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Assessment of the water quality of Lumbardhi river, Prizren (Kosovo)

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The surface waters in Kosovo are predominantly polluted, and there are still no plants for the treatment of domestic or industrial wastewaters in any of the cities in Kosovo. The main goal of this research is to analyze some environmentally toxic elements downstream the river where they end up as natural recipients. The sampling sites are geographically positioned using GIS (Geographic Information System). The results were interpreted using modern statistical methods used to locate polluted regions with abnormal concentration values. Values of selected elements were evaluated by Pearson's factor statistical analysis to identify their correlation. Concentrations of some toxic elements are as follows: Cu (1.4-4.4 μg dm^{-3}), Zn (3.2-9.4 μg dm^{-3}), Pb (1.03-2.58 μg dm^{-3}), Cd (0.03-0.13 μg dm^{-3}), Mn (10.6 -59.6 μg dm^{-3}), As (0.43-28.5 μg dm^{-3}), Cr (0.6-1.0 μg dm^{-3}), Fe (80-570 μg dm^{-3}), Ni (0.6-2.5 μg dm^{-3}), Sb (0.02-0.07 μg dm^{-3}), Al (58-195 μg dm^{-3}). The results obtained were compared with WHO and EU standards for drinking water. Even though there is no legislative convent in Kosovo for allowed concentrations of toxic metals in natural water resources, the results from this study are a small contribution to gain a clear overview of the state in this field of environmental quality assurance.

Keywords: Lumbardhi river, pollution assessment, heavy metals, physico-chemical parameters, ICP/MS, FIMS.

INTRODUCTION

Kosovo is regarded as a place with developed river network. Its small territory and dynamic topography have not created circumstances to form any major river flows. Kosovo has no navigable river but existing rivers have been the deciding factor for the development of life, the establishment of settlements and communication links through their valleys.

Scarcity and misuse of fresh water pose a serious and growing threat to sustainable development and protection of the environment. Human health and welfare, food security, industrial development and the ecosystems on which they depend, are all at risk, unless water and land resources are managed more effectively in the present decade than they have been in the past [1].

Overexploitation of nature and uncontrolled use of natural resources, including inadequate processing of industrial wastes have caused large contamination of world ecosystems by toxic metals (Hg, Pb, Cd, Cu, Zn, Ni, Mn). The major contaminants are metals and metalloids [2, 3]. They have the ability to bioaccumulate in organisms living in the water systems [4-6]. Studies on toxic metals and metalloids in lakes, rivers, groundwater and fish have been the main environmental focal spots, particularly over the last decade [7-10].

Nowadays, qualitative and quantitative determination of total metals and distribution of all their physical and chemical species in trace amounts (speciation) in natural water resources is to be considered as the main challenge for most scientists [11]. Based on the results of such studies it will be possible in the future to propose protection and detoxification measures of affected river waters and general protection and remediation of ecosystems. This work is a continuation of earlier studies of surface waters in Kosovo [12-17].

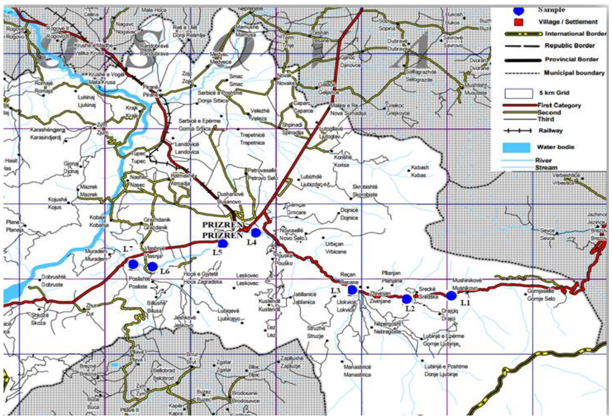

Fig. 1. Study area with sampling stations

The aim of this paper is to study the watershed of Lumbardhi river in Prizren, which belongs to the basin of Drini Bardhë, the richest basin with an annual flow of 2.200.00 million m³ and with the longest surface of 4.622 km² in the territory of the republic of Kosovo. The Lumbardhi river, Prizren has its origins from Sharr Mountains [18].

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MATERIALS AND METHODS

Samples were taken along the banks of the sampling stations in April 2013. Sampling tools were washed with water and dried before the next sample was collected. Water samples were collected from surface waters below 10 cm [19]. The collected samples were stored in polythene plastic containers. Weather was cloudy and rainy, with middle water levels, which was very suitable for sampling. Sample preparation was done according to standard methods for surface water analysis [20, 21]. The study area with the sampling locations is shown in Figure 1 and the details about all sampling sites are presented in Table 1. Geographical positions were determined by GPS, using model "geko 201, 12 channel". The number of sampling spots was 7 and at every sampling spot samples were taken in order to determine the chemical parameters. The sampling spots of water in the river of Lumbardhi Prizren, were marked by codes L_1, L_2, L_3, L_4, L_5, L_6 and L_7.

Determination of physico-chemical parameters

For determination of the quality parameters of the water we have used standard methods for water analysis including classical and modern methods. Temperature of water was measured immediately after sampling, using a digital thermometer, model "Quick 63142". Measurements of pH were performed immediately after sampling using a pH/ion-meter, model "Hanna Instruments, pH & EC". Electric conductivity was measured by a "HANNA Instrument HI 8424" conductivity meter. Total hardness of water was determined by EDTA titration using Mercurochrome black T indicator and chemicals of p.a. purity. Chlorides were determined using argentometric methods. Some physico-chemical parameters (NH_4^+, NO_3^-, PO_4^{3-}) were determined by UV-VIS spectrometry. "WTW S12 photometer", "SECOMAM Prim Light spectrophotometer" and "SECOMAM Pastel UV RS232 spectrophotometer" were used with a monochromatic irradiation in the spectral range of 190-1100 nm. The measurement region, in a cuvette of 10 mm, was 340-800 nm, for the analysis of drinking waters, discharged and sea water.

