



ASSESSMENT OF RIVER WATER QUALITY LUMBARDH OF DEÇAN (KOSOVO)

Fatmir Faiku^{[a]*}, Arben Haziri^{[a]*}, Fatbardh Gashi^[a], Naser Troni^[a] and Imer Haziri^[b]

Keywords: Water, ICP/MS, pollution assessment, Lumbardhi River.

The main research was the multielementary analyses of some environmental toxic elements downstream the river Lumbardhi Deçan (Kosovo), where they end up as natural and anthropogenic recipients. We used ICP/MS as method for the analysis. Results of some toxic elements are as: Cu ($4.3\text{--}12.6\ \mu\text{g dm}^{-3}$), Zn ($8.8\text{--}65.7\ \mu\text{g dm}^{-3}$), Pb ($1.44\text{--}8.85\ \mu\text{g dm}^{-3}$), Cd ($0.02\text{--}0.15\ \mu\text{g dm}^{-3}$), Mn ($7.6\text{--}48.8\ \mu\text{g dm}^{-3}$), As ($0.46\text{--}0.68\ \mu\text{g dm}^{-3}$), Cr ($0.3\text{--}1.1\ \mu\text{g dm}^{-3}$), Fe ($30\text{--}760\ \mu\text{g dm}^{-3}$), Ni ($0.6\text{--}3.4\ \mu\text{g dm}^{-3}$), Sb ($0.06\text{--}0.33\ \mu\text{g dm}^{-3}$), Al ($112\text{--}659\ \mu\text{g dm}^{-3}$). Also some physico-chemical parameters are determined: air temperature, water temperature, pH, electrical conductivity (EC), total hardness, sulphates, phosphates, nitrites, ammonium, dissolved oxygen and BOD₅. Results obtained by the box plot method showed the regions with determined anomalous element concentration values in the water of Lumbardhi Deçan. Even that in Kosovo we don't have yet any legislative convent for allowed concentrations of toxic metals for natural water resources, the results from this study are a small contribution to gain a clear overview of the statement in this field of environmental quality assurance.

* Corresponding Authors

E-Mail: f_faiku@hotmail.com; arbeni77chem@hotmail.com

[a] Department of Chemistry, Faculty of Natural Sciences, University of Prishtina, Kosovo

[b] Department of Veterinary, Faculty of Agriculture, University of Prishtina, Kosovo

Introduction

Rivers in Kosovo are mainly used for drinking water, agriculture, industry; however, the level of pollution is being higher and higher each day, which is a very serious concern for the citizens of Kosovo. Kosovo has a lot of problems with rivers pollution, this problem is due to non-existing wastewater treatment and waste disposal. The lowland rivers are the rivers that have the most pollution. But even in the main downstream rivers there is a lot of pollution coming in from the municipalities and different industries that are adding pollution every day to these river streams so that this water source cannot be used any way possible without some kind of treatment.¹

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 and beyond than they have been in the past.²

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). Decomposition of organic matter and pollution due to anthropogenic activity are the main sources of pollution of water and stream sediments.³⁻⁵



Figure 1. River water sampling points Lumbardhi with detailed descriptions

Nowadays, determination of total quantitative and qualitative metals and distribution of all their physical and chemical forms in traces (speciation) in natural water equilibrium resources is to be considered as the main challenge for most of the scientists.⁶ 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.⁷⁻¹³

Table 1. The water sampling points in the River Lumbardhi Deçan with detailed descriptions

Sampling point	Location	Type of relief	The water level	Potential Pollutants
L ₁	Belle	Steep	The above	Traffic, agricultural land
L ₂	Monastery near	Soft	The above	Traffic, agricultural land
L ₃	Lluk	Soft	The above	Traffic, wastewater, agricultural land
L ₄	Baran	Soft	The above	Traffic, wastewater, agricultural land

Table 2. Physico-chemical parameters determined in river waters: water temperature, air temperature, dissolved oxygen, BOD₅, electrical conductivity (EC), pH, total hardness, sulphates, nitrites, ammonium and phosphates

