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Research Paper

Heavy Metal Concentration and Physical-Chemical Characteristics of Drenica River in Gllogoc, Kosovo

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Abstract: The purpose of this research paper work is done with main intention to evaluate the water quality of the Drenica River in the part of Gllogoc municipality through monitoring and measurement of physical-chemicals and bacteriological parameters and also heavy metals in this river. This study is conducted through all seasons during the year 2014. In Gllogoc, is located and operate the smelter of NewCo Ferronikeli, the industrial complex that could contribute to Drenica River with its water discharging. The Ferronikeli complex has only one covered water discharging pipe and through this pipe (made from concrete) it releases water into the river, normally after treatment of the same water first, while the Gllogoc municipality no any system to treat the water before release into the river. Since, Gllogoc municipality no treatment system for released water, we have analyzed the water from river in few points for physical-chemical and bacteriological parameters, and heavy metals (Fe, Ni, Co and Cr) since from production process of Ferronikeli are expected to be present into the water these mentioned heavy metals. The concentrations of measured parameters were then compared with the relevant allowed limit values for a class V of river. The length in total of river Drenica is 41 km. It is a tributary of the river Sitnica that it joins at the West of Fushë Kosova, 16 km at the East of the Ferronikeli plant. The catchments area of the river is 108.35 km^2. This river is running all seasons. Visually, water quality of the river Drenica looks very poor.

Keywords: *River Drenica, slag disposal, heavy metals, total suspended solids, surface waters.*

Introduction

Water pollution is a major global problem that requires ongoing evaluation and revision of water resource policy at all levels (from international down to individual aquifers and wells). It has been suggested that it is the leading worldwide cause of deaths and diseases, and that it accounts for the deaths of more than 14,000 people daily. In addition to the acute problems of water pollution in developing countries, industrialized countries continue to struggle with pollution problems as well.

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish.

Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water. Most water pollutants are eventually carried by rivers into the oceans. In some areas of the world, the influence can be traced up to one hundred miles from the mouth by studies using hydrology transport models.

The specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens, and physical or sensory changes, such as elevated temperature and discoloration. While many of the chemicals and substances that are regulated may be naturally occurring (calcium, sodium, iron, manganese, etc.), the concentration is often the key in determining what is a natural component of water, and what is a contaminant. High concentrations of naturally-occurring substances can have negative impacts on aquatic flora and fauna. Oxygen-depleting substances may be natural materials, such as plant matter (e.g. leaves and grass) as well as man-made chemicals.

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Other natural and anthropogenic substances may cause turbidity (cloudiness) which blocks light and disrupts plant growth, clogging the gills of some fish species. Many of the chemical substances are toxic. Pathogens can produce waterborne diseases in either human or animal hosts. Alteration of water's physical chemistry includes acidity (change in pH), electrical conductivity, temperature, and eutrophication.

Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases in the primary productivity of the ecosystem. Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur, affecting fish and other animal populations.

In many recent publications about the water state in general in Kosovo the quality of the most of the rivers is not satisfactory for the main reasons due to the lack of wastewater treatment plants, and polluted water as from buildings/houses as well as from industries are released into the rivers without treatment.

The same issue about pollution is also with Drenica River that was main purpose of this study, to check and evaluate its quality in the part of Gllogoc municipality. The work is done to examine the concentration of heavy metals and other physical-chemical and bacteriological parameters in the river (surface water) and to determine the pollution level of the river.

Subject and sampling methods of study

Study area

The study area was conducted at designated points along river of Drenica in its part of Gllogoc town, as shown in Figure 1 below. In Gllogoc, is located the smelter of NewCo Ferronikeli which is an industrial complex well-known for ferronickel alloy production. Ferronikeli is the main heavy industry in that area and one source of its water discharging into the river of Drenica (Veliu A. et al. 2008). The water used in the plant for different processes, but to be clear, water for industrial processes (cooling of electric furnaces, slag granulation and water for cleaning systems for dust and gases) is not discharging into the river because this water is re-circulating, wastewater is treated in wastewater treatment plan, while run-off water is released without treatment system into the river (Veliu A. et al. 2015). Treatment system for run-off water was a condition in environmental integrated permit (IPPC) of Ferronikeli to build later (deadline - end of Dec. 2015).

Sampling points were chosen in appropriate locations in the way to cover the main part of the river Drenica (influence of houses, Ferronikeli, slag disposal, stone-quarry).

Surface water sampling

All samples were collected in wet and dry seasons in the year 2014 (a set of seven samples per each season: spring, summer, autumn and winter) in the way to capture the effects of seasonal variations. In total were collected and analyzed 28 samples (as per sampling points shown in Figure 1).

