QUALITY ASSESSMENT AND CORRELATION ANALYSIS OF CHEMICAL DATA OF THE MIROSALA WELL WATER (KOSOVO)

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In the present study, the chemical characteristics of the Mirosala well water are studied. Statistical analysis have been carried out by calculating of basic statistical parameters, anomalies (extremes and outliers) and correlation coefficients between different pairs of variables. The levels of some chemical parameters of the well water are compared with the World Health Organization directives for drinking water. From the results of field work and laboratory analyses it was found out that Mirosala well water fulfils the criteria set by the WHO. The statistical regression analysis showed that electrical conductivity is in high significant positive relationship with consumption of $KMnO_4$ and a moderately high positive correlation relationship with pH, Fe^{2+}, NO_2^- and Ca^{2+} (possible sign of lithology influence). No correlation was found with SiO_2, hardness, NO_3^-, Cl^-, Mg^{2+} and HCO_3^-. In the water sample S_3 outlier value of SiO_2 (31.9 mg L^{-1}) was registered, as possible sign of lithology influence. The distribution of low pollutants has been described as lithologically and non lithologically controlled factor.

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Introduction

The sources of physico-chemical contamination of water bodies 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.[1,2] 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.[3] The quality of drinking water is an issue of primary interest for the residents of the European Union.[4] 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.[5] Decomposition of organic matter and pollution due to anthropogenic activity are the main sources of pollution of water.[6] Therefore, multidisciplinary collaborative research is essential for understanding the pollution processes.

As reported by Brils,[7] 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.

Figure 1. Area map with study location.

Until recently, the waters of Kosovo have been poorly investigated. Gashi et al[8] 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, it 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[9-11] performed research of mass concentrations of ecotoxic metals viz. 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.[12] 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. Based on Croatian standards for drinking water, the Lumbardhi River water was classified in first and second class according to the concentrations of zinc and cadmium. It is classified in the second, third and fourth class according to the concentrations of cuprum and lead. It was concluded that water resources of Kosovo's are endangered by antropogenic pollution.[13]

Experimental

The aim of the current work is to perform, a systematic research of the well water quality in Mirosala village. Mirosala village located in the north-east of the town of Ferizaj, and is known for the hight water quality with curative properties. Mirosala water is the main source of water factory "Miros". Although there are more than 50 water quality parameters available, only 14 parameters are selected for our investigation. These parameters are: water temperature, conductivity, pH, consumption of $KMnO_4$, nitrate, nitrite, ammonia, etc. The results are interpreted using modern statistical methods that can be used to locate pollution sources.

Sampling and sample preparation

For chemical analysis water samples are collected, during September 2014 to December 2014, in plastic bottles, previously rinsed three times with sampled water, and labelled with the date and the name of the sample. These samples are transferred to refrigerator (at 4 °C) for analysis in the laboratories. All tests are performed at least thrice to calculate the average value. Sampling, preservation and experimental procedure for the water samples are carried out according to the standard methods for examination of water.[14-17] Samples are preserved in refrigerator after treatment.

Chemical characterization

Double distilled water was used in all experiments. All instruments are calibrated according to manufacturer's recommendations. Temperature of water was measured immediately after sampling. pH measurements were performed using pH/ion-meter of Hanna Instruments. Electrical conductivity (EC) is measured by InoLab WTW conductometer, chemical consumption of $KMnO_4$ using Thiemann Küebel volumetric method (boiling in acidic environment). Some of the physico-chemical parameters (NO_2^-, NO_3^- and NH_4^+) are determined using UV-VIS spectrometry method using model Merck Spectroquant NOVA 60 Fotometer.

Statistical methods

Program Statistica 6.0[18] 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 discussions

The chemical parameters i.e. water temperature, EC, pH, total hardness, consumption of $KMnO_4$ and concentrations of SiO_2, Fe^{2+}, Ca^{2+}, Mg^{2+}, Cl^-, NO_2^-, NO_3^-, NH_4^+ and HCO_3^- are presented in Table 1 and 2. The summary of descriptive statistics of the selected variables at water samples are presented in Table 3. For each variable, the values are given as arithmetic mean, geometric mean, median, minimal and maximal concentration, variance and standard deviation. Box-whiskers plot for measured variables are presented in Figure 2. Using experimental data (Table 1 and 2) and box plot approach of Tukey,[19] anomalous values (extremes and outliers) of 12 variables were determinate. Only ample S_3 showed an outlier parameter of SiO_2 (31.9 mg L^{-1}). Correlation Pearson's factor for 12 variables was calculated to see if some of the parameters were interrelated with each other and the results are presented in Table 4.