Parameters	Sampling point			
	L ₁	L ₂	L ₃	L ₄
Water temp., °C	10.2	10.7	11.7	13.2
Air temp., °C	28.7	28.9	28.9	29.2
Dissolved oxygen, mg dm ⁻³	10.2	11.1	10.7	11.9
BOD ₅ , mg dm ⁻³	1.0	1.7	1.4	1.9
EC, µS cm ⁻¹	220	240	303	341
pH	8.25	8.37	8.45	8.52
Total hardness, °D	6.5	7.0	7.5	8.2
SO ₄ ²⁻ , mg dm ⁻³	7.2	8.9	8.1	10.5
NO ₂ ⁻ , mg dm ⁻³	0.03	0.045	0.09	0.06
NH ₄ ⁺ , mg dm ⁻³	0.25	0.32	0.42	0.47
PO ₄ ³⁻ , mg dm ⁻³	0.013	0.012	0.01	0.014

Materials and methods

Sampling was done on May 2013 when the weather was sunny. The water sample was collected from the middle of the river and the samples were treated according to standards methods for surface water.^{4,14-16} The location of the study area is shown in Figure 1. The details about all sampling sites are presented in Table 1.

Determination of physico-chemical parameters

The standard methods, including classical and contemporary methods, were used for determining the quality of water parameters and water analysis. Temperature of water was measured immediately after sampling, using digital thermometer (model "Quick 63142"). pH measurements were made using pH/ion-meter (Hanna Instruments, Portugal). Electric conductivity was measured by conductometer (InoLab WTW, Weilheim, Germany). Total hardness was determined by EDTA titration using eriochrome black T as indicator. Ammonium, phosphates, nitrites and sulphates were determined with spectrophotometric method.¹⁵ using HACH DR/2010 spectrophotometer.

Determination of major and trace elements

We used the ICP/OES (inductively coupled plasma in combination with optical emission spectrophotometer) method to determine the concentration of elements.

Statistical analysis

Program Statistica 6.0 was used for all statistical calculations such as basic statistical parameters and

determination of anomalies (extremes and outliers) for solution data.¹⁷

Results and Discussion

Physico-chemical parameters

The various physico-chemical properties, measured in the water of Lumbardhi Deçan, given in Table 2. The water temperature ranged from 10.2-13.2 °C; the lowest temperature was recorded at the sampling point L₁ while the highest temperature was recorded at the sampling point L₄. pH values ranging from 8.25-8.52 suggested that the water is slightly basic. The highest conductivity was recorded in the sampling point L₄ while the lowest value was recorded at the sampling point L₁. The electrical conductivity ranged from 220-341 µS cm⁻¹. The increase in the conductivity is attributed to salts and other ingredients that contaminate the river water. The total hardness was 6.5 °D (sampling point L₁), 7.0 °D (sampling point L₂), 7.5 °D (sampling point L₃) and 8.2 °D (sampling point L₄). These results indicate that the hardness is mild.

The amount of phosphates, sulphates, ammonium, and nitrites ranged from 0.01-0.014, 7.2-10.5, 0.25-0.47 and 0.03-0.09 mg dm⁻³ respectively. These concentrations are below the maximum value allowed by the WHO¹⁸ and the EU.¹⁹

Dissolved oxygen ranged from 10.2-11.9 mg dm⁻³. The lowest BOD₅ was recorded at the sampling point L₁ (1.0 mg dm⁻³) while the highest was recorded at the sampling point L₄ (1.9 mg dm⁻³). While the lowest value was recorded at the sampling point L₁.

Table 3. Concentrations ($\mu\text{g dm}^{-3}$) of 66 elements in water of the river Lumbardhi Deçan

