Analysis of the Impact of Ferronicel Industrial Activity on Drenica River Quality

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ABSTRACT

Today, environmental water degradation all over the world comes about due to the growth of urban, industrial and agricultural activities. As a result of these discharges without any prior treatment, the quality of river waters in Kosovo has deteriorated greatly. On the basis of the research that has been done so far in the rivers of Kosovo, it was shown that Drenica is one of the rivers that are constantly exposed to the discharge of industrial waters. Therefore, the purpose of this research was to analyze the impact of water discharged from Feronikeli on the water quality of the Drenica River and the possibility of its protection. The realization of this study is focused on the evaluation of physico-chemical parameters of the water of the Drenica River, the content of heavy metals in the water, the analysis and comparison of the results obtained using the standard for the assessment of the ecological status of surface waters of Romania (GD 161). Laboratory assays were developed according to standard analysis methods (APHA). The results obtained, analyzed and compared with the values of the parameters according to the standard referred to in this research, confirm that the water of the Drenica River belongs to the class of water with "good quality" only in the source area, while in other flow stations river, especially in the third station S3 (Ferronikel industrial zone), water has "poor quality", passing into the category of "very poor quality". Therefore, in order to improve the current situation, it is recommended to apply the best environmental practices and proper management of industrial waste.

Keywords: assessment, physico-chemical parameters, impact, industrial activity, Drenica River.

INTRODUCTION

Water is the main factor for the existence of life and the elemental substance necessary for the existence of the organisms on Earth (Korça, 2003; Shala, 2015). It is the most abundant substance in the structure of all living beings, and of man, so it can rightly be argued that water is life (Durmishi, 2005).

Recognizing the importance of water for the development of life processes, since ancient times people have set up their settlements near rivers to have the access to drinking water, water for food, cleaning, as well as for various branches of production (Borah & Bera, 2003; Dreshaj, 2012). Since the necessity of water is inalienable, man needs

special care, especially in its reckless use and improper management. Although water is a renewable resource, misuse and mismanagement of the water system can cause the problems in the quality and security of drinking water. Water can be polluted in many ways, both chemical and biological, and can become unclean to drink and unfit for use in other services (Raja et al., 2008). Water resources are wasted and large water pollution is caused. This forces the population to consume polluted water (Durmishi, 2005).

Underdeveloped and developing countries have more problems in this aspect. This primarily comes from very poor water management (Chow et al., 1998). The anthropogenic factor with its activities is increasingly accelerating the

deterioration of water quality parameters both physically and chemically. Environmental water degradation today comes from the increase of municipal, agricultural and industrial activities, and their discharges without any prior treatment. Although industrialization has a significant contribution to economic growth and human well-being, it poses one of the greatest problems in terms of water pollution. Under modern living conditions, industrialism, modern agriculture, etc., not only large of water quantities but also a larger number of raw materials and agencies are used, which after application in various production processes are directly involved or indirect in the life cycle through their pre-discharge into watercourses or large bodies of water (Manahan, 2010). The heavy metals released into the environment as a result of human activities, atmospheric deposition, and erosion will eventually enter groundwater, surface, and ocean water systems. Metals are heavy, persistent and long-lasting toxins in environments where they reach the potential to combine with nutritional continuity. Thus, they are considered as one of the most important pollutants in water systems (Çullari, 2010).

The number of pollutants in the environment which are present in daily life, as well as in industrial and food production, is quite dynamic. Therefore, according to the amount of polluting waste (with special emphasis on organic ones), industrial waste are in the first place, followed by settlement waste and agricultural waste (Bertino & Zepp, 1991).

The main sources of water pollution are: industrial, domestic and uncontrolled landfills of solid substances (Andrea & Tushar, 2004). Specific problems are presented by the industries that discharge toxic substances and insoluble matter into the sewer system, which flow intact through the sewer system equipment or otherwise, to the natural recipient (Kiely, 1998).

Recently, due to the continuous discharge of industrial waste, as well as urban and agricultural waste, the quality of river water in Kosovo country has deteriorated greatly. The water resources in the country are limited (MESP 2003). The surface water in Kosovo, in addition to the pollution coming from natural roads, is also subject to the pollution from the wastewater discharged from residential and industrial activities. This is an important problem, because urban and industrial waters, without any prior treatment, flow into the nearest rivers, the inflows of which have large fluctuations during the seasons of the year. The amount of water discharged exceeds the self-cleaning capacity of the river bed. In this way, the quality of these waters is endangered and is accompanied by serious changes in their properties, which results in many undesirable effects such as: lack of dissolved oxygen, lowering the pH of wine, increasing the capacity of the complex of heavy substances, increase of toxicity and accumulation of harmful substances in the food chain, water eurotrophy, etc. (Dhaka, 2002).

On the basis of the research done so far in the rivers of the Republic of Kosovo, it was shown that one of the rivers that is constantly exposed to the discharge of industrial water is the Drenica river. This pollution comes as a result of the "Ferronikel" industry, which is one of the most worrying environmental problems due to the discharge of water into this river, which Ferronikel uses for cleaning filters and for cooling during nickel production. Many fish species have become extinct as a result of river pollution. The impact that the Ferronikel smelter may have on water pollution could be in groundwater (wells) and in the surface waters of the Drenica River.

METHODOLOGY

For the realization of this study, the authors focused on the analysis and evaluation of physico-chemical parameters of the water of Drenica River, the content of heavy metals in the water and the analysis and comparison of the results obtained using the standard for assessing the ecological status of surface waters of Romania of 2006 (GD 161).

Sampling was performed based on a preliminary study. The water samples were taken at four sampling sites, in two monitoring time periods (spring-summer period). Water sampling and conservation are performed according to standard methods for surface water sampling. Physico-chemical indicators in the Drenica river water have been researched, such as: temperature, color, smell, hardness, turbidity, suspended matter, dissolved oxygen (OT), nitrates, chemical oxygen consumption (GO), nitrites, ammonia, sulfates, chlorides and heavy metals (Pb, Cd, Cu, Zn, Ni, Cr, Fe, etc.). All laboratory determinations were performed according to standard analysis methods (APHA).

