Research Article

Determining the Level of Pollution of the River Duhlo in Rahovec, as a Result of Human and Industrial Activity, through Physico-chemical Parameters of Pollution, using Analytical Methods ICP-OES and UV-VIS

Ilir Shehu*[1], Skender Demaku[1], Blerta Gashi[1], Avni Malsiu*[1], Aziz Behrami[2]
[1]University of Pristina "Hasan Prishtina", Faculty of Natural and Mathematical Sciences, Str. "Nëna Tereze" no. 5, Pristina, Kosovo.
[2]Public University of Mitrovica, Mitrovicë.
***Corresponding author's E-mail:** ilirishehu10@hotmail.com & avni.malsiu@hotmail.com

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ABSTRACT

Based on the experimental results, using ICP-OES and UV-VIS method, we have determinate the physical and chemical parameters that influenced in the quality of the water in the river Duhlo in Rahovec. The water from the Duhlo River polluted by organic and inorganic species. During the experimental work we found lower values of dissolved oxygen, high values of phosphates, nitrites and ammonium ion. Detergents which results from use in household show higher values in third sample point. Along the river at sample points through the town of Rahovec respectively in the second sample point and third sample point, the water is polluted more by discharged waste waters without any treatment. The greater extend of the pollution is linked with several factories that operate in the city such as wine factory that operate in the town and discharge their waste water into the river without any prior treatment. This plant with its activity causes an increase in water pollution, it is confirmed by high values of phosphates, ammonia and nitrites in the second sample point. Also, a big impact comes from agricultural soils in which there is a greater use of fertilizers, which increase the concentration of nitrates, nitrites and other forms of nitrogen but also phosphates in the third sample point. The problem is that in the waters of the river Duhlo are found high value of the concentration of parameters in aspect of inorganic and organic pollution, were the values in some sample point are in ranges for ammonia up to 4.68 mg/dm^3, for phosphates up to 4.36 mg/dm^3. Also we have find a high amount of concentration of iron, that may occur as a result of mineral soil layers than from a human activity in the third sampling points.

Keywords: Water, Duhlo, River, Pollution, Rahovec, Kosovo.

INTRODUCTION

The territory of the municipality Rahovec, lies in the northern hemisphere, Ecuador with 420 degrees 30' and 420 50' northern geographic width and between 200 21' and 200 55' eastern geographic length. Settlements in the municipality are concentrated in the height of 310 m. (Mala Krusa new part of the settlement of the eastern coast of Drini River) up to 920 m altitude is concentrated Zatriq village[1]. Duhlo River traverses the city of Rahovec and some villages and finally flows into the White Drin River, where as a result of this, the river is exposed to various pollutants, such as those from agricultural lands as a result of the use of fertilizer then the city sewage waters, but also from various industries operating in the city. As a result we have the contamination from organic and inorganic chemicals in the river. The main pollutants are inorganic heavy metals, which exhibit different problems from those of organic pollutants[2]. The development of chemical and biological methods for effective monitoring of environmental levels of heavy metals poses a particular interest and a critical step for managing environmental pollution[3]. In our research we do not find a higher level of concentration of heavy metals, especially in the third sample point we have increase level of iron and manganese. Heavy metal content especially in the autumn season may come as a result of geological layers by rainfall during laundering more than by human activity[4]. Plants take iron in the form of Fe^{2+}, Fe^{3+}. Competition to connect with iron show copper, cobalt, nickel, zinc, chromium and manganese while at high pH inhibit Ca^{2+} and phosphate ions[5]. Availability of fresh water resources in worldwide countries is a principal factor to maintain life and provide the requirements for all man activities. Therefore it is necessary to protect these resource from the pollution problems[6,7]. In fact the pollution of Duhlo River come more from discharged domestic wastewater, but impact have and many factories that operating I the Town of Rahovec.

Biological, physical and chemical pollutants have negatively affected water quality and sediments[8]. Duhlo river water is used in some parts of the agricultural areas of Orahovac, then this contamination of the river water can cause negative effects in plants during irrigation[9].

