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QUALITY ASSESSMENT AND CORRELATION COEFFICIENTS STUDY OF CHEMICAL PARAMETERS OF THE WELL WATER OF PLESHINA (KOSOVA)

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Abstract. A water quality is one of the most important standards of supply service for the fact that it has a direct impact on the health of the population. In this study the assessment of water quality and correlation coefficients between different pairs of variables of 36 well water samples of Pleshina were investigated Also the quality of well water after chemical treatment was assessed. Statistical studies have been carried out by calculating of basic statistical parameters, anomalies (extremes and outliers) and correlation coefficients between different pairs of variables.. From the results of field work and laboratory analyses it was found out that well water not fulfill the criteria set by the World Health Organization and the distribution of low pollutants indicated lithological pollutants. The statistical regression analysis has been found a moderately high positive correlation relationship between EC with pH, Cl^- and NO_2^-. Turbidity showed a moderately high positive correlation relationship with NH_3. Consumption of $KMnO_4$ showed a moderately high positive correlation relationship with Mn^{2+} and NO_3^-. After chemical treatment, the study found that the Pleshina's well water was generally fulfill the criteria set by the World Health Organization.
Keywords: quality assessment, correlation coefficients, drink water, Pleshina, 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 interest for the residents of the European Union (Chirila at 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.

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 tributaryof 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) andMn(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 towardsit, 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. Based on Croatian standards for drinking water, the Lumbardhi River water was classifed 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 (Faiku et al., 2015).

Study area

Fig. 1. Area map with analysis location

The aim of the current work is to perform, a systematic research of the well water quality of Pleshina (Fig. 1), located in south weastern of Ferizaj city, at the geographical coordinates 42° 20′ 40" N and 21° 06′ 10" E (Pleshina- wikipedia). Ferizaj city is connected to the water supply system, mainly coming resource from Pleshina's well (Ferizaj-wikipedia). Although there are more than 50 water quality parameters available, only 12 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. The levels of some physico-chemical parameters of wellwaters are compared with the World Health Organization statndards for drinking water.[1,2)]

Sampling and sample preparation

For chemical analysis water samples are collected during the period from May, 2nd, 2014 to May, 30th, 2014. Samples, previously were rinsed three times with sampled water, and labeled 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[3)] (Alper et al., 2003; Dalmacija, 2000). 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 was measured by „InoLab WTW" conductometer. Depending on chemical reactions with volumetric (argentometry and oxidoreduction) methods were defined concentration of chlorides and chemical consumption of $KMnO_4$ (Thiemann Küebel volumetric method, boiling in acidic environment). Residual chlorine was determined using „DPD1"colorimetry technique. Turbidity was measured by "HANNA, HI 93703 MICROPROCESOR". Concentrations of Mn^{2+}, Al^{3+}, NO_2^-, NO_3^- and NH_4^+ were determined using UV-VIS spectrometry method, using "Merck Spectroquant NOVA 60 Fotomoter".

Statistical methods

Program Statistica 6.0[4)] 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 (of 9 well water samples befor and 27 well water samples after chemical treatment), i.e., water temperature, EC, pH, turbidity, consumption of $KMnO_4$ and concentrations of NH_4^+, NO_2^-, NO_3^-, Cl^- , residual chlorine, Mn^{2+} and Al^{3+} were presented in Tables 1 and 2. The Descriptive statistics summary 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. Frequency distributions of 9 measured parameters and box-whiskers plot for 10 measured variables are presented in Figs. 2 and 3. Using experimental data (Tables 1 and 2) and box plot approach of Tukey (1977), anomalous values (extremes and outliers) of 12 variables were determinate (Table 4). 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 5.