Definition and description of monitoring stations

Most rivers in Kosovo, as in other countries, have the spring of each river, as well as the Drenica River. Although the Drenica river is a left tributary of the Sitnica river it is about the length (50 km), the size of the basin (477 km), 16 km east of the Ferronikel industry, the surface of the river is 108.35 km^2 with a degraded bed, the waterof which is used for the irrigation needs of agricultural lands.

The water samples for analysis were taken at four sampling points along the Drenica River (Figure 1):
1) First station (S1) Pjetershtica – sampling at the source of the river,
2) Second station (S2) Drenas – sampling before discharge,
3) Third station (S3) Ferronikel – sampling during discharge,
4) Fourth Station (S4) Qikatov – sampling after discharge.

Water sampling and methods used for analysis

Water sampling for analysis was performed using equipment and containers based on the ISO 5667-6 standard, which sets out the principles to be applied in the design of sampling programs, sampling techniques and treatment of water samples from rivers and flows for physical and chemical evaluation (ISO, 2014; Shala, 2015). The samples were taken in two spring time periods, summer 2020, at four monitoring stations along the Drenica River. All chemicals used during the determination of the parameters in this paper were of purity without (pro analysis), the filter papers used during the treatment of the sample for analysis were of the German manufacturer "Masherey - Nagel" with identification code MN 640 and diameter of 125 mm, while the filtration of samples to determine the level of heavy metal content was performed with syringe and compact filters with a porosity of 0.45 μm (Shala, 2015). The analysis of water samples was performed in the laboratory of the Hydrometeorological Institute of Kosovo. Physicochemical parameters and heavy metals are determined using highly sophisticated measuring devices, such as: WTW350i for electrical conductivity, Aqualitic / PC Compact for turbulence, dissolved oxygen and oxygen saturation is determined by HI 9146, spectrophotometers with spect spectromet UV pastel, total phosphorus and ammonia ions with Secoman Prim Light, etc. In
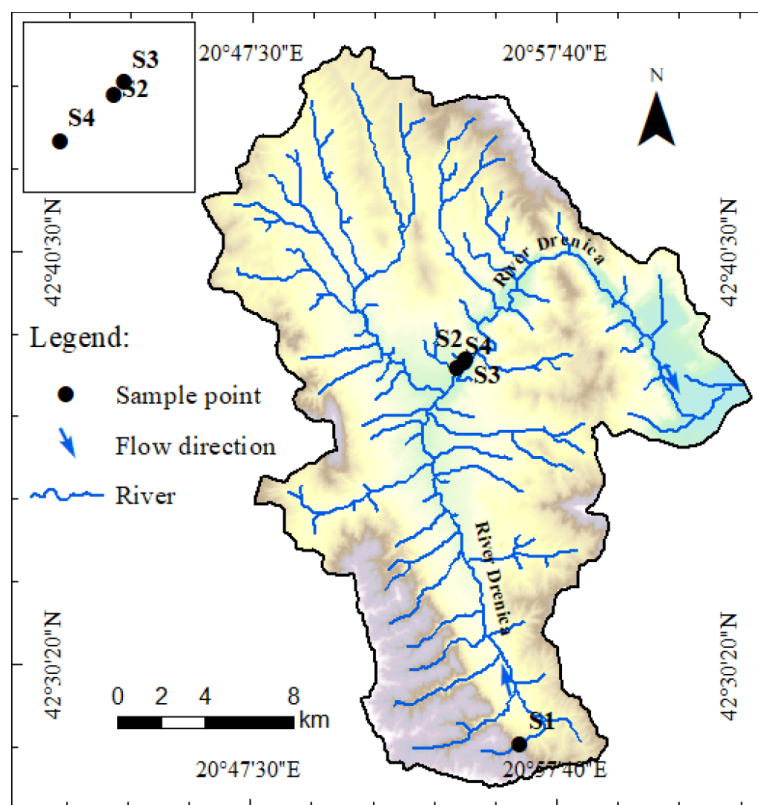

Figure 1. Study area and monitoring stations

turn, the determination of the quantity and content of heavy metals is done with spectrophoto meter of atomic absorption of the American brand "Perkin Elmer" type Analyst 400. All methods used with these devices conform to standard methods, such as: DIN, ISO and EN.

RESUTLS AND DISCUSSION

In order to interpret, compare and discuss the results obtained in this paper, the standard for assessment of the ecological status of surface waters of Romania of 2006 was used (GD 161). The following is a discussion of the results of the physical and chemical parameters analyzed during the spring and summer seasons (Table 1).

Water temperature (TU °C) – is a parameter that directly affects the development of chemical processes in water. On the basis of the results obtained from the two monitoring seasons at the metering stations of the Drenica River, it was found that the water temperature values fluctuate in the spring metering season from 10.8°C (S1) to 14.8°C (S3), while the average value is 13.45°C (Figure 2). In turn, in the summer season

the measurement values range from 16.8°C at station S1 (minimum) and 24.4°C at station S3 (maximum), while the average value of 4 monitoring points is 19.9°C. The temperature in the standard (GD 161) is not specified. Therefore, the standard for drinking water of Albania (STASH 3904-1998) was referred to. According to it, the allowed norm for temperature is from 8 to 15°C. Thus, it can be seen that the monitored waters in the course of the Drenica River in the spring season have been within the allowed norms, while in the summer season in all sampling stations have exceeded the normalized values for the temperature parameter.

Turbidity is the parameter that determines the condition and productivity of water, it is caused by the presence of suspended matter and soluble organic dyes. On the basis of the measurements analyzed in two seasons at the 4 monitoring stations, in the spring season, the values are from 6.46 NTU (S1) minimum to 49.61 NTU (S3) maximum and the average value of 29.53 NTU. In summer, the values from 0.55 NTU (S1) minimum to 4.33 NTU (S3) maximum and the average value of 2.212 NTU. According to the results obtained, the most polluted station during the two

