QUALITY ASSESSMENT OF TWO WATER RESOURCES IN MUNICIPALITY OF KAMENICA (KOSOVO)

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In this study the assessment of water quality of two water resources (depth 10-50 meters) in the municipality of Kamenica have been investigated. Concentrations of some ions are determined using UV-VIS spectrometry. Statistical studies have been carried out by calculating of basic statistical parameters and anomalies (extremes and outliers). By comparing with available results of three similar water -samples in Kosovo, it can be summarized that water quality of two water-samples in the municipality of Kamenica is similar to the well waters of Mirosala. From the results of field work and laboratory analyses it was found out that the well water does not fulfil the criteria set by the WHO. The high value of Fe, Mn and turbidity pollutants indicated pollution by natural pollutants and from anthropogenic sources like waste waters.

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Introduction

Drinking water is supposed to be pure enough to be consumed or used with low risk of immediate or long term harm.[1] Well water represents an important source of drinking water and its quality is currently threatened by a combination of overexploitation and microbiological and chemical contamination. More than four billion cases of diarrhea cause 2.2 million deaths, mostly of children under the age of five.[2] 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.[3,4] Decomposition of organic matter and pollution due to anthropogenic activity are the main sources of pollution of water.[8] Therefore, multidisciplinary collaborative research is essential for understanding the pollution processes. As reported by Brils[9], 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. Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons.[9]

Potable and safe water is gradually becoming a scarce commodity, due to mixing up of huge contaminants through natural process like soil and rock weathering and anthropogenic activities such as industrial effluents, domestic sewage, garbage, over mining activity, explosive population etc.[17,18]

Mainly there are four main approaches that can be used to assess the water quality of a water body: (1) water quality index approach, (2) trophic status index approach, (3) statistical analysis approaches of the water quality data such as correlation analysis and (4) biological analysis approaches such as Genetic Algorithms method and other different biological indices.[22] Literature has also shown that multivariate statistical methods have been proved to be one of the most useful tools for extracting meaningful information from data sets. For example applied cluster analysis (CA) to delineate monitoring sites of surface/drinking water quality while used CA and discriminant analysis (DA) to identify significant parameters and optimize monitoring network of ground water quality data. [23-26]

Until recently, the waters of Kosovo have been poorly investigated. Gashi et al.[27] performed first step with investigation of the rivers Drini i Bardhë, Morava e Binçës, Lepenc and Sitnica, which are of supra-regional interest. As Drenica River is the most important tributary of Sitnica River, the current investigation represents next step in detailed investigation and monitoring of Sitnica river watershed, which is most polluted river system in Kosovo.

Experimental

Study area

The aim of the current work is to perform, a systematic research of two water resources in Municipality of Kamenica (Figure 1). Kamenica is a town and municipality (district of Gjilane) in the eastern part of Kosovo.[34] 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 $KMnO_4$, concentration of ammonia, nitrites, nitrates, 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 well waters are compared with the World Health Organization standards for drinking water.[35,36] Finally some parameters of the present sample were compared with values of 3 well-waters in Kosovo.

Figure 1. Location of the study area and positions of sampling stations.

Sampling and sample preparation

For chemical analysis water samples are collected in July, 2015. The storage vessels were 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.[37-39] 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. TDS and pH measurements were performed using pH/ion-meter of Hanna Instruments.

Turbidity was measured using Turbidimeter HI 93703. Electrical conductivity was measured by Hanna Tetra-con 96 conductometer.

Chemical consumption of $KMnO_4$ was determined by Thiemann Küebel volumetric method of boiling in acidic environment. Concentration of calcium and chloride ion was determined by volumetric titration. Concentrations NO_2^- (at 507 nm), NO_3^- (at 500 nm) and NH_4^+ (at 655 nm) were determined by UV-VIS spectrometry method, using Aglient 8452, Spectrophotometer. Concentrations Fe^{2+} (at 510 nm) and Mn^{2+} (at 525 nm) were determined by UV-VIS spectrometry, using Spectroquant NOVA 60 photometer (Merck, Germany).