The contamination of Duhlo River with organic, inorganic matter and with heavy metals, it shows concern for the public. The possibility of their penetration to surface and underground water and then to the chain of food is very evidentioal[10].

MATERIALS AND METHODS

Sampling was done at five points along the river Duhlo. The first sampling point was made in the place of source of water of this River with coordinates 471879, 4694378. This monitoring point is defined as the point of reference, because the possibilities of the pollution of water of the river in this sampling point are minimal. The second

sample was taken about 2.0 km away from the first sample behind of the vine factory, with coordinates 471360, 4693862 after the discharged waste waters from this plant. The third sample was taken in outside of the city of Rahovec in coordinates 470095, 4692381, the sample point were all the waster waters collected in this sample point, from household waste and industrial activity from the city. The fourth sample was taken after about 4 km, from the third sample point with coordinates 466717, 4689815 and we thought that in this distance, the water can make auto purification process because in this distance have not any impact from waste waters except influence of the vine factory "Stone castle". Fifth sample and last was taken at a longer distance, after about 5.0 km, with coordinates 466296, 4686264, before joined the river Duhlo and White Drin.

Figure 1: Sample points where taken water samples

Used Equipment

1. ICP-OES, Perkin ELMER optima 2100 DV. 2. S.F.M. SECOMAM UV; 3. S.F.M. SECOMAM Premium Light; 4. F.M. WTW S12; 5. MILIPORE, Distiller; 6. WTW 340i, 7. Equipment for measurement TDS and conductivity; 8. Electronic analytical weight, AAA DAMLAB, Denver Instruments; 9. Thermo reactor, WTW CR2200; 10. Magnetic mixer, Yellow Line; 11. Consort C830 pH meter; 12. Turbid meter AQUALYTIC Compact PC; 13. Digital burettes manufacturers SOLARUS Hirschman; 14. Certified standard solutions for conductivity, pH and metal ions; 15. Kivet 10 mm quartz; 16. Container normal 1000 cm^3, 500 cm^3, 250 cm^3, 100 cm^3; 17. Laboratory glass 250 cm^3, 100 cm^3; 18. Erlenmeyer 300 cm^3, 250 cm^3, 100cm^3; 19. Paper filtering etc.

Sampling methodology

Water sampling

Sampling of water (Anonym, 2011)[11] for laboratory analysis is done carefully and is based on ISO 5667-5 standards of 2006. By following this standard we avoided the possible contamination of water samples for our study.

Preparation of sampling vessels

By (Anonym, 2011), the favorite type of bottles are glass or polyethylene but this depends on the requirements for determining the particular parameters. The bottles were cleaned with de ionized water and filled with the volume of water necessary for sampling. All bottles were sealed with a lid that hinders any contact with air or other substances.

Conservation and transport of samples

(Anonym, 2011) give some recommendation for the conservation of the samples for the analysis that means that the samples are immediately placed in refrigerated portable shaved to certain conditions.

For physic-chemical and bacteriological analysis, the time between sampling and performing analyzes if the sample are not conserved, should be much shorter. For the determination of heavy metals 100 cm^3 of each sample was taken separately and then conserved by the treatment with 0.5 cm^3 of concentrated HNO_3.

