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The Pollution of the River Sitnicë with Heavy Metals and their Determination with Spectrophotometric Methods

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Abstract: Exploitation of Pb-Zn ore, from Stari Tërgu mine and flotation of this ore in the First Tunnel flotation, and transportation of Pb and Zn concentrates it has affected on pollution of the urban environment in Mitrovicë and in surrounding. Besides the unit of Zinc Metallurgy, in the space of the MIP are wards of Chemical Industry, which as well as Zinc Metallurgy contributed directly or indirectly to the pollution of water of Sitnica river. Industrial waste, after processing of zinc, together with industrial waste of Chemical Industry are cast on Shupkovci landfill. These waste in itself contain heavy metals, which through surface and underground flowing penetrate and pollute with heavy metal the waters of Sitnica river. During our study work we aimed to investigate and verify the degree of concentration of heavy metals in the waters of river Sitnica, as a result of the impact of Shupkovci landfill, which is located on the right banks of this river.

Keywords: *Shupkovci landfill, MIP, pollution with heavy metals, Sitnica river, industrial waste, degree of concentration.*

Introduction

Besides industrial complex MIP, in south-eastern part of Mitrovica located the landfill of Shupkovc in area of 150 ha, 35.8 ha are covered with residues from Chemical industry, while 16,8 ha are industrial waste from the processing of Zinc Metallurgy. These industrial wastes, containing heavy metals, not pollute only waters of river Sitnica, but in chain order pollute the environment in general. This phenomenon occurs as a result of rainfall, sun lights, strong erosion winds and under the influence of surface and underground leaks that end up in river Sitnica. Industrial effluents and industrial waste sludge can greatly affect on the environmental pollution with different metals (Connell *et al*., 1984**)**. Almost all industrial processes that discharge waste, are potential sources of heavy metals in the aquatic environment, where we can higlight the mineralogy, smelting and processing of minerals, etc. (Denton *et al*., 2001). Chehregan & Malayer (2007) reported that high concentrations of heavy metals have severe toxic effects and are considered as potential environmental pollutants. Heavy metals can pass in the sources of drinking water, in food products and due to the high toxicity can cause serious consequences for human health, so for this reason it is essential that their presence be maintained always under control (Çullaj, 2005).

Material and Methods

During the research we have tried to present as accurately the degree of concentration and heavy metal content of the waters of the river Sitnica. For this reason in the research area we selected three monitoring points: US1 (Entry into PIM, Shupkovc), US2 (in the exit of landfill PIM) and US3 (after joining with Trepça river and exit from the PIM). Samples taken for each monitoring point were made during winter and summer season 2014/2015.

Samples were divided into separate containers and their conservation is done in accordance with the procedure of conservation American Public Health Association, 2005 (APHA, 2005). Preparation of the water samples for measurement of heavy metals based on mineralization of samples on applying the methods EPA 3015A, while sediment sample preparation was done with EPA 3051A method. Reading of water and sediment samples was done with EPA method 6010 C (H.M.1994). Samples taken were determined degree of concentration of the metals Pb, Zn, Cd, Hg, Cu, Mn and Sb in the river Sitnica. During the determination of heavy metals in water samples taken, we applied two measurement techniques:

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SAA-F measurement techniques conducted in the laboratory of environmental analysis of HMIK and measurement techniques with ICP-OES, held in private laboratory "Agrovet" accredited by the Kosovo Accreditation Agency. For the determination of physico-chemical parameters of the waters of the river Sitnica, such as temperature, turbidity, pH, electrical conductivity, nitrates, nitrites, ammonium ion, phosphates and sulphates, are using these methods: ammonia with photometric method (phenat method 417.C) and spectrophotometric (417.B Nessler method). Nitrites, nitrates and phosphates were determination with photometric method; sulphates with turbidimetric methods (426.C); turbidity-nephelometric methods; pH and electrical conductivity with potentiometric method (APHA, 1983; APHA, 2005).