Statistical Methods

Program Statistica 6.0[40] was used for the statistical analysis of data in this work, such as descriptive statistics, distribution histograms and box plot diagrams for determination of anomalies i.e. extremes and outliers.

RESULTS

The value of physico-chemical parameters from 10 water samples (at the depth of 10, 20, 30, 40 and 50 m) of two resources, i.e. water temperature, EC, pH, Turbidity, TDS, consumption of $KMnO_4$, hardness, and concentrations of Cl^-, NH_4^+, NO_2^-, NO_3^-, Ca^{2+}, Fe^{2+} and Mn^{2+} are presented in tables 1 and 2. The descriptive statistical 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. Scatter box plot diagrams of 15 measured variables are presented in Figures 2 and 3 Using experimental data and box plot approach of Tukey,[41] anomalous values (extremes and outliers) of 14 variables were determined.

Table 1. Physico-chemical parameters of water samples from two resources.

Parameter	S_{1-10m}	S_{1-20m}	S_{1-30m}	S_{1-40m}	S_{1-50m}	S_{2-10m}	S_{2-20m}	S_{2-30m}	S_{2-40m}	S_{2-50m}
Water temp. °C	10.8	10.8	10.9	10.8	10.8	10.7	10.8	10.8	10.8	10.9
EC, at 20 °C µscm^{-1}	530	530	520	490	510	500	500	510	500	500
pH	7.18	7.17	7.2	7.19	7.2	7.55	7.63	7.65	7.5	7.61
Turbidity NTU	2.32	1.66	1.88	10.5	7.42	12.88	11.73	10.39	15.9	15.8
TDS mg L^{-1}	260	260	260	260	250	250	250	260	250	250
Hardness °dH	12.19	12.75	12.61	12.89	12.05	8.83	8.83	8.69	8.83	8.81
$KMnO_4$ consumed mg L^{-1}	11.7	12.96	12.01	11.06	11.7	5.69	6.95	6.32	7.21	7.23
Cl^- mg L^{-1}	10.28	10.28	10.28	7.44	8.5	9.22	9.22	8.51	4.61	4.61
NH_4^+ mg L^{-1}	0.31	0.32	0.37	0.48	0.38	0.41	0.33	0.22	0.18	0.19
NO_2^- mg L^{-1}	0.0045	0.0082	0.0031	0.0034	0.0032	0.0012	0.0015	0.0012	0.005	0.001
NO_3^- mg L^{-1}	1.12	1.29	1.28	0.7	0.7	0.35	0.32	0.32	0.32	0.2
Fe^{2+} mg L^{-1}	2.14	2.35	2.12	1.42	1.27	0.13	0.17	0.12	0.14	0.14
Mn^{2+} mg L^{-1}	1.28	1.32	1.29	1.02	1.11	0.15	0.17	0.16	0.12	0.11
Ca^{2+} mg L^{-1}	17.94	18.74	18.74	19.14	19.4	13.95	13.95	13.95	13.95	14.2