Determination of elements

We used ICP/MS (inductively coupled plasma mass spectrometry) to determine the concentration of the target elements. Hg was determined by FIMS (flow injection Hg analysis).

Statistical analysis

Program Statistica 6.0 [22] was used in the statistical calculations of this work, such as: determination of basic statistical parameters and two-dimensional box plot diagrams for the determination of anomalies (extremes and outliers) for solution data.

Table1. Sampling stations with detailed locality description

Sample	Locality	Coordinates	Possible pollution sources
L_1	Mushnikovë	42⁰10ʾ23.75ʾʾN 20⁰53ʾ3.67ʾʾE	Throwing rubbish, Wastewater
L_2	Sredskë	42⁰10ʾ15.47ʾʾN 20⁰51ʾ5.88ʾʾE	Throwing rubbish, Wastewater
L_3	Reçan	42⁰12ʾ34.76ʾʾN 20⁰44ʾ56.25ʾʾE	Factory Fruti
L_4	Marash	42⁰12ʾ44.78ʾʾN 20⁰44ʾ40.65ʾʾE	Throwing rubbish, Traffic
L_5	Prizren	42⁰12ʾ35.53ʾʾN 20⁰44ʾ11.34ʾʾE	Throwing rubbish, Traffic
L_6	Poslisht	42⁰11ʾ5.31ʾʾE 20⁰40ʾ11.31ʾʾE	Throwing rubbish
L_7	Vlashne	42⁰11ʾʾ57.87ʾʾN 20⁰39ʾ47.31ʾʾE	Throwing rubbish, Wastewater

Table 2. Physico-chemical parameters determined in river waters: air temperature, water temperature, pH, total solids, electrical conductivity (EC), dissolved oxygen, BOD_5, total hardness, content of sulfates, nitrites, ammonium and phosphates

Parameters	Sampling station						
	L_1	L_2	L_3	L_4	L_5	L_6	L_7
Water temp./ ^{0}C	12.08	13.5	20.3	15.6	15.0	14.9	17.4
Air temp./ ^{0}C	9.8	10.3	11.1	11.4	11.9	11.7	15.7
pH	8.25	8.49	8.51	8.38	8.37	8.10	8.12
TS/ mg dm^{-3}	100	200	200	190	560	360	960
EC/µS cm^{-1}	126	159	188	178	190	226	280
DO/ mg dm^{-3}	7.7	8.2	10.5	10.0	9.8	8.5	9.1
BOD_5/ mg dm^{-3}	5.0	4.2	0.5	4.8	6.1	5.5	6.74
Total hardness / ^{0}D	6.72	11.2	7.84	7.89	6.72	16.8	26.88
SO_4^{2-}/ mg dm^{-3}	15	17	12	22	20	25	27
NO_3^-/ mg dm^{-3}	0.04	0.025	0.08	0.15	0.18	0.20	0.28
NH_4^+/ mg dm^{-3}	0.25	0.3	0.4	0.8	0.9	1.2	2.2
PO_4^{3-}/ mg dm^{-3}	0.11	0.15	0.2	0.55	0.7	0.65	0.8
Cl^-/ mg dm^{-3}	5.01	4.30	3.58	2.66	1.43	3.94	4.85

RESULTS AND DISCUSSION

Physico-chemical parameters

Table 2 shows several physico-chemical parameters measured in the water of Lumbardhi river, Prizren: air temperature, water temperature, pH, electrical conductivity (EC), dissolved oxygen, BOD_5, total hardness, content of sulfates, nitrites, ammonium and phosphates.

Temperature is a biologically significant factor which plays an important role in the metabolic activities of organisms. It is also an important parameter in determining water quality, as it influences pH, alkalinity, acidity and dissolved oxygen (DO). The temperature values recorded in the water samples from the study area range between 12.08 ^{0}C (L_1) and 20.3 ^{0}C (L_3), as summarized in Table 2 with a mean temperature of 15.54 ^{0}C. The recorded temperature values were within the WHO standard for drinking water.

The pH is a measure of the acidity or alkalinity and measures the concentration of hydrogen ions in water. Basically, pH is determined by the amount of dissolved carbon dioxide (CO_2) which forms carbonic acid in the water. The pH values of the surface water sampled in the area varied from 8.10 to 8.51 with a mean value of 8.32 (the WHO standard range is 6.50-8.50). From these data we can see that the water of the river Lumbardhi Prizren is slightly basic.

The minimum TS value of 100 mg dm^{-3} was recorded at L_1 while the maximum value of 960 mg dm^{-3} was recorded at L_7. No limit has been set by WHO for drinking water and water for domestic uses but water with values similar to these has previously been described as good [23].

Electrical conductivity (EC) is a measure of water capacity to convey electric current. It is a determination of levels of inorganic constituents in water [24]. EC values obtained for the samples were in the range of 126-280 µS cm^{-1}, which is below the WHO recommended value of 400 µS cm^{-1} indicating a low amount of dissolved inorganic substances in ionized form.

Dissolved oxygen (DO) is an important parameter in water quality assessment and reflects the physical and biological processes prevailing in the water. The DO values indicate the degree of pollution in water bodies. DO values, as shown in Table 2, varied from 7.7 to 10.5 mg dm^{-3}.

The values for biochemical demand shown in Table 2 range from 0.5 to 6.74 mg dm^{-3} with a mean of 4.69 mg dm^{-3}. The values are quite lower than the standard of 10 mg dm^{-3} recommended by WHO.

The total hardness was 6.72 ^{0}D (sampling spots L_1 and L_5), 11.2 ^{0}D (sampling spot L_2), 7.84 ^{0}D (sampling spot L_3), 7.89 ^{0}D (sampling spot L_4), 16.8 ^{0}D (sampling spot L_6) and 26.88 ^{0}D (sampling spot L_7). The lowest total hardness was observed at L_1 and L_5 spots (6.72 ^{0}D) and a higher value of the hardness was observed at spot L_7 (26.88 ^{0}D).