Table 1. Points of the sampling and their coordinates

River	Samples taken	Geographical width	Longitude	Sea level (m)
Sitnicë US_1	Entry into PIM, Shupkovc	42°52'38.15"	20°52'31.43"	502
Sitnicë US_2	In the exit of landfill PIM	42°53'15.69"	20°52'40.47"	503
Sitnicë US_3	After joining with river Trepça and exit from the PIM	42°53'22.79"	20°52'37.18"	503

Results and Discussion

Monitoring and evaluation of the water situation in the research area was done in accordance with EU regulations and directives, Directive 75/440/EEC for water, and in full compliance with the law and guidance of Kosovo on water, Administrative Instruction No.13/2008. In the early experimental stage has been monitoring the physical-chemical parameters (see table 2 to 6), with special emphasis has been monitoring the concentration of heavy metals in the river Sitnica, under certain network monitoring. They are determined the concentration of these metals in water: Pb, Zn, Hg, Cu, Mn and Sb (see table from 7 to 12).

Table 2. Concentration of physico-chemical parameters, Spring season

Sample taken MPV			Sitnicë Before PIM	Sitnicë After PIM	Sitnicë Afte Trepça
Date:07.06.2014	unit		US_1	US_2	US_3
Physical parameters					
Water temperature -T_w	^oC	25	19.7	22.2	20.6
Turbidity - TUR	NTU		19.2	14.2	16.8
Electrical conductivity-χ	µS/cm	1000	589	580	593
Chemical parameters					
Ion concentration of H^+, pH	1-14	6.5-8	7.66	7.75	7.70
Nitrates - NO_3^-	mg/dm^3	30	8.8	9.2	9.0
Nitrites- NO_2^-	mg/dm^3	0.2	0.85	0.85	0.82
Ammonia ion NH_4^+	mg/dm^3	0.2	1.60	2.55	7.71
Phosphate ion -PO_4^{3-}	mg/dm^3	1.0	1.13	1.19	1.4
Total phosphorus, P_{To}	mg/dm^3	1.0	0.41	0.48	0.46
Sulphate ion-SO_4^{2-}	mg/dm^3	150	64	69	66

Table 3. Concentration of physico-chemical parameters, Summer season

Sample taken MPV			Sitnicë Before PIM	Sitnicë After PIM	Sitnicë After Trepça
Date:05.07.2014	unit		US_1	US_2	US_3
Physical parameters					
Water temperature – T_w	^0C	25	15.1	15.0	15.1
Turbidity - TUR	NTU		14.6	16.9	17.6
Electrical conductivity-χ	µS/cm	1000	599	590	608
Chemical parameters					
Ion concentration H^+, pH	1-14	6.5-8	7.73	7.64	7.71
Nitrates - NO_3^-	mg/dm^3	30	11.4	12.6	12.3
Nitrites- NO_2^-	mg/dm^3	0.2	0.82	0.69	0.59
Ammonia ion NH_4^+	mg/dm^3	0.2	2.40	2.34	1.72
Phosphate ion -PO_4^{3-}	mg/dm^3	1.0	0.47	0.17	0.486
Total phosphorus, P_{To}	mg/dm^3	1.0	0.22	0.08	0.183
Sulphate ion-SO_4^{2-}	mg/dm^3	150	71	73	76

Table 4. Concentration of physico-chemical parameters, Summer season

Sample taken MPV			**Sitnicë Before PIM**	**Sitnicë After PIM**	**Sitnicë After Trepça**
Date:11.09.2014	unit		US_1	US_2	US_3
Physical parameters					
Water temperature – T_w	^0C	25	18.9	19.0	19.5
Turbidity – TUR	NTU		11.6	14.1	14.8
Electrical conductivity-χ	µS/cm	1000	579	1701	593
Chemical parameters					
Ion concentration H^+, pH	1-14	6.5-8	7.48	7.39	7.72
Nitrates- NO_3^-	mg/dm^3	30	15.6	7.1	10.8
Nitrites- NO_2^-	mg/dm^3	0.2	1.12	0.16	0.82
Ammonia ion NH_4^+	mg/dm^3	0.2	1.87	1.28	3.35
Phosphate ion-PO_4^{3-}	mg/dm^3	1.0	0.426	0.438	0.46
Total phosphorus, P_{To}	mg/dm^3	1.0	0.139	0.141	0.34
Sulphate ion-SO_4^{2-}	mg/dm^3	150	70	60,5	70

