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The effect of anthropogenic activity on the underground water quality in the territory of Lipjan (Kosovo). A Statistical Approach

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Abstract

Chemical contamination of underground water has several implications for human health. The study of the effect of anthropogenic activity on the underground water quality was carried out in the region of Lipjan (Kosovo). Water samples were collected in 10 sampling points and fourteen different parameters are investigated. The program “Statistica ver. 6.0” has been used for calculations of basic statistical parameters and anomalies (extremes and outliers). These statistical approaches and results yielded useful information about water quality and can lead to better water resource management. Dendograms and box-whisker plots were drawn to evaluate the chemical variation. The levels of some physico-chemical parameters of underground waters are compared with the WHO statndards for drink water. Our results show for significant pollution of underground waters as results of anthropogenic activity coming from settlements and wastewaters in the region surround.

Keywords: *Pollution, undergroud water, quality, anthropogenic activity, statistical, Lipjan.*

1. 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 [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 phisico-chemical contamination are usually immediate [3]. The quality of drinking water is an issue of primary interest for the residents of the European Union [4]. 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 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 of 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 [8]. 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 [9].

2. Materials and Methods

2.1. Study Area

The aim of the current work is to perform, a systematic research of the effect of anthropogenic activity on the underground water quality in the region of Lipjan (Kosovo). This work is a continuation of earlier studies of surface and underground waters in Kosovo [10-13]. The name of the town, Lipjan is derived from the ancient Roman toponym “Ulpiana”. The municipality of Lipjan is located in central Kosovo. It covers an area of approximately 422 km² and includes Lipjan town and 62 villages. Sampling strategy was planned in the 10 monitoring stations. Although there are more than 50 water quality parameters available, only 15 parameters are selected for our investigation. Those parameters are: water temperature, dry residue, conductivity, pH, TDS, total alkalinity, total and tempory hardness, concentration of Ca^{2+}, Mg^{2+}, OH^-, HCO_3^-, CO_3^{2-}, Cl^- and consumption of $KMnO_4$. The sampling sites are geographically positioned using geographic information system (GIS). The results were interpreted using modern statistical methods that can be used to locate pollution sources. Surface water sampling of champions were done with polyethylene non-contaminating bottles and their elaboration were done according to standards methods for underground water [14]. Some of the water samples are filtered with Whatman paper of 0.45 µm made from cellulose nitrate in the bottle of teflon under pressure of nitrogen (purity 99.99 %).

2.2. Sampling and Sample Preparation

Water samples were collected at 17 may 2013 in polyethylene bottles previously rinsed three times with sampled water, they were labeled with the date and the name of the sample. Then samples are transfered to hand refrigerator (at 4°C) to be analyzed in the chemical laboratories. All tests were performed at least three times to calculate the average value. The sampling locations were chosen at points where pollution was expected, due to closeness of factory’s, traffic, settlements or combinations of those factors. Sampling, preservation and experimental procedure of the water samples were carried out according to the standard methods for examination of water [15-18]. The study area with the sampling locations is shown in Fig. 1 and the details about all sampling sites are presented in Table 1.