Sulfate content higher than 100 mg dm^{-3} tends to give water a bitter taste and has a laxative effect on people not adapted to the water [25]. Also ailments like catarrh, dehydration and gastrointestinal irritation have been linked with high sulfate concentration. The results revealed that all analyzed water samples have a low sulfate content ranging from 12 to 27 mg dm^{-3} (Table 2). So, the concentration of sulfates is below the maximum value allowed by the WHO and the EU [23, 26].

Nitrate content in the analyzed water samples ranged from 0.025 mg dm^{-3} in L_2 to 0.28 mg dm^{-3} in L_7. These fall within the allowable value when compared to the WHO recommended guidelines. Nitrate fouls the water system and epidemiological studies have shown that exposure to nitrate causes methemoglobinemia disease [27].

The amounts of Cl^-, PO_4^{3-}, NH_4^+ ions range from 1.43 to 5.01 mg dm^{-3}, 0.11 to 0.8 mg dm^{-3}, and 0.25 to 2.2 mg dm^{-3}, respectively. Table 3 shows the concentrations of 67 elements in the water of river Lumbardhi Prizren.

Concentration of major and trace elements

Cadmium levels in all samples were in the range of 0.03-0.13 μg dm^{-3} with a mean value of 0.061 μg dm^{-3} (Table 4). The relative cadmium concentration for individual samples is indicated in Table 3. L_5 has the lowest cadmium content and L_1 has the highest one. In the case of cadmium, the highest concentration was recorded at the sampling spot L_1 (0.13 μg dm^{-3}), where this high concentration comes from the face of the earth geology. The values are lower than the WHO recommended standard of 3×10^{-3} mg dm^{-3}. Excess cadmium concentration in water is highly toxic and is responsible for adverse renal arterial changes in kidneys [28].

Copper detected in the water samples was very low and far below the recommended limits of 2.0 mg dm^{-3} set by WHO. Copper concentration was found to vary from 1.4 to 4.4 μg dm^{-3} with a mean of 3.029 μg dm^{-3} (Table 4) for all samples.

Most groundwater supplies contain some iron because it is one of the most abundant metals in the earth crust and is essential for plants and human beings. But excess iron in drinking water produces inky taste and muddy smell. The WHO recommends that the iron content of drinking water should not exceed 0.2 mg dm^{-3} because iron in water stains plumbing fixtures, cloths during laundering, incrusts well screens and clogs pipes [29]. Iron concentration was observed to vary from 80-570 μg dm^{-3} with a mean of 230 μg dm^{-3} (Table 4) for all samples. Iron concentrations in the water samples from L_4, L_5 and L_7 were above the EU guideline [26].

Magnesium ions are directly related to hardness. Magnesium content in the investigated water samples was ranging from 2120 to 7730 μg dm^{-3} which were below the WHO guidelines of 200 mg dm^{-3}. It is known that Ca^{2+} and Mg^{2+} ions in water are essential for human health and metabolism [30].

The sodium content ranged from a minimum of 2570 μg dm^{-3} to a maximum of 6750 μg dm^{-3}. The minimum values of the samples can be explained on the basis of lower microbial activity. No limit is established by the WHO for sodium in drinking water but a maximum standard of 100 mg dm^{-3} has been proposed for the general public.

The major source of potassium in natural fresh water is weathering of rocks [31]. Potassium content in the water samples varied from 790 to 1340 μg dm^{-3}. No guide and acceptable limits have been specified for potassium levels in the WHO standards for drinking water.

Aluminum levels in all samples were in the range of 58-195 μg dm^{-3} with a mean value of 126.571 μg dm^{-3} (Table 4). Relative aluminum concentration for individual samples is indicated in Table 3. L_2 has the lowest aluminum content and L_5 has the highest one. The values are lower than the WHO recommended standard of 0.2 mg dm^{-3}.

Arsenic levels in all samples were in the range of 0.43-28.5 μg dm^{-3} with a mean value of 4.487 μg dm^{-3} (Table 4). Relative arsenic concentration for individual samples is indicated in Table 3. L_1 has the lowest arsenic content and L_7 has the highest one. In the case of arsenic the highest concentration was recorded at the sampling spot L_7 - 28.5 μg dm^{-3}. Also from Table 3, we can see that arsenic (28.5 μg dm^{-3}, sample L_7) has higher concentration compared to WHO and EU standards for drinking water.

The WHO recommends that the zinc content of drinking water should not exceed 3 mg dm^{-3}. Zinc concentration was observed to vary from 3.2 to 9.4 μg dm^{-3} with a mean of 5.743 μg dm^{-3} (Table 4) for all samples, which is below the WHO guideline.

Table 3. Concentrations (μg dm^{-3}) of 67 elements in the water of river Lumbardhi Prizren

