

## QUALITY ASSESSMENT OF RIVER WATER OF GRAQANICA (KOSOVO) AND CORRELATION STUDY OF CHEMICAL DATA

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**Abstract.** In this study the assessment of river water quality and correlation coefficients between different pairs of variables of water samples, were investigated. The main objective of this study was to perform assessment of water quality of Graqanica River. Statistical studies have been carried out by calculating of basic statistical parameters, anomalies (extremes and outliers) and correlation coefficients between different pairs of variables. The statistical regression analysis has been found a high positive correlation relationship between turbidity and EC, hardness,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ . EC showed high significant positive relationship with turbidity, hardness, COD,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ . Consumption of  $\text{KMnO}_4$  showed high significant positive relationship with COD, TOC,  $\text{NO}_2^-$  and  $\text{PO}_4^{3-}$  (possible sign of waste waters from settlements influence). From the results of field work and laboratory analyses it was found out that river water quality not fulfill the criteria set by the World Health Organization and the distribution of pollutants indicated anthropogenic sources of pollutants mainly from Kishnica and Badovci flotation tailing dams and waste waters.

**Keywords:** water, quality assessment, correlation coefficients, Graqanica river, statistical analysis

### Introduction

The sources of physico-chemical contamination are numerous and include the land disposal of sewage effluents, sludge and solid waste, septic tank effluent, urban runoff and agricultural, mining and industrial practices (Close et al., 2008; Keswick et al., 1984). Chemical contamination of drinking water is often considered a lower priority than microbial contamination by regulators, because adverse health effects from chemical contaminations are generally associated with long-term exposures, whereas the effects from microbial contamination are usually immediate practices (Thompson et al., 2007). The quality of drinking water is an issue of primary in-

terest for the residents of the European Union (Chirilă et al., 2010). In peat bogs, water flows freely in the active layer of water or acrotelm. Water storage is critical to the balance of water in peat swamps and at surrounding areas. Logging activity, agriculture, peat extraction and destruction of peat swamp drainage activity also give a negative effect and has a bad implication on the hydrology (Hamilton et al., 2008). Decomposition of organic matter and pollution due to anthropogenic activity are the main sources of pollution of water (Montgomery, 1996). Therefore, multidisciplinary collaborative research is essential for understanding the pollution processes. As reported by Brils (2008), adequate water quality in Europe is one of the most eminent concerns for the future. Good management of natural and environmental waters will give results if leading institutions constantly monitor information about environmental situation. Therefore, seeing it as a challenge for environmental chemists, our goal is to determine the amount and nature of pollutants in the environment. One could claim that the most polluted areas in the world are those with the densest population. It should therefore be the foremost goal of environmentalists to prevent such pollution, and to educate the population towards proper management of ecosystems (Jbajn et al., 1998).

Until recently, the waters of Kosovo have been poorly investigated. Gashi et al. (2009) performed first step with investigation of the rivers Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica, which are of supra-regional interest. They performed investigations of mineralogical and geochemical composition and of contamination status of stream sediments of mentioned rivers of Kosovo. By comparing the concentrations of toxic elements with the existing criteria for sediment quality, in that study was found that two sites in Sitnica River are significantly polluted, especially locations in Fushë Kosova (Kosovo Polje) and in Mitrovica. This was assumed to be caused by Zn and Pb processing by flotation and Zn-electrolysis factory. In Morava e Binçës River, two sites were found to be polluted with Cd. The authors of that paper suggested future monitoring of sediments and possibly remediation of Sitnica and Morava e Binçës rivers. As Drenica River is the most important tributary of Sitnica River, the current paper presents next step in detailed investigation and monitoring of Sitnica river watershed, which is most polluted river system in Kosovo. Gashi et al. (2011; 2013; 2014) performed research of mass concentrations of ecotoxic metals: Cu(II), Pb(II), Cd(II), Zn(II) and Mn(II) in waters of four main rivers of Kosovo. The main goal of that work was to suggest to authorities concerned a monitoring network on main rivers of Kosovo (Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica). The authors also aimed to suggest application of WFD (Water Framework Directive) in Kosovo as soon as possible and performed research could be the first step towards it, giving an opportunity to plan the monitoring network in which pollution locations will be highlighted. The authors highlighted two locations in Sitnica River as very polluted with ecotoxic elements and possible remediation by Kosovo authorities concerned was suggested. Troni et al.

