Heavy metals in urine samples from residents of the Akhtala amalgamated community located in the mining region of Lori Province, Armenia

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Abstract

This study's primary focus is the determination of heavy metals (arsenic, copper, nickel, cadmium, lead) in urine samples of residents living near the Nahatak tailing pond located in Lori Province, Armenia. Sampling was conducted in the communities of Mets Ayrum, Pokr Ayrum, Chochkan, Shamugh and in the reference community in the ecologically safer Tavush Province. Previous studies of this region have proven increased risks of polluted soil with increased levels of arsenic, cadmium and nickel. This study verifies the presence of heavy metals by examining 73 urine samples in total, where 62 were urine samples of residents living in the aforementioned communities and 11 were urine samples from the reference community.

The results of this study are compared with other available results of research and biomonitoring done by teams in the USA, Czech Republic and Germany. They have proven the presence of arsenic in all samples of urine in the span from 6 to 58 µg/g of creatinine in which the population of children has shown the worst levels of its presence.

The second high-risk element that has shown increased levels of presence in urine samples in comparison with test samples is cadmium. The levels of cadmium among them have risen up to the levels of 1 µg/g of creatinine. These results confirm the findings of previous studies that have assessed increased risks of exposition to this metal.

There have been proven levels of lead and copper in a smaller portion of samples for this study. In these samples, the levels of copper have ranged in the span of 5 to 28 µg/g of creatinine whereas lead ranged from 1 to 8 µg/g of creatinine. The concentration of both lead and copper was found higher in samples coming from residents of the potentially contaminated localities. The concentration of nickel did not surpass the detection limit in all of the examined urine samples.

The results of our research confirm the heightened burden of the residents living in the metallurgically polluted location with increased levels of arsenic and cadmium in the environment. The worst effected residents of these locations are children. It will be necessary to examine more body tissues to show the presence of the observed elements to confirm general conclusions of the environmental burden of the Lori Province residents.

Content

Introduction

Arnika, the Prague, Czech Republic based NGO, in cooperation with Armenian partner the Center for Community Mobilization and Support (CCMS) and informational NGO EcoLur have been conducting research of the contamination of the environment in the Northern Armenian province Lori since 2018[1]. The pinnacle of this cooperation are the current conclusions of the potential influence on human health by heavy metal pollution using non-invasive methods of human biomonitoring.

This current research is following the previous studies which have proven the contamination of the environment in Armenia (for example in aquatic ecosystems[2]) caused by heavy metal pollution connected with hard rock mining. The studies have also confirmed possible health risks connected with mining and metallurgical industries in affected locations[3].

In 2018, the evaluation of samples of soil, river sediments, sand from children's playgrounds and human hair was conducted in the greater area of industrial locations in Alaverdi, Akhtala and Teghut where samples were also taken from the river basin of Debed. The samples were examined for the presence of heavy metals such as arsenic, cadmium, chromium, copper, molybdenum, nickel, lead and zinc[4]. Additionally, an analysis was conducted in order to determine the presence of selected persistent organic substances (dioxins, dioxin-like PCB, HCB, HCBD, HCH) in the samples of domestic hen eggs from free range hens in two locations in Alaverdi[5].

In 2019, we have evaluated the presence of heavy metals (arsenic, cadmium, copper, molybdenum, nickel, lead) in samples of human hair from residents of nine households and conducted additional monitoring of these metals in soil, in locally grown samples of fruit, vegetables and honey (in Alaverdi and Akhtala). The results of these analyses were compared with Armenian, Dutch, French, Czech and American standards for polluted soil and indicate higher concentrations especially of arsenic but also of cadmium. However, some cases included an increased concentration of other metals as well (copper, lead, nickel)[6]. These analyses also included the use of the RISC (Integrated Risk for Software) software to estimate the potential health risk due to exposure to selected heavy metals. Some results point to the possibility of increased health risks, especially in connection with arsenic exposure. In the case of arsenic, this software evaluated the overall carcinogenic risk to children in all nine monitored locations and in eight out of nine locations to adults. After the calculation of the non-carcinogenic risks, it was assessed that the number of locations that pose increased non-carcinogenic health risks are two for children and one for adults. In the case of cadmium, increased non-carcinogenic risks for children were observed in one examined location.

[1] Arnika (2018, a): Heavy metals in the surroundings of mining and metallurgical sites in the Lori region in Armenia)

[2] Gevorgyan at al.: Environmental Risk Assessment of Heavy Metal Pollution in Armenian River Ecosystems: Case Study of Lake Sevan and Debed River Catchment Basins

[3] Grigoryan at al: Risk factors for children's blood lead levels in metal mining and smelting communities in Armenia: a cross-sectional study, BMC Public Health (2016) 16:945

[4] Arnika (2018, a): Heavy metals in the surroundings of mining and metallurgical sites in the Lori region in Armenia)

[5] Arnika (2018, b) Persistent Organic Pollutants (POPs) in Chicken Eggs from Alaverdi, Armenia - Results of sampling conducted in 2018

[6] Arnika (2019): Heavy metals in soils, foodstuffs, and human hair in the mining and metallurgical communities of Alaverdi and Akthala, Lori province of Armenia

Based on the results from the analyses from the years 2018 and 2019 which suggest the possible contamination of the region's environment in connection with industrial activities, the current study focuses on the potential influence of heavy metal (arsenic, lead, cadmium, nickel, copper) pollution on human health. Additionally, based on the evaluation of academic literature[7] [8] [9], it was decided to use non-invasive methods of human biomonitoring for this study, specifically the analysis of aforementioned metals in urine and other human tissues. This study reports the results of urine samples.

[7] Wilhelm at al: Comparison of arsenic level in fingernails with urinal As species as biomarkers of arsenic in residents living close to a coal-burning power plant in Prievidza Distric, Slovakia, Journal of Exposure, Analysis and Environmental Epidemiology 2015, 15, 89-98

[8] Cottingham at al: Diet and toenail arsenic concentrations in a New Hampshire population with arsenic-containing water, Nutrition Journal 2013, 12:149

[9] Rasheed at al. Human health risk assessment for arsenic: a critical review, Critical Reviews inf Environmental Sciences and Technology, 2016, 14? 19-20, 1529-1583

1. Chosen Location

Based on the studies conducted in the years 2018 and 2019, the main focus is on the location Chochkan and neighboring locations Mets Ayrum, Pokr Ayrum in the Lori Province in northeastern Armenia, not far from the Georgian-Armenian boarder. More samples were taken from the non-burdened location in the village Achajur in the neighboring Tavush Province to provide clear comparison.

There were high concentrations of arsenic found in soil during the previous sampling in the village Chochkan and the calculation of health risks indicated increased carcinogenic and non-carcinogenic risks from arsenic exposure for both children and adults [10].

The locations are nearby the Nahatak tailing pond in which the waste from the Akhtala Mountain Enrichment Combine complex is disposed. The complex processes copper ore mined from the Shamlugh location. Two more currently unused tailing ponds are located nearby and these ponds, along with the waste from the mining industry, can be a source of heavy metal contamination of the location.

The number of residents potentially burdened with the mining activities (living in the examined locations) are presented in Table 1[11] [12].

Tab. 1 Overview of the number of residents

Overview of the number of residents		
	De jure (res.)	De facto (res.)
Achajur (Tavush Province, 2008)	4 447	-
Chochkan (Lori Province, 2001)	1 907	1 753
Mets Ayrum (Lori Province, 2001)	638	594
Pokr Ayrum (Lori Province, 2001)	171	166

[10] Arnika (2019): Heavy metals in soils, foodstuffs, and human hair in the mining and metallurgical communities of Alaverdi and Akhtala, Lori province of Armenia

[11] RA 2001 population and housing census results Available at https://www.armstat.am/file/doc/162.pdf

[12] Marzes of the Republic of Armenia in Figures, 2008 Available at https://www.armstat.am/file/article/marz_08_42.pdf

2. Monitored metals/pollutants

Following the findings of the previous studies, this project focuses on the determination of the levels of arsenic, cadmium, lead, nickel and copper in urine. These are elements typically described as heavy metals with a mutual function of persistence in the environment. Another mutual ability of these elements is that all are naturally present in nature but can be significantly affected by the human activities. The mining of hard rocks and the metallurgical industry can be a significant source of contamination in the case of all of the monitored metals.

Even though each metal differs in its metabolism, the primary form of exposure to these metals is same for all of the studied elements - 1) inhalation, either via microparticles or via vapors or 2) ingestion, i.e., the absorption into the digestive tract either via food, water, soil or dust (especially for children). Acute toxic effects of metals happen on only rare occasions (e.g., arsenic compounds have been used as poison in the past centuries), therefore the main focus is on their long term and chronic effects.

The limited capabilities of metal secretion from organisms (mainly via urine or stool) lead to different values of bioaccumulation in live organisms. This attribute raises concerns that long term exposure to even small amounts of certain metals can lead to the rise of their levels in a given organism which could lead to negative effects on its health[13].

↘ a. Arsenic

Arsenic (As) occurs in the nature in many forms, either in the form of inorganic compounds (primarily sulfides) or organic compounds as well. It occurs in larger concentrations especially as an admixture of some ore deposits such as gold, silver, lead, copper, nickel, cobalt, antimony, iron etc. It can be found in trace amounts in some coal deposits as well, especially in the case of the lesser quality lignite (brown) coal. Significant contamination of the environment occurs during the combustion of coal or during the extraction and processing of the aforementioned ores[14].

Approximately 140 million people live in areas of natural leakages of arsenic into surface or subterranean water which poses health risks for public health. A significant anthropogenic source of arsenic are the mining and metallurgical industries [15].

The compounds of arsenic in the soil enter the roots of plants and arises to the surface of agriculture plants or are washed away into the rivers and water reservoirs where they become a part of the bodies of fish, aquatic lants and other organisms that can become a part of the human food supply [16].

