

DETERMINATIONS AND INTERPRETATIONS OF THE CONTENTS OF HEAVY METALS FROM FOOD AND WATER TEST SAMPLES FROM LOCATIONS NEAR THE MINING PERIMETERS OF BAIJA MARE AND BĂIUȚ AREA

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Abstract: *The paper presents the level of heavy metal contamination in the areas located in the vicinity of the mining perimeters in Baia Mare and Băiuț and the risk of their expansion in the future. Heavy metal contamination was analysed on water samples from wells, plants and milk from animals that consumed water from polluted streams.*

Keywords: *heavy metals, sample, contamination, mining perimeters*

1. Introduction

The monitoring carried out in the recent years on the mining perimeters in Maramureș County revealed that the pollution sources are becoming more and more reactive, proving the amplifying effect of acid drainage. Also, new sources that release pollutants in the environment have been identified, either by destroying some dams or underground diversions, or by the untimely release of the precipitate accumulated on the mine drainage routes. The amount of toxic material released into rivers is constantly increasing, leading to the contamination of some areas in continuous expansion.

The impact of heavy metals on the environment and the health of the population has been studied in detail and published in numerous specialized articles. For Baia Mare area, many studies, projects, grants have been carried out, being financed by both national and international authorities [1], [2], [3], [4], [5], [6], [7], [8]. Baia Mare has a long history of heavy metal and toxic gas pollution, being the subject of study and interest for the media, NGOs, various organizations, etc. All these publications referred to the mining activity, but mainly to the metallurgical activity, being considered the main source of pollution. The paper presents the level of heavy metal contamination in the areas located near the mining perimeters of Baia Mare and Băiuț and the risk of their expansion.

2. Sampling and determination of heavy metals in Baia Mare and Băiuț area

The paper [8] presents the results of analyzes on water and sediment samples in the vicinity of mining perimeters (emissaries that are directly related to them). The aim of this paper is to assess the level of contamination of groundwater in the area of influence of mining perimeters and possibly contaminated food. With this in view, two types of locations were chosen for study. The first location is next to Tăuții de Sus tailings pond, which is apparently not in the direction of the groundwater flow. In this area, the metal content of a well located at a distance of 87 m from the pond was determined with the groundwater level in the hay at a depth of 5 m. The analyzes were performed in the laboratory of SC Vital SA.

The paper highlighted the effects of bioaccumulation of heavy metals in the food chain. In accordance, food samples (vegetables, water and milk) were taken from the vicinity of Baia Mare and from Poiana Botizei (mountain area). If the contamination levels were predictable for the area of Baia Mare, the dose of milk

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contamination in Poiana Botizei remains surprising. Goat, sheep and cow's milk were taken from this area. The animals graze in an isolated, mountainous area, they drink water from springs and streams (clean water), but during the summer they also drink water from Poieni and Cizma brooks, which cross the locality. This stream is heavily contaminated, as evidenced by the analyses of water and sediment. Milk samples showed alarming concentrations of heavy metals, especially lead, in excess of tens of times. These analyses demonstrate the impact of the irresponsible closure of Băiuț mining perimeter (respectively Cizma) with the destruction of the aquatic environment, food contamination and finally the contamination of the uninformed population on the risks to which it is exposed. More studies are needed, including information, but the most important thing is to find urgent technical solutions to stop the pollution. The reasonable solution involves the exploitation of the mineral resource from Cizma perimeter and the backfilling of the exploited space with minerals with a buffering role (limestone, zeolites) located in the area. The "concern" of the authorities so far has been to set up a protected area in the former mining perimeter, which, instead of solving the problems, has made the situation even more complicated.

Table 1 presents the analyses of the results obtained on the water and food samples from the studied locations. For each sample, a set of analyses was performed for several metals considered to be at risk of accumulation. Only metals that could be determined within the measuring limits of the devices were shown in the table (metals below the detection limit were not shown in the table).

Table 1. Values of heavy metals determined from water and food samples

No.	Food / water sampling location	U.M.	Metal	Value obtained	Maximum allowed value
1	Fountain near Tăuții de Sus pond	mg/l	nickel	0,066	0,02
			manganese	0,518	0,05
2	Land next to Tăuții de Sus pond (onion)	mg/kg	copper	0,25	*
			zinc	3,17	*
3	Land next to Tăuții de Sus pond (mixture of lettuce leaves and celery leaves)	mg/kg	lead	0,32	*
			cadmium	0,12	*
			copper	0,40	*
			zinc	8,04	*
4	Land next to Tăuții de Sus (salted goat cheese)	mg/kg	arsenic	0,07	*
			zinc	10,8	*
5	Downstream pond Leurda - Băiuț (dried onion)	mg/kg	arsenic	0,05	*
			nickel	0,03	*
			copper	0,41	*
			zinc	1,28	*
6	Downstream pond Leurda - Băiuț (garlic)	mg/kg	manganese	1,61	*
			copper	2,31	*
			zinc	4,31	*
7	Downstream Central Pond - Tăuții de Sus (dried onions)	mg/kg	manganese	3,48	*
			nickel	0,36	*
			manganese	1,20	*
8	Downstream Central Pond - Tăuții de Sus (hay water)	μg/l	lead	0,05	*
			nickel	1,4	20
9	Poiana Botizei (goat's milk)	mg/kg	manganese	81	50
			lead	0,5	*
10	Poiana Botizei (cow's milk)	mg/kg	lead	0,25	*
			manganese	0,08	*
11	Poiana Botizei (sheep's milk)	mg/kg	lead	0,47	*
			manganese	0,15	*
			lead	1,37	*