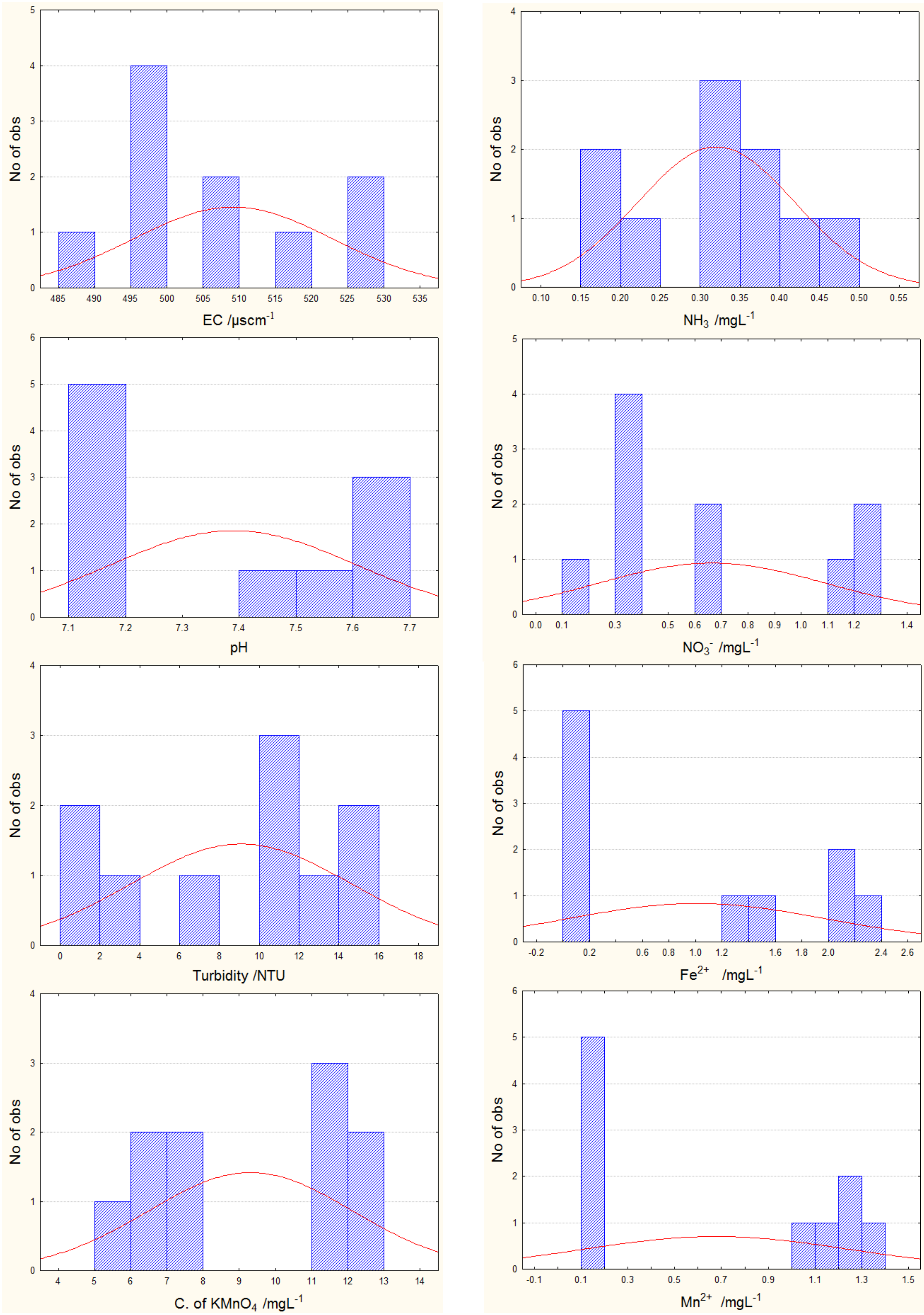

Figure 2. Frequency histograms of 8 measured variables.