(2013) compared the surface water quality in Kosovo in Lumbardhi River basin in the region of Peja. From chemical aspects are investigated some of main indicators pollution as: pH value (in situ), dissolved oxygen, lead, cadmium, copper, zinc, arsenic, cobalt, nickel, uranium, bromine, nitrites, etc.

### **Study area and sampling**

The Graqanica is a river in Kosovo, about 19 km long left bank tributary to the Sitnica River. The Graqanica River originates from Gollaku Mountain, in Prishtina region. The river originally flows to the west and receives many streams coming down from Badovci, Kishnica and Hajvalija villages. The composite valley of the river is densely populated, with several large villages (Badovci, Kishnica, Graqanica, Hajvalija, Laplje Selo, Preoci, Lepia, Dobreva e ulët and Vragolia). Near the village of Vragolia, the Graqanica River splits and empties into the Sitnica River. The Graqanica River belongs to the Black Sea drainage basin. Sampling of river water was performed at 01.04.2014. The sampling network was established in order to cover the river spatially, taking into account anthropogenic pressures, the different habitats and the hydromorphological conditions of the river. Portable instruments were used to measure water temperature, electrical conductivity (EC), pH and total dissolved solids (TDS). At each sampling location, water samples were collected in polyethylene bottles. Before taking water samples, the bottles were rinsed three times with lake's water to be collected. Water samples were collected for analysis according to the recommended procedures, near the river bank at a depth of 15 cm, put into 1dm<sup>3</sup> bottles stored at 4° C.<sup>1,2)</sup> Preservation and experimental procedure for the water samples are carried out according to the standard methods for examination of water Samples are preserved in refrigerator after treatment<sup>3)</sup> (Baba et al., 2003; Dalmacija, 2000). Geographic coordinates were measured by GPS device Extras, "GARMIN, 12 channel" and locations were well described. The levels of some physico-chemical parameters of river waters are compared with the World Health Organization standards for drinking water.<sup>4)</sup> The study area with the sampling locations is shown in Fig. 1 and the details about all sampling sites are presented in Table 1.

**Table 1.** Sampling stations with detailed description

Sample	Locality	Coordinates	Height over sea	Possible pollution sources
S <sub>1</sub>	Badovci	34T 0518013 UTH 4717512	613.0m	Mining from Hajvalia and Badovci, traffic
S <sub>2</sub>	Kishnica	34T 0517393 UTH 4716754	606.0m	Kishnica's flotation deposit, pollution from peripheral rivers, settlement and traffic

S <sub>3</sub>	Graqanica	34T 0514789 UTH 4716419	591.3m	Kishnica's flotation deposit, waste waters from Graqanica and agriculture
S <sub>4</sub>	Miradi e epërme	34T 0507132 UTH 4716510	556.3m	Settlement and agriculture
S <sub>5</sub>	Miradi e epërme	34T 0507127 UTH 4716508	552.0m	Waste waters from Miradia village, milk factory "Bylmeti" and agriculture
S <sub>6</sub>	Vragolia	34T 0505534 UTH 4717628	547.0m	Waste waters from Miradia village, agriculture and traffic



Fig. 1. Study area with sampling stations

### Materials and methods

Twice distilled water was used in all experiments. All instruments are calibrated according to manufacturer's recommendations. All tests were performed at least three times to calculate the average value. Temperature of water was measured immediately after sampling, using digital thermometer, model "Quick 63142". Measurements of pH were performed using pH/ion-meter, "Hanna Instruments". Electric conductivity was measured by conductometer "InoLab WTW", turbidity (turbidimetric method with formazine standard), chemical expense  $\text{KMnO}_4$  was determined by Thiemann Kübel volumetric method (boiling in acidic environment), chlorides was determined by argentometric titrimetric method, the alkalinity was determined by titrating it against standard HCl solution, using phenolphthalein and methyl orange indicators, total and temporary hardness of water were measured

using chemicals of p.a. purity. Total hardness was determined by EDTA titration, using eriochrome black T indicator. Temporary hardness (carbonate hardness) was also determined. It is due to the presence of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ . Some of physico-chemical parameters ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ) were determined using UV-VIS spectrometry method. “WTW S12 Photometer”, “SECOMAM Prim Light spectrophotometer”, “SECOMAM Pastel UV spectrophotometer” and “WTW S12 Photometer” are used with a monochromatic irradiation in ultraviolet (UV) and visible (VIS) spectral range of 190-1100 nm. Its measurement region, in a cavette of 10 mm, was  $\lambda = 340\text{-}800\text{ nm}$ , is dedicated for drinking waters analysis, discharged and sea water.