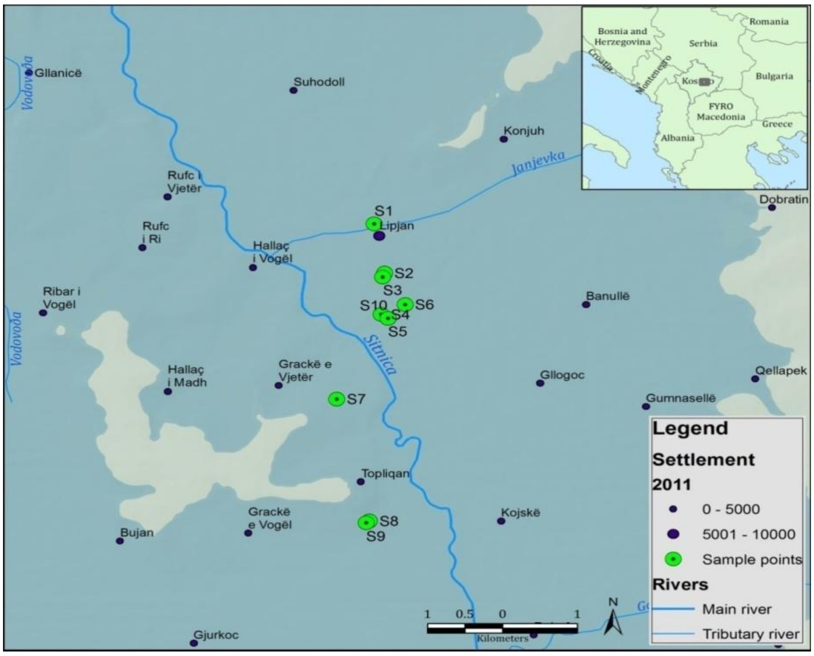

Figure 1. Study area with sampling stations

Table 1. Sampling stations with detailed description

Sample	Locality	Coordinates	Hight above sea level /m	Possible pollution sources
S_1	Lipjan	42º 31' 40" N 21º 07' 08" E	563.91	Paper factory, agriculture, waste water.
S_2	Lipjan	42º 31' 15" N 21º 07' 14" E	558.97	Settlement, trafic.
S_3	Lipjan	42º 31' 13"N 21º 07' 13" E	555.51	Settlement, trafic.
S_4	Lipjan	42º 30' 54"N 21º 07' 12" E	550.00	Settlement, trafic.
S_5	Lipjan	42º 30' 52" N 21º 07' 16" E	548.28	Settlement, trafic.
S_6	Lipjan	42º 30' 59"N 21º 07' 26" E	558.00	Settlement, trafic.
S_7	Grackë e vogël	42º 30' 11"N 21º 06' 46" E	567.00	Settlemen
S_8	Topliçan	42º 29' 09"N 21º 07' 05" E	552.37	Settlemen
S_9	Topliçan	42º 29' 08"N 21º 07' 03" E	550.38	Settlemen
S_{10}	Lipjan	42º 30' 52" N 21º 07' 16" E	548.28	Settlement

2.3. Physico-chemical Characterisation

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. Some of the parameters were measured directly in the ground (mainly physical parameters), while chemical analyses were carried out in the analytical laboratory.

Table 2. Some physico-chemical parameters determined in water

Sample	Water temp./° C	Dry res. /mgL^{-1}	EC /µScm^{-1}	pH /1	TDS /mgL^{-1}	Alk. tot. /mgL^{-1}	OH^- /mgL^{-1}	CO_3^{2-} /mgL^{-1}	HCO_3^- /mgL^{-1}
S_1	15	1120	1420	6.7	560	34.8	n.d.	52.8	51.24
S_2	24	820	1081	6.78	567	22	7.48	14.1	n.d.
S_3	19.9	360	552	7.25	252	18	2.04	31.2	n.d.
S_4	15.8	700	1091	6.84	589	16.6	0.34	32.4	n.d.
S_5	14.2	660	513	6.85	567	26.4	18.36	9.6	n.d.
S_6	14.6	700	985	6.84	523	22.2	7.14	27.6	n.d.
S_7	17.4	524	881	6.79	455	13.1	14.2	3.4	n.d.
S_8	18.1	525.9	767	6.85	396	12	11.6	2.04	n.d.
S_9	14.7	1554	2486	6.89	1292	15.3	15	3.06	n.d.
S_{10}	14.1	664	515	6.83	565	27	18.29	9.1	142

