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Water Quality Assessment of Sitnica River (Kosovo): A Statistical Evolution

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Abstract

Degradation of water quality is very important issue in Kosovo. Discharge of untreated or partially treated industrial and domestic wastewater, leaching of pesticides and residues of fertilizers; and navigation are often factors that affect the quality of water. The aim of this study was to analyze the river water quality of Sitnica. Exact geographic coordinates were measured by GPS and locations were well described. Water samples were collected in 10 sampling points and the following physico-chemical parameters were analyzed: water temperature, electrical conductivity, pH, alkalinity, total hardness, temporary hardness, total oxigeny, etc. Using UV-VIS spectrophotometry are determinated concentrations of: NO_2^-, NO_3^-, NH_4^+, Mn^{2+}, Al^{3+} and Fe^{2+}. Program Statistica 6.0 has been used for statistical calculations of basic statistical parameters and anomalies (extremes and outliers). Results obtained by the box plot method will be helpy to determiny the regions with anomalous of physic-chemical parameters. The levels of some parameters and ecotoxic ions from surface waters are compared with the results from the river source where anthropogenic effects are negative.

Keywords**:** Sitnica River; Physico-chemical Parameters; UV-VIS Spektrophotometry; Anomalies; Pollution assessment; Statistical evolution.

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1. Introduction

The increasing urbanization, industrialization, the modernization of agriculture, the increase in traffic contribute to global pollution, which requires accurate monitoring and information about the quality of water resources. The World Health Organization estimated that in developing countries about 80% of water pollution is a result of domestic waste [1]. 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 [2].

Drinking water is an essential environmental constituent and the quality of drinking water is an issue of primary interest for the residents of the European Union [3]. 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 bad implication on the hydrology [4]. Decomposition of organic matter and pollution due to anthropogenic activity are the main sources of pollution of water [5]. Therefore, multidisciplinary collaborative research is essential for understanding the pollution processes. As reported by Brils [6], 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.

This work is a continuation of earlier studies of surface waters in Kosovo [7-11]. 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 [12].

The aim of the current work is to perform, a systematic research on water of the river Sitnica. The research is based on the above factors as they affect directly and indirectly the water quality, also except the impact that they have in aquatic life (water), a major impact will be in biota where it is known that a large amount of this river flow is used for irrigation of agricultural lands and this may be an indirect impact in people's lives as they consume agricultural products and can be deposited in the organism of people through the food chain [13].

2. Materials and Methods

2.1. Study Area

The objective of this study is to estimation of water quality of river Sitnica ((length of 90 km), as surface water resource, located in middle side of Kosova. Sampling strategy was concentrate in the 10 monitoring points from the source in the mountain, downstream to the end of river within our territory near the border of Serbia. The sampling sites in Kosovo are geographically positioned using Geographic Information System. The results were interpreted using modern statistical methods that can be used to locate pollution sources.

Surface water sampling of champions and their elaboration in the depth ≥ 0.15 m were done with Pyrex noncontaminating bottles according to standards methods for surface water [14]. Some of the natural 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 3 March 2010 and 7 March 2010 in plastic bottles previously rinsed three times with sampled water, they were labeled with the date of the name of the source of samples and then are transferred to hand refrigerator (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]. According to the requirement samples were preserved in the refrigerator after treatment. Geographical positions were determined by GPS, model "GEKO, GARMIN", 12 channels. The study area with the sampling locations is shown in Figure 1 and the details about all sampling sites are presented in Table 1.

2.3. Chemical Characterization

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. Temperature of water was measured immediately after sampling, using digital thermometer, model "Quick 63142". Measurements of pH were performed using pH/ion-meter, "Hanna Instruments". Electric conductivity was measured by conductometer "InoLab WTW", turbidity (turbidimetric method with formazine standard), chemical expense $KMnO_4$ was determined by Thiemann Küebel volumetric method (boiling in acidic environment), chlorides was determined by argentometric titrimetric method, the alkalinity 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 eriochrome black T indicator. Temporary hardness (carbonate hardness) was also determined. It is due to the presence of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. Some of physic-chemical parameters (NO_2^-, NO_3^-, NH_4^+, Al^{3+}, Mn^{2+} and Fe^{2+}) were determined using UV-VIS spectrometry method. "WTW S12 Photometer", "SECOMAM Prim Light spectrophotometer", "SECOMAM Pastel UV spectrophotometer" and "WTW S12 Photometer " are used with a monochromatic irradiation in ultraviolet (UV) and visible (VIS) spectral range of 190-1100 nm. Its measurement region, in a cavette of 10 mm, was λ = 340-800 nm, is dedicated for drinking waters analysis, discharged and sea water.