Table 1. Results of physical and chemical parameters analyzed, during the spring and summer season

| Parameters	Symbol	Results							
		S1_Pjetershtivce		S2_Drenas		S3_Ferronikel		S4_Qikatove	
Weather	M	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
		Cloud	Sunny	Cloud	Sunny	Cloud	Sunny	Cloud	Sunny
Sampling time	h	10:46	10:15	11:42	11:00	11:53	11:20	12:23	11:45
Air temperature	T_A	16.8	22.4	17.2	23.7	18.2	24.1	19	24.5
Water temperature	WT	10.8	16.8	13.7	18.5	14.8	24.4	14.5	19.9
Turbidity	TUR	6.46	0.55	28.51	2.01	49.61	4.33	33.55	1.96
Electrical cond.	EC	354	450	443	610	524	760	524	655
TDS	TDS	174	225	222	305	262	381	262	277
Conc. of H^+ Ion	pH	7.12	8.02	8.35	7.70	8.69	8.98	8.48	7.73
Dissolved Oxygen	O_2	6.41	4.33	5.45	2.01	2.28	0.55	2.41	1.96
Saturation	OS	79.4	46.7	70.7	23.9	31.8	9.7	30.1	21.2
COD	COD	5.9	11.7	48.4	16.34	58.1	38.6	51.3	21.4
BOD	BOD_5	2.1	2.8	25.4	16.6	26.8	98.2	25.9	29.2
Total Organic Carbon	TOC	1.9	8.8	12.9	68.2	17.2	77.2	13.2	69.3
Nitrate	NO_3	< 0.1	2.4	0.4	20.4	0.9	24.3	0.8	21.1
Nitrites	NO_2	0.081	< 0.1	0.128	<0.1	0.462	0.3	0.157	0.3
Ammonium	HN_4^+	0.124	< 0.1	0.451	2.2	1.303	2.3	1.257	2.2
Phosphates	PO_4^{3-}	0.104	0.087	0.205	0.558	0.106	0.627	0.186	0.598
Sulphates	SO_4^{2-}	22.3	0.338	44.6	2.130	18.6	0.208	40.9	2.042
Chlorides	Cl^-	5.88	0.150	14.56	1.091	18.37	1.338	6.62	1.111

S – monitoring stations, M – Months.
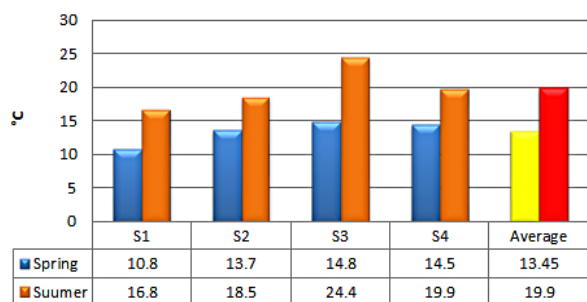
Figure 2. Water temperature according to sampling stations and seasonal variation in Drenica River water
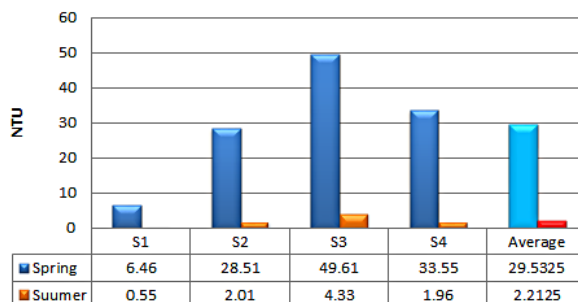

Figure 3. Seasonal variations of turbulence in the water of the Drenica River

seasons was S3, which is located at the place of discharge of water from Ferronikeli and in the vicinity of residential and urban areas, while the source area had a minimal amount of turbidity (Figure 3).

Electrical conductivity χ [μS/cm] – electrical conductivity of water shows an increasing tendency in dry periods and with low rainfall. The values of this parameter in the waters of the Drenica river have shown the following variation: in spring the lowest values (minimum) are observed in the measuring station S1 (354 μS/cm), the maximum value is found in the measuring stations S3 and S4 (524 μS/cm), while the average value is 461.25 μS/cm. In turn, in summer the lowest values (minimum) are observed at the measuring station S1 (450 μS/cm), the maximum value is found at the measuring station S3 (760 μS/cm), while the average value is 618.75 (μS/cm). From the following data it can be seen that in the source points, the values of electrical conductivity have been lower, while in the places with greater pollution the values of electrical conductivity have been higher (Figure 4).

Total dissolved substances – the obtained values of this indicator in the waters of Drinca river, are: in spring the lowest values are observed in

the measuring station S1 (174 mg/l), the maximum value is found in the measuring station S3 and S4 (262 mg/l), while the average value is 230 (mg/l). In summer, the lowest values are observed at the measuring station S1 (225 mg/l), whereas the maximum value is found at the measuring station S3 (381 mg/l), while the average value is 297 (mg/l). The analyzed results show that the source area during the two monitoring seasons had a minimum amount of total water soluble matter, while station S3 (place of discharge of water from Ferronikeli), was the station with the maximum number of total water soluble matter due to of great industrial but also urban pollution (Figure 5).

Dissolved oxygen O2 [mg/l] – is a very important parameter for determining the "state of purity" of water. The measured values of this parameter in the two seasons in the Drenica River have shown fluctuations: in spring the fluctuations of the values are from 2.28 mg/l (station S3) to 6.41 mg/l (station S1), while the average value is 4.13 mg/l (Figure 6). Compared to the standard values (GD161) it results that the water in the Drenica River in stations S3 and S4 water belongs to the fifth class (V) very poor quality, while in S1 and S2, the water belongs to the third class (III) average quality. On the basis of the average value
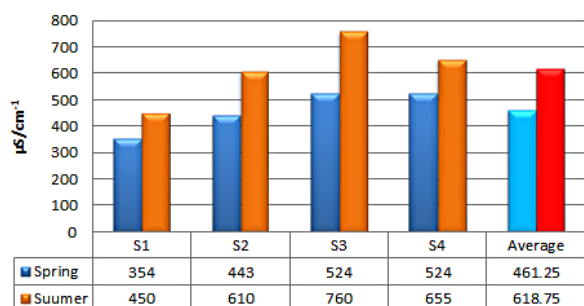

Figure 4. Electrical conductivity according to sampling stations and seasonal variation in the water of the Drenica River
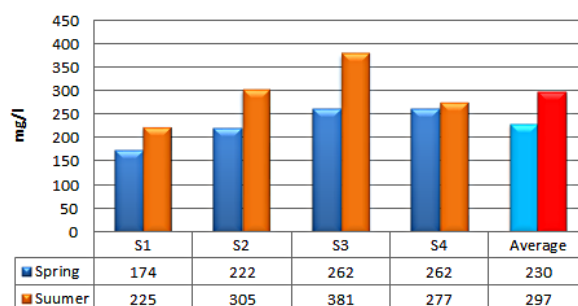

Figure 5. Total dissolved substances according to sampling stations and seasonal variation in the Drenica River water

of 4.13 mg/l in the spring season the water belongs to the second category (II) poor quality. In summer, the value fluctuations are from 0.55 mg/l minimum (S3) to 4.33 mh/l maximum (S1) while the average value is 2.21 mg/l. Compared to the standard values (GD161), it turns out that the water in station S1 water belongs to the second class (II), while in all other stations S2, S3 and S4, the water belongs to the fifth category (V). Moreover, based on the seasonal average value of 2.21 mg/l, the water of this river belongs to the fifth class (V), very poor quality.

