ESTIMATION OF THE GROUNDWATER QUALITY IN THE WESTERN PART OF LIPJAN (KOSOVO)

PROCJENA KAKVOĆE PODZEMNIH VODA U ZAPADNOM DIJELU LIPlJANA (KOSOVO)

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The study of the effect of anthropogenic activity on the water quality was carried out in the western part of Lipjan (Kosovo). The software "Statistica 6.0" was used for calculations of basic statistical parameters and anomalies (extremes and outliers). The levels of some physicochemical parameters of groundwater are compared with the World Health Organization standards for drinking water. Our results show significant pollution (high values of electrical conductivity, total dissolved solids and consumption of KMnO4) of groundwaters as a result of anthropogenic activity coming from settlements, pollution of small rivers (Vodavoda and Grika) and wastewaters in the surrounding area.

Keywords: pollution, groundwater, quality, anthropogenic activity, statistical analysis, the western, Lipjan

Studija utjecaja antropogenog djelovanja na kvalitetu vode provedena je u zapadnom dijelu Lipljana (Kosovo). Program "Statistica 6,0 "korištena je pri izračunu osnovnih statističkih parametara i anomalije (ekstrema i odstupanja). Razine nekih fizikalno-kemijskih parametara podzemne vode uspoređeni su sa standardima Svjetske zdravstvene organizacije za pitku vodu. Naši rezultati pokazuju značajno onečišćenje (visoke vrijednosti električne provodljivosti, ukupno otopljenih krutih tvari i potrošnja KMnO4) podzemnih voda kao posljedica antropogenog djelovanja koje dolazi iz naselja, zagađenim rječicama (Vodavoda i Grika) i otpadnih voda u okolici.

Ključne riječi: zagađenje, podzemne vode, kakvoća, ljudska aktivnost, statističke analize, zapadni Lipljan

Introduction

The sources of physicochemical 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 (Keswick, 1984; Close et al., 2008). 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 physicochemical contamination are usually immediate (Thompson et al., 2007). The quality of drinking water is an issue of primary interest for the residents of the European Union (Chirila et al., 2010). Water storage is critical to the balance of water in peat swamps and in 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 (Hamilton, 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 J. 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 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 (Šajn et al., 1998).

The aim of this work is to perform, a systematic research of the effect of anthropogenic activity on the groundwater quality in the western part of Lipjan. This work is a continuation of earlier studies of surface and groundwaters in Kosovo (Gashi et al., 2009; 2012a; 2012b; 2013).

Study area

The name of the town of 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 the town of Lipjan and 62 villages. Sampling strategy was planned in the 8 monitoring stations. Although there are more than 50 water quality parameters available for water quality assessment, only 15 parameters were selected for our research. Those parameters are: water temperature, dry residue, conductivity, pH, TDS, total alkalinity, total and temporary 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). Surface water sampling was carried out with no-contaminating bottles which were made according to standard methods for groundwater (Feely et al., 1991). Some of the water samples were filtered with Whatman paper of 0.45μm made from cellulose nitrate in the Teflon bottle under pressure of nitrogen (purity 99.99 %).

Materials and methods

Water samples were collected on 20 May 2013 in polyethylene bottles previously rinsed three times with sampled water. They were labeled with the date and the name of the sample. After that, the samples were transferred to hand refrigerator (at 4 °C) to be analysed at 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 traffic, small rivers, settlements or combinations of those factors. Sampling, preservation and experimental procedure of water samples were carried out according to the standard methods for examination of water (Skoog et al., 1992; Alper et al., 1998; *Standard Method for the Examination of water and waste water*, 1998; Dalmacija, 2000). The study area with the sampling locations is shown in Figure 1 and the details about all sampling sites are presented in Table 1.