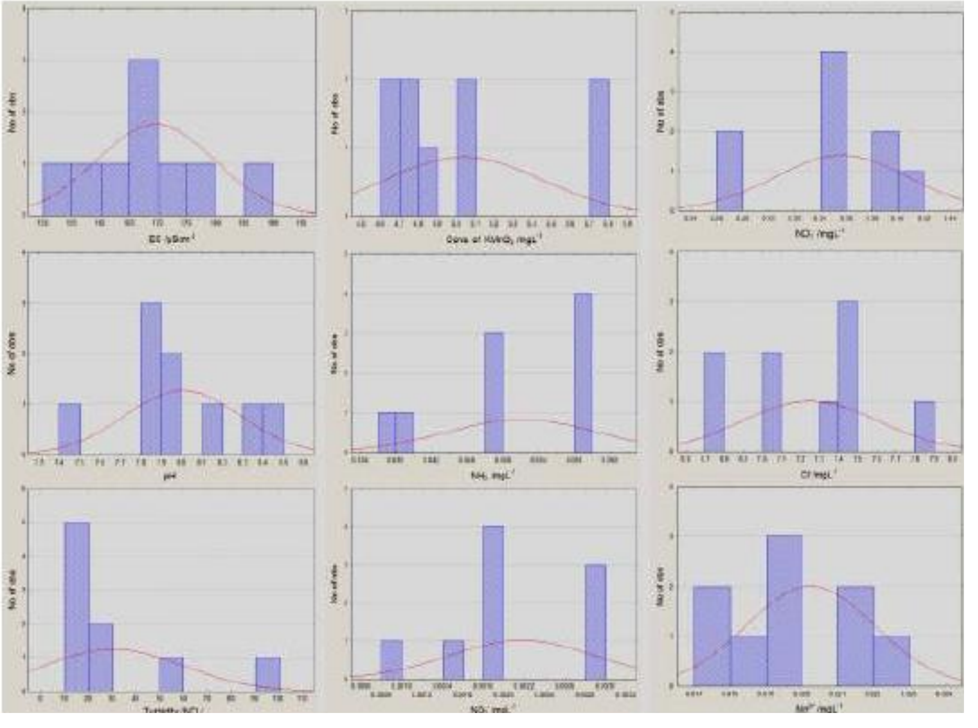

Fig. 2. The frequency histograms of 9 measured variables

Table 1. Some physico-chemical parameters of the well water in Pleshina before chemical treatment

Parameter /Unite	Sample MPL, WHO	S_1 02.05.2014	S_2 06.05.2014	S_3 08.05.2014	S_4 13.05.2014	S_5 16.05.2014	S_6 20.05.2014	S_7 23.05.2014	S_8 27.05.2014	S_9 30.05.2014
Water temp. /° C	12	12.8	12.8	13.1	13.3	13.1	14.9	15.4	15	14.6
EC /μScm^{-1}	1000	155	158	162	170	170	174	178	170	188
pH /1	6.5-8.5	7.95	7.87	8.17	7.9	7.9	7.49	7.95	8.32	8.46
Turbidity /NTU	5	99	14.3	25.71	13.59	24.49	15.47	15.19	11.38	55
C. of $KMnO_4$ /mgL^{-1}	10	5.06	5.74	5.72	4.74	4.7	4.74	4.69	4.86	5.06
NH_3 /mgL^{-1}	1.5	0.06	0.04	0.06	0.05	0.05	0.06	0.038	0.05	0.06
NO_2^- /mgL^{-1}	3	0.003	0.002	0.002	0.0015	0.002	0.002	0.003	0.001	0.003
NO_3^- /mgL^{-1}	50	0.42	0.4	0.35	0.4	0.36	0.36	0.28	0.36	0.27
Cl^- /mgL^{-1}	250	6.74	6.74	7.1	7.45	7.37	7.1	7.45	7.81	7.455
Cl (res.) /mgL^{-1}	0.3	No det.	No det.	No det.	No det.	No det.	No det.	No det.	No det.	No det.
Mn^{2+} /mgL^{-1}	0.1	0.02	0.022	0.02	0.018	0.019	0.02	0.022	0.018	0.023
Al^{3+} /mgL^{-1}	0.2	No det.	No det.	No det.	No det.	No det.	No det.	No det.	No det.	No det.

Table 2. Basic statistical parameters for 10 variables in 9 well water samples

Variable	Unite	Descriptive statistics						
		Mean	Geo. Mean	Median	Min.	Max.	Variance	Std. Dev.
Water temp.	/° C	13.8889	13.8533	13.3000	12.80000	15.4000	1.126	1.06118
EC	/μScm^{-1}	169.4444	169.1729	170.0000	155.0000	188.0000	104.2778	10.21165
pH	/1	8.0011	7.9966	7.9500	7.49000	8.4600	0.081	0.28392
Turbidity	/NTU	30.4589	22.9723	15.4700	11.38000	99.0000	840.726	28.99528

Cons. of KMnO4	/mgL-1	5.0344	5.0197	4.8600	4.69000	5.7400	0.175	0.41884
NH3	/mgL-1	0.0520	0.0513	0.0500	0.03800	0.0600	0.000	0.00872
NO2-	/mgL-1	0.0022	0.0021	0.0020	0.00100	0.0030	0.000	0.00071
NO3-	/mgL-1	0.3556	0.3520	0.3600	0.27000	0.4200	0.003	0.05151
Cl-	/mgL-1	7.2461	7.2383	7.3700	6.74000	7.8100	0.127	0.35621
Mn2+	/mgL-1	0.0202	0.0202	0.0200	0.01800	0.0230	0.000	0.00179