[13] Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

[14] Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

[15] Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

[16] Rasheed at al. Human health risk assessment for arsenic: a critical review, Critical Reviews inf Environmental Sciences and Technology, 2016, 14? 19-20, 1529-1583

Arsenic and its attributes have been known to humanity since the Ancient Era and its effects on human health has since been intensively studied, including the chronic exposure to arsenic compounds [17]. There are some locations on Earth with high levels of arsenic in the soil and water (e.g. Bangladesh) [18].

Same as the arsenic trioxide, arsenic itself was allocated by the International Agency for Research on Cancer (IARC) [19] into the group 1 as human carcinogens. According to IARC, the evidence of the connection of arsenic with the occurrence of lung and bladder cancer is considered sufficient. The IARC considers the evidence of arsenic influence on prostate, liver and kidney cancer only as partially sufficient.

Non-carcinogenic health risks of arsenic exposure are connected with the deceleration of fetal development, influencing the neuropsychic development of children, influence on the central and peripheral nervous system and to heart and vessel diseases [20].

↘ b. Cadmium

Cadmium (Cd) is a heavy metal chemically related to Zinc, which is most commonly naturally present with lead in ore as sulfides of these metals. It commonly occurs in the form of many organic and inorganic compounds, specifically in small concentrations of soil, water and air [21].

People usually obtain cadmium for their use as a byproduct during the mining of other metals such as lead, copper or zinc which also leads to the contamination of the environment. Cadmium is also used as a stabilizer of selected plastics. In the past, cadmium was abundantly used in many electric and electronic devices as well. However, this has been (with a few exceptions) banned in the European Union since 2006 [22].

Besides the mining and the metallurgy, other significant sources of environment pollution can also be the burning of fossil fuels or the processing of electronic waste. According to the European Commission, cadmium as a polluting substance currently poses the highest risks of the substances contained in phosphorus fertilizers[23]. Additionally, the use of contaminated sewage sludge as fertilizer on agriculture soil can also create significant problems.

Cadmium has the ability to accumulate within living organisms including the human body (bioaccumulation). According to the International Agency for Research on Cancer (IARC), cadmium is considered as a confirmed human carcinogen (group 1) which can disrupt the genetic information in

[17] Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

[18] M. F. Hossain. Arsenic contamination in Bangladesh—An overview,Agriculture, Ecosystems and Environment, 2006, 113: 1-4, 1-16

[19] IARC (2012): Arsenic, Metals, Fibres, and Dusts - IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Volume 100C

[20] EFSA (2009): Scientific Opinion on Arsenic in Food, EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA, Parma, Italy

[21] EFSA (2009): Scientific Opinion on Arsenic in Food, EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA, Parma, Italy

[22] EFSA (2009): Scientific Opinion on Arsenic in Food, EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA, Parma, Italy

[23] SDĚLENÍ KOMISE EVROPSKÉMU PARLAMENTU, RADĚ, EVROPSKÉMU HOSPODÁŘSKÉMU A SOCIÁLNÍMU VÝBORU A VÝBORU REGIONŮ Konzultativní sdělení o udržitelném využívání fosforu. COM/2013/0517 final

cells (genotoxicity) and cause damage to human fetuses during their prenatal development (teratogenicity). In the case of cadmium exposure, the IARC confirms the existence of sufficient evidence for lung cancer development, and additionally, the influence of cadmium was also observed in kidney and prostate cancer [24].

Cadmium can also damage the functions of kidneys (nephrotoxicity) or the nervous system (neurotoxicity). According to the European Food Safety Authority (EFSA), cadmium can also negatively influence the metabolism of bones (leading to possible osteoporosis) and can disrupt the hormonal system [25].

The tolerated daily dose of cadmium recommended by the EFSA is 2.5 micrograms per kilogram of the body weight per week. However, the main source of cadmium in these cases is via their food. More than half of the children aged 4 to 6 years of age absorb more cadmium than the mentioned recommended tolerated dose by the EFSA [26].

In addition to these findings, it is necessary to consider the major impact of cadmium effects on cigarette smokers (including passive smokers). According to experts, the cigarette smoke creates a cadmium source more than 20x greater than cadmium absorbed via food [27].

There were limits established by the Commission for biological monitoring of the Federal Republic of Germany for cadmium and other metals which were derived from the results of toxicological and epidemiological studies. These values were created as two levels, whereas HBM I (human biomonitoring value I) determines the concentration of the discussed substance, which should not pose any health risks, and which should not require further measures if the level isn't breached. The value of HBM II was defined as a level where its breach poses a significant health risk and therefore needs additional intervention and other measures. The values oscillating between the HBM I and HBM II levels require increased attention and closer observation [28]. The limit of HBM I for children, adolescents and young adults under 25 years of age was established on the level of 1 µg/g of creatinine and the limit of HBM II on 6 µg/g of creatinine. The limits of HBM I and HBM II for adults older than 25 years of age were established as 2 µg/g of creatinine and 5 µg/g of creatinine respectively [29]. The value of HBM I for children was consequentially revised and decreased to the level of 0,5 µg/g of creatinine [30].

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[24] IARC (2012): Arsenic, Metals, Fibres, and Dusts - IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Volume 100C

[25] EFSA: Cadmium dietary exposure in the European population, 2012

[26] EFSA: Cadmium dietary exposure in the European population, 2012

[27] Miroslav Šuta: Kadmium ohrožuje každého desátého Čecha. Nejčastěji děti a kuřáky, Český rozhlas, 2017

[28] Schulz et al.: The German Human Biomonitoring Commission, International Journal of Hygiene and Environmental Health, 210, 2007, 373-382

[29] SZÚ: Zdravotní důsledky expozice lidského organismu toxickým látkám ze zevního prostředí (biologický monitoring), Odborná zpráva za rok 2009, Praha 2010

[30] SZÚ: Zdravotní důsledky expozice lidského organismu toxickým látkám ze zevního prostředí (biologický monitoring), Odborná zpráva za rok 2016, Praha 2017

↘ c. Copper

Copper (Cu) is a metal naturally present especially in the forms of sulfides, oxides and carbides and to a lesser extent also in pure metal form. Copper has been used by humans for thousands of years whereas the mining and processing its ores can be a significant source of environmental contamination. This applies not only for copper but also with other metals such as lead, cadmium, zinc or molybdenum [31].

On one hand, copper, from a biological point of view, is one of the so-called essential elements that the human body in small amounts necessarily needs for its proper functioning. On the other hand, it is potentially toxic. The National Reference Laboratory for Drinking Water at the State Institute of Public Health warns that the limits of safe and toxic amounts are very close to each other in the case of copper [32].

Copper in the human body is involved in the function of many enzymes and in the catalysis of significant enzymatic processes such as cellular respiration or the formation of neurotransmitters. Above other functions, copper is also involved in blood clotting and indirectly in hematopoiesis as well thanks to its role in how the body manages its iron reserves.

Various experts somewhat differ in the recommendation what is the ideal daily dose of copper for our bodies. Most recommend the limit to be around 1 milligram of copper per day [33].

However, higher copper exposure may pose a health risk. Acute copper toxicity can result in a variety of pathological conditions and, in extreme cases, even death. Chronic toxicity can lead to liver damage and severe neurological damage. It is also discussed that excess copper could also play a role in the case of Alzheimer’s disease [34].

There is a discussion among experts over whether copper has an antioxidant effect. However, most of the available scientific studies associate increased copper exposure with the opposite effect, that being the development of oxidative stress.

For a long time has modern medicine monitored the amount of copper that people get into their bodies in food and beverages. According to these analyses, the vast majority of people, including children, have an adequate supply of copper through food. Only some women over the age of 15 have a copper intake slightly smaller than what is considered optimal.

31 Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

32 SZU: Upozornění Státního zdravotního ústavu – Národního referenčního centra pro pitnou vodu na možné zdravotní riziko pití vody z měděné nádoby, 2017

33 SZU: Upozornění Státního zdravotního ústavu – Národního referenčního centra pro pitnou vodu na možné zdravotní riziko pití vody z měděné nádoby, 2017

34 Uriu-Adams at al: Copper, oxidative stress, and human health, Molecular Aspects of Medicine, 26 (2005)268–298

↘ d. Lead

Lead (Pb) is seemingly the most common element of all heavy metals. It is naturally present especially in the forms of sulfides and carbides [35]. It continues to be generally used for the production of batteries, cables or munition regardless of its dangerous nature. Lead enters the environment via the activities of the mining and metallurgical industry, with the processing of waste, fossil fuel usage etc. A significant former source of lead was the addition of organic compounds of lead as anti-detonation additive into automobile gasoline [36].

Lead is a toxic substance with the ability to accumulate within organisms. Substantial amounts of its ill effects have been proven on the health of liver, kidneys, the nervous system and red blood cells. The IARC has placed the inorganic compounds of lead into the group of "likely" carcinogens (group 2A) with the explanation that there have been studies conducted on animals with sufficient but limited results [37].

The EFSA published a report of a panel of experts according to which there isn't evidence of the existence of a so-called "threshold dose" for negative effects of lead. Therefore, it is not possible to determine a level of lead dose that would be safe for the human organism [38].

Small children, especially those under 6 years of age, represent a group with the highest risks of lead exposure for a number of reasons. One of them is their probable higher exposure (compared to adults) to lead due to oral intake of clay and dust. Another factor is the higher level of lead absorption in children's digestive tract, and finally it should be taken into account that the developing organs of the child are more sensitive to the effects of lead. Effects on the immune systems have also been proven on children living in lead-contaminated areas, for example the influence on the levels of immunoglobins such as IgA, IgM, alpha-microglobulin and transferrin [39].