Element	Sampling station						
(μg dm^{-3})	L_1	L_2	L_3	L_4	L_5	L_6	L_7
Na	2570	2850	3080	2760	3200	6750	4850
Li	<1	<1	1	1	1	1	1
Be	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mg	2120	3400	3920	4760	4910	5460	7730
Al	80	58	111	136	195	167	139
Si	2200	2600	2700	3000	3000	3100	2900
K	790	930	1080	1060	1100	1560	1340
Ca	>20000	>20000	>20000	>20000	>20000	>20000	>20000
Sc	1	1	1	1	1	1	1
Ti	2.4	1.5	1.4	1.6	1.9	2.1	1.9
V	0.3	0.2	0.3	0.5	0.6	0.5	0.5
Cr	0.6	<0.5	0.7	0.8	1	0.9	0.7
Mn	10.6	12.3	22.2	31.3	43.2	59.6	24.7
Fe	100	80	130	210	320	200	570
Co	0.182	0.163	0.228	0.35	0.486	0.361	0.305
Ni	0.6	2	1.2	2.2	2.5	0.8	0.9
Cu	1.4	3	2.8	4.4	4	2.8	2.8
Zn	4.3	3.2	3.5	6.1	5.3	8.4	9.4
Ga	0.22	0.15	0.1	0.08	0.07	0.05	<0.01
Ge	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	0.43	0.44	0.46	0.45	0.55	0.58	28.5
Se	<0.2	<0.2	<0.2	<0.2	<0.2	0.3	0.3
Br	4	4	5	4	4	6	7
Rb	0.519	0.415	0.476	0.483	0.548	0.884	0.795
Sr	77	88.9	95.4	78.5	80.3	81.3	163
Y	0.121	0.096	0.163	0.272	0.346	0.254	0.214
Zr	0.03	0.02	0.04	0.04	0.04	0.02	0.03
Nb	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Mo	0.3	0.3	0.2	0.1	0.1	0.1	0.1
Ru	0.01	0.01	0.01	0.02	0.01	0.01	0.01
Pd	0.01	0.01	0.01	0.01	<0.01	0.01	0.01
Ag	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cd	0.13	0.05	0.07	0.04	0.03	0.05	0.06
In	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Sn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sb	0.07	0.21	0.02	0.05	0.03	0.06	0.07
Te	<0.1	<0.1	0.1	<0.1	<0.1	0.1	0.1
I	<0.1	<0.1	<0.1	<0.1	<0.1	1	1
Cs	0.01	0.008	0.009	0.013	0.014	0.014	0.013
Ba	13.7	14	13.7	23.7	24.7	25.7	74.3
La	0.181	0.115	0.145	0.276	0.33	0.228	0.186
Ce	0.474	0.247	0.336	0.653	0.743	0.373	0.332
Pr	0.036	0.027	0.04	0.074	0.084	0.061	0.048
Nd	0.145	0.1	0.157	0.288	0.316	0.255	0.181
Sm	0.028	0.032	0.039	0.072	0.093	0.069	0.047
Eu	<0.001	<0.001	<0.001	<0.001	0.004	<0.001	<0.001
Gd	0.036	0.03	0.046	0.08	0.1	0.066	0.062
Tb	0.004	0.004	0.006	0.011	0.013	0.01	0.008
Dy	0.029	0.019	0.031	0.047	0.071	0.045	0.038
Ho	0.004	0.004	0.005	0.009	0.012	0.008	0.007
Er	0.011	0.011	0.013	0.021	0.029	0.025	0.018
Tm	0.001	<0.001	0.002	0.003	0.004	0.003	0.002
Yb	0.01	0.009	0.014	0.019	0.023	0.018	0.012
Lu	0.002	0.001	0.001	0.003	0.003	0.003	0.002
Hf	0.003	0.003	0.003	0.004	0.001	0.003	0.002

Table 3. continuation.

Element ($\mu g\ dm^{-3}$)	Sampling station						
	L_1	L_2	L_3	L_4	L_5	L_6	L_7
Ta	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
W	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02
Re	0.002	0.001	0.001	0.002	0.001	0.002	0.002
Os	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Pt	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Au	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Hg	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ti	0.002	0.002	0.002	0.002	0.004	0.003	0.005
Pb	2.58	1.18	1.03	1.54	1.18	1.93	1.42
Bi	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Th	0.002	0.003	0.003	0.003	0.004	0.002	0.005
U	0.097	0.0184	0.158	0.137	0.148	0.153	0.206
Hg ($ng\ L^{-1}$)	53	27	24	23	12	<6	<6

Lead levels in all samples were in the range of 1.03-2.58 $\mu g\ dm^{-3}$ with a mean value of 1.551 $\mu g\ dm^{-3}$ (Table 4). Relative lead concentration for individual samples is also indicated in Table 3. L_3 has the lowest lead content and L_1 has the highest one. The values are lower than the WHO recommended standard of 0.01 mg dm^{-3}.

Antimony ranges from 0.02 $\mu g\ dm^{-3}$ (L_4) to 0.07 $\mu g\ dm^{-3}$ (L_1 and L_7); barium ranges from 13.7 $\mu g\ dm^{-3}$ (L_1 and L_3) to 74.3 $\mu g\ dm^{-3}$ (L_7); bromine ranges from 4 $\mu g\ dm^{-3}$ (L_1, L_2, L_4, L_5) to 7 $\mu g\ dm^{-3}$ (L_7); chromium ranges from 0.6 $\mu g\ dm^{-3}$ (L_1) to 1 $\mu g\ dm^{-3}$ (L_5); manganese ranges from 10.6 $\mu g\ dm^{-3}$ (L_1) to 59.6 $\mu g\ dm^{-3}$ (L_6); mercury ranges from 12 ng dm^{-3} (L_5) to 53 ng dm^{-3} (L_1); molybdenum ranges from 0.1 $\mu g\ dm^{-3}$ (L_4, L_5, L_6 and L_7) to 0.3 $\mu g\ dm^{-3}$ (L_1 and L_2), nickel ranges from 0.6 $\mu g\ dm^{-3}$ (L_1) to 2.5 $\mu g\ dm^{-3}$ (L_5); uranium ranges from 0.0184 $\mu g\ dm^{-3}$ (L_2) to 0.206 $\mu g\ dm^{-3}$ (L_7). So, the concentration of these elements is below the maximum value allowed by the WHO.

The data from Table 3 show that the concentrations of the elements Be, Ge, Nb, Ag, In, Sn, Ta, W, Os, Pt, Au and Bi are below the corresponding limits of detection.

The concentrations of heavy metals are almost within the allowed standard concentrations except for some sampling spots where higher concentrations of some heavy metals were found. Removing heavy metals from surface water is important. Metal ions like Cu^{2+}, $Hg^{2+,}$ $Pb^{2+,}$ $Zn^{2+,}$ $Ni^{2+,}$ $Cd^{2+,}$ represent harmful and noxious water pollutants for human and animal consumption, mostly due to their tendency to accumulate in the food chain. Their removal can be done by chemical precipitation, coagulation and flocculation, adsorption onto plant wastes and special treatments, as nanofiltration or reverse osmosis.