### Statistical methods

Program Statistica 6.0<sup>5)</sup> was used for the statistical calculations in this work, such as: descriptive statistics, Pearson’s correlation factor and two dimensional box plot diagrams for determination of anomalies (extremes and outliers) for solution data. Relationships between the observed variables were tested by means of correlation analysis. The level of significance was set at  $p < 0.05$  for all statistical analyses. It was qualitatively assumed that the absolute values of  $r$  between 0.3 and 0.7 indicate good association, and those between 0.7 and 1.0 strong association between elements.

### Results and discussion

The physico-chemical parameters: water temperature, pH, turbidity, dissolved oxygen, EC, TDS, total hardness, COD, BOD, TOC, consumption of  $\text{KMnO}_4$ , concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ -total,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , etc. are presented in Table 2. Basic statistical parameters for 19 variables in 6 water samples are presented in Table 3. Using experimental data and box plot approach of Tukey (1977), anomalous values (extremes and outliers) in waters were determined for the whole region. Two dimensional scatterplot with plots diagrams are presented in Fig. 2. Anomalous values (outliers and extremes) for some variables are presented in Table 4.

**Table 2.** The physico-chemical parameters of some parameters in water samples

Parameter	S1	S2	S3	S4	S5	S6
W. T. / ° C	16.8	19.8	14.6	14	14.9	15.4
pH /1	6.8	6.1	6.06	6.18	6.16	6.75
Turbidity /NTU	19.9	32.1	8.2	20.5	8.4	8.6

Dissolved oxygen /mgL <sup>-1</sup>	9.83	8.2	6.14	4.2	6.17	12
EC /μScm <sup>-1</sup>	1194	3010	2160	1163	1198	1173
TDS /mgL <sup>-1</sup>	15.8	54	55	4.2	12.2	9.3
Hardness (total) /°dH	35.91	99.5	66.234	27.93	30.59	30.32
COD /mgL <sup>-1</sup>	27.4	66.5	125	23.8	36.5	29
BOD /mgL <sup>-1</sup>	12.1	14.8	70	19.8	24.8	20.2
TOC /mgL <sup>-1</sup>	9.4	10.6	56	16	19.8	16.2
Cons. of KMnO <sub>4</sub> /mgL <sup>-1</sup>	35.644	45.61	80.9	61.65	45.61	68.06
Detergent /mgL <sup>-1</sup>	-	-	3.4	-	-	-
Alkalinity (total) /mgL <sup>-1</sup>	9.13	4.87	5.1	4.97	6.45	5.01
HCO <sub>3</sub> <sup>-</sup> /mgL <sup>-1</sup>	46.814	297.07	311.1	303.17	393.45	305.61
NH <sub>4</sub> <sup>+</sup> /mgL <sup>-1</sup>	-	-	2.261	6.337	6.043	5.429
NO <sub>2</sub> <sup>-</sup> (total) /mgL <sup>-1</sup>	0.064	0.151	1.008	0.281	0.384	0.225
NO <sub>3</sub> <sup>-</sup> /mgL <sup>-1</sup>	0.2	-	0.8	6.4	7	3.7
Ca <sup>2+</sup> /mgL <sup>-1</sup>	22.344	52.934	30.59	17.29	19.684	14.896
Mg <sup>2+</sup> /mgL <sup>-1</sup>	13.566	46.814	35.644	10.64	10.906	15.424
SO <sub>4</sub> <sup>2-</sup> /mgL <sup>-1</sup>	4.357	13.95	10.27	5.927	6.16	5.609
Cl <sup>-</sup> /mgL <sup>-1</sup>	49.6	15.3	19.08	26.72	34.35	38.17
PO <sub>4</sub> <sup>3-</sup> /mgL <sup>-1</sup>	0.087	0.029	2.329	2.43	1.647	1.542

**Table 3.** Descriptive statistics of the 19 variables in 6 cases

Variable	Descriptive statistics						
	Mean	Geometric	Median	Min.	Max.	Var.	Std.Dev.
W. T.	15.917	15.807	15.150	14.000	19.800	4.5	2.1245
pH	6.342	6.334	6.170	6.060	6.800	0.1	0.3387
Turbidity	16.283	14.070	14.250	8.200	32.100	93.5	9.6700
Diss. oxygen	7.757	7.321	7.185	4.200	12.000	8.1	2.8384