In the present study, the temperature varied from 14.8–16° C and there are higher than the temperatures (7.3°C) of both Rječina and Kupa karstic springs in Croatia, reported by Frančišković-Bilinski et al.[20] This is usual behavior of most of ground waters. As thermostat adjustment of the instrument for conductivity measurement was not done, temperature of water sample was measured and with approximate correction factor, f, which for water, in temperature range from 10 to 25˚C, is 0.02˚C^{-1}, it was calculated to temperature of 20˚C by Eqn. 1.

$$K_{20} = K_t\left[1 + f(20 - t)\right] \qquad (1)$$

Table 1. Mean value of some physico-chemical parameters of the well water.

Sample	Date	Water temp. °C	EC, µScm^{-1}	pH	Hardness, °dH	Consumption of $KMnO_4$, mgL^{-1}
S_1	11.09.14	16.0	478	7.93	10.08	12.64
S_2	15.09.14	15.8	475	7.84	11.20	9.72
S_3	10.12.14	14.8	471	7.90	11.77	9.03
S_4	23.12.14	15.7	478	8.08	10.98	12.64
S_5	26.12.14	15.5	476	8.06	11.20	10.53
S_6	29.12.14	15.4	475	8.04	9.74	9.72

Table 2. Mean value of some chemical parameters of the well water.

Sample	SiO_2,	Fe^{2+}	Ca^{2+}	Mg^{2+}	Cl^-	NO_2^-	NO_3^-	NH_4^+	HCO_3^-
S_1	19.2	< 0.03	41.6	23.04	17.016	0.018	0.02	n.d.	286.7
S_2	22.5	0.03	41.0	23.41	16.1	0.027	0.5	n.d.	284.5
S_3	31.9	0.03	38.9	24.68	18.7	0.020	0.2	n.d.	280.6
S_4	21.6	0.03	38.4	24.96	15.95	0.025	0.03	n.d.	274.5
S_5	20.8	0.03	36.1	26.40	14.18	0.025	0.2	n.d.	335.2
S_6	18.30	0.03	40.4	23.76	15.61	0.016	0.33	n.d.	366.0

Note: Concentration of ammonium ion was not determined. All concentrations are in mg L^{-1}.

Table 3. Basic statistical parameters for 12 variables in 6 water samples.

Variable	Descriptive Statistics						
	Mean	Geo. mean	Median	Minimum	Maximum	Variance	SD
EC, µS cm^{-1}	475.5000	475.4941	475.5000	471.0000	478.0000	6.700	2.58844
pH	7.9750	7.9745	7.9850	7.8400	8.0800	0.010	0.09834
Hardness, tot., °dH	10.8283	10.8054	11.0900	9.7400	11.7700	0.586	0.76557
HCO_3^-, mg L^{-1}	304.5833	302.7988	285.6000	274.5000	366.0000	1382.550	37.18265
C. of MnO_4^-, mg L^{-1}	10.7133	10.6208	10.1250	9.0300	12.6400	2.453	1.56619
SiO_2, mg L^{-1}	22.3833	21.9975	21.2000	18.3000	31.9000	24.102	4.90934
Fe^{2+}, mg L^{-1}	16.8583	0.1161	0.0300	0.0300	101.0000	1699.157	41.22083
Ca^{2+}, mg L^{-1}	39.4033	39.3589	39.6500	36.1000	41.6000	4.121	2.02999
Mg^{2+}, mg L^{-1}	24.3750	24.3493	24.2200	23.0400	26.4000	1.526	1.23512
Cl^-, mg L^{-1}	16.2593	16.2017	16.0250	14.1800	18.7000	2.279	1.50968
NO_2^-, mg L^{-1}	0.0218	0.0214	0.0225	0.0160	0.0270	0.000	0.00445
NO_3^-, mg L^{-1}	0.2133	0.1258	0.2000	0.0200	0.5000	0.033	0.18283

Table 4. Matrix of correlation coefficients (*r*) of selected 12 variables.