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 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.

3. Results

3.1. The Physico-chemical Analysis

The physico-chemical parameters: water temperature, EC, pH, turbidity, total alkalinity, total hardness, temporary hardness, total oxygen, consumption of $KMnO_4$, concentration of Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}, Mn^{2+}, NH_4^+ -tot. HCO_3^-, NO^-_2, NO_3^-, and Cl^- are presented in Table 2.

Table1: Sampling stations with detailed description

Sample	Locality	Coordinates	Height above sea level (m)	Possible pollution sources
S_1	Jezerc	34T 0501340 UTH4689442	790	Settlement
S_2	Rubofc	34T 0511168 UTH0701529	554	Waste water, agriculture
S_3	Lypjan	34T 0509360 UTH4706698	542	Road, waste water from Lypjan
S_4	Lismir	34T 0505443 UTH4721072	539	Settlement, agriculture, flotation waste, wastewater from Prishtina
S_5	Palaj	34T 0504992 UTH4725302	531	Agriculture, wastewater from Fushë kosova
S_6	Plemetin	34T 0503152 UTH4728263	526	Thermo power plant, waste water from Obiliq
S_7	Pestova	34T 0499284 UTH4736665	523	Agriculture
S_8	Vushtrri (exit)	34T 0496273 UTH4741288	516	Agriculture, tin factory, wastewater from Vushtrria
S_9	Mitrovica (exit)	34T 0490408 UTH4749416	508	Phosphate and accu factory, settlement, road, waste water from Mitrovica
S_{10}	Zveqan	34T 0487012 UTH4754445	504	Road, waste water from Mitrovica

3.2. Determination of Basic Statistical Parameters and Anomalous Values

Basic statistical parameters for 9 variables (μg dm^{-3}) in 10 water samples are presented in Table 3. Using experimental data (Table 2) and box plot approach of Tukey [20], anomalous values (extremes and outliers) in waters were determined for the whole region. Frequency distributions of each measured ions and two dimensional scaterplot with plots diagrams are presented in Figure 2 and 3. Anomalous values (outliers and extremes) for 9 variables are presented in Figure 4.

Figure 1: Study area with sampling stations

Table 2: Some physic-chemical parameters determined in river water

Parameters /mgdm^{-3}	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Water temp. / ° C	12.0	12.1	11.8	11.9	11.8	11.9	11.9	11.9	12.0	11.9
EC, /µScm^{-1}	400	295	305	590	428	442	437	453	461	442
pH /1	7.18	7.34	7.39	7.09	7.93	7.84	7.51	7.73	7.68	7.68
Turbidity /NTU	0.13	95	79	52	91	92	61	69	59	59
Total alkalinity /mgdm^{-3}	45.8	42.5	48.5	57.0	53.5	47.5	50.5	53.8	40.25	44.5
Total hard. /◦H	12.88	8.40	8.68	10.92	13.16	14.00	13.44	12.88	13.16	14.00
Temp. hard. /ºH	1.28	1.19	1.36	1.59	1.49	1.16	1.41	1.56	1.12	1.24
TO / mgdm^{-3}	9.4	8.3	7.8	7.1	7.7	7.8	7.8	8.0	7.3	8.1
Cons. of	11.6	37.93	28.44	37.6	26.86	23.7	24.65	24.33	30.02	22.12

$KMnO_4$ /mgdm^{-3}										
Ca^{2+} / mgdm^{-3}	69.97	3.99	3.99	51.98	47.97	47.99	49.97	44.98	44.39	43.99
Mg^{2+} / mgdm^{-3}	17.39	20.84	22.45	20.8	36.88	41.54	36.86	59.28	39.76	44.9
Fe^{2+} / mgdm^{-3}	0.05	0.46	0.61	0.36	1.85	0.64	0.45	0.82	0.37	0.48
Al^{3+} / mgdm^{-3}	0.034	0.02	0.043	0.019	0.094	0.047	0.028	0.051	0.025	0.031
Mn^{2+} / mgdm^{-3}	0.03	0.98	0.94	0.77	1.44	1.08	0.62	0.75	0.65	0.66
HCO_3^- / mgdm^{-3}	279.38	259.2	295.8	347.7	362.3	289.7	308.0	328.18	245.5	271.4
NH_4^+ / mgdm^{-3}	0.06	0.09	0.08	0.17	0.38	0.50	0.27	0.22	0.28	0.23
NO_2^- / mgdm^{-3}	0.005	0.06	0.05	0.11	0.05	0.04	0.04	0.04	0.04	0.04
NO_3^- / mgdm^{-3}	0.05	0.5	0.5	0.5	0.5	1.2	1.4	0.5	0.5	0.5
Cl^- / mgdm^{-3}	2.5	14.6	12.0	19.7	26.2	29.0	16.1	17.3	18.1	19.9