Experts consider the so-called developmental neurotoxicity, i.e. damage to brain development in childhood, to be a possible critically negative effect of lead that can severely impact the children. This was the strongest argument for banning the addition of lead to motor gasoline in the past. It was proven that children exposed to higher doses of lead from car exhausts had lower IQs than children in the control group [40]. Experts consider the negative effects on kidneys (nephrotoxicity) and on systolic blood pressure to be critical in the case of adults [41].

It is prohibited to add lead into automobile gasolines in the European Union due to its dangerousness it is also strictly regulated by the RoHS directive in electrical and electronic devices [42]. Other lead regulations involve e.g. paints, water pipes or jewelry.

Meat and game offal are the most commonly served meals in which have experts found extremely high concentrations of lead [43]. Several studies have also shown that more frequent consumption of game shot by lead ammunition affects the lead levels in consumers' bodies [44].

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35 Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

36 Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

37 IARC (2006) IARC MONOGRAPHS VOLUME 87

38 EFSA (2010): Scientific Opinion on Lead in Food, EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA, Parma, Italy

39 Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

40 Grant, L. D. and Sors A. (eds.): Lead exposure and child development. An international Assessment, MPT Press, 1990

41 EFSA (2010): Scientific Opinion on Lead in Food, EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA, Parma, Italy

42 Miroslav Šuta: Zákaz některých chemikálií v nových spotřebičích, Odpady, 9/2006

43 EFSA (2012): Lead dietary exposure in the European population, European Food Safety Authority, Parma, Italy

44 BfR: Lead ammunition results in higher lead concentrations in game meat. 06/2013

↘ e. Nickel

Nickel (Ni) is present in the environment especially in the form of sulfides and silicates. The contamination of the environment occurs primarily with the ore mining and as a consequence of the metallurgical industry [45].

Nickel in its metal form is a silver-white, very shiny metal and is especially used in the metallurgical industry, in a similar way as chromium or manganese for steel alloying. It serves as an ingredient to enable greater durability and to secure protection against corrosion and high temperatures. Nickel is also used as a component for variety of special alloys characterized by higher strength. The application of a thin layer of nickel is performed in order to protect the less durable metals against atmospheric influences and water, most commonly electrolytically. However, nickel is also used for the production of some types of batteries or as a catalyst in the chemical and food industries [46].

The IARC has classified some compounds of nickel as confirmed human carcinogens (group 1) and nickel itself into the group 2B which is the classification of possible carcinogens. Some studies on animals have proven a variety of damage done to hereditary information - DNA [47].

Moreover, considering its health impacts, nickel also acts as a very strong contact allergen. Nickel is the most common cause of contact dermatitis in the world [48]. This problem is present with approximately 10% of women and 2-6% of men in Europe [49]. The high occurrence of allergies is related to a broad spectrum of nickel usage most notably with the production of stainless steel or for nickel-plating of surfaces of other metals. Therefore, nickel is found in many items of basic daily use such as buttons, zippers, spectacle frames, jewelry, tools or electronic devices[50].

The so-called "Nickel Directive" was accepted in 1994 by the European Union to combat the increased occurrence of allergic reactions which has limited the amount of nickel released from products [51]. This regulation became a part of the new complex chemical policy of the EU in 2009 when the REACH directive was established [52].

Some allergic individuals who originally had reactions only when directly contacted with material containing nickel can gradually develop an allergic reaction to nickel present in food as well. Whereas in the case of contact allergic reactions the solution is to completely avoid contact with metals containing nickel, this is not possible in the case of food allergies [53].

[45] Bencko, Cikrt, Lener: Toxické kovy v životním a pracovním prostředí, Grada 1995

[46] Miroslav Šuta, Dokáže potrápit na knoflíku i v potravinách. Nikl škodí také kuřákm e-cigaret, Český rozhlas, 2018

[47] IARC (2012): Arsenic, Metals, Fibres, and Dusts - IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Volume 100C

[48] Ahlstrom at al: Nickel allergy and allergic contact dermatitis: A clinical review of immunology, epidemiology, exposure, and treatment. Contact Dermatitis. 2019; 81:227–241.

[49] Suková: Alergie na nikl, Agronavigator, 23. 2. 2004

[50] Garg at al: Nickel allergy following European Union regulation in Denmark, Germany, Italy and the U.K., Br J Dermatol. 2013 Oct;169(4):854-8

[51] EUROPEAN PARLIAMENT AND COUNCIL DIRECTIVE 94/27/EC of 30 June 1994 amending for the 12th time Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations

[52] ECHA: ANNEX XVII TO REACH – Conditions of restriction, Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles, Entry 27, Nickel

[53] EFSA: Scientific Opinion on the risks to public health related to the presence of nickel in food and drinking water, 2015

It has been known to experts for centuries, that there are significant amounts of nickel in cigarette smoke and studies have proven the increased occurrence of nickel in the lungs of smokers. High concentrations of nickel can be present in the fumes of e-cigarettes as well [54].

[54] Lukasz,at al: Levels of selected carcinogens and toxicants in vapor from electronic cigarettes, Tob Control. 2014 March; 23(2): 133–139

3. Sampling and analysis

The monitored locations of interest were selected based on the results of previous studies. Urine samples were taken in the Lori Province, namely at Mets Ayrum, Chochkan, Pokr Ayrum and Shamlugh near the Nahatak tailing pond. The distance of the sampling locations from the tailing pond ranged from 50 to 3500 meters. The Achajur community (in Tavush Province) was chosen as the reference site, which is not burdened with the mining or metallurgical industries (Fig.1, Fig.2).

Figure 1 Overview of sampling locations (hot spot a reference location)

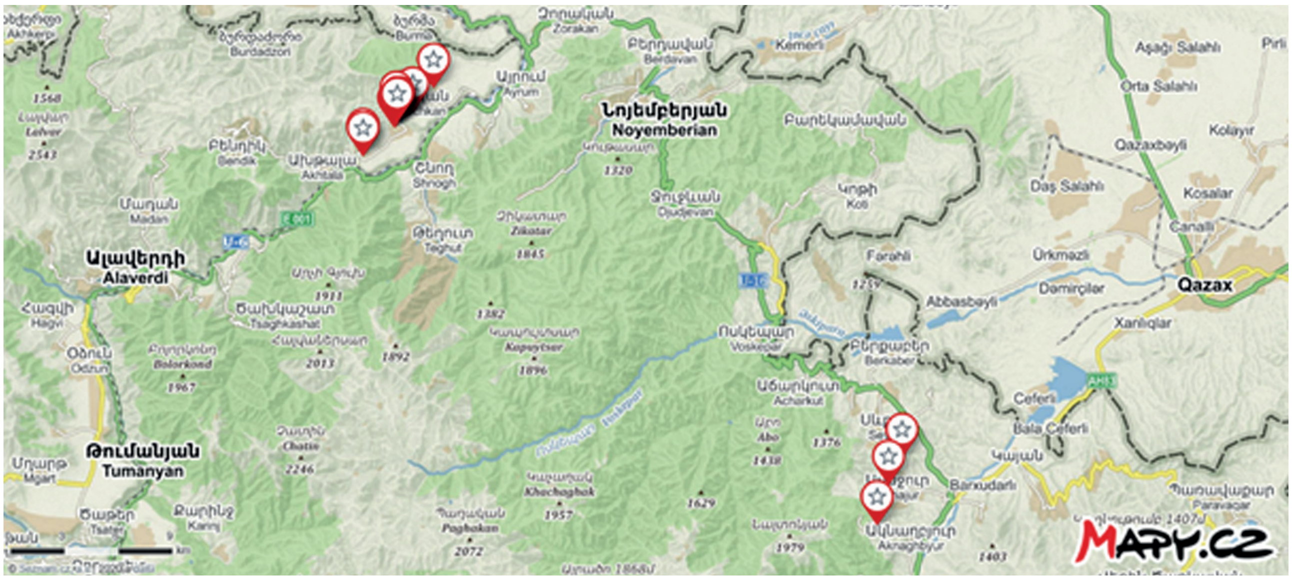
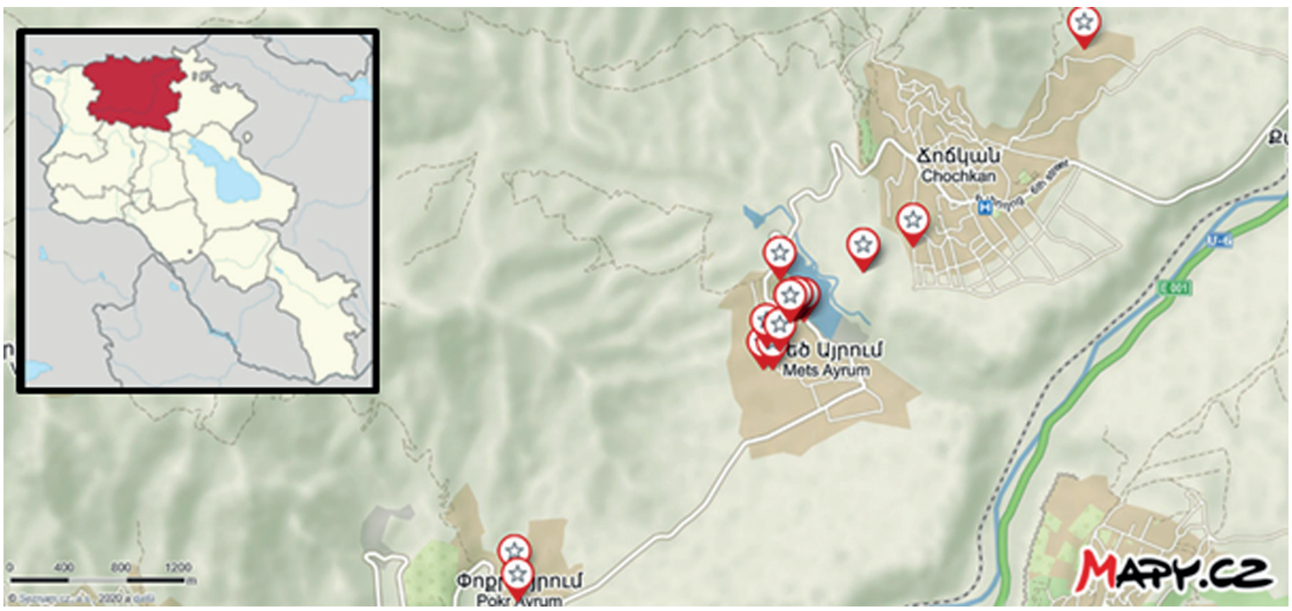


Figure 2 Overview of sampling sites at location of interest



A total of 73 urine samples were collected for the study, including 62 samples from the area of interest and 11 samples from the reference location. Samples were provided by 46 women (63%) and 27 men (27%) in the age range from 0.3 to 83 years (Figure 3). Qualifying conditions for the participants in this research were a) non-smoking person and b) long-term stay at the sampling site.