Element, $\mu\text{g dm}^{-3}$	Sampling point			
	L ₁	L ₂	L ₃	L ₄
Na	686	717	585	857
Li	<1	<1	2	<1
Be	<0.1	<0.1	<0.1	<0.1
Mg	2350	2400	3480	2820
Al	144	112	659	147
Si	1780	1780	2180	2080
K	455	485	995	575
Ca	20000	20000	20000	20000
Sc	1	1	1	1
Ti	1.3	1.7	2.3	1.8
V	0.28	0.28	1	0.4
Cr	1.6	0.3	1.1	0.6
Mn	11.9	7.6	48.8	20.6
Fe	145	105	265	145
Co	0.18	0.14	0.42	0.27
Ni	3.3	3.2	3.4	0.6
Cu	12.6	5.3	31	4.3
Zn	16.1	65.7	57.1	8.8
Ga	0.025	0.025	0.75	0.04
Ge	<0.01	<0.01	<0.01	<0.01
As	0.46	0.46	0.68	0.51
Se	<0.2	<0.2	<0.2	<0.2
Br	4	3	15	3
Rb	0.30	0.33	1.04	0.35
Sr	56.1	60.1	137	79.3
Y	0.12	0.09	0.55	0.34
Zr	0.02	0.05	0.20	0.02
Nb	0.005	0.005	0.005	0.005
Mo	0.3	0.2	0.2	0.2
Ru	<0.01	<0.01	<0.01	<0.01
Pd	<0.01	<0.01	<0.01	<0.01
Ag	<0.2	<0.2	<0.2	<0.2
Cd	0.06	0.02	0.15	0.025
In	0.001	0.001	0.001	0.001
Sn	1	0.18	6.0	19.6
Sb	0.33	0.06	0.22	0.08
Te	<0.1	<0.1	<0.1	<0.1
I	1	1	1	1
Cs	0.01	0.01	0.16	0.01
Ba	9.7	10.2	45.5	14.5
La	0.05	0.1	0.45	0.26
Ce	0.2	0.23	0.93	0.59
Pr	0.018	0.018	0.1	0.06
Nd	0.1	0.08	0.44	0.28
Sm	0.02	0.01	0.1	0.07
Eu	0.01	0.01	0.03	0.02
Gd	0.02	0.01	0.12	0.08
Tb	0.01	0.01	0.02	0.01
Dy	0.02	0.01	0.09	0.06
Ho	0.01	0.01	0.03	0.03
Er	0.02	0.01	0.05	0.04
Tm	0.001	0.01	0.01	0.01
Yb	0.01	0.01	0.04	0.03
Lu	<0.001	<0.001	0.01	0.01
Hf	<0.001	<0.001	<0.001	<0.001
Ta	0.001	0.001	0.001	0.001

contg. Table 3.

Re	0.001	0.001	0.001	0.001
Os	0.002	0.002	0.002	0.002
Pt	<0.3	<0.3	<0.3	<0.3
Au	0.002	0.002	0.002	0.002
Ti	<0.001	<0.001	<0.001	<0.001
Pb	7.9	1.44	8.85	2.32
Bi	<0.3	<0.3	<0.3	<0.3
Th	<0.001	<0.001	0.01	0.01
U	0.21	0.20	0.28	0.27
Hg	<0.2	<0.2	<0.2	<0.2

The concentrations of 67 elements determined in the river water are given in Table 3. The highest concentration of lead was recorded at the sampling points L₁ (7.9 µg dm⁻³) and L₃ (8.5 µg dm⁻³) situated at the outskirts of the city. The highest concentrations of toxic elements was also recorded at these sampling points because of the pollution from the city waste water and other wastes etc. are discharged at these points.

The highest cadmium concentration was recorded at the point L₃ (0.15 µg dm⁻³) where it comes from the face of the earth geology. Arsenic is also present in concentration (0.68 µg dm⁻³) at this point whereas the concentration of zinc at points L₂ and L₃ was 65.7 and 57.1 µg dm⁻³ respectively and is due to the flow of various pollutants from traffic, sewage, waste etc.

The levels of nickel, aluminium, manganese and iron were highest at the point L₃, whereas the higher concentrations of copper and chromium was recorded at the point L₁ because of the inflow of various pollutants from traffic, sewage, waste etc. at this point.

The amount of sodium ranged from 585 µg dm⁻³ (L₃) to 857 µg dm⁻³ (L₄), potassium from 455 µg dm⁻³ (L₁) to 995 µg dm⁻³ (L₃), silicon from 1780 µg dm⁻³ (L₁ and L₂) to 2180 µg dm⁻³ (L₃), barium from 9.7 µg dm⁻³ (L₁) to 45.5 µg dm⁻³ (L₃) and uranium from 0.20 µg dm⁻³ (L₂) to 0.28 µg dm⁻³ (L₃).