Table 1 Sampling stations with detailed description

Sample	Locality	Coordinates	Possible pollution sources
S_1	Gllanicë	N 42˚32'24.8" E 21˚03'41.7"	Agriculture, small rivers of Vodavoda and Grika, waste water
S_2	Dobrajë e madhe	N 42˚32'35.9" E 21˚02'40.5"	Settlement, small rivers of Vodavoda and Grika, waste water
S_3	Dobrajë e madhe	N 42˚29.09'8" E 21˚07'07"	Settlement, Sitnica River, waste water
S_4	Dobrajë e madhe	N 42˚32'35.9" E 21˚02'40.8"	Settlement, small river of Vodavoda and Grika, waste water
S_5	Dobrajë e madhe	N 42˚32'17.7" E 21˚02'47.7"	Settlement, small rivers Vodavoda and Grika, waste water
S_6	Dobrajë e madhe	N 42˚32'17.7" E 21˚02'47.7"	Settlement, small rivers Vodavoda and Grika, waste water
S_7	Dobrajë e madhe	N 42˚02'54.2" E 21˚02'54.2"	Settlement, small rivers of Vodavoda and Grika, waste water
S_8	Llugë	N 42˚32'71.7" E 21˚02'44.3"	Settlement small rivers of Vodavoda and Grika, waste water, petrol station