Regarding sampling, morning urine from a middle stream was collected into plastic sampling boxes. They were stored immediately after sampling in a cold environment for a short time, and afterwards frozen and stored in a freezer for transport to the laboratory.

The determination of heavy metals was performed by a specialized laboratory of the Health Institute in Ústí nad Labem. Analyzing the pollutants of interest was performed according to accredited methodologies.

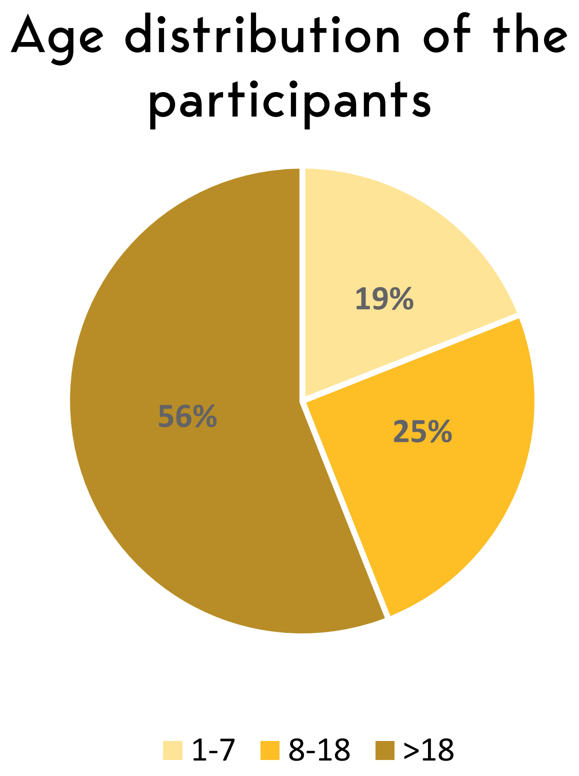
The determination of creatinine was performed according to the SOP 503 methodology and is based on its reaction in an alkaline environment with picric acid to form a yellow-orange complex. The color intensity, which is directly proportional to the creatinine concentration in the sample, is measured photometrically.

Heavy metals were determined according to the SOP 201.03 by mass spectrometry with inductively coupled plasma (ICP-MS). The final concentrations of the individual metals were subsequently converted on a per gram of creatinine basis in order to reduce distortion caused by the concentration function of kidneys.

For the determination of arsenic in urine, the recommended amount of creatinine should be in the range of 0.3 to 3.0 g/l. Samples with low creatinine content were excluded from the evaluation of biomonitoring, specifically samples with code numbers **5, 13, 19,24, 30, 32, 44, 60**.

In the next phase of the study, the content of heavy metals in nails of local residents and in dust samples taken from households will also be examined.

Figure 3 Pie Chart describing the age distribution of the participants of this study



4. Results and discussion

Described in Table 2 are ranges and basic statistics of measured concentrations of heavy metals in urine samples from burdened (and reference) locations. Nickel values in all samples came in lower than the limit of detection. Detailed information concerning the values of specific metals is described in the Annex (Table 7, Table 8).

Table 2 Overview of metal concentration values in urine samples taken from the population residing in the locations of interest and reference, values in µg/g of creatinine

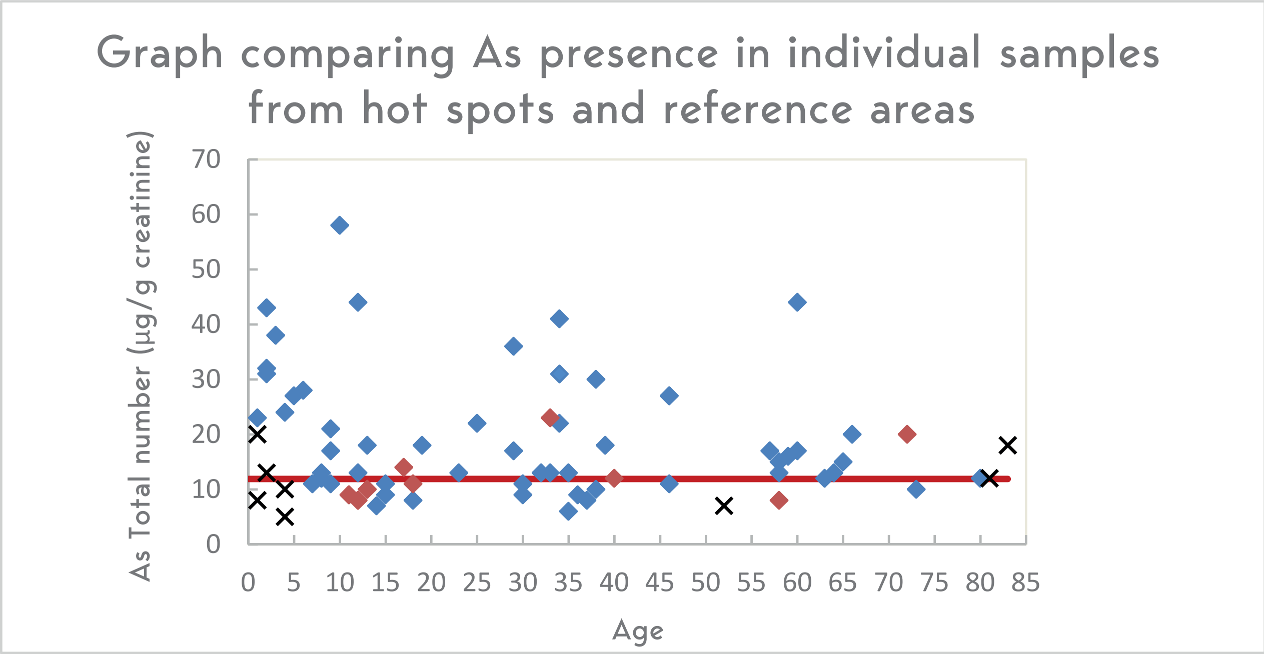
Hot spot (ref.)	Min	Max	Ar. Mean	Gm. Mean	Median	90 percentile	Number of samples
As	6 (8)	58 (23)	19,6 (12,7)	17,0 (11,9)	16,5 (11,5)	37,0 (19,4)	56 (9)
Cu	5 (5)	28 (10)	10,4 (7,2)	9,3 (7,1)	8,0 (7,0)	17,2 (9,2)	55 (9)
Cd	0,1 (-)	1 (-)	0,34 (-)	0,29 (-)	0,3 (-)	-	19 (-)
Pb	1 (1)	8 (2)	2,2 (1,5)	1,8 (1,4)	2 (1,5)	-	35 (2)
Ni	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

↘ a. Arsenic

The resulting values from the locality of interest ranged from 6 to 58 µg/g creatinine (Table 2). Moreover, the limit of professional exposure of the Czech Republic was exceeded in one measured case. It should be emphasized that this sample did not belong to an employee of the metallurgical industry, but to a 10-year-old child living in the Pokr Ayrum community, where professional exposure is not expected. In four cases, the measured value was close to the exposure limit from samples of participants aged 2, 12, 34 and 60 years (samples 29, 11, 53, 52).

For the determination of arsenic in urine, the recommended amount of creatinine is in the range of 0.3 to 3.0 g/l. In eight samples taken at the location of interest, the creatinine level deviated from this range (there were 7 cases with levels lower than this range), and therefore the recalculated arsenic values for these samples may be underestimated. At first, we considered it useful to keep them in the basic data set (Fig. 4), however, these samples were later excluded during statistical data processing.

Figure 4 Graph comparing As presence in individual samples from hot spots and reference areas (blue marks-samples from hot spot, red marks-samples from reference location, red line-geometric mean of reference location, black crosses-excluded samples)



The results of our analyses of samples taken at the Chochkan / Mets Ayrum site near the mining tailing pond confirm the hypothesis of increased arsenic exposure to people living in the vicinity of copper ore tailing ponds compared to residents from locations without mining and metallurgical waste. The average concentration of arsenic in the affected location was thus more than 20% higher than in the reference location with the median difference being even higher (by 40%). The median value indicates the level of metal which half of the samples exceed. The findings of the theoretical risk assessment carried out in 2019 by the RISC software, which assumed a higher health risk for children compared to adults, are also confirmed in this study. In particular, the levels of arsenic measured in children under 7 years of age in the area of interest reach significantly higher values than in the case of adults from the same area.