Most of the samples were collected in the river (6 of them) while only one sample was collected in a small open water channel (sample no. 5) where effluent flowing from Ferronikeli slag disposal into the river.

Sampling and the examination methods of water samples are done according to standard method guideline for environment impact assessment of surface and ground water (APHA, 1998) as well as per standard method ISO 5667-1 (2006). Some parameters are measured in-situ, while for other analyses samples are treated as per standard procedures.

Results and Discussion

The tables below show the results of analyzed parameters in all seasons of 2014 of these collected samples (marked from S1 to S7) taken during this assessment study. For clarification samples represents as follow: S1- river sample upstream of Ferronikeli; S2 – water released after treatment from Ferronikeli plant; S3 – river sample downstream of Ferronikeli; S4 – river sample (upstream of this sample is located one private stone-quarry); S5 – sample from open channel that come from slag disposal of Ferronikeli; S6 – river sample downstream of slag disposal; and S7 – river sample.

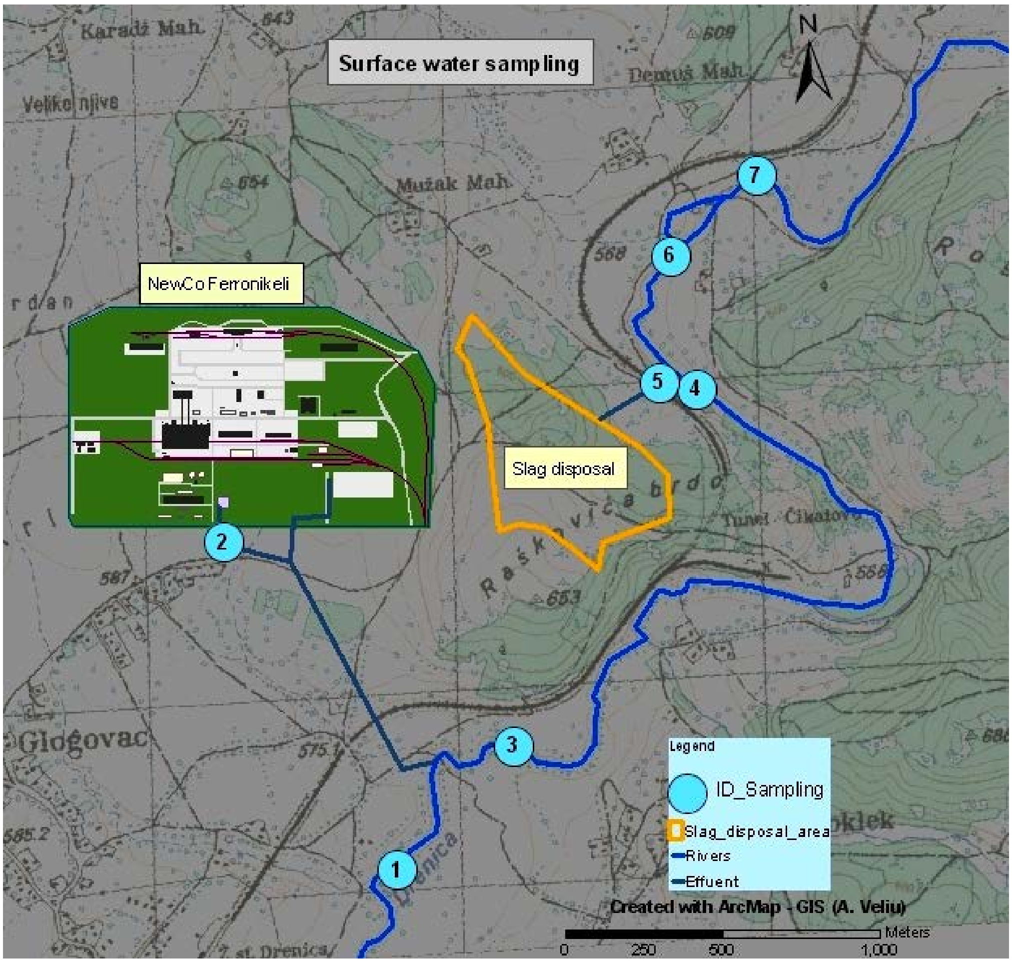

Figure 1: Sampling points of surface water

The results of monitoring are compared with Kosovo Administrative Instruction 'AI 13/2008' for the limited values of the effluents that discharged on water bodies and on the system of public canalization – table 4 of this AI, column for water of class V. This Regulation (AI) was in force in the time period of this study (until the end of December 2014) but also it was under drafting for new water Regulation for future.