O_2 saturation – based on the monitored stations in spring, the values range from a minimum value of 30.1% (S4) to a maximum of 79.4% (S1) and an average of 53%. Compared to the standard values (GD161) in stations S3 and S4, the water belongs to the fourth class (IV) poor quality, while in S1 and S2, the water belongs to the second class (II) good quality. In summer, the values range from 9.7% (S3) minimum to 46.7% (S1) maximum and an average of 25.37%. Compared to the standard values (GD161) only in station S1 the water belongs to the second class (II) poor quality, while in other stations S2, S3 and S4, the water belongs to the first class (I) very poor quality (Figure 7).

Concentration of hydrogen ions (pH) – the pH values in the spring season are presented with small variations (minimum value 7.12 in S1 and maximum 8.69 in S3, while the average is 8.16). In summer, the pH values reached the minimum pH 7.7 in S2 and the maximum pH 8.98 in S3, while the average value of pH measurements in the 4 stations is around 8.1 (Figure 8). The monitored pH values in the water of the Drenica River are compared with the respective values of the GD161 standard. From this comparison, it results that only in station S3 during the two monitoring seasons the maximum values were exceeded, which shows that in this station there are impacts of industrial discharges in the monitored water of the river Drenica. In other stations, the measured pH values are within the standard values.

Chemical oxygen demand – COD⁻ [mg/l] – this parameter explains the rapid acid oxidation. The values measured have shown fluctuations of this parameter: in spring the minimum value is observed in S1 (5.9 mg/l), the maximum value is found in S3 58.1 (mg/l), while the average value is 40.92 mg/l. Compared to the standard values of GD161, it turns out that the water in the Drenica river water belongs to the second class (II) good

quality only in the first station (source) S1, in the second station S2 the water belongs to the fourth class (IV) poor quality, while at stations S3 and S4 it belongs to the fifth class (V) very poor quality. In summer, the minimum value is observed in S1 (11.7 mg/l), the maximum value is found in S3 38.6 (mg/l), while the average value is 22.01 mg/l (Figure 9). Compared to the standard values, it turns out that the water in stations S1 and S2 belongs to the third class (III) of average quality, while in stations S3 and S4 it belongs to the fourth class (IV) of poor quality.

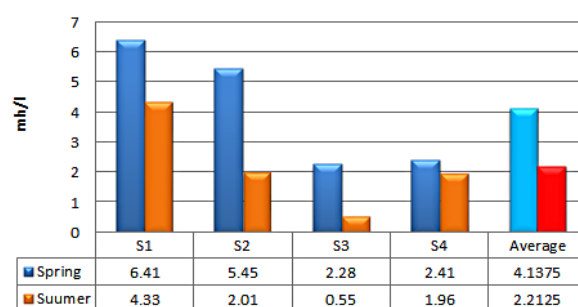Biological oxygen demand BOD_5 [mg/l] – indicates the level of organic water pollution. The

	S1	S2	S3	S4	Average
Spring	6.41	5.45	2.28	2.41	4.1375
Suumer	4.33	2.01	0.55	1.96	2.2125

Figure 6. Dissolved oxygen according to sampling stations and seasonal variation in the Drenica River water

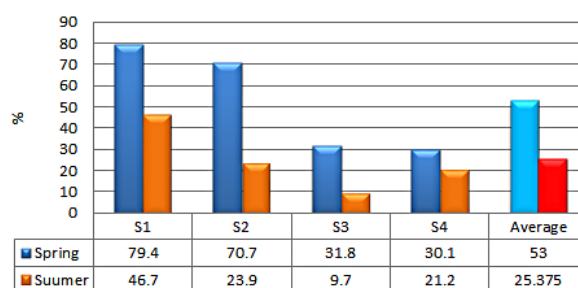|	S1	S2	S3	S4	Average
Spring	79.4	70.7	31.8	30.1	53
Suumer	46.7	23.9	9.7	21.2	25.375

Figure 7. Oxygen saturation of water according to sampling stations and seasonal variation in the water of the Drenica River

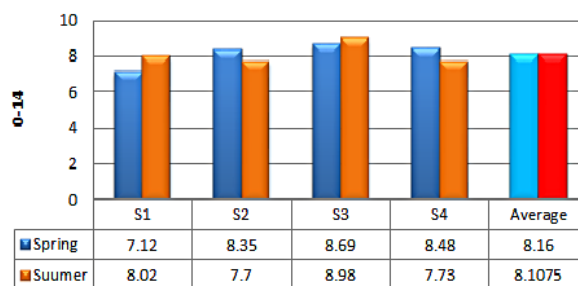|	S1	S2	S3	S4	Average
Spring	7.12	8.35	8.69	8.48	8.16
Suumer	8.02	7.7	8.98	7.73	8.1075

Figure 8. The pH according to sampling stations and seasonal variation in the Drenica River water

greater the biological demand for oxygen, the greater the amount of biologically degradable substances and the higher the degree of their organic pollution. The measured values at the four monitoring stations on the Drenica River yielded the following results: in spring the minimum value of 2.1 mg/l is found at station S1, the maximum 26.8 mg/l at station S3, while the average value is 20.05 mg/l. The values obtained for BOD_5, compared to the values of standard GD161, show that the water in the Drenica river belongs to the first class (I) very good quality only in the first station (source) S1, while in stations S2, S3 and S4 it belongs to the fifth class (V) very poor quality. In summer, the minimum value is found in S1 (2.8 mg/l), the maximum value is observed in S3 98.2 (mg/l), while the average value is 36.7 mg/l (Figure 10). Compared to the standard values, it turns out that the water in stations S1 belongs to the first class (I) very good quality, in station S2 it belongs to the fourth class (IV) poor quality, while in stations S3 and S4 it belongs to the fourth class (V) very poor quality.