The fact that even the lowest level of arsenic in the urine of children from the locality of interest (12.7 µg/g creatinine) is significantly higher than the levels found in the Czech Republic during the monitoring of children's health statuses (2.5 to 5.25 µg/l) is considered significant. The levels of arsenic in the urine of children from the location of interest also exceeded the values discovered in the assessment of health risks of children living in the Kutná Hora - Kaňk area. This area is historically heavily contaminated due to mining and processing of silver ores, where the arithmetic mean with children aged 2 to 15 years was 16.64 µg/g of creatinine, and the median being 10 µg/g of creatinine.

Urinary arsenic concentrations are expected to reflect its ingested and inhaled amounts after its uptake into blood, and therefore provide a more relevant reflection of the possible daily dose than the amount of As in other tissues (e.g. nails)[55]. The values measured by us reflect the amount of arsenic to which the children were exposed several days before the actual collection (hair samples would otherwise reflect the long-term impact of arsenic exposure). The rate of contaminant elimination depends on a number of parameters of a given individual.

The determination of arsenic in urine is also used as a biological exposure test in occupational medicine to assess health risks. For this purpose, there was a concentration limit for arsenic in urine set by Decree 432/2003 Coll. for the protection of worker's health in the Czech Republic. According to Annex No. 2 to Decree No. 432/2003 Coll. on the established limit values of biological exposure test indicators and the conditions for the collection of biological material for the performance of biological exposure tests, the limit for urinary arsenic is 0.05 mg/g creatinine or 0.075 μmol/mmol creatinine for the samples taken at the end of the working week [56].

There are many studies that have evaluated the amount of total arsenic or some of its forms or metabolites in urine. Many studies report levels of arsenic or its compounds in micrograms per liter of urine, while only some report a more valid conversion of arsenic to creatinine. Detailed information is given in Tab. 3. where the determined values of heavy metals in human urine are described. The table contains the results of this study and the results from the available literature.

Table 3 Overview of the arsenic content found in this study and the academic sources

Country	Arithmetic Mean (μg/g creat.)	Geometric Mean (μg/g creat.)	Median (μg/g creat.)	Note	Reference
Armenia – Interest location	19,6	17,0	16,5	Whole population	
Armenia – Interest location	26,4	23,5	23,8	Children 2 to 12 years of age	
Armenia – Control location	12,7	11,9	11,5	Whole population	
USA		8,24		whole population	57
USA		8,25		children 6 to 12 years of age	58
USA		6,11		12 to 19 years of age	59
USA		8,64		above 20 years of age	60

55 Bencko, Symon: Exposure Test of Environmental Exposure and Hearing Changes in Exposed Children, Environmental Health Perspectives, 19, 95-111, 1977

56 Vyhláška č. 432/2003 Sb., kterou se stanoví podmínky pro zařazování prací do kategorií, limitní hodnoty ukazatelů biologických expozičních testů, podmínky odběru biologického materiálu pro provádění biologických expozičních testů a náležitosti hlášení prací s azbestem a biologickými činiteli

57 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

58 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

59 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

60 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

Germany	7,64	4,60	4,9	whole population	61
South Korea	49,4	41,1	41,2	whole population	62
China	46,0			open fireplaces	63
China	117,0			Strongly contaminated groundwater	64
China Hubei	20,20			Children 2 to 12 years of age	65
China Gansu	15,59			Children 2 to 12 years of age	66
China Guanding	9,10			Children 2 to 12 years of age	67
Nepal	11-51,4			Contaminated drinking water	
France	94,8			Women, fish and seafood consumers	68
France	59,7			Men, fish and seafood consumers	69
Spain	5,37	2,438	3,398	Children	70
Spain Andalusia		1,44		Industrial area	71
Spain Andalusia		1,26		Control location	72
Czech Republic Kaňk	16,64		10	Children, historically contaminated location	73
Czech Republic Kaňk	28			historically contaminated location	74
Czech Republic	10			biomoniotring	75

[61] Seifert et al: The German Environmental Survey 1990/92 (GerES II): reference concentrations of selected environmental pollutants in blood, urine, hair, house dost, drinking water and indoor air, Journal of Exposure Analysis and Environmental Epidemiology (2000) 10, 552-565

[62] Lee at al: Korea National Survey for Environmental Pollutants in the Human Body 2008: Heavy metals in the blood or urine of the Korean population International Journal of Hygiene and Environmental Health, 215 (2012) 449– 457

[63] Sengupta et al: Pathogenesis, clinical features and pathology of chronic arsenicosis. Indian J Dermatol Venereol Leprol. 2008; 74: 559-70.

[64] Liu at al: Biomarkers for the evaluation of population health status in 16 years after the intervention of arsenic contaminated groundwater in Xin-jing, China, J Hazard mater 262,1159-1166

[65] Zhang et al: Total arsenic concentrations in Chinese children’s urine by different geographic locations, ages, and genders, Environ Geochem Health (2018) 40:1027–1036

[66] Zhang et al: Total arsenic concentrations in Chinese children’s urine by different geographic locations, ages, and genders, Environ Geochem Health (2018) 40:1027–1036

[67] Zhang et al: Total arsenic concentrations in Chinese children’s urine by different geographic locations, ages, and genders, Environ Geochem Health (2018) 40:1027–1036

[68] Sirot at al: Dietary exposure and biomarkers of arsenic in consumers od fish and shelfish from France, Sci Totl Env, 407, 1875-1885

[69] Sirot at al: Dietary exposure and biomarkers of arsenic in consumers od fish and shelfish from France, Sci Totl Env, 407, 1875-1885

[70] Molina-Villalba at al: Biomonitoring of arsenic, cadmium, lead, manganese and mercury in urine and hair of children living near mining and industrial areas, Chemosphere 124 (2015) 83–91

[71] Aguilera et al, Biomonitoring of urinary metals in a population living in the vicinity of industrial sources: A comparison with the general population, Sci Total Environ (2008)

[72] Aguilera et al, Biomonitoring of urinary metals in a population living in the vicinity of industrial sources: A comparison with the general population, Sci Total Environ (2008)

[73] ZÚ Ústí nad Labem: Dílčí hodnocení zdravotního rizika obyvatel lokality Kutná Hora – Kaňk, 2015

[74] ZÚ Ústí nad Labem: Dílčí hodnocení zdravotního rizika obyvatel lokality Kutná Hora – Kaňk, 2015

[75] SZÚ: Systém monitorování zdravotního stavu ve vztahu k životnímu prostředí, Souhrnná zpráva 2005

When comparing the results of this study, significant levels of As can be observed in urine samples across the whole age spectrum of humans, as well as in individual age groups (e.g. 2-12 years). It is also possible to observe higher levels of As in our interest location compared to the results of biomonitoring performed in the Czech Republic, USA, Germany and studies in China, Spain, Nepal. It was also found that the 90% percentile for As in the location of interest was 37 μg/l, in comparison with the reference location which was almost a half lower (19.4 μg/l). The 90% percentile indicates the level of values that 90 percent of the set results are either equal to or below this value.

On the other hand, it should be noted that the values recorded in the location of interest do not reach the extreme values described by the literature in highly contaminated areas, where the main source of exposure is surface or groundwater with a high arsenic content. Arsenicosis (a multisystem disease caused by chronic exposure to high doses of arsenic, which involves cutaneous, neurological, cardiovascular, airway, kidney or liver disorders)[76] with levels of 46 μg of arsenic per liter of urine has been observed in Chinese rural areas where people have used open coal fires as heating [77].

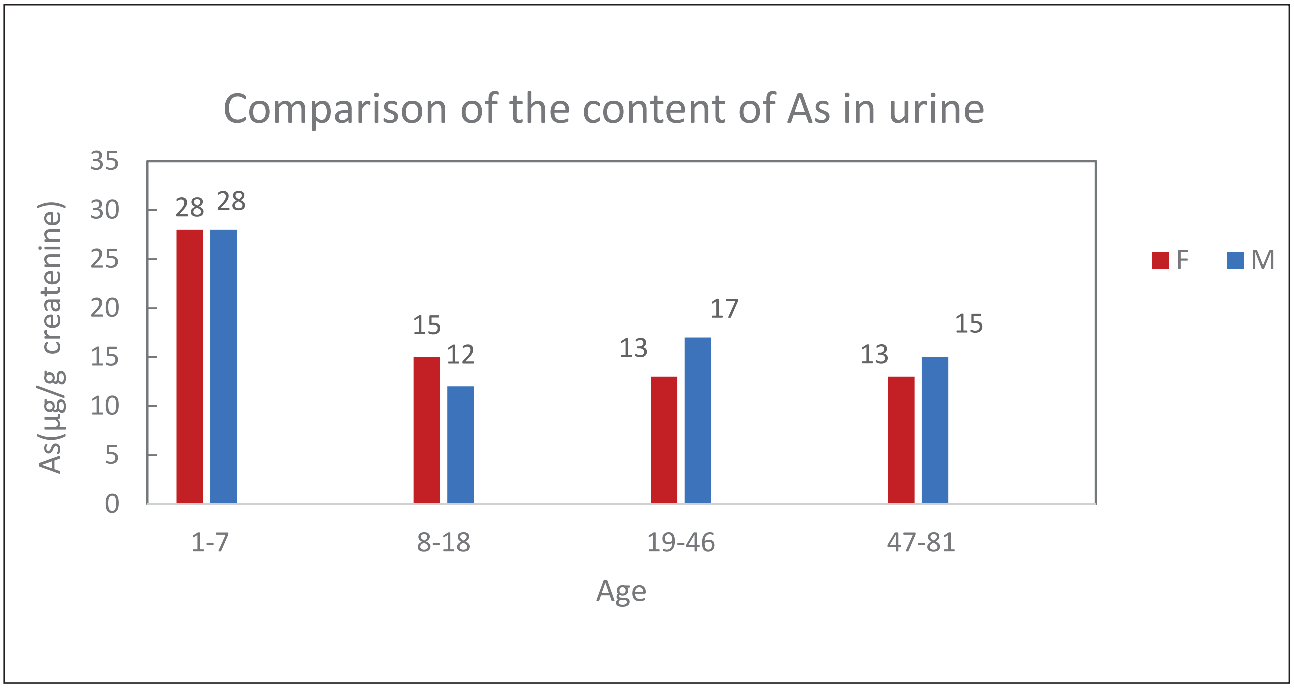
Residents of the municipalities of Pokr and Mets Ayrum are potentially exposed to arsenicoses, where in 6 samples the As values ranged from 39.6 to 97.44 μg arsenic per liter of urine, while these values were in the samples of both children (samples 16, 57, 58) and adult population in their reproductive age (samples 53, 56, 59). The maximum measured value of 97.44 μg arsenic per liter of urine found in a sample of a ten-year-old child (sample 58) is up to twice as high as the value reported in the literature.