Table 3. Some physic-chemical parameters determined in water

Sample	Tot. hard. /°D	Temp. hard. /°D	Ca^{++} /mgL^{-1}	Mg^{++} /mgL^{-1}	Cons. of $KMnO_4$ /mgL^{-1}	Cl^- /mgL^{-1}
S_1	7.56	0.728	38.02	9.70	63.22	1008.7
S_2	5.04	0.342	30.02	3.64	47.41	643.8
S_3	2.24	0.325	14.02	1.21	10.63	257.5
S_4	3.64	0.308	24.02	1.21	79.02	586.6
S_5	3.96	0.392	24.02	2.60	79.02	643.9
S_6	3.96	0.375	22.02	3.82	110.63	608.1
S_7	2.8	0.398	10.01	6.07	94.84	579.6
S_8	3.64	0.325	27.02	2.43	63.22	357.4
S_9	3.96	0.420	24.02	2.34	158.04	2038.5
S_{10}	3.96	0.392	24.02	2.60	79.09	643.7

Temperature of water was measured immediately after sampling, using digital thermometer, model "Quick 63142". Measurements of pH and TDS were performed using pH/ion-meter, model "Hanna Instruments". Conductivity was measured by conductometer "InoLab WTW". Depending on chemical reactions volumetric (alkalimetry, complexometry, argentometry and oxidoreduction) with these methods

were defined: total alkalinity, total and temporary hardness, concentration of chlorides and chemical consumption of $KMnO_4$. The alkalinity of water sample 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 Erichrome Black T indicator. Temporary hardness (carbonate hardness) was also determined. It is due to the presence of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. Chemical consumpion of $KMnO_4$ was determined by Thiemann Küebel volumetric method (boiling in acidic environment).

2.4. Statistical Methods

Program Statistica 6.0 [19] was used for all statistical calculations in this work, such as: determination of basic statistical parameters (mean, geo. mean, median, max. min, varance and std. deviation) and determination of anomalies (extremes and outliers) for solution data. Outlier values are between 1.5 and 3, and extreme values above 3 standard deviations.

Table 4. Basic statistical parameters for 14 variables in 10 underground water samples

Variable	Descriptive Statistics						
	Mean	**Geo. mean**	**Median**	**Min.**	**Max.**	**Variance**	**Std. Dev.**
W. temp. /º C	16.780	16.5395	15.4000	14.1000	24.000	10.1	3.1804
Dry res. /mgL^{-1}	762.790	705.1683	682.0000	360.0000	1554.000	117830.3	343.2642
EC /µScm^{-1}	1029.100	913.3792	933.0000	513.0000	2486.000	348082.5	589.9852
pH /1	6.862	6.8606	6.8400	6.7000	7.250	0.0	0.1460
TDS /mgL^{-1}	576.600	532.6463	562.5000	252.0000	1292.000	74242.9	272.4756
Alk. tot. /mgL^{-1}	20.740	19.6782	20.0000	12.0000	34.800	51.3	7.1618
HO^- /mgL^{-1}	19.545	8.8960	12.9000	0.3400	101.000	858.3	29.2972
CO_3^{2-} /mgL^{-1}	18.530	11.4435	11.8500	2.0400	52.800	282.0	16.7930
Tot. Hard. /°D	4.076	3.8827	3.9600	2.2400	7.560	2.1	1.4337
Temp. hard. /°D	0.401	0.3883	0.3835	0.3080	0.728	0.0	0.1210
Ca^{++} /mgL^{-1}	23.719	22.3944	24.0200	10.0100	38.020	60.0	7.7486
Mg^{++} /mgL^{-1}	3.562	2.9265	2.6000	1.2100	9.700	6.6	2.5761
Cons. of $KMnO_4$ /mgL^{-1}	78.512	66.3337	79.0200	10.6300	158.040	1518.5	38.9682
Cl- /mgL^{-1}	736.780	633.6804	625.9000	257.5000	2038.500	247978.7	497.9746