Table 1: Standard methods for measurements of water parameters

No.	Parameters	symbol	Meas unit	Standard Methods	Equipment
			Physical		
1	Time	00:00	h	-	-
2	Weather	-	view	-	-
3	Water temperature	-	°C	DIN 38404-C4	Termometer
4	Turbidity	Tur	NTU	ISO7027	Photometri
5	Conductivity	χ	µScm-1	ISO 7888	Electrochemistry
6	Water soluble substances	WSS	mg/dm^3	ISO 7888:1985	Electrochemistry
7	Hydrogenium jon concentration	pH	0-14	ISO 787-9	Electrochemistry
8	Dissolved Oxygen	DO	mg/dm^3	DIN EN 25814-G22:1992-11	Electrochemistry
9	Total disolved solid	TdS	mg/dm^3	IS 3025	UV Spectroscopy
10	Total phosphorus	Ptot	mg/dm^3	USEPA 8048	VIS Spectroscopy
11	Ammonyum jone	NH_4^+	mg/dm^3	ISO 7150/1	VIS Spectroscopy
12	Nitrites	NO_2^-	mg/dm^3	EN 26 777	VIS Spectroscopy
13	Nitrates	NO_3^-	mg/dm^3	ISO 7890/1	UV Spectroscopy
14	Detergents (SURFACATNTS)	Det	mg/dm^3	ISO 2870	UV Spectroscopy
15	Heavy metals	M	mg/dm^3	ISO 15586	ICP-OES

RESULTS AND DISCUSSION

Table 2: Results of the experimental analysis in the water of the Duhlo River–physic-chemical parameters

Parameters	Unit	Standard methods	First sample	Second sample	Third sample	Fourth sample	Fifth sample
Coordinates	UTM 34T		X-471879 Y-4693862 Z-424 m	X-471360 Y-4693862 Z-388 m	X-470095 Y-4692381 Z-388 m	X-466717 Y-4686264 Z-307 m	X-466296 Y-4686264 Z-307 m
Temperature	°C	DIN 38404-C4:1976-12	14.3	17.5	20.5	23.0	21.4
Conductivity	µs/cm	ISO 7888:1985	680.0	730.0	790.0	750.0	680.0
pH	1-14	DIN 38404-5	6.8	7.7	7.6	7.8	7.8
Oxygen	mg/L	DIN EN 25814-G22:1992-11	8.6	3.4	1.0	6.9	8.3
TDS	mg/L	IS 3025	412.0	386.0	430.0	408.0	378.0
Anionic detergents	mg/L	EN903:200P	<0.06	0.12	0.20	0.11	0.10
Hardness	mg/L	Volumetric	16.56	13.49	14.05	18.59	16.63
Chlorides	mg/L	Volumetric	14.88	32.35	34.76	24.31	22.23
Alkalinity	mol/L	Volumetric	0.50	2.50	2.80	1.40	1.12
Acidity	mg/L	Volumetric	359.9	408.7	402.6	372.1	335.5
Phosphates	mg/L	USEPA 8048	0.14	2.27	4.36	1.45	1.46
Ammonium	mg/L	USEPA 8155	0.12	3.43	4.68	2.70	2.06
Nitrites	mg/L	USEPA 8507	0.012	0.270	0.610	0.470	0.300
Nitrates	mg/L	USEPA 8192	1.0	6.2	5.4	3.0	1.7
Sulphates	mg/L	ISP10304-1	23	57	59	42	45
Ca	mg/L	Volumetric	14.05	11.76	12.88	16.06	15.40
Mg	mg/L	Volumetric	18.04	12.43	15.60	18.19	21.14

Table 3: Results of the experimental analysis in the water of the Duhlo River-heavy metals

Parameters	Unit	Standard methods	First sample	Second sample	Third sample	Fourth sample	Fifth sample
As	mg/L	EPA 3015A:2007 EPA 6010C:2007	< 2 ppb	0.008	0.009	0.0	< 2 ppb
Cd			< 0.1 pbb	< 0.1 pbb	< 0.1 pbb	< 0.1 pbb	< 0.1 pbb
Co			< 0.2 ppb	< 0.2 ppb	< 0.2 ppb	< 0.2 ppb	< 0.2 ppb
Cr			< 0.2 ppb*	< 0.2 ppb*	0.018	0.0	0.0
Cu			<0.4 ppb*	0.15	0.13	<0.4 ppb*	< 0.4 ppb*
Fe			0.03	0.15	0.28	0.ë	0.ë
Mn			0.001	0.04	0.13	0.1	0.0
Ni			< 0.5 ppb*	< 0.5 ppb*	0.006	<0.5 ppb*	< 0.5 ppb*
Pb			< 1ppb	0.01	0.006	<1 ppb	< 1 ppb
Zn			< 0.2 ppb	0.023	0.0ë2	<0.2 ppb	< 0.2 ppb