The highest As values were found in preschool children (29.5 μg/g creatinine in girls samples and 25.0 μg/g creatinine in boys samples), which can be observed in Fig. 5, where the amount of As content is divided by age. Combined with the fact that 3 out of 5 samples that exceeded or approached the above-mentioned Czech exposure limit (0.05 mg/g creatinine), the results contribute to the considerable concern about the health risks of children in the region.

[76] Sengupta et al: Pathogenesis, clinical features and pathology of chronic arsenicosis. Indian J Dermatol Venereol Leprol. 2008; 74: 559-70.

[77] Zhang et al: Unventilated indoor coal-fired stoves in Guizhou China: Cellular and Genetic damage in villagers exposed to arsenic in food and air, Environmental Health Perspectives, 115: 653-658 (2007)

Figure 5 Comparison of the amount of As in the samples of urine from the interest location based on the age of participants



As part of the discussion regarding the obtained results, it is necessary to state that the groups monitored by us are relatively small. Therefore, it is necessary to approach them with some caution in terms of its significance. On the other hand, along with samples of urine, samples of nails and household dust were also taken for analysis. The results of laboratory analyses of these matrices will be available during further studies and may be an important guide for a more comprehensive assessment of arsenic exposure at the location of interest.

In the event of discovering high levels of arsenic in individual cases, broader investigation of the given family possibly accompanied with a detailed medical examination of individuals should be recommended.

If a connection between the high values of As found in urine and the contamination of household dust is confirmed, it should be appropriate to recommend measures to reduce the environmental exposure of the concerned population and to remediate the sources of environmental contamination in the location of interest.

↘ b. Cadmium

Urine cadmium concentrations recorded for this study at the site of interest in Armenia ranged from undetectable levels to 1.00 μg/g creatinine within the non-smoking population. On the contrary, the values in the control group were below the limit of detection (Table 2).

While stating the cadmium level in blood is used for the current exposure determination and it is possible to estimate the intake of Cd in recent months using this method, the determination of cadmium concentration in urine is mainly considered as an indicator of both total body exercise and total level of Cd accumulated in the body. The biological half-life of cadmium is very long and is estimated to be in the range of 15 to 30 years. Usual urinary cadmium levels for non-smokers range from 0.1 to 0.7 μg/g of creatinine but may be higher for smokers. In a study brought out by Swedish researchers, cadmium levels for non-smoking women and men were 0.27 and 0.18 μg/g of creatinine[78].

It was determined by our study that urinary cadmium levels were 0.7 μg/g of creatinine in a sample taken from Pokr Ayrum (Sample 52) and 1 μg/g creatinine from Metz Ayrum (Sample 14). While the highest concentrations do not exceed the values of HBM I and HBM II for the adult population, it is necessary to note that in two cases higher amounts of cadmium was detected in the female non-smoking population. Additionally, it can be noted that these values exceeded the cadmium values found in biomonitoring in the USA (Table 4).

Due to the difference between the values found in the samples taken at the site of interest and at the control site, it cannot be ruled out that there is a slightly higher environmental exposure to cadmium at the site of interest.

[78] OLSSON, Ing-Marie, et al. Cadmium in blood and urine--impact of sex, age, dietary intake, iron status, and former smoking--association of renal effects. Environmental health perspectives, 2002, 110.12: 1185-1190.

Table 4 Overview of cadmium values mentioned in the academic literature

Country	Arithmetic Mean (μg/g creatinine)	Geometric Mean (μg/g creatinine)	Median (μg/g creatinine)	Note	Reference
USA		0,181		Biomonitoring 1999-2000	79
USA		0,199		Biomonitoring 2001-2002	80
USA		0,210		Biomonitoring 2003-2004	81
USA		0,075		Biomonitoring 2001-2002	82
USA		0,090		Biomonitoring 2003-2004	83
Spain	0,56	0,37	0,32	Ria of Huelva	84
Spain	0,77	0,39	0,31	Andalusia	85
Spain	1,37	0,747	0,853	Ria of Huelva	86
CZ	0,29			Biomonitoring of children 2008	87

It will be possible to draw a more definite conclusion about possible health risks after evaluating other samples (nails and household dust).

In individual cases of findings of high concentrations of cadmium, further investigation within the given family and possible more detailed medical examination of specific persons should be recommended.

If the connection between the high levels found in urine and the contamination of household dust is confirmed, it will be appropriate to recommend measures to reduce the environmental exposure of the discussed population and to remediate the sources of environmental contamination in the location of interest.

79 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

80 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

81 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

82 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

83 CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

84 Aguilera et al, Biomonitoring of urinary metals in a population living in the vicinity of industrial sources: A comparison with the general population, Sci Total Environ (2008)

85 Aguilera et al, Biomonitoring of urinary metals in a population living in the vicinity of industrial sources: A comparison with the general population, Sci Total Environ (2008)

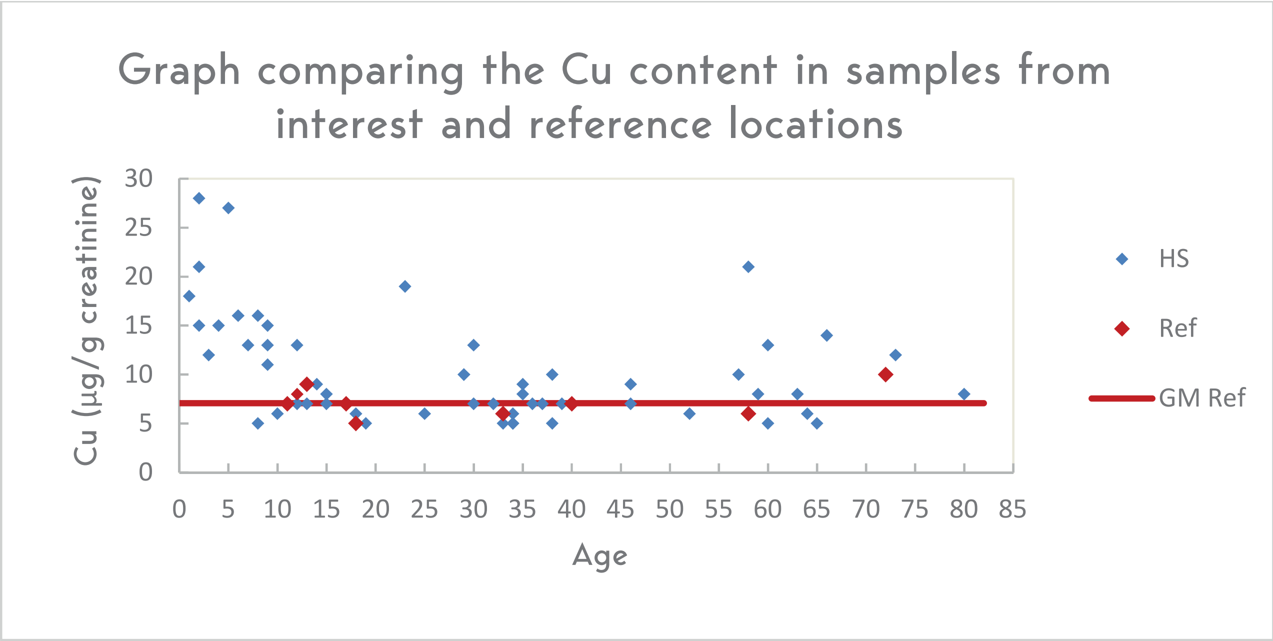
86 Molina-Villalba at al: Biomonitoring of arsenic, cadmium, lead, manganese and mercury in urine and hair of children living near mining and industrial areas, Chemosphere 124 (2015) 83–91

87 Beneš at al: Determination of Normal Concentration Levels of Cd, Pb, Hg, Cu, Zn and Se in Urine of the Population in the Czech Republic, Cent Eur J Public Health, 2002 Jun;10(1-2):3-5

↘ c. Copper

Out of all 73 urine samples, detectable values were found in 72 samples (Table 2). A detailed overview of the found Cu values is shown in Figure 6. The 90% percentile was also calculated, which set the values of 17.2 µg/g creatinine for the site of interest and 9.2 µg/g creatinine for the reference site.

Figure 6 Final overview of the Cu content in urine samples



Copper as an element is usually included in biomonitoring due to its biological significance, while the available values in the academic literature relate to the levels in whole blood, blood serum, hair or urine. Urinary copper concentrations usually range from 6 to 50 µg/g of creatinine [88]. In the samples analyzed in our study, the values of copper were in the range of 6 to 28 µg/g of creatinine, therefore no large deviations from the norm were observed. Additionally, the amount of Cu in the samples did not significantly differ from the values reported in the literature in Table 5.