The data from Table 3 further shows that the concentrations of beryllium, ruthenium, selenium, palladium, silver, tellurium, sulfur, platinum, bismuth, titanium, hafnium and mercury are below the permissible limits.

Results of heavy metals indicate that their concentrations are present almost within the allowed standard concentrations, except at some places the increasing concentration of some heavy metals were found.

Removal of heavy metals from surface water is important. Metal ions such as Cu²⁺, Hg²⁺, Pb²⁺, Zn²⁺, Ni²⁺ and Cd²⁺ are harmful and noxious water contaminants for human and animal consumption, mostly due to their tendency to be accumulated in the food chain. These can be removed by chemical precipitation, coagulation and flocculation, by adsorption onto plant wastes and special treatments such as nano-filtration or reverse osmosis.

So these kind of waters must be treated by 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) before being utilized by humans. 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 hazardous substances accumulated in the food chain. Water resources in Kosovo are limited and the major ingredients of surface water are rivers except some artificial lakes.

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

Statistical Analysis

Determination of basic statistical parameters

Table 4 presents basic statistical parameters for 67 elements in four samples, which can be considered as preliminary values until a larger dataset is collected. For each element, the values are given as arithmetic mean, geometric mean, median, minimal and maximal concentration, standard deviation, skewness and kurtosis. From experimental data (Table 3) and box plot approach of Tukey²⁰, we have determined the abnormal data (extremes and outliers) for some elements in the river Lumbardhi Deçan.

Figure 2 shows the Scatter/box two dimensional diagrams for heavy metals arsenic, copper, cadmium, zinc, lead, iron, manganese, chromium, nickel and cobalt in the water of the river. Arsenic, copper, cadmium, zinc lead, iron, manganese, chromium, nickel and cobalt do not show any extreme and outlier in water samples.

In Kosovo we don't have standards yet, so we decided to use the Croatian standards to classify the water quality of the river (Narodne Novine 107/95, 1998).²¹

Table 4. Basic statistical parameters for four major and 66 minor elements in samples of river Lumbardhi Deçan