So, before human utilization, this kind of waters must be subjected to intensive physical and chemical treatment, extended treatment and disinfection, e.g., chlorination to break-point, coagulation, flocculation, decantation, filtration, adsorption (activated carbon), disinfection (ozone, final chlorination). The vulnerability of water quality is followed by serious changes of its properties resulting in undesirable effects like: lack of oxygen, reduction in pH value, increase of heavy metal complexation capacity, increase of toxicity and accumulation of hazardous substances in the food chain. Water resources in Kosovo are limited and the major ingredients of surface water are rivers except for some artificial accumulation lakes.

Global concern for environment, in spite of the fact that efforts were done and are being done to overcome pollution, permanent monitoring of polluted waters now and in the future will be a big challenge for us and all scientific institutions in entire Kosovo. Water like a natural resource of general interest should be rationally used and protected from eventual degradation.

Statistical Analysis

Determination of basic statistical parameters

Table 4 presents the basic statistical parameters for 67 elements in four samples, which can be considered as preliminary values until a larger data set will be compiled. For each element, the values are given as arithmetic mean, geometric mean, median, minimal and maximal concentration, variance and standard deviation. From the experimental data (Table 3) and the box plot approach of Tukey [32], we have determined the abnormal data (extremes and outliers) for some elements in the river Lumbardhi Prizren.

Table 4. Basic statistical parameters for four major and 67 minor elements in samples of river Lumbardhi Prizren

Variables	Descriptive Statistics (Spreadsheet1)						
	Mean	Geom. Mean	Median	Minimum	Maximum	Variance	Std. Dev.
Na	3722.857	3506.865	3080.000	2570.000	6750.000	2356457	1535.076
Li	29.571	3.738	1.000	1.000	101.000	2381	48.795
Mg	4614.286	4315.420	4760.000	2120.000	7730.000	3118262	1765.860
Al	126.571	117.921	136.000	58.000	195.000	2279	47.738
Si	2785.714	2769.457	2900.000	2200.000	3100.000	98095	313.202
K	1122.857	1098.811	1080.000	790.000	1560.000	65424	255.781
Sc	1.000	1.000	1.000	1.000	1.000	0	0.000
Ti	1.829	1.800	1.900	1.400	2.400	0	0.355
V	0.414	0.389	0.500	0.200	0.600	0	0.146
Cr	15.100	1.549	0.800	0.600	101.000	1435	37.879
Mn	34.029	28.079	31.300	10.600	59.600	422	20.534
Fe	230.000	186.903	200.000	80.000	570.000	29067	170.489
Co	0.296	0.277	0.305	0.163	0.486	0	0.114
Ni	1.457	1.282	1.200	0.600	2.500	1	0.761
Cu	3.029	2.875	2.800	1.400	4.400	1	0.969
Zn	5.743	5.335	5.300	3.200	9.400	6	2.392
Ga	14.524	0.266	0.100	0.050	101.000	1454	38.132
Ge	86.573	27.057	101.000	0.010	101.000	1457	38.171
As	4.487	0.863	0.460	0.430	28.500	112	10.589
Se	72.229	19.154	101.000	0.300	101.000	2414	49.137
Br	4.857	4.740	4.000	4.000	7.000	1	1.215
Rb	0.577	0.559	0.519	0.415	0.884	0	0.165
Sr	94.914	91.707	81.300	77.000	163.000	944	30.717
Y	0.209	0.192	0.214	0.096	0.346	0	0.089
Zr	0.031	0.030	0.030	0.020	0.040	0	0.009
Mo	0.171	0.151	0.100	0.100	0.300	0	0.095
Ru	0.011	0.011	0.010	0.010	0.020	0	0.004
Pd	14.437	0.037	0.010	0.010	101.000	1457	38.171
Cd	0.061	0.056	0.050	0.030	0.130	0	0.033
Sb	0.073	0.057	0.060	0.020	0.210	0	0.063
Te	57.757	5.209	101.000	0.100	101.000	2909	53.933
I	72.429	27.018	101.000	1.000	101.000	2381	48.795
Cs	0.012	0.011	0.013	0.008	0.014	0	0.003
Ba	27.114	22.520	23.700	13.700	74.300	463	21.517
La	0.209	0.197	0.186	0.115	0.330	0	0.075
Ce	0.471	0.443	0.474	0.247	0.743	0	0.176
Pr	0.053	0.049	0.048	0.027	0.084	0	0.021
Nd	0.206	0.192	0.181	0.100	0.316	0	0.081
Sm	0.054	0.050	0.047	0.028	0.093	0	0.024
Eu	86.572	23.737	101.000	0.004	101.000	1457	38.173
Gd	0.060	0.056	0.062	0.030	0.100	0	0.025
Tb	0.008	0.007	0.008	0.004	0.013	0	0.004

Table 4 continuation.

Variables	Descriptive Statistics (Spreadsheet1)						
	Mean	Geom. Mean	Median	Minimum	Maximum	Variance	Std. Dev.
Dy	0.040	0.037	0.038	0.019	0.071	0	0.017
Ho	0.007	0.006	0.007	0.004	0.012	0	0.003
Er	0.018	0.017	0.018	0.011	0.029	0	0.007
Tm	14.431	0.011	0.003	0.001	101.000	1457	38.173
Yb	0.015	0.014	0.014	0.009	0.023	0	0.005
Lu	0.002	0.002	0.002	0.001	0.003	0	0.001
Hf	0.003	0.003	0.003	0.001	0.004	0	0.001
Ta	101.000	101.000	101.000	101.000	101.000	0	0.000
W	86.574	29.873	101.000	0.020	101.000	1457	38.167
Re	0.002	0.001	0.002	0.001	0.002	0	0.001
Tl	0.003	0.003	0.002	0.002	0.005	0	0.001
Pb	1.551	1.481	1.420	1.030	2.580	0	0.543
Th	0.003	0.003	0.003	0.002	0.005	0	0.001
U	0.155	0.151	0.153	0.097	0.206	0	0.035
Hg	48.714	37.097	27.000	12.000	101.000	1430	37.810

Frequency histograms and two-dimensional scatter with plot diagrams of 12 measured elements are presented in Figures 2 and 3. Using experimental data and the box plot approach of Tukey [32], anomalous values (extremes and outliers) of some elements were determined **(**Table 5). It was found that cadmium shows an outlier (L_1), arsenic - an extreme (L_7) and antimony - an extreme (L_2).