Total Organic Carbon – the values of Total Organic Carbon in spring have fluctuated in the range of 1.9 mg/l, the minimum is found in station S1, the maximum value of 17.2 mg/l is observed in station S3, while the average value is 11.3 mg/l. In summer the values have fluctuated

in the range of 8.8 mg/l, the minimum value is observed at station S1, the maximum value 77.2 mg/l is found at station S3, while the average value is 55.87 mg/l (Figure 11).

Nitrates NO_3^- [mg/l] – small quantities are present in surface water, while larger quantities are found in groundwater. The measured values for nitrates are as follows: in spring, the minimum value in S2 is 0.4 mg/l, the maximum is 0.9 mg/l (S3), while the average value is 0.7 mg/l. In the first locality, the values were below the level of detection. (<0.01). Compared to the values of the GD161 standard, it turns out that the water in the Drenica River in stations S2 S3 and S4 is of the first class (I). In summer, the minimum is 2.4 mg/l (S1), the maximum 24.3 mg/l (S3), while the average value is 17.05 mg/l (Figure 12). On the basis of the ecological status of surface waters (GD161), the water in station S1 is of the second class (II), while in the other stations the water is of the fifth class (V). On the basis of the seasonal averages of the four stations based on (GD161), the water in spring belongs to the first class (I) while in the summer to the fifth class (V). Thus, it is seen that the greatest deterioration of river water quality in terms of this parameter is observed in S3.

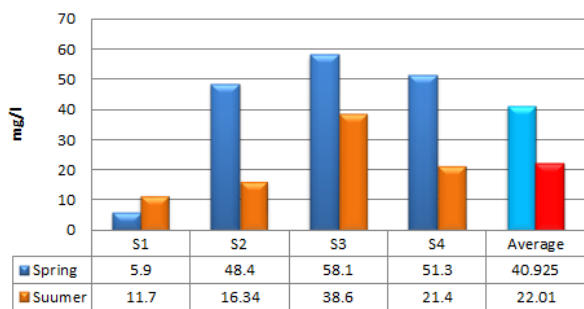Nitrites NO_2^- [mg/l] – are terrestrial and their amount in drinking water is maximized, they are

Figure 9. COD according to sampling stations and seasonal variation in the water of the Drenica River
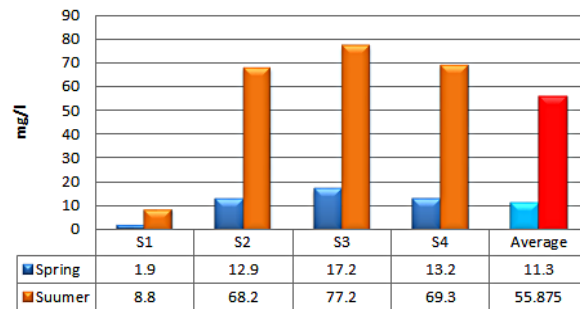
	S1	S2	S3	S4	Average
Spring	5.9	48.4	58.1	51.3	40.925
Suumer	11.7	16.34	38.6	21.4	22.01

Figure 11. TOC according to sampling stations and seasonal variation in the water of the Drenica River

	S1	S2	S3	S4	Average
Spring	1.9	12.9	17.2	13.2	11.3
Suumer	8.8	68.2	77.2	69.3	55.875
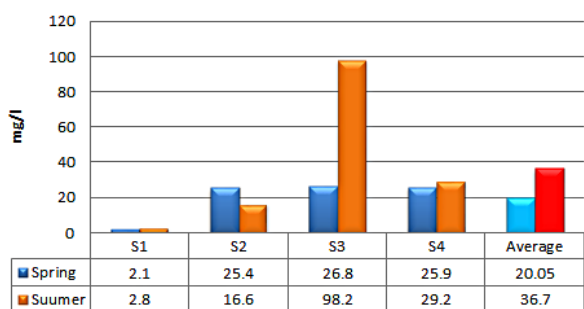
Figure 10. BOD according to sampling stations and seasonal variation in the water of the Drenica River

	S1	S2	S3	S4	Average
Spring	2.1	25.4	26.8	25.9	20.05
Suumer	2.8	16.6	98.2	29.2	36.7
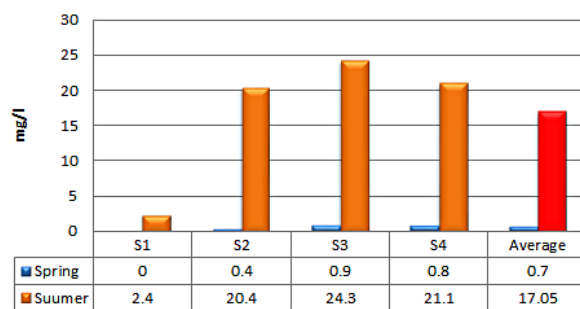
Figure 12. Nitrates according to sampling stations and seasonal variation in the Drenica River water

	S1	S2	S3	S4	Average
Spring	0	0.4	0.9	0.8	0.7
Suumer	2.4	20.4	24.3	21.1	17.05

formed with the dissolution of biological and industrial pollution. The results measured in the two seasons in the Drenica river have shown the following values: in the spring season, the minimum is 0.081 mg/l (S1), the maximum 0.462 mg/l (S3), while the average value is 0.207 mg/l (Figure 13). Compared to the standard (GD161) in the first station S1, the water belongs to the fourth class (IV) poor quality, while in the other three stations S2, S3 and S4 it belongs to the fifth class (V) very poor quality.

In summer, at the first and second monitoring stations S1 and S2, it did not turn out to have nitrite1, as the values were below the deduction level. In contrast, the values of nitrites in station S3 and S4 are 0.3 mg/l and the water of these stations belongs to the fourth category (IV) poor quality.