EC	1649.667	1527.190	1196.000	1163.000	3010.000	597327.5	772.8696
TDS	25.083	16.785	14.000	4.200	55.000	533.7	23.1022
Hardness	48.414	42.781	33.250	27.930	99.500	829.7	28.8040
COD	51.367	42.311	32.750	23.800	125.000	1541.3	39.2594
BOD	26.950	22.341	20.000	12.100	70.000	464.6	21.5534
TOC	21.333	17.491	16.100	9.400	56.000	303.3	17.4157
Co. of $\text{KMnO}_4$	56.246	54.135	53.630	35.644	80.900	285.5	16.8955
Alkalinity	5.922	5.757	5.055	4.870	9.130	2.8	1.6787
$\text{HCO}_3^-$	276.202	232.441	304.390	46.814	393.450	13922.3	117.9927
$\text{NO}_2^-$	0.352	0.249	0.253	0.064	1.008	0.1	0.3394
$\text{Ca}^{2+}$	26.290	23.836	21.014	14.896	52.934	199.7	14.1310
$\text{Mg}^{2+}$	22.166	18.533	14.495	10.640	46.814	233.6	15.2855
$\text{SO}_4^{2-}$	7.712	7.098	6.044	4.357	13.950	13.3	3.6532
$\text{Cl}^-$	30.537	28.241	30.535	15.300	49.600	162.8	12.7609
$\text{PO}_4^{3-}$	1.344	0.575	1.595	0.029	2.430	1.1	1.0573

**Table 4.** Water samples with anomalous values (extremes and outliers) of some physico-chemical parameters in water samples

Sample	Extremes of parameters (x)	Outliers of parameters (o)
$S_1$	No reg.	No reg.
$S_2$	No reg.	No reg.
$S_3$	TOC (56 $\text{mgL}^{-1}$ )	$\text{NO}_2^-$ (1.008 $\text{mgL}^{-1}$ )
$S_4$	No reg.	No reg.
$S_5$	No reg.	No reg.
$S_6$	No reg.	No reg.

Water temperature varied at different locations and ranged from 14.0-19.8°C, what might be due to the rate of chemical reactions and the nature of biological processes taking place in aquatic system. The pH affects chemical and biological processes and temperature affects the availability of oxygen concentration in the water. Based on pH measurements, the river water is slightly acidic with values ranging from 6.06-6.80, what is much lower than the values found in karstic rivers of Croatia (pH up to 8.7) reported by Frančišković-Bilinski et al. (2013). The lower pH at stations  $S_2$ ,  $S_3$ ,  $S_4$ , and  $S_5$  may be due to the dissolution and decomposition of sulfide minerals including metal sulphides deposited in flotation tailings in Kishnica.

Turbidity ranged from 8.2-32.1 NTU, (what is not in agreement with the WHO standards) as influence from deposited flotation tailings in Kishnica and waste waters from milk factory "Bylmeti". Another common measurement often taken is