[88] SZÚ: Zdravotní důsledky expozice lidského organismu toxickým látkám ze zevního prostředí (biologický monitoring), Odborná zpráva za rok 2009, Praha 2010

Table 5 Overview of the contents of Cu determined in this study and in the academic literature

Country	Arithmetic Mean (µg/g creatinine)	Geometric Mean (µg/g creatinine)	Median (µg/g creatinine)	Note	Ref
ARM-interest I	**10,38**	**9,26**	**8,0**		
ARM-control I	**7,77**	**7,08**	**7,00**		
Germany	8,88	6,93	6,7	Biomonitoring of the whole population	89
Spain Andalusia	11,69	8,39	8,62	Industrial area	90
Spain Andalusia	12,60	8,60	8,69	Control location	91
CZ			16 to 26	Biomonitoring, 4 cities 2009	92
CZ	16,2			Biomonitoring of children	93
CZ	10,6			Biomonitoring of adults	94

Figure 7 shows the distribution of copper content in urine among several age groups. Significantly and exponentially higher amounts of copper were determined in urine samples of preschool children (1 to 7 years). The difference in this case is due to their slower metabolism or more frequent ingestion of dust particles, soil, etc [95]. Additionally, the child's body may be more sensitive to the effects of copper as well. In 3 of 4 age categories, the Cu content in the urine of women was higher than the Cu content in the urine of men.

[89] Seifert et al: The German Environmental Survey 1990/92 (GerES II): reference concentrations of selected environmental pollutants in blood, urine, hair, house dost, drinking water and indoor air, Journal of Exposure Analysis and Environmental Epidemiology (2000) 10, 552-565

[90] Aguilera et al, Biomonitoring of urinary metals in a population living in the vicinity of industrial sources: A comparison with the general population, Sci Total Environ (2008)

[91] Aguilera et al, Biomonitoring of urinary metals in a population living in the vicinity of industrial sources: A comparison with the general population, Sci Total Environ (2008)

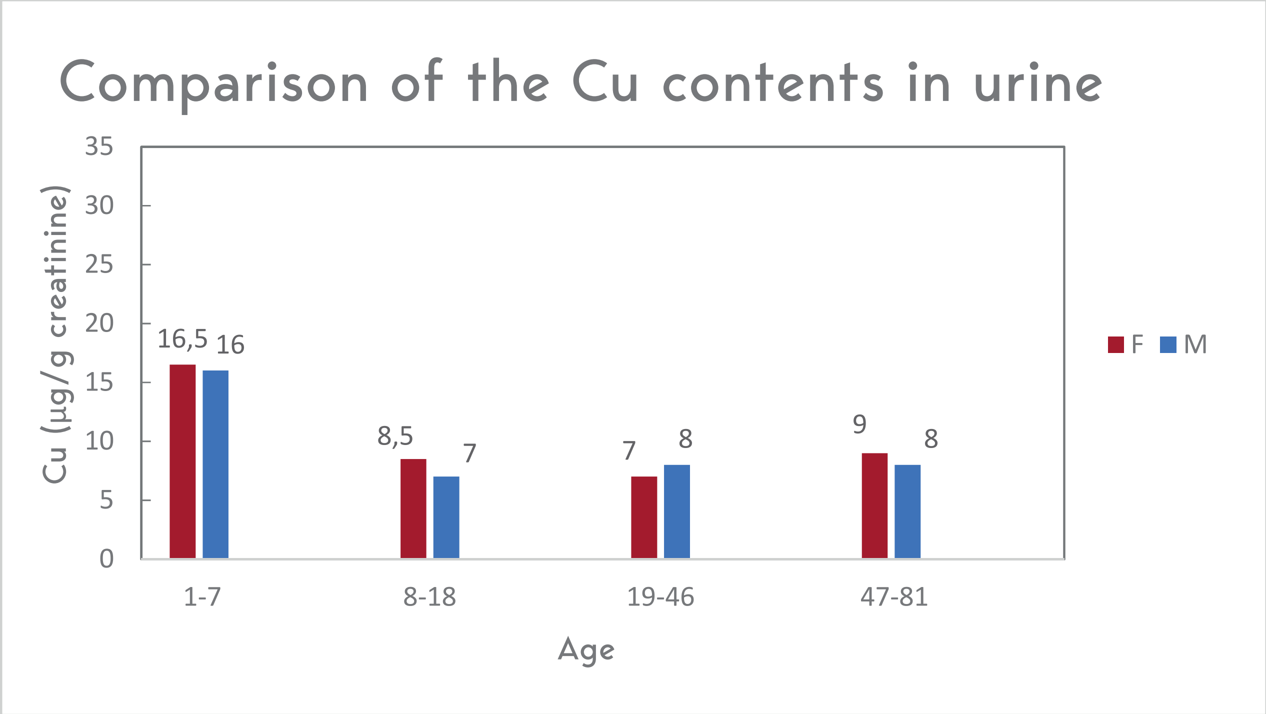
[92] SZÚ: Zdravotní důsledky expozice lidského organismu toxickým látkám ze zevního prostředí (biologický monitoring), Odborná zpráva za rok 2009, Praha 2010

[93] Beneš at al: Determination of Normal Concentration Levels of Cd, Pb, Hg, Cu, Zn and Se in Urine of the Population in the Czech republic, Cent Eur J Public Health, 2002 Jun;10(1-2):3-5

[94] Beneš at al: Determination of Normal Concentration Levels of Cd, Pb, Hg, Cu, Zn and Se in Urine of the Population in the Czech republic, Cent Eur J Public Health, 2002 Jun;10(1-2):3-5

[95] Moya, J., Phillips, L. A review of soil and dust ingestion studies for children. J Expo Sci Environ Epidemiol 24, 545–554 (2014). https://doi.org/10.1038/jes.2014.17

Figure 7 Comparison of the Cu contents in urine samples from the interest location, based on age



Despite the limited extent of sampling at the location of interest should be taken into account, it can be stated that the recorded levels of copper in the urine do not deviate from the values determined in the biomonitoring of the general population where an occupational exposure is not expected. However, a more precise conclusion about possible health threats will be possible after evaluating other samples (those of hair and household dust). These samples will be evaluated in later study.

↘ d. Lead

Considering the limited range of sampling in Armenia, it can be stated that the recorded levels of lead in urine are within the range of lead levels commonly found during biomonitoring of the population with no expected occupational exposure. When comparing with the available information from the academic literature, we can note a significant difference between the values found in this study and values from the US biomonitoring performed between 1999 and 2004.

In contrast, when comparing with the values from biomonitoring in the Czech Republic, the Pb concentrations from Armenia are lower (Table 6).

Table 6 Lead concentration in urine detected by different types of studies

Country	Arithmetic Mean (µg/g creatinine)	Geometric Mean (µg/g creatinine)	Median (µg/g creatinine)	Note	Reference
Armenia - interest location	**2,23**	**1,83**	**2,0**		
Armenia - control location	**1,50**	**1,41**	**1,50**		
USA		0,721		Biomonitoring 1999-2000	96
USA		0,639		Biomonitoring 2001-2002	97
USA		0,632		Biomonitoring 2003-2004	98
Czech Republic	1		1,1	Biomonitoring 2009	99
Czech Republic	4,8			Biomonitoring of children 2008	100
Czech Republic	3,3			Biomonitoring of adults 1996-2000	101

Of all samples, only 37 out of 65 had values exceeding the detection limit of the method of determination (Table 2). For this reason, a more definite conclusion about possible health risks can be made after evaluating other samples (e.g. blood, nails and household dust).

Exposure to lead can pose health risks especially to children, during both intrauterine development and in pre-school age - especially with regard to the developmental and neurobehavioral changes it can cause in the body. Monitoring of the level of lead in blood (plumbemia) is usually used for biomonitoring, while its adverse effects in the case of children have already been demonstrated at values around 100 µg/l.

[96] CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

[97] CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

[98] CDC: Fourth National Report on Human Exposure to Environmental Chemicals, 2009

[99] SZÚ: Zdravotní důsledky expozice lidského organismu toxickým látkám ze zevního prostředí (biologický monitoring), Odborná zpráva za rok 2009, Praha 2010

[100] Beneš at al: Determination of Normal Concentration Levels of Cd, Pb, Hg, Cu, Zn and Se in Urine of the Population in the Czech Republic, Cent Eur J Public Health, 2002 Jun;10(1-2):3-5

[101] Beneš at al: Determination of Normal Concentration Levels of Cd, Pb, Hg, Cu, Zn and Se in Urine of the Population in the Czech Republic, Cent Eur J Public Health, 2002 Jun;10(1-2):3-5

↘ e. Nickel

The amount of nickel in the urine samples taken at the location of interest in Armenia and from the control group was below the limit of detection (Table 2).

Based on the results being below the detection levels, it can be assumed that the environment in the location of interest is likely not a significant source of nickel exposure. However, a more definite conclusion regarding possible health risks will be possible after the evaluation of other samples (e.g. nails, blood or household dust).

5. Conclusion

In this study, urine samples were analyzed for the presence of heavy metals, specifically As, Cd, Cu, Ni and Pb from the Akhtala community in the Lori Province. Sampling took place in the communities of Mets Ayrum, Chochkan, Pokr Ayrum where an estimated 2,700 people live. Analyses of urine samples taken from residents living in the mining region where copper ore is processed confirm the hypothesis of increased exposure of the population to arsenic compared to people living in the non-mining Tavush Province. The analyses also confirm the higher exposure of the child population compared to the adult population.

In this study, the presence of arsenic poses the greatest risks. Residents of mining areas are on average 20% more burdened with the negative health effects of arsenic than in the reference municipality of Achajur (Tavush Province). Additionally, the median indicates an even higher burden (by 40%) in the location of interest than in the reference location. A total of 4 samples approached or exceeded the Czech exposure limit (50 μg/g of creatinine), of which 3 samples belonged to individuals from the child population (up to 12 years). Our results point to a higher burden on the child population compared to adults, which confirms earlier findings from a theoretical risk assessment conducted in 2019 using the RISC software, which assumed a higher health risk for children compared to adults. Arsenic is a human carcinogen, it slows fetal development, affects the children's development, the nervous system and causes damage to the function of the heart and blood vessels.