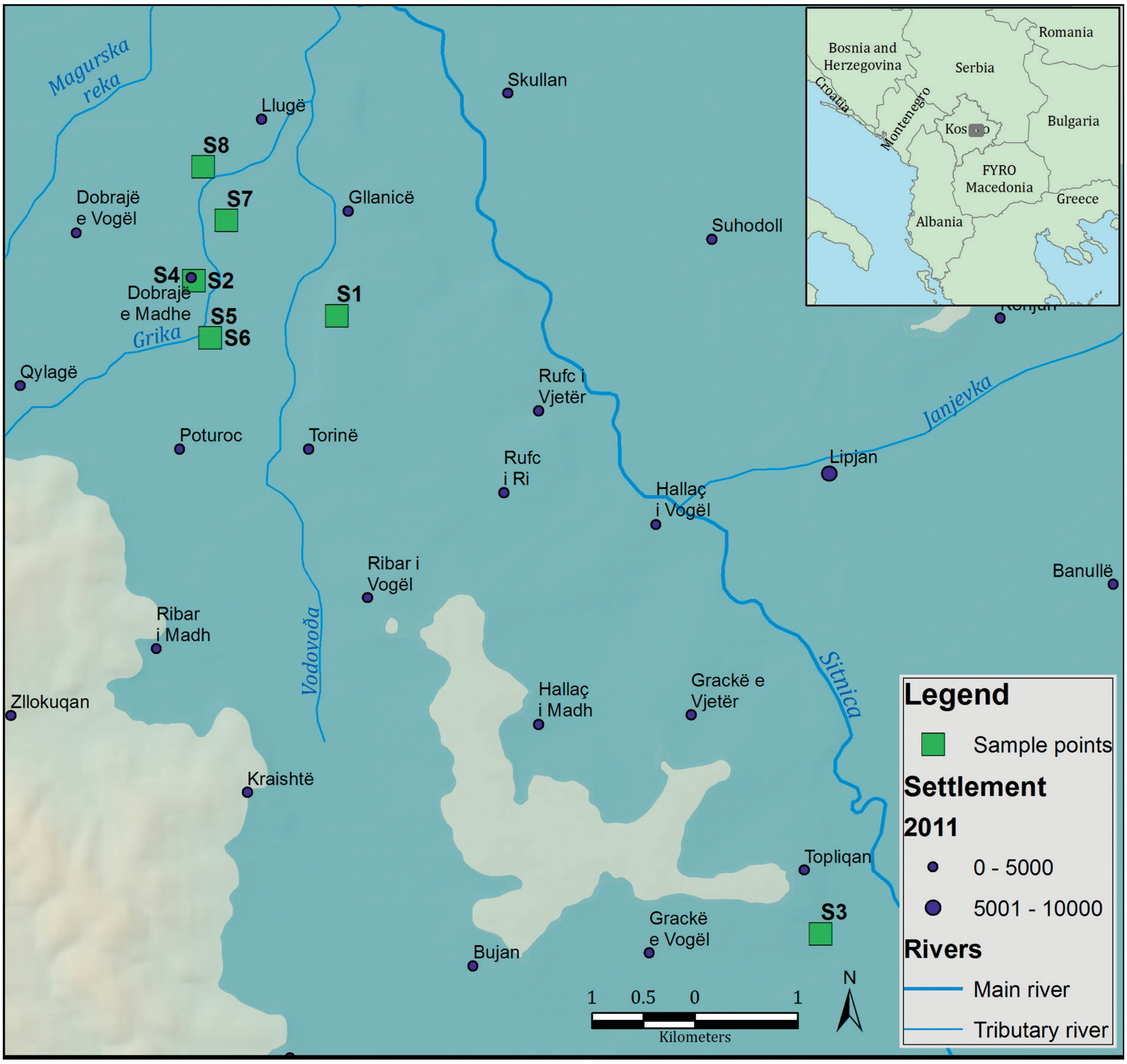

Figure 1 Study area with sampling stations

Physicochemical characterization

Redistilled water was used in all experiments. All instruments were calibrated according to the manufacturer's recommendations. Some of the parameters were measured directly in the ground (mainly physical parameters), while chemical analyses were carried out in the analytical laboratory. Water temperature 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 methods (alkalimetry, complexometry, argentometry and oxidoreduction) were used to determine: 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 caused by the presence of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. Chemical consumption of $KMnO_4$ was determined by Thiemann Küebel volumetric method (boiling in acidic environment). Analytical method and detection limit for some parameters measured are given in Table 2.

Statistical methods

The results were interpreted using modern statistical methods that can be used to locate pollution sources. Software Statistica 6.0 was used for all statistical calculations in this work, such as: determination of basic statistical parameters (Tab. 3). Frequency distributions and Two Dimensional Scatter with Plot diagrams of some measured parameters are presented in Figures 2 and 3. Determination of anomalies (extremes and outliers) for solution data are presented in Table 4. Outlier values are between 1.5 and 3 and extreme values above 3 standard deviations.

Results and discussions

The physicochemical parameters: water temperature, dry residue, EC, pH, total dissolved solids (TDS), consumption of $KMnO_4$, total alkalinity, total and temporary hardness of water, concentration of OH^-, CO_3^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+} and Cl^- are presented in Table 2.

In the present study, the temperature varied at different locations. Water temperature is lowest (13.2 °C) at the station S_3 and this is higher than temperatures (7.3 °C) of both Rječina and Kupa karstic springs in Croatia, reported by S. Frančišković-Bilinski et al. (2013). This is the usual characteristics of most of groundwaters. The dry residue of the examined samples was ranging from 50 to 540 mgL^{-1}. Except for stations S_3 and S_5 all samples were found to be under recommended WHO standards for drinking water (500 mgL^{-1}). As thermostat adjustment of the instrument for conductivity measurement had not been carried out, the temperature of water sample was measured and using the approximate correction factor, f, which is 0.02 $°C^{-1}$ for water in temperature range from 10 to 25 °C. The quantity of dry residue was calculated for the temperature of 20°C using the following formula:

$$\kappa_{20} = \kappa_t[1+f(20-t)]$$

EC values are relatively high in the all samples. Lowest value of 653 μScm^{-1} was measured at station S_3 and the highest value of 3250 μScm^{-1} which was measured at station S_8. All those values are much higher than all values found in the Kupa River and Rječina, Croatia, where the values range from 200 to 250 μScm^{-1}. Those higher values of EC might be a sign of anthropogenic environmental pollution. Values of pH are highest at station S_3 (7.22), which is much lower than the values found in karstic rivers of Croatia (pH up to 8.7). It could be due to

Table 2 Some physicochemical parameters determined in groundwater

Variable	Det. limit	Station							
		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
W. T./°C	0.01	15.1	13.2	17.7	16.9	15.8	19.9	16.6	20.0
Dry res./mgL^{-1}	0.01	90.0	70.0	540.4	50.0	50.0	502.1	270.0	71.0
EC/μScm^{-1}	0.01	1216	1119	653	800	826	990	894	3250
pH/1	0.01	6.94	6.98	6.80	6.80	7.01	6.67	7.22	6.59
TDS/mgL^{-1}	0.01	632	581	340	416	426	515	463	1690
Alk. T./mgL^{-1}	0.01	17.0	20.33	15.16	20.50	15.00	21.16	19.33	27.33
$KMnO_4$/mgL^{-1}	0.01	98.20	93.82	79.02	94.82	110.60	126.43	94.82	142.20
T. hard./°dH	-	5.32	4.20	3.64	5.32	4.76	5.04	5.88	7.28
OH^-/mgL^{-1}	-	17	Not det.	192.44	Not det.	255.00	30.90	79.39	113.22
CO_3^{2-}/mgL^-	2.00	600.0	639.6	460.8	600.0	Not det.	700.8	399.6	560.0
HCO_3^-/mgL^{-1}	-	Not det.	264.74	Not det.	640.5	Not det.	Not det.	Not det.	Not det.
Ca^{2+}/mgL^{-1}	0.01	53.2	33.6	25.2	14.0	39.2	30.8	25.2	78.4
Mg^{2+}/mgL^{-1}	0.01	19.55	15.10	13.09	19.55	17.11	18.11	21.13	26.17
Cl^-/mgL^{-1}	0.01	122.90	77.90	42.98	64.97	85.90	89.90	189.90	329.80