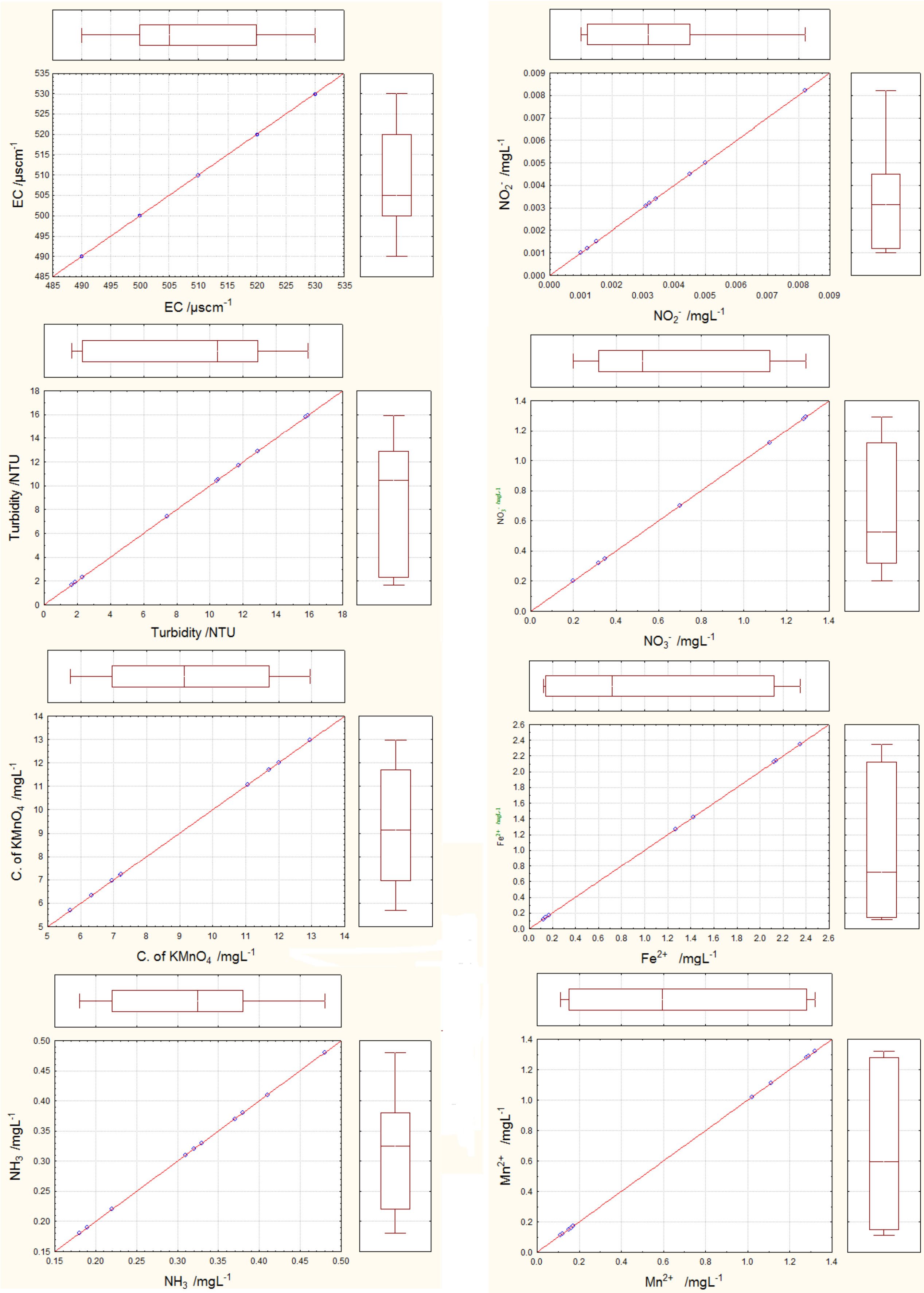

Figure 3. Frequency histograms of some measured variables.