In table 1 are presented results for winter season sampled in February 2014 for measured parameters. In all samples for physical-chemical for this period of the year is noticed that color in samples S1 (in green) and S4 (in yellow) is not as per Regulation (class V of water from AI 13/2008); turbidity is important parameter of river pollution and this study shows the turbidity in the range of 2.6 (S5) – 13.7 (S2) NTU. The highest desirable limits for turbidity are 5 NTU and maximum permissible limit 50 NTU (Mandal et al. 2012), so in few samples the value of turbidity is above 5 NTU but no one above 50 NTU; pH is exceeding only in S5 (but in low level); and ammonium ion is exceeding allowed values in samples: S1, S3, S4, S6 and S7, but not in samples S2 and S5 where expected to have influence Ferronikeli plant and its slag disposal; while bacteriological parameters and heavy metals are within the permissible limits.

In table 2 are presented results for spring season sampled in May 2014. In all samples for physical-chemical is noticed only a color (brown) in samples S2 and S3 due to influence of Ferronikeli plant that discharge its runoff water without treatment; turbidity is in range 4.5-81.4 NTU (only S2 is above 50 NTU, and is a pollution indication due to lack of runoff water treatment system); while other parameters for physical-chemical, bacteriological and heavy metals are within the permissible limits for class V of water.

Table 1: Results for winter season – sampled in February 2014

Parameter	Unit	S1	S2	S3	S4	S5	S6	S7	UA 13/2008*
Odor	-	no	no	no	no	no	no	no	poor
Color	-	green	no	no	yellow	no	no	no	poor
Temperature	^0C	7.6	10.2	9.0	9.9	14.5	9.7	9.5	35
Turbidity	NTU	4.4	13.7	7.6	8.2	2.6	8.6	8.1	-
pH	-	8.22	8.34	8.21	8.29	8.65	8.33	8.30	6-8.5
Elec. conductivity	µS/cm	680	310	685	670	665	670	665	1500
$KMnO_4$ consumption	mg/l	60.89	83.33	68.90	70.22	134.61	72.36	71.61	-
Dissolved oxygen	mg/l	6.68	10.55	5.35	7.65	10.37	7.43	7.48	3
Chlorides	mg/l	53	16	51	46	41	46	49	250
BOD_5	mg/l	3.63	5.26	1.86	4.68	2.72	3.11	3.14	80
Ammonia (NH_3)	mg/l	1.46	0.23	1.47	1.50	0.55	1.52	1.52	2.5-8
Ion ammonium NH_4^+	mg/l	1.54	0.24	1.56	1.59	0.58	1.61	1.62	1.0
Nitrites NO_2-N	mg/l	0.066	0.049	0.052	0.050	0.014	0.047	0.048	1.5
Nitrates NO_3-N	mg/l	1.2	2.5	1.4	1.4	4.6	1.8	1.6	40
Sulfate	mg/l	98	94	96	95	420	186	180	250
Phosphates	mg/l	2.9	1.2	2.8	2.7	3.4	3.2	3.1	4
Suspended solids	mg/l	4	13	9	6	2	8	9	150
Total coliforms	cfu/100 ml	251	192	104	176	815	243	158	<6000
Escherichia coli	cfu/100 ml	no	no	no	no	no	no	no	Not allowed
Fe	mg/l	0.203	0.150	0.200	0.247	0.212	0.265	0.285	5.0
Ni	mg/l	trace	trace	trace	trace	trace	trace	trace	1.5
Co	mg/l	trace	trace	trace	trace	trace	trace	trace	1.5
Cr	mg/l	trace	trace	trace	trace	trace	trace	trace	1.75