Table 5. Anomalous values (extremes and outliers) of concentrations for particular elements (μg dm^{-3}).

Sample	Extremes of elements (*)	Outliers of elements (o)
L_1	-	Cd (0.13 μg dm^{-3})
L_2	Sb (0.21 μg dm^{-3})	-
L_3	-	-
L_4	-	-
L_5	-	-
L_6	-	-
L_7	As (28.5 μg dm^{-3})	-

The results from Pearson's correlation factors displayed in Table 6 for some elements as sodium show an excellent and very high positive relationship (>0.65) compared with K, Mn, Zn and Br but it is in high negative relationship with Hg (-0.69). Magnesium is in excellent and very high positive relationship compared with K, Mn, Fe, Zn, As, Br, Sr, Ba, Th and U but is in very high negative relationship with Hg (-0.87). The concentration of aluminum in water samples is in excellent correlation and in very high positive relationship with V, Cr, Mn, and Co. No correlations were found for Sb and Hg.

As it belongs, the concentration of chromium in the same samples is in excellent and very high positive relationship with Co (0.96) but in high negative relationship with Sb (-0.69). The calculated iron concentration from the program data is in excellent and very high positive relationship with Zn, As, Sr, Ba and Th, but no correlation with the concentration of Hg was found. The results from the correlation factors displayed on Table 6 for the concentration of nickel are in excellent and very high positive relationship with Cu (0.85), but in very high negative relationship with Cd (-0.72). It is worth mentioning that the manganese concentration is in high positive relationship with Fe (0.77), Co (0.70), Zn (0.92) and Br (0.76) but in very high negative relationship with Hg (-0.88).

Discussing the arsenic concentration from the program data it is evident that it is in excellent and very high positive relationship with Br, Sr, Ba and Th. Finally, the cobalt concentration is in very positive relationship with Cu (0.67). No correlation with concentrations of Cd (-0.65) and Hg (-0.66) was found.

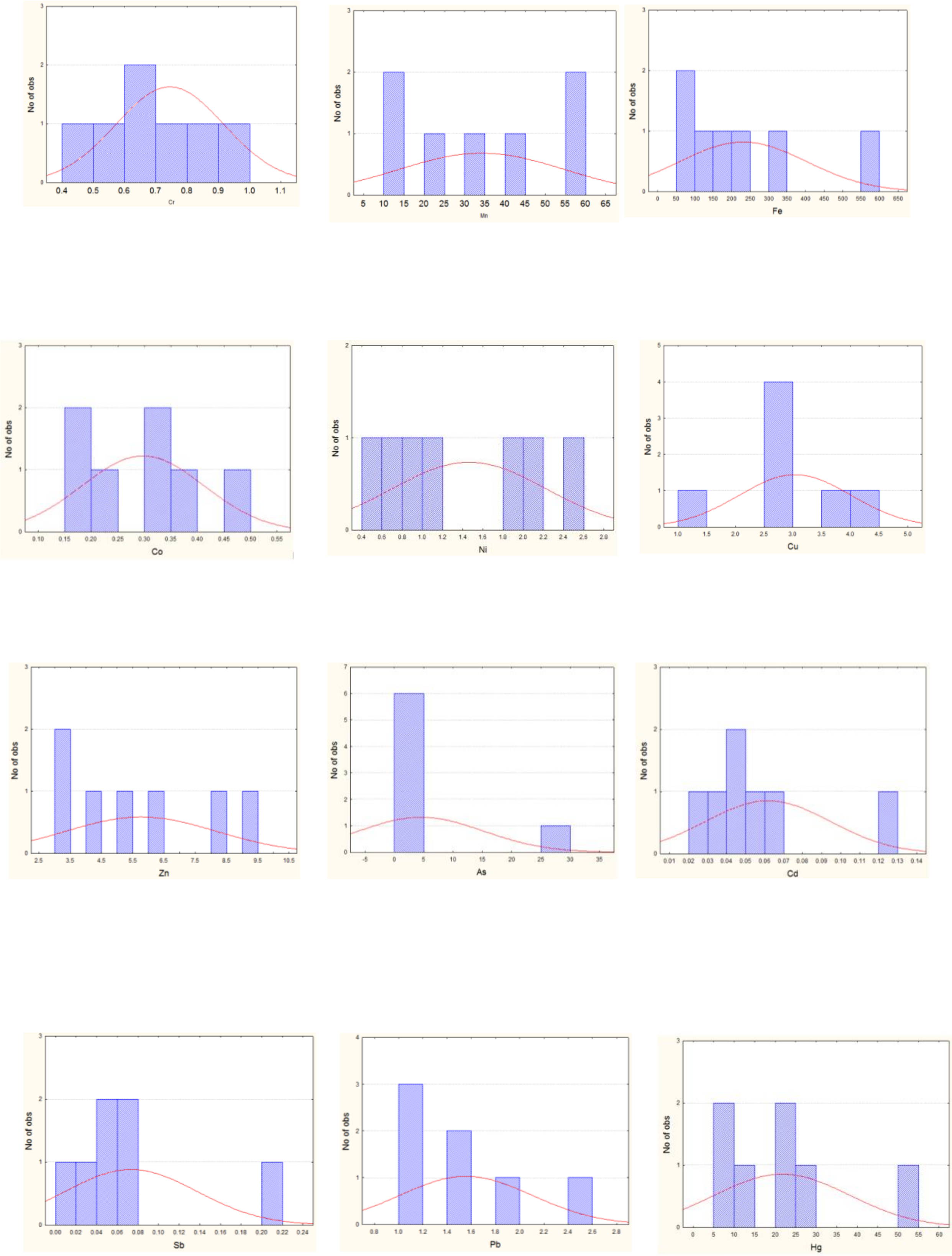

Fig. 2. Frequency histograms of 12 measured elements.