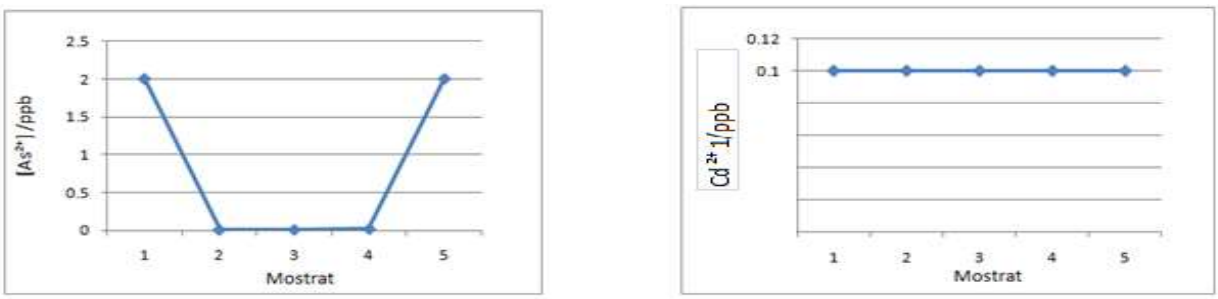
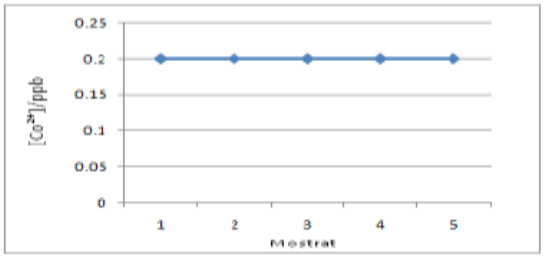


Figure 2: Concentration in µg/L As and Cd in water samples



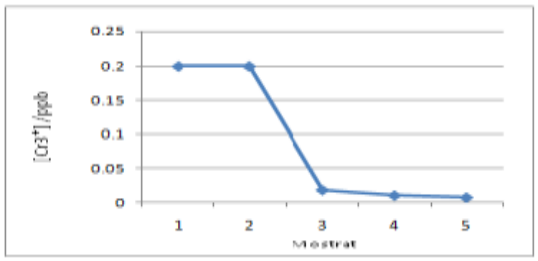
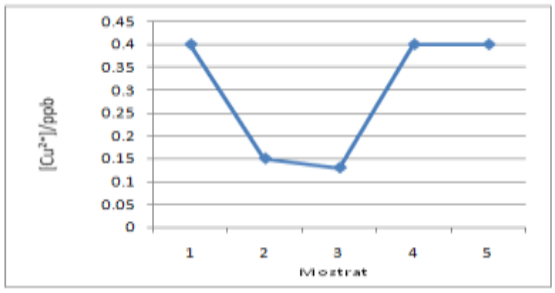


Figure 3: Concentration in µg/L Co^{2+} and Cr^{3+} in water samples



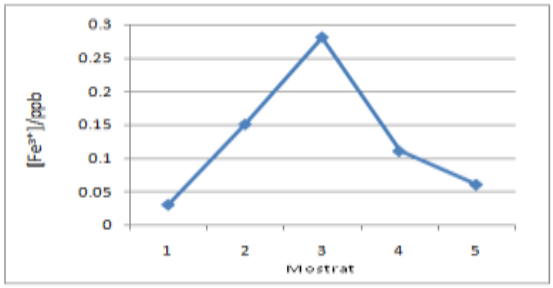
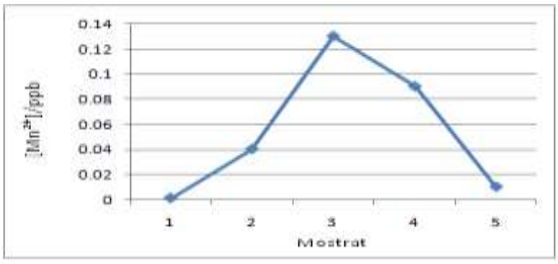


