8	0.4	73.7	38	NA	0.0123	NA	40	13	NA	71
MLGH-SED-06/23	5.4	0.3	75.8	37	NA	0.0275	NA	53	14	NA	92
MLGH-SED-07/23	20.0	0.5	64.2	41	NA	0.0238	NA	48	23	NA	101
ARARAT-SED-01/23	14.9	0.2	74.5	35	NA	0.0321	NA	68	12	NA	72
ARARAT-SED-02/23	12.8	0.1	56.1	22	NA	0.0148	NA	43	12	NA	58
SRNVN-SED-03/23	16.6	0.2	66.3	31	NA	0.0188	NA	61	10	NA	62

Table VII: Heavy metals concentrations in samples of waste (mg/kg DW).

ID	As	Cd	Cr	Cu	Fe	Mo	Ni	Pb	V	Zn
MGHR-WASTE-02/22	36.1	0.6	4.1	88	23,500	1.4	6	27	NA	123
MGHR-WASTE-01/22	39.7	0.9	7.7	158	31,000	1.8	4	40	NA	203
KARAB-WASTE-01/22	10.7	1.9	2.9	402	24,900	5.3	3	15	81.2	220

Table VIII: Heavy metals concentrations in the fish sample (mg/kg FM).

ID	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SRNVN-FISH-01/23	0.09	<LOQ	<LOQ	0.41	0.052	<LOQ	<LOQ	29.8

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