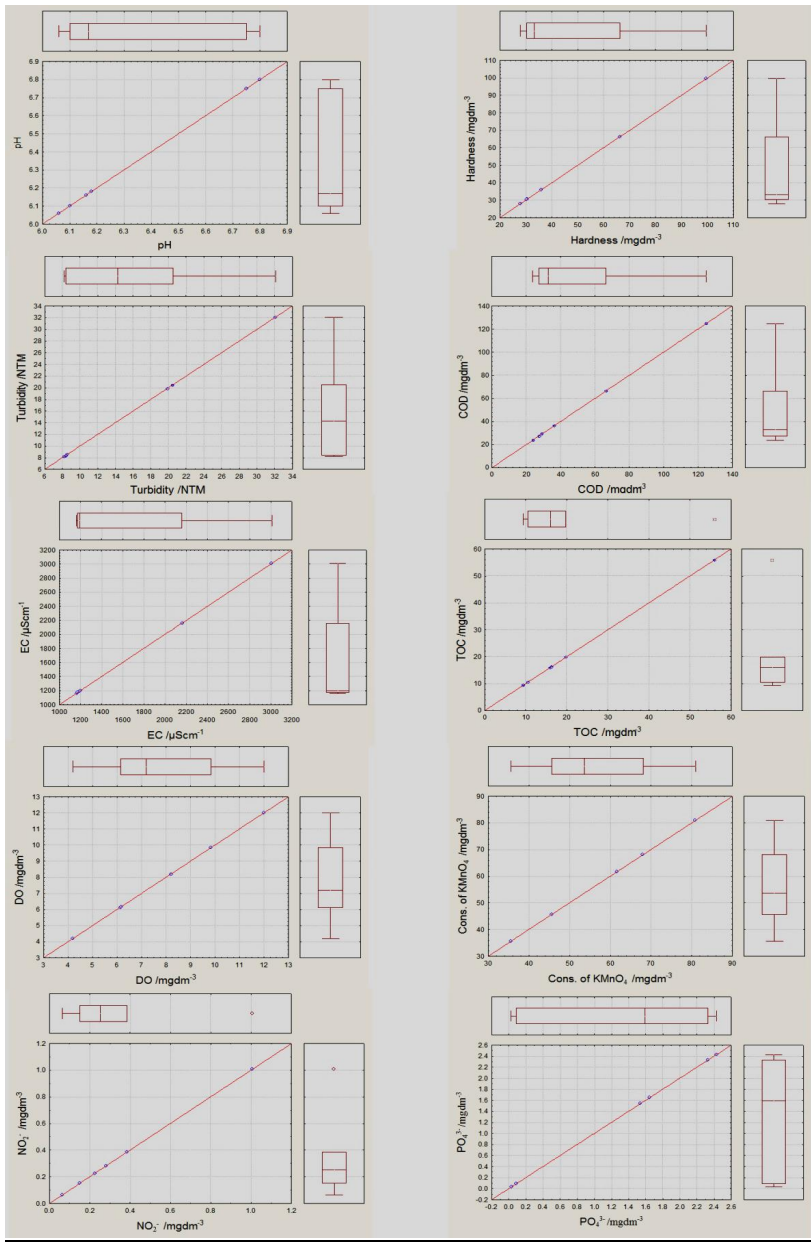


Fig. 2. Scatter box plot diagrams of selected parameters in water samples



dissolved oxygen (DO), which is a measure of how much oxygen is dissolved in the water. Dissolved oxygen can tell us a lot about water quality. Rapidly moving water in river, tends to contain a lot of dissolved oxygen, whereas stagnant water contains less. Bacteria in water can consume oxygen as organic matter decays. Thus, excess organic material in rivers can cause eutrophic conditions, which is an oxygen-deficient situation that can cause a water body "to die". Dissolved oxygen ranged from  $4.2\text{--}12.0\text{mgL}^{-1}$ , and these values exceed WHO highest desirable limit from  $7.5\text{mgL}^{-1}$ . Those low values of diss. oxygen in samples  $S_3$ ,  $S_4$ , and  $S_5$ , might be sign of anthropogenic environmental pollution as influence from waste waters from settlement of Gračanica, Hajvalija, Laplje Selo, Preoci, Lepia, Dobrova e ulët and waste waters from milk factory. Mean values of EC values are relatively high in the whole course of Gračanica River, and were about three times higher than values measured in karstic Kupa and Rječina Rivers (Croatia), reported by Frančisković-Bilinski et al. (2013), and these values are above highest desirable World Health Organization limit ( $1000\mu\text{Scm}^{-1}$ ) as influence of pollution from mining activities from Hajvalija and Kishnica mines and from deposits of the flotation tailings of Kishnica and Badovci. Going downstream EC values are gradually decreasing to the lowest value of  $1163\mu\text{Scm}^{-1}$ , which is measured at station  $S_4$ . TDS give information on the total cations and anions in waters, which are also a possible sign of anthropogenic influence. The effluent draining and mine wastes contained elevated levels of those ions. TDS values (behave similarly as EC), of all water samples ranged from  $9.3\text{--}55\text{mgL}^{-1}$ . Values of total hardness depend upon dissolved salts present in water. They are very high and are ranged  $27.93\text{--}99.50^\circ\text{dH}$ , as influence from deposited flotation tailings in Kishnica. Chemical oxygen demand (COD) and Biological oxygen demand ( $\text{BOD}_5$ ) show moderate enrichment values ranging from  $23.8\text{--}125\text{mgL}^{-1}$  and  $12.1\text{--}70\text{mgL}^{-1}$ , respectively. Total organic carbon (TOC) of the investigated samples was ranging from  $9.4\text{--}56\text{mgdm}^{-3}$ . Except station  $S_1$ , all stations were found to be over recommended WHO standards for drinking water ( $10\text{mgL}^{-1}$ ). Chemical consumption of  $\text{KMnO}_4$  ranged from  $35.644\text{--}80.9\text{mgL}^{-1}$ , and these values exceed WHO highest desirable limit from  $10\text{mgL}^{-1}$ . Those higher values of consumption of  $\text{KMnO}_4$  might be sign of anthropogenic environmental pollution as influence from deposited flotation tailings in Kishnica, waste waters from Gračanica city and waste waters from milk factory. Total alkalinity was ranging from  $4.87\text{--}9.13\text{mgL}^{-1}$  and all stations were found to be under recommended World Health Organization standards for drinking water (MPV,  $250\text{mgL}^{-1}$ ). Concentration of  $\text{HCO}_3^-$  was ranging from  $46.814\text{--}393.45\text{mgL}^{-1}$  and all stations were found to be under recommended World Health Organization standards for drinking water (MPV,  $635\text{mgdm}^{-3}$ ). Detergent of the investigated samples was detected only in station  $S_3$ . The presence of the detergents is due to the discharge of household waste waters from settlements of Gračanica city. Going downstream, detergents in river water are gradually decreasing to the lowest value. Concentrations of  $\text{NH}_4^+$  were ranging