Variable	EC,µS cm^{-1}	pH	Hardness total, °dH	HCO_3^- mg L^{-1}	C_{KMnO4}, mg L^{-1}	SiO_2 mg L^{-1}	Fe^{2+} mg L^{-1}	Ca^{2+} mg L^{-1}	Mg^{2+} mg L^{-1}	Cl^- mg L^{-1}	NO_2^- mg L^{-1}	NO_3^- mg L^{-1}
EC, µScm^{-1}	1.00											
pH	0.44	1.00										
Hardness total, °dH	-0.52	-0.29	1.00									
HCO_3^-, mg L^{-1}	-0.04	0.48	-0.54	1.00								
C_{KMnO4}, mg L^{-1}	0.89	0.38	-0.35	-0.34	1.00							
SiO_2, mg L^{-1}	-0.81	-0.44	0.80	-0.49	-0.51	1.00						
Fe^{2+}, mg L^{-1}	0.47	-0.22	-0.48	-0.24	0.60	-0.32	1.00					
Ca^{2+}, mg L^{-1}	0.09	-0.60	-0.51	-0.18	0.07	-0.19	0.53	1.00				
Mg^{2+}, mg L^{-1}	-0.09	0.59	0.52	0.19	-0.08	0.19	-0.53	-1.00	1.00			
Cl^-, mg L^{-1}	-0.54	-0.60	0.27	-0.58	-0.17	0.73	0.25	0.44	-0.44	1.00		
NO_2^-, mg L^{-1}	0.15	-0.08	0.65	-0.42	0.05	0.11	-0.42	-0.41	0.42	-0.36	1.00	
NO_3^-, mg L^{-1}	-0.46	-0.46	0.11	0.30	-0.77	0.05	-0.52	0.21	-0.20	-0.16	0.23	1.00

