Research Article

Evaluation of the Concentration of Heavy Metals in the Waters and Soil Around the Kishnicë Landfill

Islam Krasniqi[1], Skender Demaku[2], Ilir Shehu[1*]

[1]University of Pristina "Hasan Prishtina", Faculty of Education, str. "George Bush" Pristina, Kosovo.

[2]University of Pristina "Hasan Prishtina", Faculty of Mathematical and Natural Sciences, Dept of Chemistry, str. Pristina, Kosovo.

[1*]University of Pristina "Hasan Prishtina", Faculty of Mathematical and Natural Sciences, Dept of Chemistry, str. Pristina, Kosovo.

***Corresponding author's E-mail:** ilirishehu10@hotmail.com

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ABSTRACT

Waste after the flotation process discharged in the landfill near the kishnica flotation process. Direct effects of these residues appear in the lands around the landfill as well as surface and underground waters. The concentration of heavy metals has been researched in the years 2004 and 2010. We have researched the level of concentration of heavy metals in 2016, by AAS method, to see the level of their accumulation in soils around the landfill. The results show an increase in the value of the concentration of heavy metals in the soil as well as in water bodies. Given that the flotation factory in Kishnicë is active and repeatedly deposit residue in the area and the level of concentration of the metals increased, if we consider that half-time of these metals is very long and heavy metals bioaccumulate are difficulties. In this work we have done research on concentration of heavy metals in the same sampling points that which we have also researched in 2004 and 2010, to see that if we have increase or decrease the concentration of heavy metals in the area. Obtained results show that we have an increase in concentration. Therefore it is the responsibility of governing bodies to think seriously about the environment in this area.

Keywords: Heavy metals, waste, flotation process, water, soil, Kishnica.

INTRODUCTION

Although the process of production from mines in Kosovo is not very intensive, wastes which have been before and those which are now stored, directly affecting pollution.

Production from mining is an economic importance for development of Kosova. The mining in Kishnica is a part of industrial complex of Trepça which are located in the northeastern part of Kosovo, near of capital city Prishtina.

Mines produce large amounts of waste because the ore is only a small fraction of the total volume of the mined material[1].

The European directives, classified with annex the disposal operations as D1 Deposit into or on to land (e.g. landfill, etc.) and D2 Land treatment (e.g. biodegradation of liquid or sludgy discards in soils, etc.)[2]. Recent years flotation factory at Kishnica works with added capacity compared with year 2004 and in the 2016 the capacity are in the same level.

This mining with her activity gain a considerable amount of residue that remains after the flotation process of the minerals. Generally, the following two types of mine effluents persist:[1, 4-5]

1. Effluents originating from deep mines, which are neutral or mildly alkaline, and systematically segregated according to salt content. Effluents possessing low concentrations of salt are utilized as industrial water, whilst those with high salt content are collected separately and disposed of in an orderly, and planned, manner.

2. Effluent originating from open cut operations. Sulphur often persists within these discharges in the form of pyrites. During leaching and extraction, the following chemical reactions take place:

$$2\,FeS_2 + 7O_2 + H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

$$4Fe^{2+} + +O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

The reaction velocity of the oxidation process depends on pH, concentration of oxygen, concentration of FeS_2, and the presence of chemoautotrophic microorganisms oxidising Fe^{2+} to Fe^{3+} [3,4,5].

This mining activity causes pollution in water and land around it, because in the composition of waste after the flotation process, participate heavy metals Pb, Zn, Cu and Cd in form of inorganic compounds.

Waste waters deriving from ore processing plants are contaminated with: Insoluble substances, predominantly waste sludge (finely ground waste rock).

The concentrations of these solids are usually within the range of 20–300 g/L. Soluble substances, which are extracted from the ore (heavy metals, sulphates) Chemical used in the flotation process[6].

Heavy metals are not biodegradable and are involved in biogeochemical cycles by which they are concentrated in sediment and biota[7].

Purpose of this research work has been the level concentration of heavy metals from landfill waste before and after coverage with soil and mining activity in Kishnica in pollution of water and soil around mining until 2016.

MATERIALS AND METHODS

In Figure 1, are shown the position of samples (sampling points) for water, waste after the flotation process, and soil. With blue color, we show the five positions of samples taken for water. With red color we are present three positions of samples for waste after the flotation process in landfill in Kishnica, and green color are used to show the position of samples taken for soil.

Two vertical arrows indicate the position of landfills wastes and horizontal arrow indicate Badovci Lake.

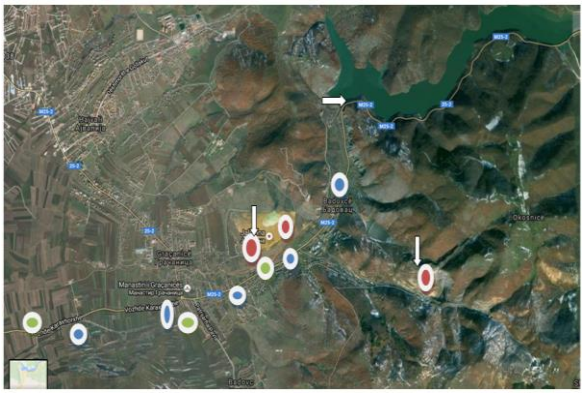

Figure 1: Presentation of the Sample Positions (Sampling Places) taken for the Analysis.