the composition of rocks in the area, as mentioned Croatian rivers are situated in karst, while our stations are situated in the area of acid magmatic rocks. TDS values (behave similarly as EC), are also a possible sign of anthropogenic influence. TDS of the tested samples was ranging from 340 mgL^{-1} to 1690 mgL^{-1} and stations S_1, S_2, S_6 and S_8 were found to be above the recommended WHO standard for drinking water (500 mgL^{-1}). Generally speaking, groundwaters of Kosovo are enriched in dissolved solids, as a consequence of aquifer lithology and residence time of ground water. Waters with high TDS usually appear in metamorphic and igneous environments, while waters with low TDS occur in carbonate rocks. Total hardness, temporary hardness, total alkalinity, concentration of Ca^{2+}, Mg^{2+}, HCO_3^- and OH^- of examined samples showed that all water samples are in low values. Hydroxides, carbonates and hydrogen carbonates and alkaline earth metals, mainly Na, Ca and Mg cause water alkalinity. 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. If the median values of some macro components of groundwaters of Europe are compared with those in groundwaters of Kosovo, it is obvious that Kosovo waters are richer in Mg, Na, and K, besides high values of EC and TDS. Except for station S_8 chlorides in all samples were found to be under recommended WHO standards for drinking water (250mgL^{-1}). Those higher values of chlorides might be the result of groundwater treatment with chlorine products. Consumption of $KMnO_4$ was ranging from 79.02 to 142.2 mgL^{-1} and all groundwater samples were found to be above recommended WHO standard for drinking water (10 mgL^{-1}). Such high values of consumption of $KMnO_4$ might be a sign of anthropogenic environmental pollution. Based on the anomalous values (Fig. 3 and Tab. 4) from 15 experimental data in sample S_8 we registered extreme values of TDS and electrical conductivity and outlier values of total hardness and chlorides.

Table 3 Basic statistical parameters for 12 selected variables in 8 groundwater samples

Variable	Mean	Geometric mean	Median	Minimum	Maximum	Variance	Standard Deviation
Dry res. /mgL^{-1}	205.4	130.0	805.0	500.0	540.4	43205.9	207.9
EC /μScm^{-1}	1218.5	1067.7	9420.0	6530.0	3250.0	706200.0	840.4
pH /1	6.9	6.9	68.7	65.9	7.2	0.0	0.2
TDS /mgL^{-1}	632.9	554.3	4890.0	3400.0	1.7	191223.6	437.3
HO^- /mgL^{-1}	111.2	83.5	1010.0	170.0	255.0	6260.6	79.1
CO_3^{2-} /mgL^{-1}	507.7	450.0	5800.0	1010.0	700.8	36249.9	190.4
HCO_3^- /mgL^{-1}	188.9	143.5	1010.0	1010.0	640.5	36579.0	191.3
Tot. Hard. /°D	5.2	5.1	51.8	36.4	7.3	1.2	1.1
Ca^{2+} /mgL^{-1}	37.5	3.3	322.0	140.0	78.4	405.3	20.1
Mg^{2+} /mgL^{-1}	18.7	18.4	188.3	130.9	26.2	15.8	4.0
Cl- /mgL^{-1}	125.6	103.3	879.0	429.8	329.9	8786.3	93.7
Cons. of $KMnO_4$ /mgL^{-1}	110.6	108.4	1027.1	790.2	142.2	570.3	23.9