from 2.261-6.337mgL<sup>-1</sup>. The concentration of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> in all samples did not exceed recommended standards for drinking water. Stations S<sub>3</sub>-S<sub>6</sub> was found to be above recommended norms, as possible sign of anthropogenic influence, mainly from wastewaters and agricultural land use. Concentration of Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> at all station were found to be under recommended standards. Concentration of PO<sub>4</sub><sup>3-</sup> at stations S<sub>3</sub>-S<sub>6</sub> were found to be above recommended norms, as possible sign of anthropogenic influence, mainly from agricultural land use.

**Table 5.** Matrix of correlation coefficients (r) of selected 14 variables  
Correlations

Marked correlations are significant at p < 0.050	pH	Turb	Diss. Oxygen	EC	Hard.	COD	TOC	C. of KMnO <sub>4</sub>	NO <sub>2</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>
pH	1.00	-0.14	0.81	-0.55	-0.49	-0.56	-0.46	-0.28	-0.55	-0.48	-0.48	-0.66	0.86	-0.38
Turb.	-0.14	1.00	-0.05	0.56	0.58	-0.14	-0.55	-0.52	-0.55	0.69	0.46	0.49	-0.30	-0.64
DO	0.81	-0.05	1.00	-0.07	-0.02	-0.24	-0.35	-0.16	-0.43	-0.05	0.01	-0.16	0.50	-0.55
EC	-0.55	0.56	-0.07	1.00	1.00	0.66	0.21	0.06	0.21	0.97	0.99	0.98	-0.79	-0.36
Hard.	-0.49	0.58	-0.02	1.00	1.00	0.64	0.18	0.01	0.17	0.98	0.98	0.97	-0.73	-0.43
COD	-0.56	-0.14	-0.24	0.66	0.64	1.00	0.87	0.57	0.85	0.51	0.74	0.67	-0.66	0.21
TOC	-0.46	-0.55	-0.35	0.21	0.18	0.87	1.00	0.78	0.99	0.02	0.31	0.27	-0.44	0.61
C. of KMnO <sub>4</sub>	-0.28	-0.52	-0.16	0.06	0.01	0.57	0.78	1.00	0.77	-0.18	0.17	0.16	-0.45	0.77
NO <sub>2</sub> <sup>-</sup>	-0.55	-0.55	-0.43	0.21	0.17	0.85	0.99	0.77	1.00	0.02	0.30	0.28	-0.49	0.66
Ca <sup>2+</sup>	-0.48	0.69	-0.05	0.97	0.98	0.51	0.02	-0.18	0.02	1.00	0.93	0.93	-0.67	-0.53
Mg <sup>2+</sup>	-0.48	0.46	0.01	0.99	0.98	0.74	0.31	0.17	0.30	0.93	1.00	0.96	-0.76	-0.32
SO <sub>4</sub> <sup>2-</sup>	-0.66	0.49	-0.16	0.98	0.97	0.67	0.27	0.16	0.28	0.93	0.96	1.00	-0.87	-0.22
Cl <sup>-</sup>	0.86	-0.30	0.50	-0.79	-0.73	-0.66	-0.44	-0.45	-0.49	-0.67	-0.76	-0.87	1.00	-0.25
PO <sub>4</sub> <sup>3-</sup>	-0.38	-0.64	-0.55	-0.36	-0.43	0.21	0.61	0.77	0.66	-0.53	-0.32	-0.22	-0.25	1.00