Obs. * the values interpreted in point 2

3. Interpretations of heavy metal contents in relation to the legislation in force

The values obtained were compared with the values settled by Law no. 458/2002 on drinking water quality [10]. By relating the values determined in the laboratory to the values in the law, exceeding values were obtained for manganese (10.36 times) and for nickel (3.3 times) (in the case of sample 1, determinations were made in the laboratory of Vital SA).

A sample of a mixture of lettuce leaves and celery leaves (sample 3) and a goat cheese sample (sample 4) were taken from this location. In this area there is a goat farm that grazes near the pond. The cheese was preserved in brine. The determinations were performed in the ICIA laboratory - the branch of the Research Institute for Analytical Instrumentation in Cluj-Napoca.

The second location is downstream the mining perimeters: downstream Leurda - Băiuț pond; downstream Central - Tăuții de Sus / Baia Mare pond and downstream Cizma mining perimeter in Poiana Botizei locality. A sample of garlic (sample 6) and a sample of dried onion (sample 5) were taken from Leurda pond downstream location.

A goat's milk sample was taken from Poiana Botizei (sample 9); cow's milk sample (sample 10); sampled sheep's milk (sample 11).

For the milk samples from Poiana Botizei (cow, goat and sheep) there is evidence of contamination with heavy metals, even if they are fed with grass from the mountain area, but are watered during the summer from tributaries of Poiana Botizei brook (uncontaminated) and sporadically from the Poiana Botizei brook (with Cizma tributary, heavily contaminated). In the case of cow's milk, it should be noted that the cows were given in the last 5 months (winter months) only spring water, uncontaminated water. In this way, the influence of food contamination in an emissary can be noticed even if the animals' water drinking occurs only at certain times of the year and not permanently. From discussions with farmers, they said that some animals sometimes refuse water from the stream. The level of contamination of the stream is so strong that there are no signs of life in it. It was also found that these farmers are not informed about the risks they are exposed to by using water contaminated by animals.

Regarding the risk of consuming these contaminated products, reports have been made to different legislations: Romanian, European, American, IARC (International Agency for Research on Cancer) and WHO. [13], [14]. The common principle of these legislations is given by the level of contamination accumulated over a certain period of time expressed in units of metal / kg body. In order to distinguish separately the risk posed by heavy metals, the problem is complicated by the addition of contaminants of other products related to the eating habits of those persons. For example, the literature specifies the contamination of rice with cadmium. If a person constantly consumes rice to which are added the contaminated products from the mining areas, the level of risk is easily reached. A calculation made for the situation of people who grow their salad in Tăuții de Sus (sampling area) shows that an average consumption of 1 kg of salad/week reaches a level of major risk of cancer (strictly from salad).

In the case of the milk taken from Poiana Botizei in which the lead content was 1.37 mg / kg dry matter, respectively 1370 micrograms / kg, while assuming a consumption of one kg of cheese (produced from this milk) for a child of 20 kg during two weeks, it determined the accumulation in the body, strictly from this product, of 34.25 micrograms, exceeding the maximum value allowed by the WHO of 25 micrograms / kg body /week. If a consumption of 1 kg / week is reached, 68.5 micrograms / kg body weight is accumulated. These calculations are performed on the assumption that the person concerned would have no other source of exposure, including remanence.

In the case of the salad mixture, at a consumption of 1 kg / week for a child of 20 kg, the value of 6 micrograms / kg of cadmium body is reached, and in two weeks, 12 micrograms / kg of body is accumulated. According to the WHO, the limit is 7 micrograms / kg body weight / week of cadmium.

By reference to Commission Regulation (EU) 2015/1005 of 25th of June 2015, amending Regulation (EC) No. 1831/2006 as regards the maximum levels of lead in certain foods, in which the values for milk are 0.02 mg / kg, the exceeding value, in the case of the goat milk samples (Poiana Botizei), is 12.5 times higher, for sheep's milk 68.5 times, and for cow's milk 23.5 times. Another way of assessing the risk of lead consumption given by the WHO is 0.5 micrograms / kg body weight / day which leads to an excess of 8.56 times in the case of consumption of 250 grams of cheese by an adult with a mass of 80 kg (assuming the only source of lead contamination). These scenarios show the risks to which the population in these areas is exposed through consuming contaminated products and water. [12]

By reference to Regulation (EU) no. 488/2014 of the Commission of 12th of May 2014, amending Regulation (EC) no. 1831/2006, as regards maximum cadmium levels in foodstuffs, the limit set for leafy vegetables is 0.05 milligrams / kg, which is 2.4 times the case for lettuce and celery leaves for Tăuții sample and 3.2 times lead (with a limit of 0.1 mg / kg). [12]