Figure 4: Concentration in µg/L Cu^{2+} and Fe^{3+} in water samples



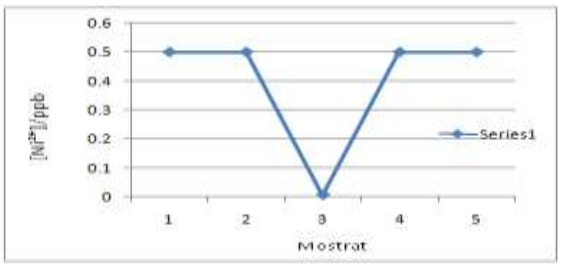
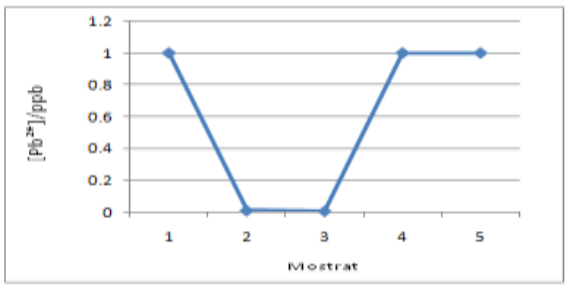


Figure 5: Concentration in µg/L Mn^{2+} and Ni^{2+} in water samples



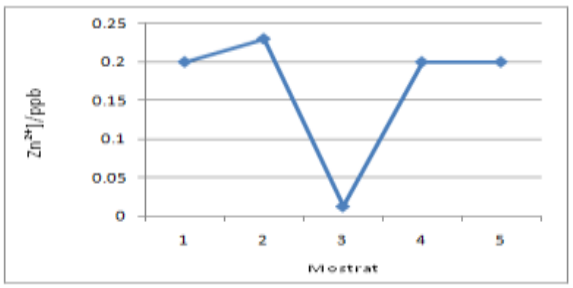


Figure 6: Concentration in µg/L Mn^{2+} and Ni^{2+} in water samples

The water temperature in the sampling points varies from 14.3-23.0 °C (Table 2). The lowest temperature was recorded at the first sampling point 14.3, this temperature is expected, given that we are dealing with the water source while the highest was recorded at the fourth sampling point 23.4° C. The measured pH value varies from 6.8-7.8, based on those isn't any significant change of the pH value. Conductivity varies from 680 to 790 µS/cm, from these values it can be concluded that the increase of the conductivity values in the third sampling points can be a result of discharging waters of Rahoveci town, from household waste waters and from industrial activity.

The dissolved oxygen varies from the highest value 8.6 mg/L at first sample point, this value expected, because in this sample point we have water source and the possibility of the contamination at this point is too small from natural agents. In the third samples we have strongly decrease value of dissolved oxygen which arrived to 1.0 mg/L, (Table 2). On the basis of literature known to the waters that have low levels of dissolved oxygen, we conclude that we are dealing with pollution of water as well as in organic terms in the inorganic as spent to make oxidation of these substances by oxygen. Reducing the concentration of dissolved oxygen due to respiration of plants, animals and aerobic bacteria and chemical oxidation reactions (e g Fe_2^+ to Fe_3^+). The Total dissolved solids in our sample points are in the value that allowed by European Directive, Directive 2000/60/EC[12].

Based on our results obtained, shows that do not have deviations of this parameter in the samples analyzed, the highest value recorded in the third samples about 430

mg/L, which is lower than the maximum value allowed under the European directives for surface waters which is around 450 mg/L, (Table 2).

Detergents in our results which coming from experimental analysis, ranging from values 0,06 mg/L in reference point as the minimum value, up to the values 0.2 mg/L, (Table 2), in the third sample point, which found in output of the city as maximum level. Detergents from waters usually are the result of human activity, from used in households which also prove that our results in the third sampling point coming from discharge of the wastewater that collected from all of the city.