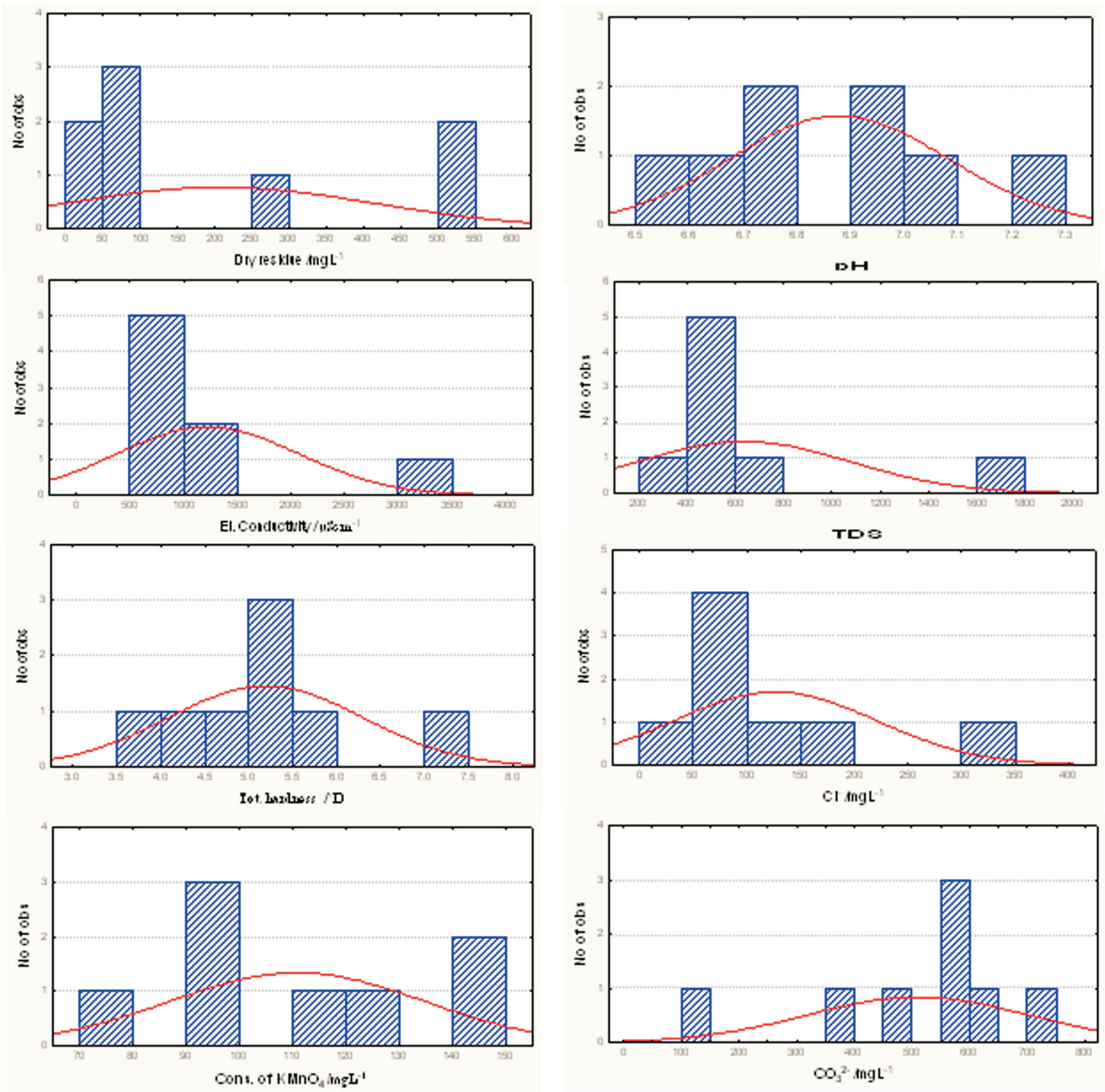

Figure 2 Frequency histograms of some measured variables

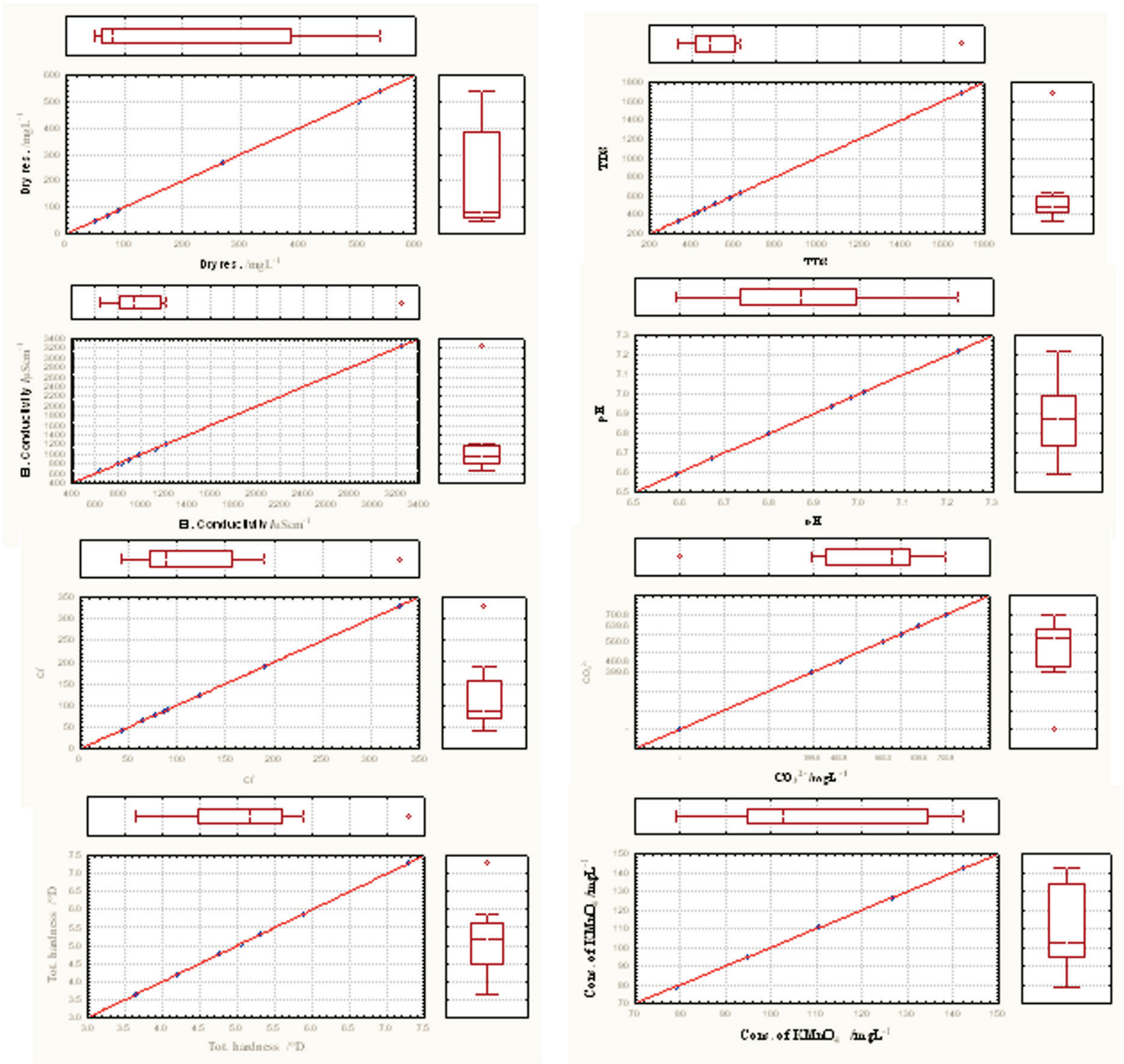

Figure 3 Scatterplot with box plot diagrams of some measured variables

Table 4 Water samples with anomalous values (outliers and extremes)

Sample	Outliers of parameters	Extremes of parameters
S_1	Not reg.	Not reg.
S_2	Not reg.	Not reg.
S_3	Not reg.	Not reg.
S_4	Not reg.	Not reg.
S_5	Not reg.	Not reg.
S_6	Not reg.	Not reg.
S_7	Not reg.	Not reg.
S_8	Cl^- (329.89 mgL^{-1}), Tot. Hardness (7.28 °dH)	TDS (1690 mgL^{-1}), EC (3250 μScm^{-1})

Conclusion

The physicochemical analysis indicates that groundwater in the western part of Lipjan is polluted. High values of TDS, EC and consumption of $KMnO_4$ may indicate a possible sign of anthropogenic influence. Faecal contamination from anthropogenic activity in some groundwater samples is an indication that contamination is beginning to reach the aquifer. A long and uncontrolled discharge of municipal waste water caused a change in water quality. For this reason, we recommend avoiding discharges of wastewater without treatment, mainly from septic tanks, which are extensively used in the area. Also, further research of water in the studied region, including concentrations of heavy metals and possibly organic pollutants, is suggested to get a better insight into degree of pollution.

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