DISCUSSION

In the present study, the temperature of 10 water samples in two resources varied from 10.7–10.9 °C, with a low standard deviation of 0.0032, an usual behavior of most of well waters. As thermostat adjustment of the instrument for conductivity measurement wasn't 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. The electrical conductivity (EC) of water samples varied from 490-530 μScm^{-1} as a sign of natural pollution, and are higher than the values for Izbitac karstic spring on the slopes of Mt. Biokovo in Croatia (362.5 μScm^{-1}), which is known to be under the significant anthropogenic influence.[42] Turbidity values in all water samples varied from 1.66 to 15.90 NTU and its value in samples S_1 at the depths 40 m and 50 m, and in all samples from S_2 exceeded recommended WHO norms for drinking waters. TDS values in all water samples varied from 250 to 260 mg L^{-1} and no sample exceeded the recommended WHO norms of 1500 mg L^{-1} for drinking waters. pH values varied from 7.17-7.76 and it could be because of the composition of rocks in that area. Total hardness was ranging from 8.69 to 12.89 °dH and were found to be well below the recommended standards for drinking water (30 ° dH). Increased hardness on those locations is of natural origin, due to presence of gravel, sand, sandy clay and tuffs deposits.[43] Consumption of $KMnO_4$ ranged from 5.69 to 12.9 mg L^{-1} and the value in all the samples were found to be within the recommended norms for drinking water. Similarly, concentrations of calcium, chlorides, ammonia, nitrites and nitrates in all the samples were found to be within recommended WHO standards for drinking water. The concentration of iron in all the samples exceeded the recommended WHO norms of 0.3 mg L^{-1} for drinking waters. Similarly, manganese in all the water samples from S_1, exceed recommended WHO norms of 0.1 mgL^{-1} for potable water.

Table 2. Mean values of some physico-chemical parameters of water from two resources.

Parameter	WHO standard	Resource (mean value) 1	Resource (mean value) 2
Temp. °C	8-12	10.84	10.84
EC μscm^{-1}	1000	516	498
pH	6.5-8.5	7.18	7.58
Turbidity NTU	5	13.34	4.75
TDS mgL^{-1}	1500	258	258
Hardness °dH	<30	12.498	8.798
$KMnO_4$ consumed mg L^{-1}	250	13.86	6.5
Cl^- mg L^{-1}	30	9.35	7.23
NO_3^- mg L^{-1}	50	1.018	0.298
NO_2^- mg L^{-1}	3	0.0042	0.00198
NH_3 mg L^{-1}	0.5	0.37	0.26
Fe^{2+} mg L^{-1}	0.3	1.86	0.14
Mn^{2+} mg L^{-1}	0.1	1.2	0.142
Ca^{2+} mg L^{-1}	200	18.74	14

Basic statistical parameters for the 14 parameters analyzed in water samples from two water resources are presented in Table 3. Based on the frequency histograms (Figure 2) and two dimensional scatter box plot diagrams (Figure 3), anomalous values (extremes and outliers) were not registered.

When values of 10 selected measured parameters in waters of Kamenica are compared with similar well waters in Kosovo (Table 4), following facts can be observed: EC and concentrations of NH_3, NO_2^-, NO_3^-, Ca^{2+}, Fe^{2+} and Mn^{2+}, water resources of Kamenica were approximately the same with well waters of Mirosala.

Table 3. Statistical analysis of 14 variables of water from two resources.

Variable	Mean	Geometric	Median	Minimum	Maximum	Variance	Std. Dev.
Temp. °C	10.8100	10.8099	10.8000	10.7000	10.9000	0.0032	0.05676
EC µs cm^{-1}	509.0000	508.8352	505.0000	490.0000	530.0000	187.7778	13.70320
pH	7.3880	7.3852	7.3500	7.1700	7.6500	0.0462	0.21498
Turbidity NTU	9.0480	6.8348	10.4450	1.6600	15.9000	30.2450	5.49955
TDS mg L^{-1}	255.0000	254.9510	255.0000	250.0000	260.0000	27.7778	5.27046
Hardness ° dH	10.6480	10.4842	10.4400	8.6900	12.8900	3.8628	1.96540
$KMnO_4$ consumed mg L^{-1}	9.2830	8.8862	9.1450	5.6900	12.9600	7.9380	2.81745
Cl^- mg L^{-1}	8.2950	7.9869	8.8650	4.6100	10.2800	4.6122	2.14760
NH_3^- mg L^{-1}	0.3190	0.3043	0.3250	0.1800	0.4800	0.0096	0.09803
NO_2^- mg L^{-1}	0.0032	0.0026	0.0032	0.0010	0.0082	0.0000	0.00225
NO_3^- mg L^{-1}	0.6600	0.5392	0.5250	0.2000	1.2900	0.1834	0.42825
Fe^{2+} mg L^{-1}	1.0000	0.5012	0.7200	0.1200	2.3500	0.9250	0.96178
Mn^{2+} mg L^{-1}	0.6730	0.4096	0.5950	0.1100	1.3200	0.3213	0.56682
Ca^{2+} mg L^{-1}	16.3960	16.2169	16.0700	13.9500	19.4000	6.5200	2.55343