Landfill Waste After the Flotation Process Analyzing

To analyze the heavy metals in landfill waste after the flotation process, we took 3-5 kg of landfill waste in three different places. First samples we took in landfill waste in the north site, second samples we took in front of "Flotation Factory". Third sample we took in the south site of landfill waste. From these samples we have prepared the representative samples for the analysis. First we have mixed and homogenized the samples and then we have separate in four part about 1 kg. This amount of sample we have mixed and pressed in pestle, then we used separator with 100 to 200 mesh.

Soil Analyzing

We took also four different samples of soil. First samples we took in area with low influence of landfill waste. In football area was taken second samples. Third samples we took between landfill waste and Graçanica town in agricultural area and fourth samples of soil was taken in agricultural area one kilometer away from Graçanica. The samples were dried in 105 °C till constant mass.

Water Analyzing

Water for the analysis was taken on the river Graçanka and in discharge tube of flotation factory. First sample was taken in Graçanka River near the dam of Badovci Lake; second sample we took in the discharge tube of flotation factory, third samples was taken in Graçanka River 300 m after drainage of discharge tube. Fourth sample was taken at the beginning of the town of Graçanica. In the river Graçanka, one kilometer from Graçanica town we took sample number five. Water samples were taken in polietilen bottles and HNO_3 was used to conserve samples. Then samples we keep in the temperature of 4^{o}C till we have analyzed. Water was first evaporating till 10 ml then we have acidified with 1 ml of HCl.

General Treatment of Landfill Waste After the Flotation Process and Soil Samples

All these samples we have to bring in solution form before we have analyzed. To do that, for soil and landfill waste we used mixture of perchloric acid and nitric acid in the ratio 1:4. We took 0.25 g of dried sample then we dissolved with 10 ml of the mixture of perchloric acid and nitric acid 1:4. Samples are evaporated in sand bath till dry. Then the residue was treated with 10 ml HCl 1M till 100ml. The silicates which were not dissolved, we have removed by filtration.

RESULTS AND DISCUSSION

Our results we give in table and graphical form. Results are given as arithmetic average value of analyzed samples. In five different places of river Graçanka we have determined the concentration of heavy metals (Pb, Zn, Cu, and Cd), also we have determined heavy metals in four places of soil and three places of landfill waste after flotation process.

All samples were taken at July 2016 in the same sample places which are taken at July of year 2004 and year of 2010.

Landfill waste samples were taken in the area with high indication of pollution, notably in front of flotation factory. In those three samples, we found that the concentration of heavy metals were: Pb 4.480 at 2004, 11.150 at 2010 and 12.12 mg/kg at 2016; Zn 2.900at 2004,8.700 at 2010 and 10.12 mg/kg at 2016; Cu 6.180 at 2004, 10.20 at 2010 and 9.26 mg/kg at 22106 and Cd 3.700 at 2004, 5.2 at 2101 and 7.28 mg/kg at 2016, (Table 1.). As we see, the Lead and Copper was in higher concentration compared to Zinc and Cadmium in our samples. The landfill waste contains also a high amount of Cadmium. Large amounts of landfill waste have a big influence in the pollution of air, water and soil. Also are a potential pollutant for the human health. Environmental degradation, landscape appearance, heavy traffic load, noise, dusts, fumes and odor emissions, render these facilities environmental stressor with negative impact on life quality of the surrounding communities[8]. Environmental inequality studies show that waste facilities are disproportionally located in the areas where more deprived, or minority groups reside[9,10,11]. The level of heavy metals concentrations in landfill waste presents a worry. The possibility of their penetration to surface

and underground waters and through then to the chain of food is very evidential, because this landfill waste permeated river Graçanka. The "landfill waste" from flotation process has direct influence in the river Graçanka because this landfill waste found in the edge of river Graçanka. Created disposal from residue after the industrial process are near the river and in the permanent way have impact in the quality of its water[7].

Discharge tube from flotation factory without preventive treatment has a higher influence in pollutions of river Graçanka. We have analyzed the concentration of heavy metals in the water of river Graçanka.

The concentration of heavy metals in the water of river Graçanka were: Pb 0.080 at 2004, 11.40 at 2010 and 14.52 mg/dm at 2016[3]; Zn 0.480 at 2004, 5.700 at 2010 and 6.45 mg/dm[3]and 6.45 at 2106; Cu 0.760 at 2004, 10.20 at 2010 and 11.45 mg/dm[3] at 2016. Cd 0.460 at 2004, 5.020 at 2010 and 4.96 mg/dm[3] at 2016, (Table 2).