Basic statistical parameters (Mean, Geometric mean, Median, Minimum, Maximum, Variance and Standard deviation) for 19 parameters analyzed in water samples are presented in Table 3. Based on the two dimensional scatter box plot diagrams (Fig. 2) from 10 experimental data were constructed and anomalous values (extremes and outliers) were registered in Table 4. In the sample S<sub>3</sub> the extreme value of TOC (56mgL<sup>-1</sup>) and the outlier values of NO<sub>2</sub><sup>-</sup>, (1.008mgL<sup>-1</sup>) were registered. The statistical regression analysis has been found a highly useful technique for the linear correlating between various water parameters. The correlation coefficient (Table 5) indicates posi-

tive and negative significant correlation of variables with each other. Positive correlation mean one parameter increase with other parameters and negative correlation mean one parameter increase with other parameters decrease. In study period, pH showed high significant positive relationship with diss. oxygen and Cl<sup>-</sup>, as possible sign of anthropogenic influence. Turbidity showed high significant positive relationship with EC, hardness, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. Diss. oxygen showed high significant positive relationship with pH and Cl<sup>-</sup>. EC showed high significant positive relationship with turbidity, hardness, COD, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup>. Total hardness, showed high significant positive relationship with EC, COD, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup>. COD showed high significant positive relationship with EC, hardness, TOC, consumption of KMnO<sub>4</sub>, NO<sub>2</sub><sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> (possible sign of anthropogenic influence and chemical treating of waters). TOC showed high significant positive relationship with COD, consumption of KMnO<sub>4</sub>, NO<sub>2</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>. Consumption of KMnO<sub>4</sub> showed high significant positive relationship with COD, TOC, NO<sub>2</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> (possible sign of waste waters from settlements influence). NO<sub>2</sub><sup>-</sup> showed high significant positive relationship with COD, TOC, consumption of KMnO<sub>4</sub> and PO<sub>4</sub><sup>3-</sup>. Ca<sup>2+</sup> showed high significant positive relationship with turbidity, EC, hardness, COD, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. Cl<sup>-</sup> showed high significant positive relationship with pH, diss. oxygen and Ca<sup>2+</sup>. PO<sub>4</sub><sup>3-</sup> showed high significant positive relationship with TOC, consumption of KMnO<sub>4</sub> and NO<sub>2</sub><sup>-</sup>.

### **Conclusions**

Generally, well waters of Kosovo are enriched in dissolved solids, as the consequence of aquifer lithology and residence time of ground water. The main objective of this study was to perform assessment of water quality of Graqanica River. The statistical regression analysis has been found a high positive correlation relationship between turbidity and EC, hardness, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. EC showed high significant positive relationship with turbidity, hardness, COD, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup>. Consumption of KMnO<sub>4</sub> showed high significant positive relationship with COD, TOC, NO<sub>2</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> (possible sign of waste waters from settlements influence). From the results of field work and laboratory analyses it was found out that river water quality not fulfill the criteria set by the World Health Organization and the distribution of pollutants indicated anthropogenic sources, mainly from Kishnica and Badovci flotation tailing dams and waste waters.

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## NOTES

1. [http://www.who.int/water\\_sanitation\\_health/dwq/fulltext.pdf](http://www.who.int/water_sanitation_health/dwq/fulltext.pdf)
2. [http://apps.who.int/iris/bitstream/10665/43285/1/9789241546768\\_eng.pdf](http://apps.who.int/iris/bitstream/10665/43285/1/9789241546768_eng.pdf)
3. [http://www.mwa.co.th/download/file\\_upload/SMWW\\_1000-3000.pdf](http://www.mwa.co.th/download/file_upload/SMWW_1000-3000.pdf)
4. [http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151\\_eng.pdf](http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf)
5. [https://www.statsoft.com/Portals/0/Products/PCA\\_Analysis\\_with\\_STATISTICA.pdf](https://www.statsoft.com/Portals/0/Products/PCA_Analysis_with_STATISTICA.pdf)

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