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Turbidity	/NTU	30.4589	22.9723	15.4700	11.38000	99.0000	840.726	28.99528
Cons. of $KMnO_4$	/mgL^{-1}	5.0344	5.0197	4.8600	4.69000	5.7400	0.175	0.41884
NH_3	/mgL^{-1}	0.0520	0.0513	0.0500	0.03800	0.0600	0.000	0.00872
NO_2^-	/mgL^{-1}	0.0022	0.0021	0.0020	0.00100	0.0030	0.000	0.00071
NO_3^-	/mgL^{-1}	0.3556	0.3520	0.3600	0.27000	0.4200	0.003	0.05151
Cl-	/mgL^{-1}	7.2461	7.2383	7.3700	6.74000	7.8100	0.127	0.35621
Mn^{2+}	/mgL^{-1}	0.0202	0.0202	0.0200	0.01800	0.0230	0.000	0.00179

Table 4. Anomalous values (extremes and outliers) determined in the well water of Pleshina

Sample	Outliers of parameters (o)	Extremes of parameters (¤)
S1	No reg.	Turbidity (99NTU)
S2	Cons. of KMnO4(5.74 mgL-1)	No reg.
S3	Cons. of KMnO4 (5.72 mgL-1)	No reg.
S4	No reg.	No reg.
S5	No reg.	No reg.
S6	pH (7.49)	No reg.
S7	No reg.	No reg.
S8	No reg.	No reg.
S9	Turbidity (55 NTU) KMnO4 (0.27 mgL-1)	No reg.

Table 5. Matrix of correlation coefficients (r) of selected 10 variables

Variable	Water temp.	EC	pH	Turbidity	Cons. of $KmnO_4$		NO_2^-	NO_3^-	Cl^-	Mn^{2+}
Water temp.	1.00									
EC	0.75	1.00								
pH	0.12	0.29	1.00							
Turbidity	-0.33	-0.23	0.21	1.00						
Cons. of $KMnO_4$	-0.53	-0.52	0.22	0.08	1.00					
NH_3	-0.12	0.03	0.13	0.53	0.05	1.00				
NO_2^-	0.05	0.20	0.05	0.64	0.01	0.10	1.00			
NO_3^-	-0.71	-0.85	-0.44	0.15	0.21	0.07	-0.42	1.00		
Cl^-	0.64	0.67	0.46	-0.44	-0.58	-0.13	-0.38	-0.52	1.00	
Mn^{2+}	0.18	0.32	0.17	0.21	0.35	-0.14	0.76	-0.57	-0.32	1.00

Discussion of chemical parameters of well water (before chemical treatment)

In the present study, the temperature of 9 samples of Pleshina's well water varied from 12.8–15.4° C, as usual behavior of most of well 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 Eq. (1):$_{20}$

$$k_{20}=k_t[1+f\,(20-t)] \qquad (1)$$

Mean value of EC (169.44 μScm^{-1}), as sign of natural pollution, were lower than value of Izbitac karstic spring on the slopes of Biokovo Mt. in Croatia

(362.5 μScm^{-1}), which is known to be under the significant anthropogenic influence (Matić et al., 2012). pH values were varied from 7.95-8.46, and It could be from composition of rocks in the area. Turbidity in water is because of suspended solids and colloidal matter. If sewage solids are present, pathogens may be encased in the particles and escape the action of chlorine during disinfection. In the present study, turbidity was ranged from 11.39-99.00 and all samples were found to be were found to be under recommended World Health Organization standards for drinking water, as possible sign of lithology influenc. That higher values of consumption of $KMnO_4$ might be sign of natural pollution. Consumption of $KMnO_4$ was ranging from 4.69-5.74 and all samples were found to be under limit of recommended WHO standard for drinking water (10mgL^{-1}). Concentrations of chlorides, ammonia, nitrites, manganese and aluminium in all samples were found to be under recommended WHO standards for drinking water. Residual chlorine and aluminium were not detected.

Basic statistical parameters (Mean, Geometric mean, Median, Minimum, Maximum, Variance and Standard deviation) for 10 parameters analyzed in 9 water samples are presented in Table 3. Based on the frequency histograms from experimantal data (Fig. 2) and the two dimensional scatter box plot diagrams (Figure 3) from experimantal data were constructed and anomalous values (extremes and outliers) were registered in Table 4. In samples S_2, S_3 and S_9 outliers' value of consumption of potassium permanganate was registered. In the S_6 outlier value of pH was registered. In the S_1 and S_6 extreme and outlier respectivly values of turbidity was registered.