Ammonia NH_4^+ [mg/l] – the values of this parameter in the water of the Drenica river are as follows: the minimum values during the two seasons were measured at the first station (0.124 mg/l and <0.1 mg/l), while the maximum values also in the two seasons are registered in the third station S3 (1,303 mg/l and 2.3 mg/l, whereas the average values in spring are 0.783 mg/l and summer are 2.23 mg/l (Figure 14). Compared to the values of the Romanian standard for assessment of ecological status of surface waters (GD161), it turns out that in station S1 in spring the water belongs to the first class (I) while in summer the values of ammonia in this station are below the values of dedication. In the third station in the two seasons, the water belongs to the fourth class (IV) poor quality.

Chromium – measurements for Cr^{3+} in the water of the Drenica River yielded the following results: in both monitoring seasons (spring and summer) the lowest values were recorded at station S1 and compared to the reference standards, the water belongs to the first category (I) (Figure 15). In turn, the highest values during the two seasons are recorded in the third station (S3 at the place of discharge of water from Ferronikeli) and the water belongs to the third category (III – summer) and the fourth category (IV – spring).

Cadmium (Cd^{2-}) – as a pollutant in water, it can come from industrial discharges and mineral waste. In the water of the Drenica river, the following values of cadmium were recorded: in the first station S1 in the two monitoring seasons (spring and summer) the values are below the values of dedication (Figure 16). While in other stations S2, S3 and S4 in both seasons the values turned out to be above the maximum values, which – compared to the values of the standard of the Republic of

Romania for the assessment of the ecological status of surface waters (GD161) – rank the water of this river in fifth grade (V) very poor quality. The highest values were recorded at the third S3 station during the two monitoring seasons.
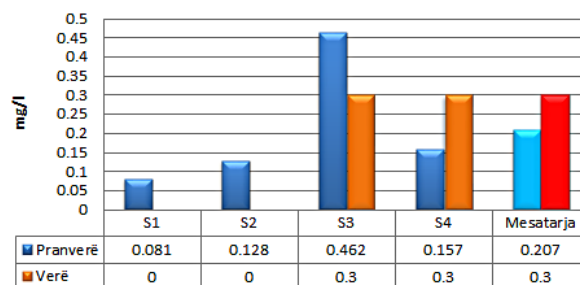

	S1	S2	S3	S4	Mesatarja
■ Pranverë	0.081	0.128	0.462	0.157	0.207
■ Verë	0	0	0.3	0.3	0.3

Figure 13. Nitrite according to sampling stations and seasonal variation in the Drenica River water

	S1	S2	S3	S4	Average
■ Spring	0.124	0.451	1.303	1.257	0.78375
■ Suumer	0	2.2	2.3	2.2	2.233333333
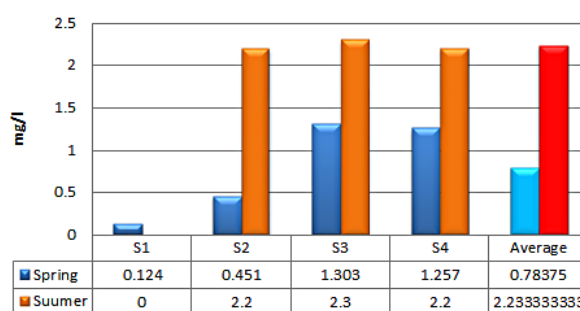
Figure 14. Ammonium according to sampling stations and seasonal variation in the Drenica River water

	S1	S2	S3	S4	Average
■ Spring	0.002	0.038	0.104	0.032	0.044
■ Suumer	0.003	0.051	0.099	0.048	0.05025

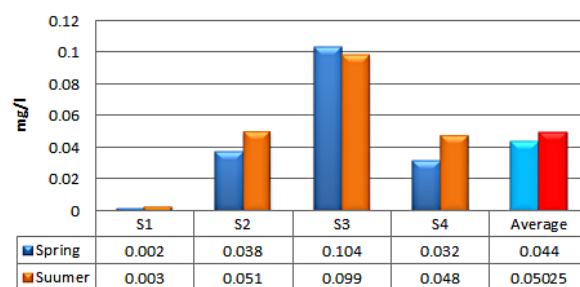**Figure 15.** Chromium content (mg/l) in the analyzed water samples and seasonal variation in the water of the Drenica River

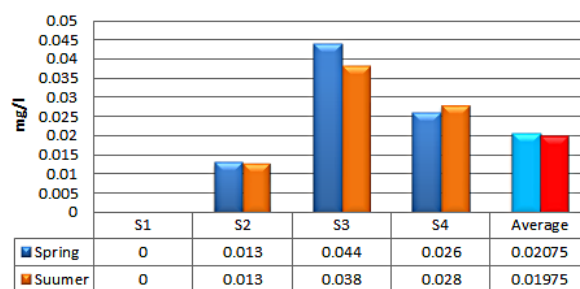|	S1	S2	S3	S4	Average
■ Spring	0	0.013	0.044	0.026	0.02075
■ Suumer	0	0.013	0.038	0.028	0.01975

Figure 16. Cadmium content (mg/l) in the analyzed water samples and seasonal variation in the water of the Drenica River

Nickel (Ni^{2+}) – from the analysis of the samples from two seasons at monitoring stations in the Drenica River, is was observed that the nickel values in the spring season range from 0.009 mg/l (S2) minimum to 0.038 mg/l (S3) maximum, with an average value of 0.014 mg/l. In summer, the minimum value is 0.008 mg/l (S1), while the maximum value is 0.052 mg/l (S3) and the maximum value is 0.02 mg/l (Figure 17).

Zinc (Zn^{2+}) – measurements of zinc in the water of the river Drenica turned out to be within the minimum values, which – compared to the values of the standard of the Republic of Romania for assessment of ecological status of surface waters (GD161) – is within limits and water of this river ranks in first grade (Figure 18).

Manganese (Mn^{2+}) – the Manganese values in the water of the Drenica River measured in the two seasons in all monitoring stations have turned out to be above the maximum values, which – compared to the values of the standard of the Republic of Romania for assessing the ecological status of waters surface (GD161) – classifies the water of this river in the fifth class (V) (Figure 19).

Copper (Cu^{2+}) – the values of copper in the water of the river Drenica measured in the two seasons are: in station S1, in both seasons, the

values obtained were below the values of dedication. In spring, the values range from 0.006 mg/l (S2) minimum to 0.022 mg/l (S3) maximum. In summer, the values range from 0.008 mg/l (S2) minimum to 0.028 mg/l (S3) maximum. In both seasons, the highest values are recorded in the third station S3, where – based on the reference standard – the water of this station belongs to the second class (II) (Figure 20).