Table 5. Concentration of physico-chemical parameters, Autumn season

Sample taken MPV			**Sitnicë Before PIM**	**Sitnicë After PIM**	**Sitnicë After Trepça**
Date:16.11.2014	unit		US_1	US_2	US_3
Physical parameters					
Water temperature –T_w	^0C	25	4.8	5.0	5.1
Turbidity – TUR	NTU		14.6	15.6	17.7
Electrical conductivity-χ	µS/cm	1000	710	744	704
Chemical parameters					
Ion concentration H^+, pH	1-14	6.5-8	7.74	7.74	7.8
Nitrates - NO_3^-	mg/dm^3	30	12.4	12.4	12.3
Nitrites- NO_2^-	mg/dm^3	0.2	0.21	0.20	0.23
Ammonia ion NH_4^+	mg/dm^3	0.2	1.78	1.23	3.79
Phosphate ion -PO_4^{3-}	mg/dm^3	1.0	0.412	0.453	1.25
Total phosphorus, P_{To}	mg/dm^3	1.0	0.128	0.135	0.574
Sulphate ion-SO_4^{2-}	mg/dm^3	150	75	80	84

Table 6. Concentration of physico-chemical parameters, Winter season

Sample taken MPV			**Sitnicë Before PIM**	**Sitnicë After PIM**	**Sitnicë After Trepça**
Date: 11.03.2015	unit		US_1	US_2	US_3
Physical parameters					
Water temperature– T_w	^0C	25	5.0	4.9	4.9
Turbidity– TUR	NTU		11.9	8.4	7.4
Electrical conductivity χ	µS/cm	1000	541	543	544
Chemical parameters					
Ion concentration H^+, pH	1-14	6.5-8	8.11	8.05	8.21
Nitrates - NO_3^-	mg/dm^3	30	9.6	9.8	9.8
Nitrites- NO_2^-	mg/dm^3	0.2	0.26	0.06	0.2
Ammonia ion NH_4^+	mg/dm^3	0.2	0.68	0.20	1.05
Phosphate ion -PO_4^{3-}	mg/dm^3	1.0	0.675	0.599	0.782
Total phosphorus, T_o	mg/dm^3	1.0	0.256	0.234	0.328
Sulphate ion-SO_4^{2-}	mg/dm^3	150	70.3	70.89	74.8

Getting started from the fact that near the Sitnica river, positively to complex of MIP landfill, there is a residue from the time of production of NPK fertilizer, then automatically wonder whether rapid development of flora in this part of the river Sitnica at sampling points that monitored, occur as a result of the presence of NO_2^-, NH_4^+ and PO_4^{3-}.

If you look at the table shows that the sampling US2 and US3 we have increase the value of Pb. In US3 sampling the concentration of Pb it is near the limit value and seen the maximum value reaches

at 0.043 mg/dm^3, while sampling US2 the concentration of Pb exceeds recommended value. Sharma and Dubey (2005) reported that among the heavy metals, lead is one of the most dangerous pollutants of the environment and Pb pollution in air, water and agricultural land is ecological problem because of its impact on human health and the environment. In sampling US1 and US2 the Zn lies within the limits of the maximum recommended value. The table shows that the sampling US3 we have increase the value of Zn concentrations up to 0.645 mg / dm^3. The results obtained in site-sampling US1 and US2 show a pronounced presence of Hg, where maximum concentration value reaches 0.006 Hg on US1, and 0.0088 mg/dm^3 in the US2. From the tabular results from sampling US2 note that the concentration of Cu exceeds recommended value.