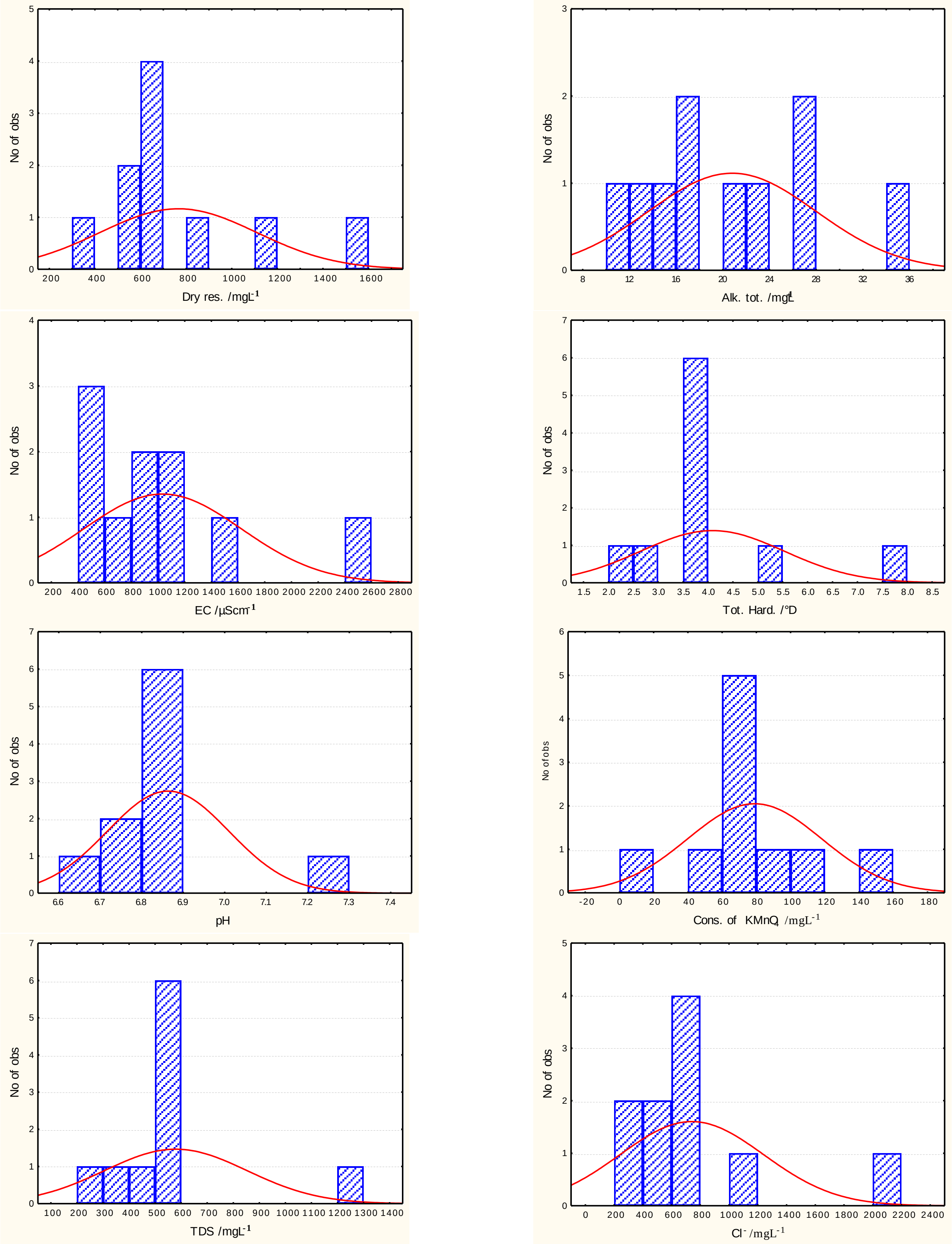

Figure 2. Frequency histograms of some measured variables

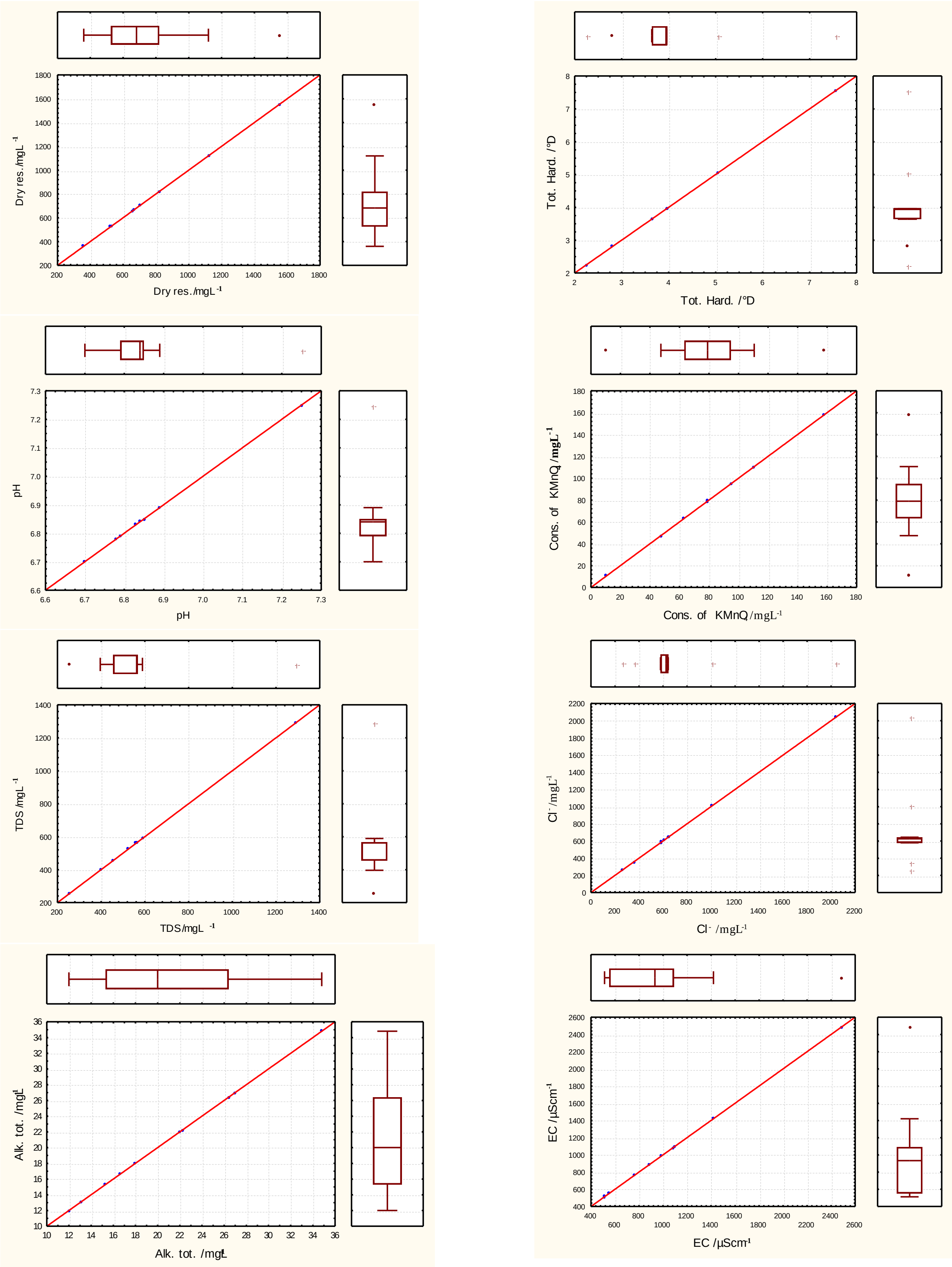

Figure 3. Scatterplot with box plots diagrams of some measured variables

Table 5. Water samples with anomalous values (outliers and extremes) from 14 variables

Sample	Outliers of elements (¤)	Extremes of elements (o)
S_1	-	Hard. tot (7.56°dH), Cl^- (1008.7mgL^{-1})
S_2	-	Hard. Tot (5.04°dH)
S_3	-	pH (7.25)
S_4	-	-
S_5	-	-
S_6	-	-
S_7	-	-
S_8	-	-
S_9	Dry res. (1554 mgL^{-1}), EC (2486 μScm^{-1}), Cons. of $KMnO_4$ (158.04mgL^{-1})	TDS (1292 mgL^{-1}), Cl^- (2038.5mgL^{-1})
S_{10}	-	-