Iron (Fe^{2+}) – is an important metal for living things, but becomes toxic in high doses. The values of Fe^{2+} measured in the two seasons in the water of the Drenica river in all monitoring stations turned out to be above the maximum values, which – compared to the values of the standard of the Republic of Romania for the assessment of ecological status of surface waters (GD161) –classified this river in the fifth category (V) (Figure 21).

Lead (Pb^{2+}) – is also a heavy metal (poisonous) that in aquatic environments comes from various industrial sources and mines. Lead poisoning of humans causes disorders in the functioning of the kidneys, reproductive system, liver and nervous system. The Pb values in the water of the Drenica River in spring range from 0.001 mg/l (S1) minimum to 0.056 mg/l (S3) maximum, with an average value of 0.025 mg/l. In summer, the
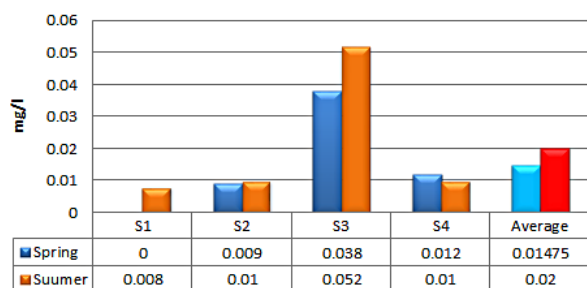

	S1	S2	S3	S4	Average
Spring	0	0.009	0.038	0.012	0.01475
Suumer	0.008	0.01	0.052	0.01	0.02

Figure 17. Nickel content (mg/l) in the analyzed water samples and seasonal variation in the water of the Drenica River

	S1	S2	S3	S4	Average
Spring	0.028	0.062	0.103	0.083	0.069
Suumer	0.035	0.087	0.095	0.088	0.07625

Figure 19. Manganese content (mg/l) in the analyzed water samples and seasonal variation in the water of the Drenica River

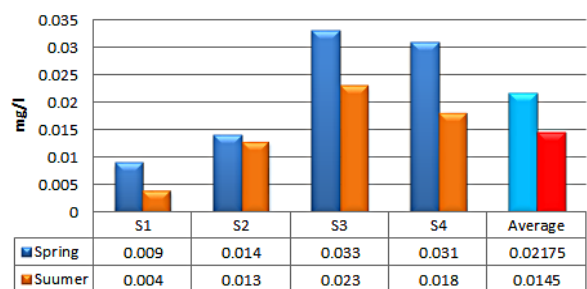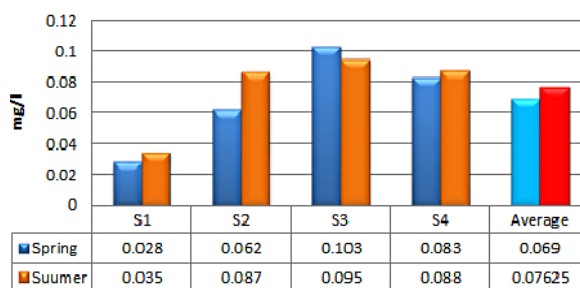|	S1	S2	S3	S4	Average
Spring	0.009	0.014	0.033	0.031	0.02175
Suumer	0.004	0.013	0.023	0.018	0.0145

Figure 18. Zinc content (mg/l) in the analyzed water samples and seasonal variation in the water of the Drenica River

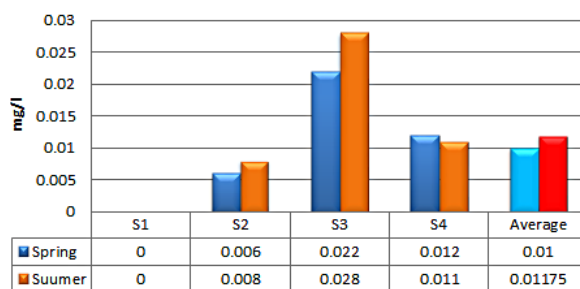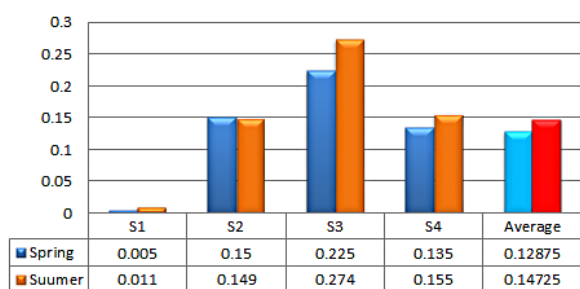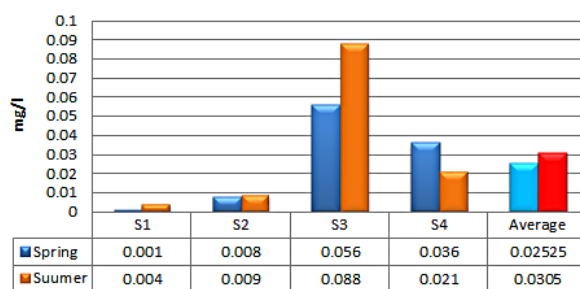|	S1	S2	S3	S4	Average
Spring	0	0.006	0.022	0.012	0.01
Suumer	0	0.008	0.028	0.011	0.01175

Figure 20. Copper content (mg/l) in the analyzed water samples and seasonal variation in the water of the Drenica River

Figure 21. Iron content (mg/l) in the analyzed water samples and seasonal variation in the water of the Drenica River

Figure 22. Lead content (mg/l) in the analyzed water samples and seasonal variation in the water of the Drenica River

Table 2. Heavy metal results measured in the Drenica River water, mg/L

Metals	Symbols	Results							
		S1_Pjetershtice		S2_Drenas		S3_Ferronikel		S4_Qikatove	
Chromium	Cr	0.002	0.003	0.038	0.051	0.104	0.099	0.032	0.048
Cadmium	Cd	<0.001	<0.001	0.013	0.013	0.044	0.038	0.026	0.028
Nickel	Ni	<0.006	0.008	0.009	0.010	0.038	0.052	0.012	0.016
Zinc	Zn	0.009	0.004	0.014	0.013	0.033	0.023	0.031	0.018
Manganese	Mn	0.028	0.035	0.062	0.087	0.103	0.095	0.083	0.088
Copper	Cu	<0.002	<0.002	0.006	0.008	0.022	0.028	0.012	0.011
Iron	Fe	0.005	0.011	0.125	0.149	0.225	0.274	0.135	0.155
Leaden	Pb	0.001	0.004	0.008	0.009	0.056	0.088	0.036	0.021
Sodium	Na	11.875	13.364	9.982	12.615	3.238	6.426	8.533	12.214
Potassium	K	0.630	1.224	4.078	4.621	0.652	2.321	3.325	4.222

values range from 0.004 mg/l (S1) minimum to 0.088 mg/l (S3) maximum, with an average value of 0.030 mg/l. In both seasons, the highest values are recorded in the third station S3, where – based on the reference standard – the water of this station belongs to the fifth class (V) (Figure 22).