EC is significantly lower than that of the well waters of Lipjan and pH is approximately the same with well waters of Sprig and well waters of Istog, but higher than that in well waters of Lipjan. pH is significantly lower than that in the well waters of Mirosala. Consumption of $KMnO_4$ were significantly lower than that in the well waters of Lipjan and Mirosala.

Concentrations of NH_3, NO_2^-, NO_3^- and Ca^{2+} of waters of Kamenica were significantly lower than in spring and well water of Istog. Concentration of Fe^{2+} in waters of Kamenica is approximately similarly with spring and well water of Istog. Concentrations of Mn^{2+} were significantly higher than in spring and well water of Istog. The distribution of Fe and Mn pollutants indicated natural pollutions and this may be a direct impact from geological constitution of rocks i.e. marlstone, claystone, sandstone, partly tuffstone, lignite, gravel, sand, sandy clay and tuffs deposits.

Table 4. Comparison of properties of water of Kamenica wells with those of water in similar wells in Kosovo.

Parameter	Kamenica well	Istog well[44]	Lipjan well[45]	Mirosala well[146]
EC µS cm^{-1}	490-530	696.3	1029.1	475.5
pH	7.17-7.65	7.2	6.86	7.98
$KMnO_4$ consumed mgL^{-1}	6.5-13.86	-	78.512	10.7133
NH_3 mg L^{-1}	0.26-0.37	2.372	-	-
NO_2^- mg L^{-1}	0.00198-0.0042	0.0617	-	0.0218
NO_3^- mg L^{-1}	0.298-1.018	19.04	-	0.2133
Cl^- mg L^{-1}	7.23-9.35	24.63	736.78	16.2593
Ca^{2+} mg L^{-1}	14-18.74	85.313	23.72	39.4033
Fe^{2+} mg L^{-1}	0.14-1.86	0.5287	-	16.858

CONCLUSIONS

Generally, waters of Kosovo wells 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 of water resources in Kamenica were investigated. In comparison with available results of three similar well waters in Kosovo, it can be summarized that water quality of resources in Kamenica were approximately the similarly with well waters of Mirosala. Results from physico-chemical analyses were used to compare the obtained value of the selected parameters with the WHO existing criteria of drinking water. Turbidity from the first well water (S_1), generally appeared to be significantly high, and exceed recommended WHO norms for drinking waters. The concetration of iron from the first well water (S_1), also appeared to be significantly high and exceed recommended WHO norms from 0.3 mg L^{-1} for drinking waters. The concentration of manganese in both well waters appeared to be significantly high and exceed recommended WHO norms of 0.1 mg L^{-1} for drinking waters. From the results of field work and laboratory analyses it was found out that the water from two well of Kamenica not fulfill the World Health Organization criteria set for drinking waters and can not be used as potable water.

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 pollutants indicated anthropogenic sources of pollutants, waste waters and small rivers in suburb. The distribution of Fe and Mn pollutants indicated natural pollutions and this may be a direct impact from geological constitution of rocks: marlstone, claystone, sandstone, partly tuffstone, lignite, gravel, sand, sandy clay and tuffs deposits.

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