Table 2: Results for spring season – sampled in May 2014

Parameter	Unit	S1	S2	S3	S4	S5	S6	S7	UA 13/2008*
Odor	-	no	no	no	no	no	no	no	poor
Color	-	no	brown	brown	no	no	no	no	poor
Temperature	^0C	13.6	16.7	14.6	14.5	18.2	14.8	13.6	35
Turbidity	NTU	7.8	81.4	13.4	10.8	4.5	6.4	7.8	-
pH	-	8.28	8.31	8.30	8.34	8.44	8.37	8.28	6-8.5
Elec. conductivity	µS/cm	550	620	560	525	710	520	550	1500
$KMnO_4$ consumption	mg/l	33.40	30.06	31.05	45.42	44.08	38.20	33.40	-
Dissolved oxygen	mg/l	6.12	9.39	6.53	5.52	10.17	6.23	6.12	3
Chlorides	mg/l	25	34	26	24	54	27	25	250
BOD_5	mg/l	3.72	5.38	3.82	2.81	2.89	3.06	3.72	80
Ammonia (NH_3)	mg/l	0.71	0.23	0.64	0.60	0.38	0.57	0.53	2.5-8
Ion ammonium NH_4^+	mg/l	0.76	0.25	0.68	0.64	0.40	0.61	0.56	1.0
Nitrites NO_2-N	mg/l	0.063	0.032	0.060	0.061	0.077	0.083	0.080	1.5
Nitrates NO_3-N	mg/l	2.2	1.1	2.8	2.4	4.2	3.0	3.1	40
Sulfate	mg/l	68	64	60	65	460	68	67	250
Phosphates	mg/l	2.6	1.4	2.5	2.6	3.0	2.8	2.7	4
Suspended solids	mg/l	6	111	28	21	11	8	7	150
Total coliforms	cfu/100 ml	120	80	60	140	130	170	110	<6000
Escherichia coli	cfu/100 ml	no	no	no	no	no	no	no	Not allowed
Fe	mg/l	0.150	0.135	0.131	0.152	1.102	0.135	0.170	5.0
Ni	mg/l	trace	trace	trace	trace	trace	trace	trace	1.5
Co	mg/l	trace	trace	trace	trace	trace	trace	trace	1.5
Cr	mg/l	trace	trace	trace	trace	trace	trace	trace	1.75

In table 3 are presented results for summer season sampled in August 2014. From all samples is noticed out of limits for physical-chemical parameters: a brown color in S2 and S3 (main influence of runoff water from Ferronikeli without treatment); dissolved oxygen (DO) in S1; ammonium ion in samples: S1, S3, S4, S6 and S7, not in samples S2 and S5; turbidity is in range of 7.9 – 38.4 NTU (high values of turbidity is coming from runoff water from Ferronikeli that discharging into the river without treatment); and phosphates (PH_4^-) in most of samples, except in S5 and very slightly in S2; while bacteriological parameters and heavy metals are within the permissible limits.

In the last table 4 are presented results for autumn season sampled during November month of 2014. From all samples is noticed out of limits for physical-chemical parameters: color in most of samples which is present from rain in this period and also from Ferronikeli plant runoff water, except in S1 and S5; turbidity is in range of 5.92 – 57.5 NTU; phosphates (PH_4^-) in most of samples except in S2 and S5; while other bacteriological parameters and heavy metals are within permissible limits.

Table 3: Results for summer season – sampled in August 2014

Parameter	Unit	S1	S2	S3	S4	S5	S6	S7	UA 13/2008*
Odor	-	no	no	no	no	no	no	no	poor
Color	-	no	brown	brown	no	no	no	no	poor
Temperature	^0C	18.4	18.7	21.5	21.2	20.7	20.9	21.0	35
Turbidity	NTU	7.9	37.6	38.4	30.7	7.7	9.6	8.1	-
pH	-	7.82	7.87	8.09	8.00	8.22	7.91	8.01	6-8.5
Elec. conductivity	µS/cm	760	550	670	735	1200	780	755	1500
$KMnO_4$ consumption	mg/l	53.49	30.47	33.65	43.26	29.11	40.22	41.98	-
Dissolved oxygen	mg/l	1.33	7.67	4.44	3.86	7.89	2.98	3.41	3
Chlorides	mg/l	33	31	31	32	96	54	51	250
BOD_5	mg/l	23.1	4.07	13.99	10.23	1.93	8.33	8.24	80
Ammonia (NH_3)	mg/l	3.84	0.91	2.34	2.22	0.36	2.11	2.08	2.5-8
Ion ammonium NH_4^+	mg/l	4.06	0.96	2.47	2.35	0.38	2.23	2.20	1.0
Nitrites NO_2-N	mg/l	0.027	0.115	0.051	0.043	0.058	0.049	0.044	1.5
Nitrates NO_3-N	mg/l	1.4	1.2	1.3	1.2	2.8	1.6	1.5	40
Sulfate	mg/l	38	49	41	44	80	58	52	250
Phosphates	mg/l	19.22	4.85	18.68	20.09	1.12	19.88	20.86	4
Suspended solids	mg/l	8	30	36	23	5	12	10	150
Total coliforms	cfu/100 ml	470	220	190	530	280	140	310	<6000
Escherichia coli	cfu/100 ml	no	no	no	no	no	no	no	Not allowed
Fe	mg/l	0.404	0.403	0.305	0.200	0.082	0.212	0.217	5.0
Ni	mg/l	trace	trace	trace	trace	trace	trace	trace	1.5
Co	mg/l	trace	trace	trace	trace	trace	trace	trace	1.5
Cr	mg/l	trace	trace	trace	trace	trace	trace	trace	1.75