4. Conclusions

This paper highlights the new context of pollution in Maramureș County generated by an irresponsible action on how to close the mining perimeters. These closure activities have been described and detailed in previous works [8], which pointed out the new problem given by the magnitude of the phenomenon of release of ever-increasing quantities through another transport vector, namely mine waters through acid drainage. Mine water discharges are limited and variable (depending on the level of precipitation with relatively constant flows), to which are added discharges with uncontrollable and very high flows, called untimely discharges. If studies to date have shown high levels of heavy metals, especially in soils and restricted areas, in the future the risks to the environmental impact of heavy metals will be posed by the expansion of these areas through the transport of pollutants by contaminated rivers. Most of the studies were performed for Baia Mare and the belonging localities for which the contamination levels were shown, but the new studies must be directed on the widest possible areas and in close relation with the contaminated rivers. For example, discharges from Băiuț - Căvnic area have contaminated Căvnic and Lăpuș rivers in important parts, turning them into dead rivers. The two rivers intersect, causing contamination of Someș River. In addition to the two rivers, Săsar River and numerous other streams that drain the eastern part of Maramureș mining basin (Săsar, Nistru, Băița, Ilba perimeter) contribute to the contamination of Someș River. Another area with the same environmental impact is located in the north of the county, in Borșa mining perimeter, from which two important rivers are contaminated: Cîsla and Vaser, which reach Vișeu river and later the Tisza.

The intake of heavy metals in water and soil contributes to their bioaccumulation in the food chain. On the alignment of Lăpuș and Someș, the main activity of the population is agriculture and fishing, which endangers their health, including the people who buy their products. In this context, time will not lead to a decrease in pollution despite the closure of mining, on the contrary, it will lead to an increase. Due to the complexity of the mineralization in the vein area, the multitude of heavy metals leads to a synergistic effect, further amplifying the impact.

References

- [1] **Coroian Aurelia, Miresan Vioara, Cocan Daniel, Răducu Camelia, Longodar Adina Lia, Pop Alexandra, Feher Grațian, Andronie Luisa, Marchis Zamfir**, 2017
Physical-chemical parameters and the level of heavy metals in cow milk in the Baia Mare area, Banat's Journal of Biotechnology
- [2] **Roba Carmen Andreea, Băciu Călin, Rosu Cristina, Pîstea Ioana Cristina**, 2015
Heavy metals in soils from Baia Mare mining impacted area (Romania) and their bioavailability, Geophysical Research Abstracts, Volume 17 / 2015
- [3] **Big Cristina-Laura, Lăcătușu Radu, Floarea Damian**, 2012
Heavy metals in soil-plant system around Baia Mare, Carpathian Journal of Earth and Environmental Sciences
- [4] **Mihali Cristina, Oprea Gabriela, Michnea Angela, Jelea Stela-Gabriela, Jelea Marian, Man Călin, Șenilă Marin, Grigor Laura**, 2013
Assessment of heavy metals content and pollution level in soil and plants in Baia Mare area, NW Romania, Carpathian Journal of Earth and Environmental Sciences, Volume 8, Issue 2 / 2013
- [5] **Bora Florin Dumitru, Bunea Claudiu Ioan, Chira Romeo, Bunea Andreea**, 2020
Assessment of the Quality of polluted Areas in Northwest Romania Based on the Content of Elements in Different Organs of Grapevine, MDPI Molecules
- [6] **Boros Melania-Nicoleta, Smical Irina, Micle Valer, Lichtscheidl-Schultz Irene**, 2015
Heavy metals pollutions of soils from Baia Mare – case study: Cuprom Industrial Area, Environmental Engineering, Volume IV / 2015
- [7] **Miclean Mirela, Cadar Oana**, 2021
Dietary Metals (Pb, Cu, Cd, Zn) Exposure and Associated Health Risks in Baia Mare Area, Northwestern Romania, Journal of Biomedical Research
- [8] **Bud A.**, 2022
Determinations and interpretations of heavy metal analysis in the sediments and water of Căvnic and Lăpuș rivers, Revista Minelor, nr. 1 / 2022

[9] ***

NTPA 001

[10] ***

Law no. 458/2002 regarding the quality of drinkable water

[11] ***

EU Regulation no. 488 / 2014 of the E.C. from 12th May 2014, modifying the E.C. Regulation no. 188 / 2006 regarding the maximum admissible levels of Cadmium from aliments.

[12] ***

EU Regulation no. 1005 / 2015 of the E.C. from 25th June 2015, modifying the E.C. Regulation no. 188 / 2006 regarding the maximum admissible levels of Lead from various aliments.

[13] **The National Institute of Public Health, 2020**

Informative Guide regarding the new Romanian legislation

[14] **International Agency for Research on Cancer, World Health Organization, 2020**

IARC Monographs on the evaluations of carcinogenic risks to human, Arsenic, metals, fibers, and dusts, A review of carcinogens, Volume 100 C



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