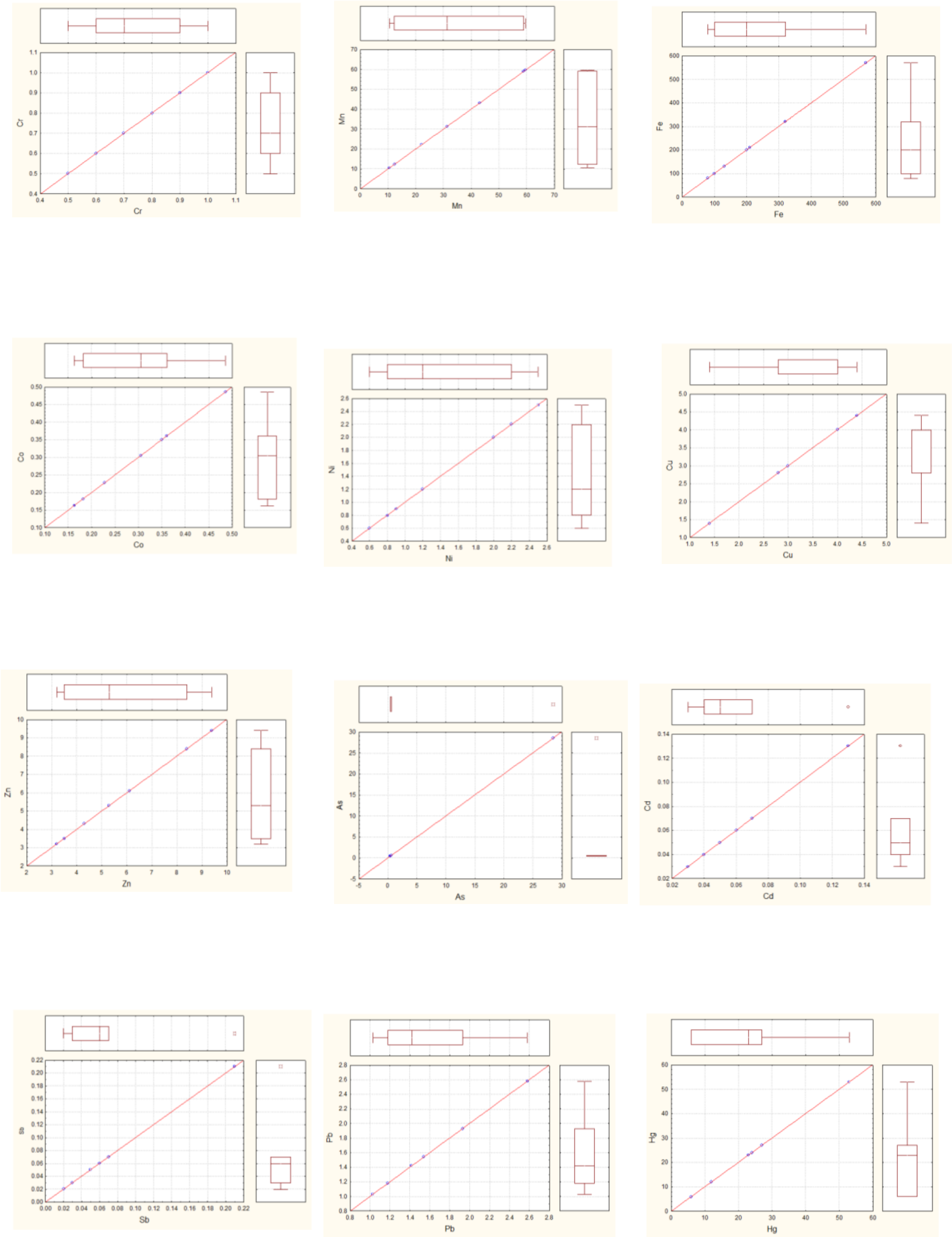

Fig. 3. Scatter box plot diagrams of 12 measured elements.

Table 6. Correlation factors for 23 elements (µg dm^{-3}) in 7 water samples.