Results from the residents of mining areas indicate they are burdened with cadmium in higher rates than residents from control locations. The cadmium levels were already confirmed as higher risks for this region in a 2019 study using RISC software. Cadmium is a carcinogenic element that damages the kidneys, nervous system or the hormonal system.

Only non-smokers participated in this study, therefore higher levels of heavy metal are not associated with active smoking.

The presence of copper and lead in urine samples was detected in smaller amounts. However, it was revealed that the urine of the population living in the mining area is also more burdened with copper than in the control location and higher levels of copper were also detected in samples from preschool children living in the location of interest. Although it is a biogenic element, long-term higher exposure can cause liver damage and neurological damage.

The results of our screening investigation, especially regarding the levels of arsenic (and partially also cadmium), require increased attention and point to the need to verify them through further examination of other human tissues. The first step in this direction will be a laboratory analysis of already taken samples of nails and dust from households.

6. Annex

Table 7 Overview of the urine samples taken from the interest and reference locations (excluded samples are highlighted red)

Sample number	Sex	Age	Location
1	F	66	Mets Ayrum
2	M	3	Mets Ayrum
3	M	5	Mets Ayrum
4	M	38	Mets Ayrum
5	**F**	**2**	**Mets Ayrum**
6	F	35	Mets Ayrum
7	M	46	Mets Ayrum
8	F	39	Mets Ayrum
9	M	19	Mets Ayrum
10	M	18	Mets Ayrum
11	F	12	Mets Ayrum
12	F	23	Mets Ayrum
13	**M**	**1**	**Mets Ayrum**
14	F	57	Mets Ayrum
15	M	63	Mets Ayrum
16	M	6	Mets Ayrum
17	F	9	Mets Ayrum
18	F	29	Mets Ayrum
19	**M**	**1**	**Mets Ayrum**
20	M	8	Mets Ayrum
21	F	14	Mets Ayrum
22	F	35	Mets Ayrum
23	M	9	Mets Ayrum
24	**F**	**4**	**Mets Ayrum**
25	F	80	Mets Ayrum
26	F	30	Mets Ayrum
27	F	73	Mets Ayrum
28	F	9	Mets Ayrum
29	F	2	Mets Ayrum
30	**F**	**83**	**Mets Ayrum**
31	F	25	Mets Ayrum
32	**M**	**0,3**	**Mets Ayrum**
33	M	4	Mets Ayrum
34	F	2	Mets Ayrum

35	M	33	Mets Ayrum
36	F	37	Mets Ayrum
37	M	15	Mets Ayrum
38	F	12	Mets Ayrum
39	F	64	Mets Ayrum
40	F	58	Mets Ayrum
41	F	46	Mets Ayrum
42	M	32	Chochkan
43	F	58	Chochkan
44	**M**	**52**	**Chochkan**
45	F	46	Chochkan
46	M	60	Chochkan
47	F	59	Chochkan
48	F	34	Chochkan
49	M	1	Chochkan
50	F	29	Chochkan
51	F	8	Chochkan
52	F	60	Pokr Ayrum
53	M	34	Pokr Ayrum
54	F	30	Pokr Ayrum
55	M	2	Pokr Ayrum
56	M	38	Pokr Ayrum
57	F	13	Pokr Ayrum
58	M	10	Pokr Ayrum
59	F	34	Pokr Ayrum
60	**F**	**81**	**Achajur**
61	F	58	Achajur
62	F	33	Achajur
63	M	11	Achajur
64	F	13	Achajur
65	F	72	Achajur
66	F	40	Achajur
67	F	18	Achajur
68	F	17	Achajur
69	M	12	Achajur
70	F	65	Achajur
71	F	36	Pokr Ayrum
72	M	15	Pokr Ayrum
73	F	7	Pokr Ayrum

Table 8 Overview of the urine results taken from the interest and reference locations (excluded samples are highlighted red)

Sample number	Creatinine (g/l)	As (mg/g creatinine)	Cd (mg/g creatinine)	Cu (mg/g creatinine)	Ni (mg/g creatinine)	Pb (mg/g creatinine)
1	0,73	0,020	0,0005	0,014	<0,007	<0,001
2	0,43	0,038	<0,0005	0,012	<0,012	<0,002
3	0,43	0,027	<0,0005	0,027	<0,012	<0,002
4	0,95	0,010	<0,0002	0,010	<0,005	<0,001
5	**0,13**	**<0,015**	**<0,0015**	**0,030**	**<0,039**	**0,008**
6	0,38	0,013	<0,0005	0,009	<0,013	<0,003
7	0,83	0,027	<0,0002	<0,004	<0,006	0,002
8	1,88	0,018	0,0002	0,007	<0,003	0,001
9	0,73	0,018	<0,0003	0,005	<0,007	<0,001
10	1,80	0,008	<0,0001	0,006	<0,003	0,001
11	0,43	0,044	<0,0005	0,013	<0,012	<0,002
12	1,33	0,013	0,0003	0,019	<0,004	<0,001
13	**0,08**	**0,026**	**<0,0003**	**0,039**	**<0,063**	**<0,013**
14	1,90	0,017	0,0010	0,010	<0,003	0,002
15	1,78	0,012	0,0002	0,008	<0,003	0,001
16	1,45	0,028	<0,0001	0,016	<0,003	0,003
17	0,78	0,021	<0,0003	0,013	<0,006	0,002
18	0,98	0,036	0,0002	0,010	<0,005	<0,001
19	**0,20**	**0,016**	**<0,0010**	**0,024**	**<0,025**	**<0,005**
20	2,23	0,012	0,0002	0,016	<0,002	0,001
21	1,83	0,007	<0,0001	0,009	<0,003	0,001
22	1,70	0,006	0,0003	0,008	<0,003	0,001
23	0,70	0,011	<0,0003	0,011	<0,007	0,002
24	**0,05**	**<0,040**	**<0,0040**	**<0,060**	**<0,100**	**<0,020**
25	1,10	0,012	0,0003	0,008	<0,005	<0,001
26	0,48	0,009	<0,0004	0,007	<0,010	<0,002
27	0,65	0,010	0,0003	0,012	<0,008	<0,002
28	0,38	0,017	<0,0005	0,015	<0,013	<0,003
29	0,43	0,043	<0,0005	0,028	<0,012	<0,002
30	**0,18**	**0,017**	**<0,0011**	**<0,017**	**<0,028**	**<0,006**
31	0,58	0,022	<0,0003	0,006	<0,009	<0,002
32	**0,10**	**<0,020**	**<0,0020**	**<0,030**	**<0,050**	**<0,010**
33	1,05	0,024	<0,0002	0,015	<0,005	0,002
34	0,33	0,031	<0,0006	0,021	<0,015	<0,003
35	1,65	0,013	<0,0001	0,005	<0,003	<0,001

36	1,35	0,008	<0,0001	0,007	<0,004	0,001
37	1,73	0,011	<0,0001	0,007	<0,003	0,002
38	0,75	0,013	<0,0003	0,007	<0,007	0,008
39	1,60	0,013	0,0002	0,006	<0,003	0,001
40	0,53	0,013	<0,0004	<0,006	<0,009	<0,002
41	0,55	0,027	<0,0004	0,007	<0,009	<0,002
42	1,60	0,013	0,0001	0,007	<0,003	0,002
43	2,05	0,015	0,0004	0,021	<0,002	0,002
44	**3,81**	**0,007**	**0,0003**	**0,006**	**<0,001**	**0,005**
45	0,68	0,011	0,0004	0,009	<0,007	<0,002
46	1,63	0,017	0,0004	0,005	<0,003	0,001
47	0,58	0,016	<0,0003	0,008	<0,009	0,004
48	0,88	0,022	<0,0002	0,006	<0,006	0,002
49	0,60	0,023	<0,0003	0,018	<0,008	0,004
50	1,25	0,017	<0,0002	0,010	<0,004	0,002
51	0,93	0,013	<0,0002	0,005	<0,005	0,001
52	0,88	0,044	0,0007	0,013	<0,006	0,002
53	1,55	0,041	0,0001	0,005	<0,003	0,001
54	1,38	0,011	0,0003	0,013	<0,004	<0,001
55	0,55	0,032	<0,0007	0,015	<0,009	0,003
56	2,25	0,030	0,0002	0,005	<0,002	0,001
57	2,20	0,018	<0,0001	0,007	<0,002	0,001
58	1,68	0,058	<0,0001	0,006	<0,003	0,002
59	1,73	0,031	<0,0001	0,005	<0,003	0,002
60	**0,28**	**0,012**	**<0,0007**	**<0,011**	**<0,018**	**<0,004**
61	0,73	0,008	<0,0003	0,006	<0,007	<0,001
62	1,65	0,023	0,0003	0,006	<0,003	0,001
63	0,43	0,009	<0,0005	0,007	<0,012	<0,002
64	0,45	0,010	<0,0004	0,009	<0,011	<0,002
65	0,48	0,020	<0,0004	0,010	<0,010	<0,002
66	0,75	0,012	<0,0003	0,007	<0,007	0,002
67	1,75	0,011	<0,0001	0,005	<0,003	<0,001
68	0,75	0,014	<0,0003	0,007	<0,007	<0,001
69	0,50	0,008	<0,0004	0,008	<0,010	<0,002
70	0,60	0,015	0,0006	0,005	<0,008	<0,002
72	0,98	0,009	<0,0002	0,008	<0,005	0,002
73	0,95	0,011	<0,0002	0,013	<0,005	0,002

Figure 8 Nahatak tailing pond

Figure 9 Nahatak tailing pond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