Variable	Descriptive Statistics									
	Mean	Geometric	Median	Minimum	Maximum	Variance	Std.Dev.	Skewness	Kurtosis	
Na	711.25	704.68	701.50	585.00	857.00	12617.6	112.3280	0.50234	1.27625	Na
Li	1.25	1.19	1.00	1.00	2.00	0.3	0.5000	2.00000	4.00000	Li
Be	0.10	0.10	0.10	0.10	0.10	0.0	0.0000	-	-	Be
Mg	2762.50	2727.58	2610.00	2350.00	3480.00	273225.0	522.7093	1.17511	0.39816	Mg
Al	265.50	198.81	145.50	112.00	659.00	69069.7	262.8111	1.97793	3.93059	Al
Si	1955.00	1946.88	1930.00	1780.00	2180.00	42500.0	206.1553	0.19974	-4.85813	Si
K	627.50	596.09	530.00	455.00	995.00	62625.0	250.2499	1.76375	3.11237	K
Ca	20000.00	20000.00	20000.00	20000.00	20000.00	0.0	0.0000	-	-	Ca
Sc	1.00	1.00	1.00	1.00	1.00	0.0	0.0000	-	-	Sc
Ti	1.77	1.74	1.75	1.30	2.30	0.2	0.4113	0.35572	1.28215	Ti
Cr	0.90	0.75	0.85	0.30	1.60	0.3	0.5715	0.38563	-1.64869	Cr
Mn	22.23	17.36	16.25	7.60	48.80	343.1	18.5236	1.52457	2.23850	Mn
Fe	165.00	155.52	145.00	105.00	265.00	4800.0	69.2820	1.53960	2.88889	Fe
Co	0.25	0.23	0.23	0.14	0.42	0.0	0.1242	1.00914	0.16023	Co
Ni	2.63	2.15	3.25	0.60	3.40	1.8	1.3525	-1.97816	3.92734	Ni
Cu	13.30	9.71	8.95	4.30	31.00	152.9	12.3664	1.51721	2.00860	Cu
Zn	36.95	27.01	36.65	8.80	65.70	821.3	28.6576	0.01974	-5.25505	Zn
Ga	0.21	0.07	0.03	0.03	0.75	0.1	0.3601	1.99770	3.99218	Ga
Ge	0.01	0.01	0.01	0.01	0.01	0.0	0.0000	-	-	Ge
As	0.53	0.52	0.48	0.46	0.68	0.0	0.1044	1.71617	2.86668	As
Se	0.20	0.20	0.20	0.20	0.20	0.0	0.0000	-	-	Se
Br	6.25	4.82	3.50	3.00	15.00	34.2	5.8523	1.96190	3.86360	Br
Rb	0.51	0.44	0.34	0.30	1.04	0.1	0.3573	1.98009	3.93494	Rb
Sr	83.13	77.80	69.70	56.10	137.00	1392.5	37.3169	1.59558	2.38166	Sr
Y	0.28	0.21	0.23	0.09	0.55	0.0	0.2146	0.74357	-1.72510	Y
Zr	0.07	0.04	0.04	0.02	0.20	0.0	0.0862	1.84628	3.41230	Zr
Nb	0.01	0.01	0.01	0.01	0.01	0.0	0.0000	-	-	Nb
Mo	0.23	0.22	0.20	0.20	0.30	0.0	0.0500	2.00000	4.00000	Mo
Ru	0.01	0.01	0.01	0.01	0.01	0.0	0.0000	-	-	Ru
Pd	0.01	0.01	0.01	0.01	0.01	0.0	0.0000	-	-	Pd
Ag	0.20	0.20	0.20	0.20	0.20	0.0	0.0000	-	-	Ag
Cd	0.06	0.05	0.04	0.02	0.15	0.0	0.0602	1.52749	2.05701	Cd
In	0.00	0.00	0.00	0.00	0.00	0.0	0.0000	-	-	In
Sn	6.70	2.14	3.50	0.18	19.60	80.6	8.9796	1.55385	2.18243	Sn
Sb	0.17	0.14	0.15	0.06	0.33	0.0	0.1269	0.58750	-2.50871	Sb
Te	0.10	0.10	0.10	0.10	0.10	0.0	0.0000	-	-	Te
I	1.00	1.00	1.00	1.00	1.00	0.0	0.0000	-	-	I
Cs	0.05	0.02	0.01	0.01	0.16	0.0	0.0750	2.00000	4.00000	Cs
Ba	19.97	15.98	12.35	9.70	45.50	294.2	17.1525	1.90858	3.66210	Ba
La	0.22	0.16	0.18	0.05	0.45	0.0	0.1805	0.80040	-1.02263	La
Ce	0.49	0.40	0.41	0.20	0.93	0.1	0.3441	0.76695	-1.69230	Ce
Pr	0.05	0.04	0.04	0.02	0.10	0.0	0.0393	0.81438	-1.49974	Pr
Nd	0.23	0.18	0.19	0.08	0.44	0.0	0.1692	0.70214	-1.98557	Nd
Sm	0.05	0.03	0.05	0.01	0.10	0.0	0.0424	0.36665	-3.43827	Sm
Eu	0.02	0.02	0.01	0.01	0.03	0.0	0.0096	0.85456	-1.28926	Eu
Gd	0.06	0.04	0.05	0.01	0.12	0.0	0.0519	0.45651	-3.10982	Gd
Tb	0.01	0.01	0.01	0.01	0.02	0.0	0.0050	2.00000	4.00000	Tb
Dy	0.04	0.03	0.04	0.01	0.09	0.0	0.0370	0.47503	-2.71624	Dy
Ho	0.02	0.02	0.02	0.01	0.03	0.0	0.0115	-0.00000	-6.00000	Ho
Er	0.03	0.03	0.03	0.01	0.05	0.0	0.0183	0.00000	-3.30000	Er
Tm	0.01	0.01	0.01	0.00	0.01	0.0	0.0045	-2.00000	4.00000	Tm