Table 3: Basic statistical parameters for 9 chemical variables (µg dm^{-3}) in 10 water samples

Variable / mgdm^{-3}	**Mean**	**Geo. mean**	**Median**	**Min.**	**Max.**	**Variance**	**Std. Dev.**
Al^{3+}	0.0392	0.03495	0.03250	0.0190	0.094	0.00049	0.022150
Fe^{2+}	0.6090	0.45637	0.47000	0.0500	1.850	0.23125	0.480889
Mn^{2+}	0.7920	0.60529	0.76000	0.0300	1.440	0.13446	0.366691
NO_2^-	0.0475	0.03914	0.04000	0.0050	0.110	0.00068	0.026167
NO_3^-	0.6150	0.48051	0.50000	0.0500	1.400	0.15225	0.390192
NH_4^+	0.2280	0.18739	0.22500	0.0600	0.500	0.01935	0.139108
OT	7.9300	7.90886	7.80000	7.1000	9.400	0.39122	0.625478
Co. of $KMNO_4$	26.6710	25.44406	25.75500	11.0600	37.930	60.37728	7.770282
Cl^-	17.4800	15.15020	17.50000	2.5000	29.000	53.55511	7.318136

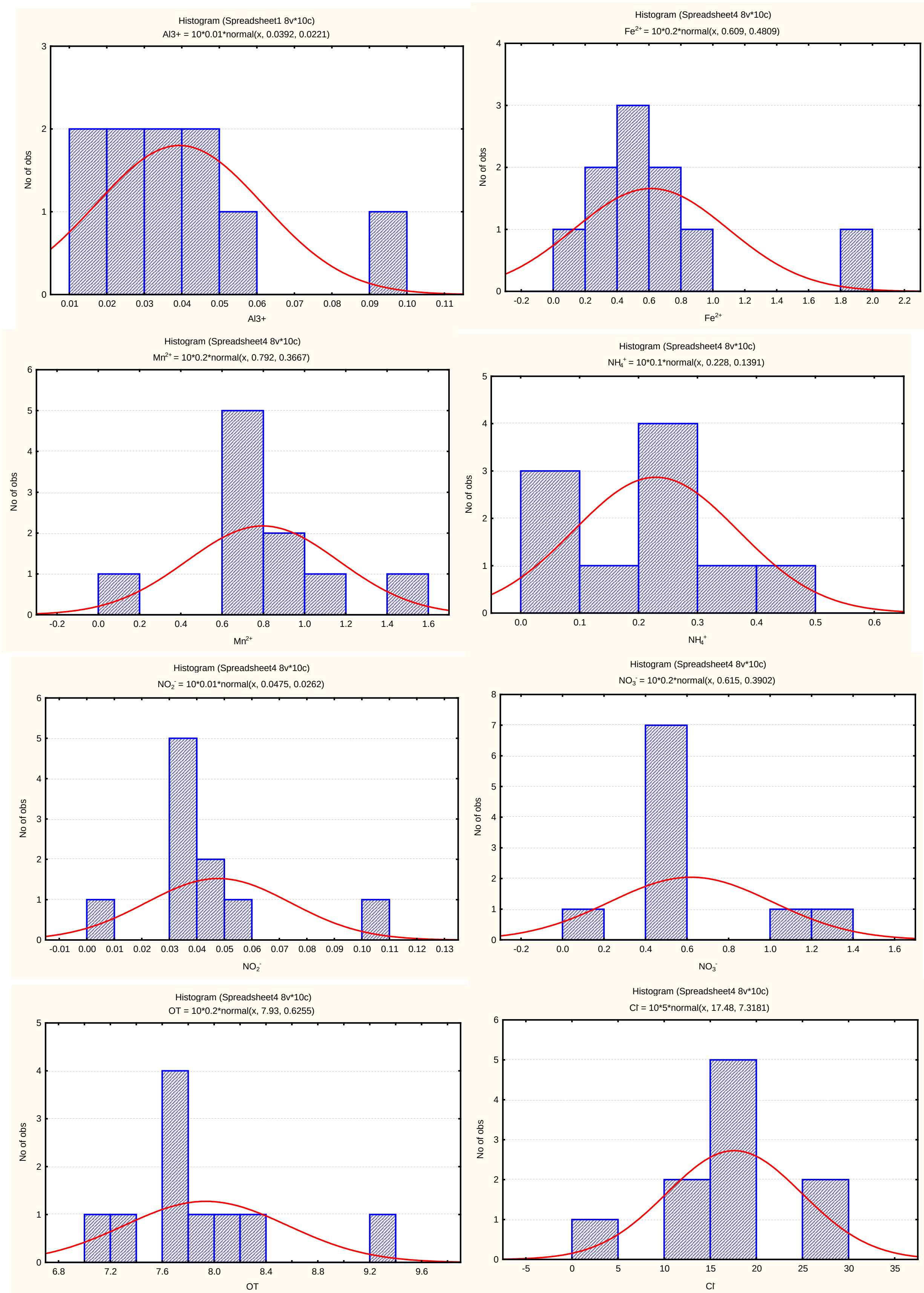

Figure 2: Frequency Histograms of some measured parameters

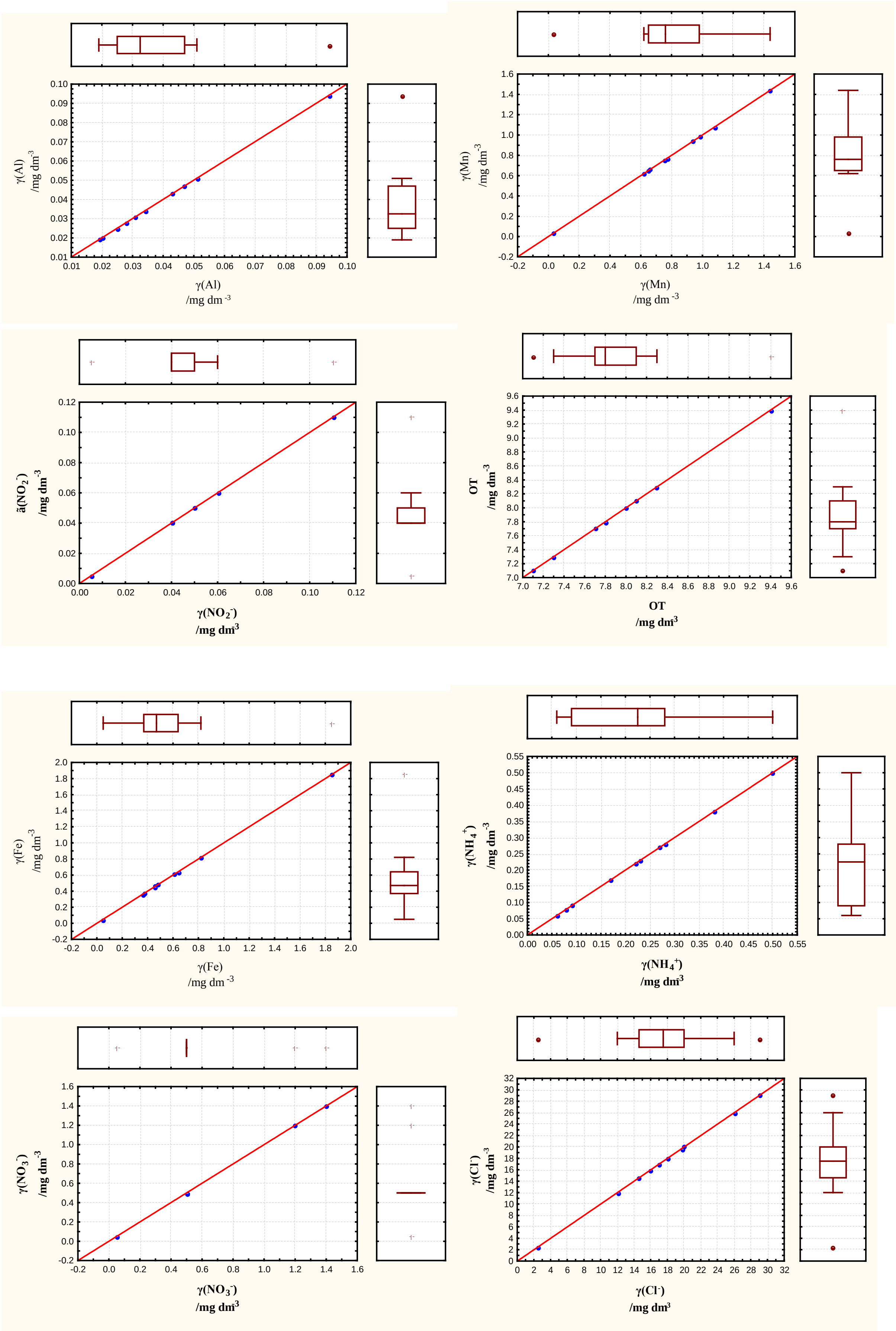

Figure 3: Two dimensional scaterplot with plots diagrams of some measured parameters

Table 4: Water samples with anomalous values (outliers and extremes) from 9 variables

Sample	Outliers of elements (¤)	Extremes of elements (o)
S_1	-	-
S_2	-	-
S_3	-	-
S_4	-	NO_2^- (0.094 µg dm^{-3})
S_5	Al^{3+} (0.094 µg dm^{-3}) Mn^{2+} (1.44 µg dm^{-3}) NH_4^+ (0.5 µg dm^{-3}) Cl^- (29 µg dm^{-3})	Fe^{2+} (1.85 µg dm^{-3})
S_6	-	NO_3^-(1.2 µg dm^{-3})
S_7	-	NO_3^-(1.4 µg dm^{-3})
S_8	-	-
S_9	-	-
S_{10}	-	-

4. Discussion