In the analyzed samples have content of phosphates as follows: in the first sample or reference sample we have low levels of phosphates because the surrounding environment do not have major impact, but we have changes on the course of the river. In the second sample, we have an increased values of phosphates to 2.27 mg/L and in the third sample points, we have very high value 4:36 mg/L,(Table 2), compared with other samples. This amount of the content of phosphates in this sampling points predominantly can be a result of discharging water of the city but the amount of phosphates may coming as a result of organic waste and decomposition of aquatic organisms.

The main source of pollution from ammonium is wastewater discharges and liquid animal waste. Significant impact can also have a reducing environment in the wells of hydrocarbons and sulfur compounds, which can cause reduction of nitrates and nitrites to ammonia. In analyzed samples in the river Duhlo we have these values: the first sample indicates a minimum load of content of ammonia but the next samples have results that show pollution of the water. In the second sample we have value 3.43 mg/L of ammonia that indicates that the water of the body of the Duhlo River, received large compounds loads of nitrogen. In the third sample we have a very high value of ammonia content to 4.68 mg/L, which is also a very safe result for Duhlo river pollution that cause from the discharge water of the town of Rahovec.

Along the river in samples 4 and 5, we have a mitigation value of ammonia, although values are still high but this reduction has come as a result of auto purification of the water.

Nitrates are not toxic, but they can return in nitrites form or organic compound as nitrosamine and a little participation of them by only 1 mg/L, have a potential carcinogenic risk.

All samples analyzed were below the level recommended by the European Union and WHO recommendations which limit the nitrate content of up to 50 mg NO_3^- mg/L, (Table 2).

Sulfate ions are among the major anions found in natural waters and water discharges. In natural unpolluted waters, sulfate ion concentration is between 5 and 100 mg/L, while in wastewater and salty it could reach much higher concentrations (up to 4000-5000 mg / L). In the analyzed samples has no high value content of sulfates, higher value ranges in the third sample of approximately 56 mg/L (Table 2).

The existence of heavy metals in aquatic environments may have different backgrounds, among which the main role is played from anthropogenic sources less than from their origin from ores. They can be found in the form of organ metallic and inorganic, which may be soluble or insoluble. Heavy metals are present in natural waters in a variety of chemical forms, such as particle shape as well as dissolved. Dissolved phase includes hydrated ions, organic and inorganic complexes, species associated with colloidal particles and organ metallic compounds. The toxicity of heavy metals in natural waters varies depending on the type of species and environmental conditions in which they are located. We can say that heavy metals exhibit their toxic effect in the form of complexes with organic substances. Consequently, biological molecules lose their functions, which leads to change and often the death of the affected cells. When analyzing water samples taken along the river Duhlo not notice any pronounced heavy metal values compared to standard values for surface waters.

CONCLUSION

Based on the obtained results in our study we can conclude:

1. Based on the obtained results for water quality as TDS, OT, pH value, the waters from the Duhlo river are loaded highly by polluting substances, which also show very low values of dissolved oxygen.
2. Concentrations of nutritive as P-PO_4^{3-}, NO_3^- N, N-NO_2^- and N-NH_4^+, can say that in terms of the content of nitrate and nitrite ions do not have any deviations but high concentrations of ammonium ion are concerning for quality of water of the river.
3. Based on the results of measurements of the levels of concentration of heavy metals as: As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, we can conclude that the deviation of the concentration of these metals from European directives for surface waters have to iron in the third sample, deflection of value of lead or load, have also focused on the second sample but also have a deviation of concentration levels permitted under European directives for the surface waters to manganese in the fourth sample.

In addition to evaluating the real situation regarding the quality of the river Duhlo in the town of Rahovec, the objective of this research is to inform the public opinion of city residents but also villages that crosses the river, about the side effects that can have water pollution of Duhlo River, because a large part of the pollution can

spend time in the pollution of land around the river, which utilized more land in cultivation of vegetables.

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