Table 7. Pb concentration (mg/dm^3) by site-sampling and seasons of the year

Pb (mg/dm^3)	**US$_1$**	**US2**	**US3**
June, ICP-OES	< 0,001	0,096	0,032
July, SAA-F	<0,05	<0,05	<0,05
September ICP-OES	0,002	0,042	0,035
November, SAA-F	<0,05	<0,05	<0,05
March IP-OES	0,003	0,048	0,043
Direc.75/440EEC	0,05	0,05	0,05
UA,13/2008, Kosovë	0,2	0,2	0,2

Table 8. Zn concentration (mg/dm^3) by site-sampling and seasons of the year

Zn(mg/dm^3)	US1	US2	US3
June ICP-OES	0,052	0,466	0,318
July SAA-F	0,016	0,197	0,061
September ICP-OES	0,092	0,148	0,104
November, SAA-F	0,079	0,345	0,645
March IP-OES	0,094	0,156	0,114
Direc.75/440EEC A2/G	1	1	1
UA 13/2008, (Dir.75/440, A1/I)	0,5	0,5	0,5

Table 9. Hg concentration (mg/dm^3) by site-sampling and seasons of the year

Hg(mg/dm^3)	US1	US2	US3
June, ICP-OES	0,002	<0,001	<0,001
September, ICP-OES	0,0057	0,0068	0,0005
March, ICP-OES	0,006	0,0088	0,0007
Direc.75/440EEC,A1/I	0,001	0,001	0,001
UA 13/2008, Kosovë	0,005	0,005	0,005

Table 10. Cu concentration (mg/dm^3) by site-sampling and seasons of the year

Cu(mg/dm^3)	US1	US2	US3
June, ICP-OES	0,002	0,028	0,01
Korrik ,SAA-F	<0,02	<0,02	<0,02
September, ICP-OES	0,004	0,002	0,015
November, SAA-F	<0,02	<0,02	<0,02
March, ICP-OES	0,006	0,005	0,004
Direc.75/440EEC,A1/I	0,02	0,02	0,02
UA 13/2008, Kosovë	0,1	0,1	0,1

Mn concentration by site-sampling and seasons of the year presented in the table, shows the exceedance in the three sampling points, until in the US2, Mn has reached maximum value of 5.46 mg/dm^3, which is much higher than the value recommended by the Directive 75/\440EEC A1 / I and according to AI 13/2008. During the research it was observed that the degree of concentration of Sb from samples taken US1 has increased to US2 sampling in the amount of 0,013 mg/dm^3, while sampling US3 is achieved maximum value Sb with 0,008 mg/Sb dm^3. The exceedance with Sb face ina all sampling points.

Table 11. Mn concentration (mg/dm^3) by site-sampling and seasons of the year

Mn(mg/dm3)	US1	US2	US3
Qershor,ICP-OES	0,037	0,057	0,055
Korrik ,SAA-F	0,298	5,46	0,182
Shtator,ICP-OES	0,045	0,059	0,066
Nentor,SAA-F	0,178	0,189	0,142
Mars, ICP-OES	0,049	0,062	0,075
Direc.75/440EEC	0,05	0,05	0,05
UA 13/2008, Kosovë	1,5	1,5	1,5

Table 12. Sb concentration (mg/dm^3) by site-sampling and seasons of the year

Sb (mg/dm^3)	US1	US2	US3
June, ICP-OES	0,002	0,002	0,002
September, ICP-OES	< 0,002	0,012	0,006
March, ICP-OES	< 0,002	0,013	0,008
Direc.75/440EEC	0,001	0,001	0,001
UA,13/2008, Kosovë	0,001	0,001	0,001

Conclusions

The obtained results show that the concentration of heavy metals in the river Sitnica somewhere exceeds reference values set out in Directive 75/440 / EEC as well as in Kosovo and Administrative Instruction No.13/2008. The presence of heavy metals in the water of this river is not always the same, because of their presence varies from season to season and from one point to another monitoring point. Research and realize analysis give us to understand that potential pollutants of the water of the river,

as in the past and now continues to be the dump with industrial wastes of MIP in Shupkovc, which is located on the banks of the river Sitnica, in the south-eastern part of Mitrovica.

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