Results obtained for heavy metals in water compared to the EU standards, show a higher increasing of their concentrations (Directive 2008/105/EC).

Many of the studies on health impact of waste treatment plant lack direct exposure information, relying only on residential distance from the site[12]. Scientific literature provides some indications of an association between adverse health effects and the residence distance from the landfill site but the level of epidemiological evidence is "inadequate" or "limited" with a general lack of consistency in the results for cancer incidence and mortality studie[13,12,14,15]. From these results we see that these concentrations of heavy metals in landfill waste have a high negative influence in quality of surface water. From the results we can see that the water of the river Graçanka is contaminated with heavy metals.

From the (Table 3), we can see that the concentration of heavy metals in soil is not very high, but as we now heavy metals are not degraded pollutants.

The heavy metals can deposit for a long time. In soil around the landfill waste in Kishnica, concentrations of heavy metals were: Pb 1.000 at 2004, 3.700 at 2010 and 3.4 mg/kg at 2016; Zn 2.000 at 2004, 3.20 at 2010 and 5.12 mg/kg at 2016; Cu 2.0 at 2004, 4.180 at 2010 and 6.45 mg/kg at 2016. Cd 1.500 at 2004, 3.80 at 2010 and 4.89 mg/kg at 2016. From these results we see that the soil was contaminated with heavy metals from the landfill waste. Heavy metals in soils were deposited from landfill waste by time.

Table 1: Concentration of Heavy Metals (in mg/kg) in Landfill Waste After Flotation Process

Metals mg/kg	Pb			Zn			Cu			Cd		
Years	2004	2010	2016	2004	2010	2016	2004	2010	2016	2004	2010	2016
Sample B_1	8.9	7.7	9.12	5.4	4.9	5.62	8.7	6.5	9.26	5	3.8	6.13
Sample B_2	11.15	10.2	12.12	6	7.14	7.79	8	6.9	8.12	5.2	4.9	6.23
Sample B_3	4.48	6.2	6.8	2.9	8.7	10.12	6.18	10.2	7.69	3.7	4.1	7.28

Table 2: Concentration of Heavy Metals (in mg/dm^3) in Water of River Graçanka

Metals mg/dm^3	Pb			Zn			Cu			Cd		
Years	2004	2010	2016	2004	2010	2016	2004	2010	2016	2004	2010	2016
Sample A_1	0.9	0.08	0.89	0.98	0.48	0.78	1.07	0.76	2.1	0.86	0.76	0.96
Sample A_2	7.2	8.6	9.12	3	4.9	4.612	9	10.2	11.35	3	2.7	4.12
Sample A_3	10	11.04	14.52	4.15	5.7	6.45	9.98	10.2	11.45	4.19	5.02	4.96
Sample A_4	6.7	6.9	8.69	2.1	3.7	3.45	3.7	4.8	2.45	2.8	2.9	4.01
Sample A_5	2.3	4.7	3.68	1.08	1.9	2.02	4.7	3.8	5.02	0.9	0.96	0.98

Table 3: Concentration of Heavy Metals (in mg/kg) in Soil around of Landfill Waste

Metals mg/kg	Pb			Zn			Cu			Cd		
Years	2004	2010	2016	2004	2010	2016	2004	2010	2016	2004	2010	2016
Sample C_1	2	2.14	3.12	2.1	3.2	3.56	3.4	3	5.16	1.7	1.9	2.56
Sample C_2	3.7	3.6	3.46	2.1	2	3.45	4.1	4.18	5.26	1.5	1.8	3
Sample C_3	1.05	1	2.02	2.4	2.3	5.12	2.2	2	6.45	3	2.9	4.02
Sample C_4	2.7	2.8	3.01	2.9	2.08	4.19	3.8	3.7	5.16	3.8	3.19	4.89

CONCLUSION

According to the experimental results obtained in this work, we can conclude that:

- The landfill waste which is located in front of the flotation factory has high amounts of heavy metals. Even though the landfill waste is covered with soil, the concentration of heavy metals is approximately same. Covering of the landfill waste only has prevented the transfer of particles through the air. In landfill waste, we found even higher amount in 2016.
- The water from flotation process, without preventive treatment is discharged into the river Graçanka. It has high negative influence in pollution of water. As we seen from our results the concentration of heavy metals are very higher compared with EU standards for surface waters. Pb and Cu were present in water of the river Graçanka in very high amount especially at year 2016.
- The concentrations of heavy metals in soil, near the landfill waste, in football area, and in the agricultural area differ place to places. All heavy metals were in lower concentration compared to the concentrations founded in wastes after flotation process. Comprehensive analyses of the possible industrial waste waters fitoremmedy and recultivation practices for the land contaminated by the heavy metals based on the best management practices (Galiulin). As we know heavy metals are not degraded pollutants, so they have deposited, by time, in soil. Potential contamination of soil from the landfill is evident and should take measures to improve the conditions of the landfill and the production process of the ores.

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