Correlations
Case N=7

Variable	Na	Mg	Al	K	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Sr	Cd	Sb	Ba	Pb	Th	U	Hg
Na	1.00																						
Mg	0.62	1.00																					
Al	0.49	0.60	1.00																				
K	0.94	0.78	0.65	1.00																			
Ti	0.30	-0.08	0.17	0.07	1.00																		
V	0.42	0.67	0.95	0.58	0.25	1.00																	
Cr	0.41	0.42	0.97	0.55	0.17	0.90	1.00																
Mn	0.83	0.90	0.80	0.92	0.20	0.80	0.67	1.00															
Fe	0.39	0.90	0.55	0.52	0.12	0.67	0.35	0.77	1.00														
Co	0.33	0.53	0.97	0.51	0.11	0.95	0.96	0.70	0.50	1.00													
Ni	-0.46	-0.08	0.24	-0.25	-0.54	0.25	0.30	-0.13	-0.04	0.45	1.00												
Cu	-0.08	0.37	0.54	0.20	-0.56	0.56	0.55	0.29	0.23	0.67	0.85	1.00											
Zn	0.79	0.86	0.59	0.82	0.36	0.69	0.44	0.92	0.78	0.48	-0.32	0.11	1.00										
As	0.33	0.78	0.12	0.38	0.09	0.26	-0.11	0.54	0.88	0.04	-0.32	-0.10	0.68	1.00									
Br	0.79	0.80	0.29	0.80	0.13	0.29	0.11	0.76	0.69	0.10	-0.58	-0.19	0.81	0.78	1.00								
Sr	0.30	0.75	0.04	0.37	-0.07	0.14	-0.18	0.48	0.82	-0.05	-0.32	-0.11	0.57	0.98	0.79	1.00							
Cd	-0.24	-0.54	-0.57	-0.48	0.55	-0.52	-0.54	-0.50	-0.32	-0.65	-0.72	-0.89	-0.25	-0.02	-0.08	-0.05	1.00						
Sb	-0.14	-0.24	-0.67	-0.28	-0.19	-0.62	-0.69	-0.39	-0.29	-0.56	0.13	-0.15	-0.29	-0.02	-0.19	0.02	-0.02	1.00					
Ba	0.45	0.89	0.34	0.53	0.13	0.48	0.12	0.71	0.95	0.26	-0.23	0.06	0.81	0.97	0.80	0.92	-0.19	-0.12	1.00				
Pb	0.14	-0.34	-0.17	-0.12	0.87	-0.06	-0.12	-0.10	-0.21	-0.22	-0.61	-0.63	0.17	-0.11	-0.04	-0.25	0.73	-0.07	-0.11	1.00			
Th	-0.01	0.72	0.32	0.19	-0.28	0.41	0.14	0.43	0.85	0.35	0.30	0.38	0.37	0.77	0.40	0.78	-0.43	-0.08	0.77	-0.59	1.00		
U	0.35	0.71	0.06	0.47	-0.51	0.05	-0.12	0.45	0.57	0.02	0.11	0.25	0.36	0.65	0.61	0.75	-0.55	0.35	0.64	-0.68	0.70	1.00	
Hg	-0.69	-0.87	-0.71	-0.86	0.25	-0.65	-0.60	-0.88	-0.65	-0.66	-0.20	-0.55	-0.67	-0.42	-0.63	-0.44	0.80	0.18	-0.58	0.54	-0.54	-0.70	1.00

Table 7. Classification of the water of Lumbardhi river, Prizren based on some trace metals as pollution indicators

Element	Water class				
(μg dm^{-3})	I	II	III	IV	V
	<2	2 – 10	10 – 15	15 – 20	>20
Cu	L_1	$L_2 – L_7$			
	<50	50 – 80	80 – 100	100 – 200	>200
Zn	$L_1 – L_7$				
	<0.1	0.1 – 2.0	2.0 – 5.0	5.0 – 80	>80
Pb		$L_2 – L_7$	L_1		
	<0.1	0.1 – 0.5	0.5 – 2.0	2.0 – 5.0	>5.0
Cd	$L_2 – L_7$	L_1			

In Kosovo there are no standards for water quality yet, that is why we decided to use the Croatian standards to classify the water quality of the Lumbardhi river, Prizren [33]. Table 7 shows the classification of the water samples of the Lumbardhi river, Prizren, based on the concentrations of toxic metals.

Based on Croatian standards for drinking water, the water from the Lumbardhi river, Prizren is classified in first class (no anthropogenic pollutions) according to the concentrations of zinc. Based on lead the samples L_2- L_7 are in second class (the concentrations of toxic metals are higher than their natural concentrations) and L_1 in third class (the toxic metal concentrations are lower than their permanent levels). Based on copper the sample L_1 is classified in first class and L_2-L_7 in second class. Based on cadmium the samples L_2-L_7 are classified in first class and L_1 in second class.

CONCLUSIONS

Based on our results we can conclude:

- Our analyses of the water of the river Lumbardhi of Prizren relate the water quality as good except for some spots where anthropogenic pollutants probably appear.
- Results of heavy metals show that their concentrations are within the standard concentrations except for some spots where higher concentrations of some heavy metals are observed.
- According to pH the water is basic (pH=8.10-8.51).
- Based on Croatian standards for drinking water the Lumbardhi water was classifed in the first class according to the concentration of zinc.
- Based on Croatian standards for drinking water the Lumbardhi water was classified in the second and third class according to the concentration of lead.
- Based on Croatian standards for drinking water, the Lumbardhi water was classified in the first and second class according to the concentrations of copper and cadmium.
- Although Kosovo has no legislative prohibition for exceeded concentrations of toxic metals in the natural water resources until now, the results from this study represent a small contribution to gain a clear overview of the state in this field of environmental quality assurance.
- We have thus concluded that water resources of Kosovo’s are put at risk by anthropogenic pollution. As a first step further forward, surface water pollution has to be prevented, managed and its condition continually improved.

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ОЦЕНЯВАНЕ НА КАЧЕСТВОТО НА ВОДИТЕ НА РЕКА ЛУМБАРДИ, ПРИЗРЕН, КОСОВО

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(Резюме)

Повърхностните води в Косово са предимно замърсени, като все още няма пречиствателни станции за битови и промишлени води. Главната цел на настоящето изследване е да се анализира съдържанието на някои токсични елементи по течението на реката. Местата за пробовзимане са разполоени спрямо географска информационна система(GIS). Резултатите са интерпретирани с помощта на съвременни методи за локализирането на замърсените райони с повишени концентрации. Стойностите на подбраните елементи са оценени с факторен статистически анализ по Pearson за намирането на корелации. Концентрациите на токсичните елементи са както следва: Cu (1.4-4.4 μg dm^{-3}), Zn (3.2-9.4 μg dm^{-3}), Pb (1.03-2.58 μg dm^{-3}), Cd (0.03-0.13 μg dm^{-3}), Mn (10.6 -59.6 μg dm^{-3}), As (0.43-28.5 μg dm^{-3}), Cr (0.6-1.0 μg dm^{-3}), Fe (80-570 μg dm^{-3}), Ni (0.6-2.5 μg dm^{-3}), Sb (0.02-0.07 μg dm^{-3}), Al (58-195 μg dm^{-3}). Получените резултати са сравнени със стандартите на Светованта здравна организаия (WHO) и на Европейския съюз за питейна вода. Въпреки, че в Косово няма законови ограничения за допусими концентрации на токсични метали в природните води, настоящите резултати са скромен принос към получаването на ясен поглед състоянието на околната среда и нейното подобряване.