Yb	0.02	0.02	0.02	0.01	0.04	0.0	0.0150	0.37037	-3.90123	Yb
Lu	0.01	0.00	0.01	0.00	0.01	0.0	0.0052	0.00000	-6.00000	Lu
Hf	0.00	0.00	0.00	0.00	0.00	0.0	0.0000	-	-	Hf
Ta	0.00	0.00	0.00	0.00	0.00	0.0	0.0000	-	-	Ta
Re	0.00	0.00	0.00	0.00	0.00	0.0	0.0000	-	-	Re
Os	0.00	0.00	0.00	0.00	0.00	0.0	0.0000	-	-	Os
Pt	0.30	0.30	0.30	0.30	0.30	0.0	0.0000	-	-	Pt
Au	0.00	0.00	0.00	0.00	0.00	0.0	0.0000	-	-	Au
Hg	0.20	0.20	0.20	0.20	0.20	0.0	0.0000	-	-	Hg
Tl	0.00	0.00	0.00	0.00	0.00	0.0	0.0000	-	-	Tl
Pb	5.13	3.91	5.11	1.44	8.85	14.3	3.7870	0.00766	-5.42673	Pb
Bi	0.30	0.30	0.30	0.30	0.30	0.0	0.0000	-	-	Bi
Th	0.00	0.00	0.00	0.00	0.00	0.0	0.0000	-	-	Th
U	0.24	0.24	0.24	0.20	0.28	0.0	0.0408	-0.00000	-5.41200	U

Table 5 shows the classifications of water samples of the river investigated and is based on the concentrations of toxic metals.

Table 5. Classification of water Lumbardhi Deçan based on some trace metals as pollutant indicator.

Metal, $\mu\text{g dm}^{-3}$	Water class				
	I	II	III	IV	V
Cu	<2	2-10 L ₂ , L ₄	10-15 L ₁	15-20	>20 L ₃
Zn	<50	50-80	80- 100	100- 200	>200
Pb	L ₁ , L ₄ <0.1	L ₂ , L ₃ 0.1- 2.0	2.0- 5.0	5.0-80	>80
Cd	<0.1	L ₂ 0.1- 0.5	L ₄ 0.5- 2.0	L ₁ , L ₃ 2.0-5.0	>5.0
	L ₁ , L ₂ , L ₄	L ₃			

Based on zinc, the samples L₁ L₄ are classified in first class (no anthropogenic pollutions) and L₂, L₃ in second class (the concentration of toxic metals are more pronounced than usual concentrations of their natural). Based on lead the sample L₂ are in second class, L₄ in third class (the toxic metal concentrations are lower than those of their permanent level) and L₁, L₃ in fourth class (temporary metal concentrations are more pronounced than those of their permanent level of toxic and do not cause permanent toxic effects). Based on cadmium the samples L₁, L₂, L₄ are classified in first class and L₃ in second class. Based on copper the samples L₂, L₄ are classified in second class, L₁ in third class and L₃ in fifth class (metal concentrations are higher than the level of their permanent acute toxic and polluting permanent).

Conclusion

Based on our results, it is concluded that the quality of the river water is good, except at some sample points where it appeared like anthropogenic pollutants. The results of heavy metals show that their concentrations are within the permissible concentrations, except at some sample places where higher concentrations of some heavy metals were detected.

According to WHO and EU norms, about the drinking water, result shows that some high concentrations of some elements are below the maximal allowed value.

According to pH the water is basic (pH = 6.5-8.52) and according to hardness the water is more or less mild (7.2-8.2 °D).

Based on Croatian standards for drinking water, the Lumbardhi water was classified in first and second class according to the concentrations of zinc and cadmium. It is classified in the second, third and fourth class according to the concentration of cuprum and lead, and based on copper it is placed in second, third and fifth class.

Even that in Kosovo we don't have yet any legislative prohibition for exceeded concentrations of toxic metals for natural water resources, the results from this study are a small contribution to gain a clear overview of the statement in this field of environmental quality assurance. We have concluded that water resources of Kosovo's are endangered by the pollution caused from human beings. As first step further, surface water pollution has to be stopped and to improve the existing condition. We are very concerned about these facts but we hope that is still time to prevent the quality deterioration of Kosovo's surface waters.