Statistical methods were applied to find anomalous values of parameters (Table 4). From the results, obtained from sample S_2 and S_3 of the river, we can see that the water in these two samples are soft (in the mean of hardness) but other samples show increase in the value of hardness. Temperature varied at different locations of the river as indicated by the in situ readings. It is not considered coming from heat contamination sources, but from natural warming in different parts of Kosovo. The pH of the investigated samples was ranging from 7.09 to 7.93 and showing that all water samples are slightly alkaline. These values are within highest desirable limit (HDL) prescribed by World Health Organization.

Electrical conductivity ranged from 295-590 µS m^{-1}, and these values are within highest desirable limit (HDL). If we compare EC separately, the lowest value is observed at S_2 station and the highest value is observed at S_4 station. Higher EC values indicate the presence of higher content of dissolved salts in the water. The lowest value of Turbidity is observed at point S_1 (near of river source) while at all ponts we have higher values from settlements, gravel separations and anthropogenic waste. Total hardness of water have described positive correlation of total hardness with Mg and Ca in the water. The lowest total hardness is observed at S_2 station (8.4° H) and the higher value of the hardness was observed at station S_6 and S_{10} (14° H). Bicarbonate hardness reaches maximum values at S_5 station (362.35 mg dm^{-3}). The alkalinity (mA) is found to be in range 40.25 (at S_9) -57 (at S_4). Consumption of $KMnO_4$ has maximum values in S_2 and S_4 while the lowest vale we found at S_1. The values of chlorides are found to be in range 2.5 mg dm^{-3} (at sours of river, S_1) and 29 mg dm^{-3} (at S_6). We found that total oxygeny (TO) is in the range of 7.1 mg dm^{-3} (at S_4) and 9.4 mg dm^{-3} (at sours of river, S_1). Total ammonia values have been changed due to downstream of the river and lower value we found at point S_1 and higher value at points S_5 and S_6. Values of NO_2^- have been changed due to downstream of the river and we found highest value at points S_4. Also we noticed that the pollution from iron and manganese, wich causing significant toxic effects is found at stations S_2 – S_{10}. In this range our proposal is the natural pollution and as such sorrounding iron mongery. Values for Al^{3+} and NO_3^- are within highest desirable limit (HDL) according to WHO and EU for drinking water and EU directive 152/99/ET for surface waters.

5. Conclusions

According to the performed chemical analyses, we have noticed that the most of pollution in this river is the sampling spots S_4, S_5, S_6 and S_7. These are the locations in Fushë Kosova (S_4-S_6) and in Vushtrria (S_7). The high values from iron and manganese, wich causing significant toxic effects is found at stations S_2 and S_{10}, (natural and antropogenic pollution).

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