3. Results and Discussions

The physico-chemical parameters: water temperature, dry residue, EC, pH, total dissolved solids (TDS), total alkalinity, concetration of OH^-, CO_3^{2-} and HCO_3^- are presented in Table 2. In Table 3 are presented: total and temporary hardness of water, consumption of $KMnO_4$, concetration of Ca^{2+}, Mg^{2+} and Cl^-. In the present study, the temperature varied at different locations. Water temperature is lowest (14.1°C) at the station S_{10} and this is higher than temperatures (7.3°C) of both Rječina and Kupa karstic springs in Croatia, reported by Frančišković-Bilinski et al.[21]. This is usual behavior of most of underground waters. The dry residue of the investigated samples was ranging from 360-1554mgL^{-1}. Except station S_3, all samples were found to be above recommended WHO standards (500 mgL^{-1}). EC values are relatively high in the all samples. Lowest value of 513 μScm^{-1} is measured at station S_5 and the highest value of 2486 μScm^{-1} which is measured at station S_9. All those values much higher of all values found in Kupa and Rječina rivers, Croatia, where values range from 200–250 μScm^{-1}. That higher values of EC might be sign of anthropogenic environmental pollution. Values of pH are highest at station S_3 (7.25), what is much lower than the values found in 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. TDS values (behave similarly as EC), are also a possible sign of anthropogenic influence. TDS of the investigated samples was ranging from 252-1292mgL^{-1} and except station S_3 and S_7 all underground water samples were found to be above recommended WHO standard for drink water (500 mgL^{-1}). Total hardness, temporary hardness, total alkalinity, concentration of Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^- and OH^- of investigated samples showing that all water samples are in lower values. Consumption of $KMnO_4$ was ranging from 10.63-158.04mgL^{-1} and all underground water samples were found to be above recommended WHO standard for drink water (10 mgL^{-1}). That higher values of consumption of $KMnO_4$ might be sign of anthropogenic environmental pollution. The concentration of chlorides in all underground water samples were found to be above recommended WHO standard for drink water (250 mgL^{-1}). That higher values of chlorides might be from underground water treatment

using chlorine products. The basic statistics of the measured data set and anomalous values (outliers and extremes) from 14 variables on water are summarized in Table 4 and 5. Using experimental data (Table 2 and 3) and box plot approach of Tukey [20], anomalous values (extremes and outliers) in waters were determined for the whole region. Based on the anomalous values (Table 5) from 14 experimantal data, in samples S_1 and S_2 we have registred extrem values in total hardness. In the samples S_1 and S_9 we have registred extrem values of chlorides. In the sample S_3 we have registred extreme value of pH. In the sample S_9 we have registred extremes values of TDS. In the sample S_9 we have registred outler values of dry residue, el. conductivity and consumption of $KMnO_4$.

4. Conclusions

The physico-chemical analysis shows that underground water in the region of Lipjan is highly polluted. Therefore this water cannot be used without previous physical and chemical treatment. Based on the anomalous values (Table 4) in some samples ($S_{1,}$ S_2 S_3 and S_9) we have registred extrem and outler values for chlorides, pH, TDS, dry residue, el. conductivity and consumption of $KMnO_4$. The high values of TDS, EC and consumption of $KMnO_4$ showed a possible sign of anthropogenic influence. Our results show for significant pollution of underground waters as results of anthropogenic activity coming from settlements, pollution from rivers (Sitnica and Janjevka) and wastewaters in the region surround. The faecal contamination from anthropogenic activity in some underground water samples is an indication that contamination is beginning to reach the aquifer. A long and uncontrolled discharge of municipal waste water inflicted the change of water quality. For this reason, we recommended avoiding discharges of wastewater without treatment, mainly from septic tanks, which are extensively used in the area.

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