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 5) showed a moderately high positive correlation relationship with pH, Cl^- and NO_2^-. No correlation was found with consumption of $KMnO_4$, turbidity and NO_2^-. pH showed a moderately high positive correlation relationship with Cl^- and no correlation was found with NO_3^-. Turbidity showed a moderately high positive correlation relationship with NH_3. Consumption of $KMnO_4$ showed a moderately high positive correlation relationship with $Mn^{2+}$and NO_3^-. The nitrite ion showed a moderately high positive correlation relationship with Mn^{2+}. From the results of field work and laboratory analyses it was found out that Pleshina wellwater not fulfill the criteria set by the World Health Organization.

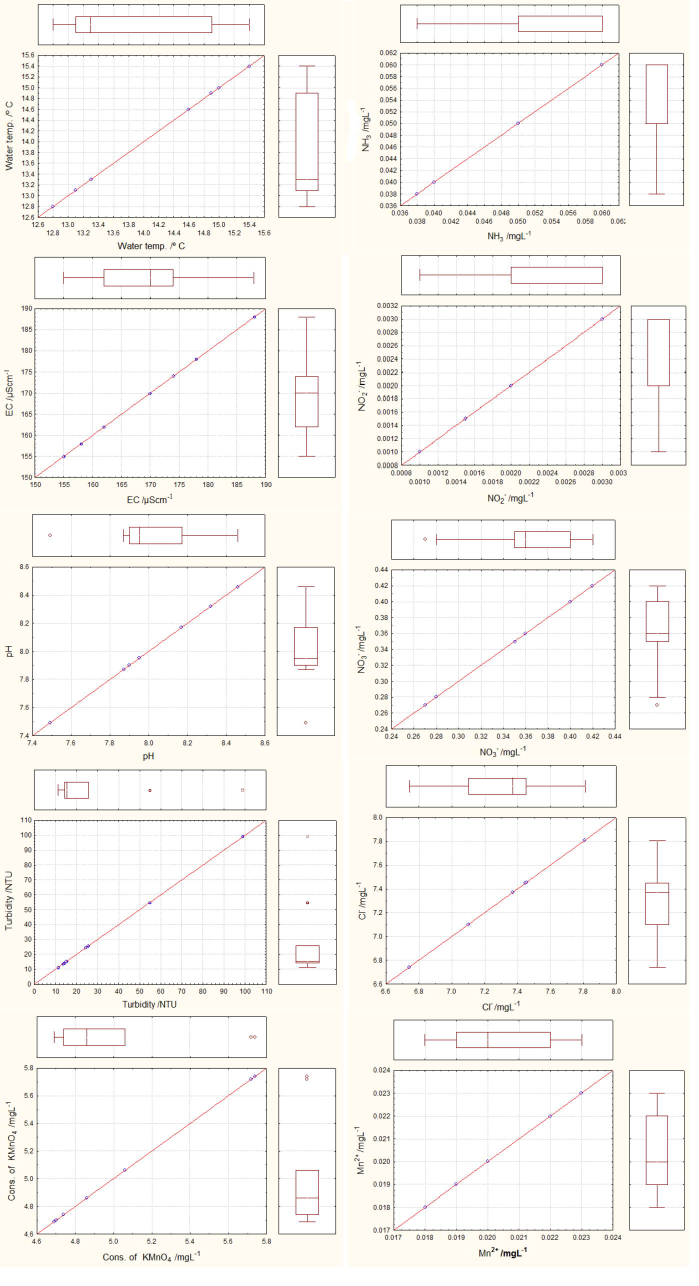

Fig. 3. Scatter box plot diagrams of 10 measured variables

Discussion of chemical parameters of well water (after chemical treatment)

The study found that generally physico-chemical parameters of chemical treated wellwaters, were well within the WHO recommended limits for drinking water. However, the physico-chemical parameters of stored water exhibited variations, but chemically, the water was potable for consumption.

Conclusions

Generally, well waters of Kosovo are enriched in dissolved solids, as the consequence of aquifer lithology and residence time of ground water. In this study the assessment of water quality and correlation coefficients between different pairs of variables of well water of Pleshina were investigated. From the results of field work and laboratory analyses it was found out that well water not fulfill the criteria set by the World Health Organization and the distribution of low pollutants indicated lithologica pollutants. The statistical regression analysis has been found a moderately high positive correlation relationship between EC with pH, Cl^- and NO_2^-. Turbidity showed a moderately high positive correlation relationship with NH_3. Consumption of $KMnO_4$ showed a moderately high positive correlation relationship with Mn^{2+} and NO_3^-. After chemical treatment, the study found that the Pleshina's well water was generally good for consumption.

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NOTES

1. http://www.who.int/water_sanitation_health/dwq/GDWQ2004web.pdf
2. http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf
3. http://www.mwa.co.th/download/file_upload/SMWW_1000-3000.pdf
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