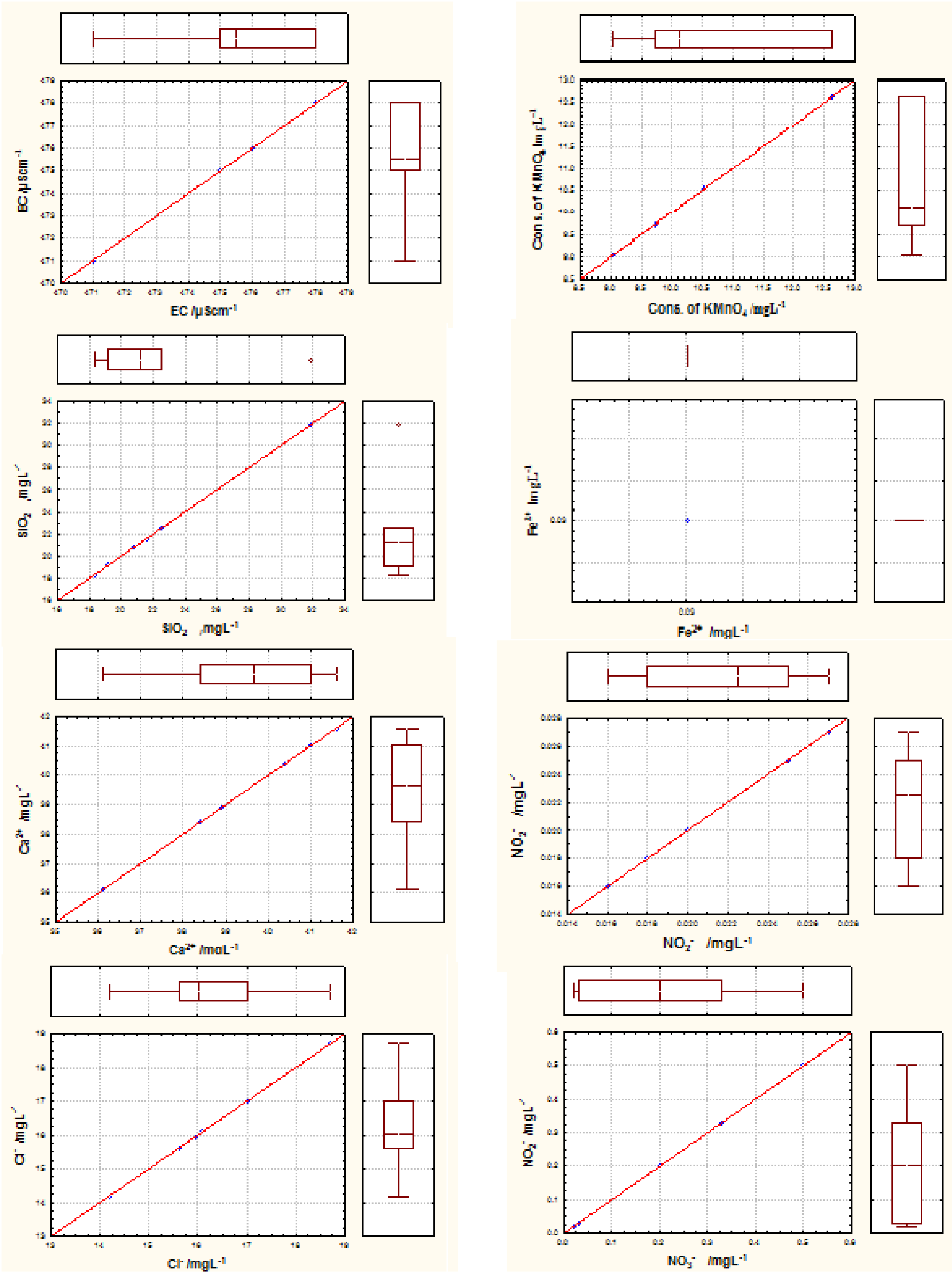

Figure 2. Scatter box plot diagrams of some measured variables

EC values are relatively high in the all samples. Lowest value of 471 μS cm^{-1} is measured at station S_3 and the highest value of 478 μS cm^{-1} which is measured at stations S_1 and S_4. All those values much higher of all values found in Kupa and Rječina rivers, Croatia, where values range from 200–250 μS cm^{-1}. The higher values of EC might be sign of natural pollution. Values of pH varied from 7.84-8.08, which is lower than the values found in water of karstic rivers of Croatia (pH up to 8.7). It could be due to composition of rocks in the area, as mentioned Croatian rivers are situated in karst, while our stations is situated in area of acid magmatic rocks. Total hardness, concentrations of SiO_2, Fe^{2+}, Ca^{2+}, Mg^{2+}, Cl^-, NO_2^- and NO_3^- and HCO_3^- of the investigated samples showing that all water samples were in lower values. Concentrations of ammonium ion in all samples were under detection limit. Hydroxides, carbonates and hydrogen carbonates of alkali and earth alkaline metals, mainly Na, Ca and Mg make water alkaline. Macro components of ground water are controlled by weathering of rocks (water-rock interactions). Thus, prevailing components in water show the major impact of aquifer lithology. Chlorides in all samples were found to be under recommended WHO standards for drinking water (250 mg L^{-1}). Consumption of $KMnO_4$ was ranging from 9.03-12.64 and all samples were found to be in the limit of recommended WHO standard for drinking water (12 mg L^{-1}). Higher values of consumption of $KMnO_4$ might be sign of natural pollution.

Statistical interpretation

Basic statistical parameters (Mean, Geometric mean, Median, Minimum, Maximum, Variance and Standard deviation) for 12 parameters analyzed in 6 water samples are presented in Table 3. Based on the two dimensional scatter box plot diagrams (Figure 2) from 12 experimental data were constructed and anomalous values (extremes and outliers) have been determined. In the S_3 outlier value of SiO_2 (31.9 mgL^{-1}) was registered, possible sign of lithology influence. The statistical regression analysis has been found a highly useful technique for the linear correlating between various water parameters. The correlation coefficient indicates positive 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, EC (Table 4) showed high significant positive relationship with consumption of $KMnO_4$ and a moderately high positive correlation relationship with pH, Fe^{2+}, NO_2^- and Ca^{2+}. No correlation was found with SiO_2, hardness, NO_3^-, Cl^-, Mg^{2+} and HCO_3^-. pH showed a moderately high positive correlation relationship with Mg^{2+}, consumption of $KMnO_4$ and HCO_3^-. No correlation was found with SiO_2, hardness, NO_3^-, NO_2^-, Ca^{2+} and Cl^-. Hardness showed high significant positive relationship with SiO_2, a moderately high positive correlation relationship with Mg^{2+}, Cl^-, NO_3^-, NO_2^- (possible sign of lithology influence). No correlation was found with consumption of $KMnO_4$, Fe^{2+}, Ca^{2+} and HCO_3^-. The bicarbonate ion showed a moderately high positive correlation relationship with Mg^{2+} and NO_3^-. Consumption of $KMnO_4$ showed a moderately high positive correlation relationship with Fe^{2+}, Ca^{2+} and NO_2^-. SiO_2 showed a high significant positive correlation relationship with Cl^- and a moderately high positive correlation relationship with Mg^{2+}, NO_3^- and NO_2^- (possible sign of lithology influence). Fe^{2+} showed a moderately high positive correlation relationship with Ca^{2+} and Cl^-. Ca^{2+} showed a moderately high positive correlation relationship with NO_3^- and Cl^-. Mg^{2+} showed a moderately high positive correlation relationship with NO_2^-. The nitrite ion showed a moderately high positive correlation relationship with NO_3^-.