Table 4: Results for autumn season – sampled in November 2014

Parameter	Unit	S1	S2	S3	S4	S5	S6	S7	UA 13/2008*
Odor	-	no	no	no	no	no	no	no	poor
Color	-	no	brown	yellow	yellow	no	yellow	yellow	poor
Temperature	^0C	9.6	16.3	9.8	9.2	13.2	9.5	9.3	35
Turbidity	NTU	16.63	57.5	24.3	36.4	5.92	28.2	31.4	-
pH	-	7.85	8.00	7.87	7.93	8.18	7.93	7.95	6-8.5
Elec. conductivity	µS/cm	480	505	500	490	715	500	495	1500
$KMnO_4$ consumpt.	mg/l	39.28	31.15	26.42	46.05	27.76	43.81	42.66	-
Dissolved oxygen	mg/l	7.50	8.76	7.70	8.34	9.60	8.01	8.34	3
Chlorides	mg/l	34	33	32	33	64	34	30	250
BOD_5	mg/l	3.92	4.39	6.01	5.72	1.42	2.98	4.33	80
Ammonia (NH_3)	mg/l	0.36	0.73	0.51	0.46	0.67	0.38	0.32	2.5-8
Ion amonium NH_4^+	mg/l	0.39	0.80	0.56	0.50	0.70	0.41	0.35	1.0
Nitrites NO_2-N	mg/l	0.002	0.099	0.008	0.006	0.001	0.004	0.003	1.5
Nitrates NO_3-N	mg/l	0.4	2.76	0.6	0.5	0.6	0.8	0.7	40
Sulfate	mg/l	10	70	15	15	100	19	16	250
Phosphates	mg/l	8.16	2.76	8.14	8.10	3.22	7.94	8.26	4
Suspended solids	mg/l	16	56	23	29	10	22	27	150
Total coliforms	cfu/100 ml	230	140	290	80	120	250	480	<6000
Escherichia coli	cfu/100 ml	no	no	no	no	no	no	no	Not allowed
Fe	mg/l	0.108	0.262	0.103	0.135	0.139	0.179	0.174	5.0
Ni	mg/l	trace	trace	trace	trace	trace	trace	trace	1.5
Co	mg/l	trace	trace	trace	trace	trace	trace	trace	1.5
Cr	mg/l	trace	trace	trace	trace	trace	trace	trace	1.75

Conclusions

This study work has presented the level of physical-chemical, bacteriological and heavy metals parameters and the current state of the river water samples collected from the river Drenica during the year 2014. The results presented in tables above (table 1 – table 4) revealed that there was an indication of water pollution (compared with allowed limit for class V of water from AI 13/2008) with some parameters as: color in few samples; turbidity, that in most of cases has high value in sample S2 (water discharging pipe from Ferronikeli) that is mainly runoff water released without treatment system in that time; ammonium ion in few samples during winter season but not in other seasons; phosphates are exceeding allowed limit during summer and autumn seasons, but not is samples S2 and S5 that means that phosphates in the river are not coming from Ferronikeli plant, but from water discharging from houses and Gllogoc municipality without prior treatment of water. Bacteriological parameters measured (total coliform and Escherichia coli) are within acceptable limit in all samples and during all seasons.

Also, all measurements in all seasons clearly indicate that heavy metals in collected samples are in very low level (acceptable range). Analyze of heavy metals is done with AAS and from tables above it shown that is detected only iron in all samples while other three metals were in ‘trace’. This explain poor dissolving of these heavy metal in the water and don`t show the contamination from the site of Ferronikeli plant.

The water quality of the river Drenica remains poor mainly from organic pollution caused by wastewater discharging from the Gllogoc municipality and the surroundings villages without any sanitary treatment and is not suitable to use for recreational purposes, while it can be used for irrigation purposes.

Conclusion or recommendation is also for the further studies (especially for ‘new’ researchers) of water quality in all Kosovo rivers to use appropriate national regulations or legislation on force for ‘allowed limits’ during their studies, not like in many cases where researchers have studied surface water quality while comparison is done for drinking water guidelines or regulations.

Thus this work will serve as baseline information for the state of Drenica River done during this study period for future work in terms of environmental management. In order to protect the water from further contamination, a designing of a detail monitoring network and reducing the anthropogenic discharges is suggested.

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