All heavy metal results measured in the Drenica river water are shown in Table 2.

CONCLUSIONS

On the basis of the processing, analysis and comparison of the results found from the experimental part of this research, it can be concluded that all analyzed parameters of the Drenica River water have shown fluctuations of values from one monitoring station to another, during the two monitoring seasons. Thus, it can be stated that the environmental condition of the Drenica River in the first station S1 (at the source of the river) is relatively good, while in the other three monitored stations there is a significant pollution, especially in the third station S3 (at the place of discharge of water from Ferronikeli). In the third station S3, a deterioration of the values of the monitored parameters which determine the water quality is observed. This confirms the impact of various polluting pressures, in particular on the third station S3 pollution, coming as a result of water discharges from Ferronikeli. The obtained and analyzed results show that the water quality of the Drenica River, compared to the values of the parameters according to the standard referred to for the assessment of the ecological status of the surface waters of Romania in 2006 (GD 161) used in this paper, confirm that the water of the Drenica river belongs to the class of water of "good quality" only in the source area (where there are no significant influences of anthropogenic factor), while in other stations in the rest of the river flow and especially in the station third S3 water has "poor quality", passing into the category of "very poor quality". The results for determining the amount of heavy metals analyzed in the 4 monitoring stations in the water of the river Drenica confirm the presence of metals (Cr, Cd, Ni, Zn, Mn, Cu, Fe, Pb, Na and K) monitored

during the two seasons (spring and summer) at almost all monitoring stations. According to the obtained results, the highest values of metal concentration during the two monitored time periods were found in the third S3 sampling site (which is thought to be due to the influence of emissions from Ferronikel industrial waste), followed by the fourth S4 sampling site. Compared to the standard referred to (GD 161) in this paper for the reference values of heavy metals, it was found that the level of their concentration in the water of the Drennica river has been high. Therefore, based on the values of the results obtained for all presented physico-chemical parameters, including heavy metals, it can be concluded that the third station S3 has the most impact on water pollution of the river Drenica as a result of impact of discharged waters from the Ferronikel industrial area.

REFERENCES

1. Abazi A.S. 2015. Disertacioni i doctorates. Analizimi i ndikimit te aktivitetit bujqësor dhe industrial në cilësin e ujërave dhe disa parametrave mjedisor të lumit Sitnuica, Kosovë.

2. American Public Health Asociaton. 1992. Standard Methods for the Examination of Water and Wastewater, 18 Ed., Washington D.C.

3. Arbneshi T., Mehmeti A., Beqa L., Hasimj H., Rugova M. 2004. The level concentration of lead cadmium, copper, zinc and phenols in the water river of Sitnica. In: 19 FECS Conference and 2 SCF meeting on Chemistry and the Environment, Bordeaux, 434.

4. Bisëas A.K. 2002. International Review for Environmental Strategies, 3(2). https://pub.iges.or.jp/pub/international-revieË-environmental-29.

5. Cullari A. 2010. Kimia e mjedisit.

6. DA, MMPH. 2003. Raport mbi gjendjen ambientale në Kosovë, Prishtinë.

7. DA, MMPH. 2010. Raport mbi gjendjen e ujrave në Kosovë, Prishtinë.

8. Daka, S. 2002. Ndikimi i ndotjes së lumenjeve në ujrat nëtokësorë. Në përmbledhje punimesh. Seminari I dytë nga hidroteknika, Prishtinë.

9. Gallopín G.C. 2050. Global Water futures 2050. Five Stylized Scenarios.

10. https://www.h2oconcepts.com/health-WHO.php

11. Klasnja M. 2014. Voda uprehrambenjoj I idustrijuj.

12. Lazo P., Çullaj A. 2008. Script metoda tëanalizes. Tiranë.

13. Manahan S.E. 2010. Water Chemistry: Green Science and Technology of Nature's Most Renewable Resource. CRC Press.

14. Menaxhimi i Burimeve Natyrore në Evropën Juglindore: Pyjet, Tokat dhe Ujrat, 2017.

15. Montogomery M.J. 1984. Water treatment principles and desing, New York.

16. QAP. Prishtinë Shtator. 2014. Hartuest tëRaportit: Agim Kelmendi dhe Milaim Morina.

17. Rastovčan-Mioč A. 2009. Uvodu u ekologiju. Skrip.

18. Sofili T. Ekotoksikologija. 2014.

19. Štrkalj A. 2014. Oneçisçenje I zaštitavoda.

20. Tauxe-Wuersch A., De Alencastro L.F., Grandjean D., Tarradellas J. 2005. Occurrence of several acidic drugs in sewage treatment plants in Switzerland and risk assessment. Water Research, 39(9), 1761-1772

21. The United Nations World Water Development Report. 2015.

22. UNICEF-WHO. 2016. Progress on sanitation and drinking Water: 2015 Update and MDG assessment. Geneva: WHO Press.

23. Walakira P. 2011. BSc Tehnologia-Kimia. A dissertation submited in partial fulfillment of the requinrements for the award of Master of Science in Environmental and Natural Resources of Makerere University.

24. Water Quality Monitoring - A Practical Guide to the Design and Implementation of Fresh Water Quality Studies and Monitoring Programmes.

25. Watershed Indicators, EPA, USA. 6. http://www.ammk-rks.net/

26. WHO. 2011. Library cataloguing-in-publication data guidelines for drinking water quality, 4th ed. World Health Organization.