Conclusions

In this study the assessment of water quality and correlation coefficients between different pairs of variables of the Mirosala well water has been investigated. Generally, ground waters of Kosovo are enriched in dissolved solids, as the consequence of aquifer lithology and residence time of ground water. From the results of field work and laboratory analyses it was found out that Mirosala well water fulfils the criteria set by the World Health Organization. In the S_3 outlier value of SiO_2 (31.9 mgL^{-1}) was registered, possible sign of lithology The statistical regression analysis showed that EC is in high significant positive relationship with consumption of $KMnO_4$ and a moderately high positive correlation relationship with pH, Fe^{2+}, NO_2^- and Ca^{2+} (possible sign of lithology influence). The distribution of low pollutants indicated lithology pollutants from waste water.

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References

[1]Close, M., Dann, R., Ball, A, Pirie, R., Savill, M., Smith, Z., *J. Water Health*, **2008**, *6*, 83-98.

[2]Keswick, B. H., *Groundwater Pollution Microbiology*. John Wiley and Sons, New York, **1984,** 39-64.

[3]Thompson, T., Fawell, J., Kunikane, S., Jackson, D., Appleyard, S., Callan, P., Bartram, J., Kingston, P., *Chemical safety of drinking-water: Assessing priorities for risk management*, World Health Organization, **2007.**

[4]Chirila, E., Bari, T., Barbes, L., *Ovidius Univ. Ann. Chem*., **2010**, *21*, 87-90.

[5]Hamilton, L. S., Forests and Water: A Thematic Study Prepared in the Framework of the Global Forest Resources Assessment. *1st Edn., Agriculture Organization of the United Nation, Rome*, **2008**, 78.

[6]Montgomery, J. M., *Water Treatment, Principles and Design*, John Wiley & Sons, New York, **1996,** 474.

[7]Brils, J., *Ann. Inst. Superiore Sanita.* **2008**, *44,* 218–223.

[8]Gashi, F., Franciskovic-Bilinski S., Bilinski, H., *Fres. Environ. Bull.*, ***2009,*** *18*. 1462-1471.

[9]Gashi, F., Frančišković-Bilinski, S., Bilinski, H., Troni, N., Bacaj, M., Jusufi, F., *Environ. Monit. Assess.*, **2011**, *175***,** 279–289.

[10]Gashi, F., Troni, N., Faiku, F., Laha, F., Haziri, A., Kastrati, I., Beshtica, E., Behrami, M., *Am. J. Environ. Sci.*, **2013**, *9*, 142-155.

[11]Gashi, F., Troni, N., Hoti, R., Faiku, F., Ibrahimi, R., Laha, F., Kurteshi, K., Osmani S., Hoti, F., *Fresenius Environ. Bull.*, **2014,** *23,* 91-97.

[12]Troni, N., Faiku, F., Gashi, F., Hoti, R., Teneqja, V., Laha F., Berisha, R., *Int. J. Green Herbal Chem.*, **2013,** *2,* 203-207.

[13]Faiku, F., Hazir, I., Gashi, F., Troni, N., Haziri, I., *Eur. Chem. Bull.*, **2015,** *4,* 169-176.

[14]Skoog, D. A., West, D. M., Holler, F. J., *Fundamentals of Analytical Chemistry.* College Publishing, Philadelphia, **1992.**

[15]APHA, AWWA and WEF, *Standard Method for the Examination of water and waste water*, 20th ed. American Public Health Association, Washington D.C., **1998.**

[16]Alper, B., Abidin, K. Yuksel, K. B., *Water Air Soil Pollut*., **1998**, *149***,** 93–111.

[17]Dalmacija, B., *Water Quality Control in Towards of Quality Management, Text book,* Novi Sad, **2000. [**In Serbian].

[18]Stat Soft, Inc. STATISTICA (data analysis software system), ver. 6. http://www.statsoft.com. **2001.**

[19]Tukey, J. W., *Exploratory data analysis*, Addison-Wesley. Reading, **1977.**

[20]Frančišković-Bilinski, S., Cuculić, V., Bilinski, H., Häusler, H., Stadler, Ph., *Chem. Erde,* **2013,** *73,* 293–308.

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