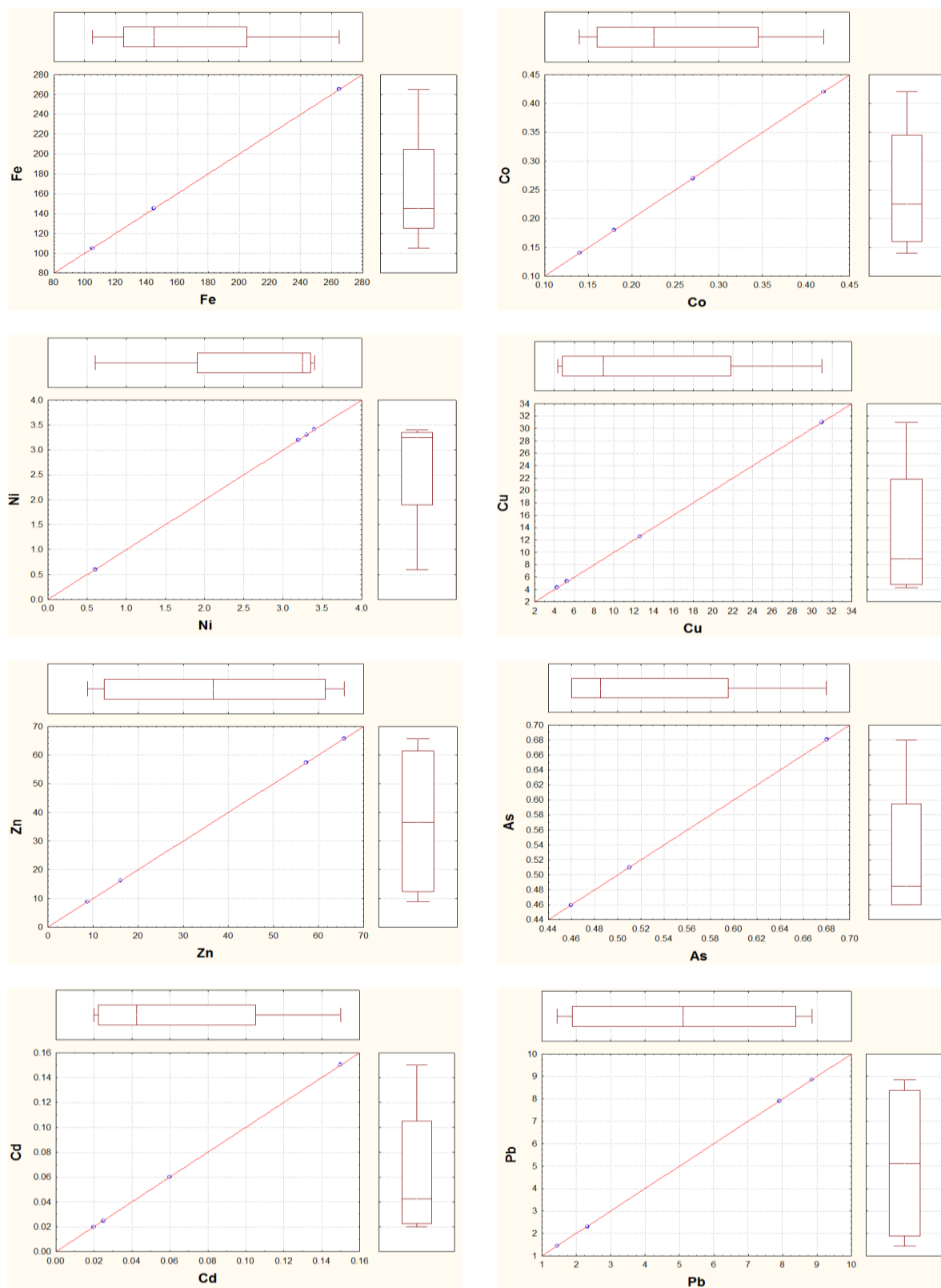


Figure 2. Scatter/box two dimensional diagrams for arsenic, copper, cadmium, zinc, lead, iron, manganese, chromium, nickel and cobalt

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Received: 01.03.2015

Accepted: 06.04.2015.