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Chemical Characterization of Some Toxic Elements of Lumbardhi River

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Abstract: Generally, the surface waters in our country are permanent polluted and is the matter of fact that our cities are yet without any treating equipment program of urban and industrial wastewaters. The main goal of this research was to analyze some environmental toxic elements downstream the river were they end up as natural recipients. Development and modernization of new techniques of measurement are used successfully with very sensitive methods and new electrodes, to detect different chemical and physical forms of metal traces and distribution of their ionic species in the natural equilibrium of waters. Even these methods are based on chemical-physical treatment of champions by displacing certain metal concentrations of all forms through displacement equilibrium into free ionic metal statements, from analytical aspects determination of all active ionic chemical species in model systems is the real overview. The mass concentration of some ecotoxic elements of the river Lumbardhi are determined with DPASV and they are compared with the results of ICP/MS techniques. It is important to point the fact that also this river is permanent polluted from every kind of trash yard from urban centers, which are discharged in the river watercourse. The mass concentrations of lead, zinc and copper ions in the analyzed samples were evidently higher than their natural

concentrations levels in this kind of water, while the cadmium ions were generally in their natural concentrations levels. Concentration of toxic elements which we received from surface waters are compared with the results received for the source where anthropogenic effects aren't present (the part of river in the mountain). We have conclude that water resources of Kosovo's are endangered by the pollution caused from human bean. As first step further, surface water pollution has to be stopped and to improve the existing condition. It is necessary prevention, monitoring and reduce of scale pollution, to ensure the quality level, biological equilibrium and these water ecosystem and at those places where quality rehabilitation is possible.

Key words: Wastewaters, Anthropogenic Effects, Trace, Metals, River Water, ICP/MS

INTRODUCTION

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.Over the last two decades enormous progress has been made with respect to the knowledge of distributions and chemical behavior of trace elements in earth hydrology. Chemical determination of trace elements and distribution of all physical and chemical forms in traces (speciation) in natural water equilibrium resources recently is considering as the main challenge for most of the scientists[1,2].

Important factors initiating these advantages were the application of 'clean techniques' for collection and storage of samples and major advances in analytical methods and instrumentation. We now know the concentrations and distributions for most of the elements in the Periodic Table. It is gained much more insight into their biogeochemical behavior in the oceans and generally the investigators accepted that the interaction of dissolved trace elements with particles suspended in seawater is the predominant mechanism of the observed concentration and distribution patterns[3].

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms. Among environmental pollutants, metals are of particular concern, due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems[4].Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota which generally exist in low levels in water and attain considerable concentration in sediments and biota[5].

Experimentally is proved that the influence of metal concentration in biologic processes depends primary from the free ionic metal and in natural equilibrium of water resources each of physical and chemical forms in traces has the different toxicity[6-9]. It is known that the considerable amount of metal concentrations of aluminum, copper, cadmium, lead etc. are the most toxics but the chemical physical connection with natural ligands reduces physiologic activity, therefore their toxicity for the flora and fauna in general. Development and modernization of new measure techniques applying very sensitive methods as are mass spectrometric methods (ICP/OES, ICP/MS and voltammetric stripping methods (ASV, CSV) are used successfully to detect different chemical and physical forms of trace elements in natural waters[10]. The ASV methods are based on chemical-physical treatment of samples by transforming certain metal concentrations of all forms through displacement equilibrium into free ionic metal statements and, from analytic aspect easy can be determinate. Most of instrumental methods currently available do not provide the sensitivity or freedom from the matrix interferences to

determine trace elements in natural waters at the picomolar and nanomolar level directly. Therefore in most cases a pre-concentration step is necessary before instrumental detection. These steps may be selected from a wide variety of selective techniques: for example, liquid-liquid extraction with chelating agents such as dithiocarbamates, chelating cation exchange with resins (Chelex 100) or electrochemical pre-concentration in ASV and CS Voltammetry.

MATERIALS AND METHODS

Surface sampling is not only the first but also often the most critical step in natural analyses. Even that the aim of this study was the quantitative determination and chemical characterization of some environmental toxic elements in the Lumbardhi river, as surface water resource located in west side of Kosova, we pay it enough attention in the extraction and elaboration of samples and it is done according to standards methods for surface water[11]. Our sampling strategy were concentrate in the six monitoring points from the source in the mountain downstream to the end of river Lumbardhi within our territory near the border of Albania. Surface water sampling of champions and their elaboration in the depth ≥0.20 m were done with non-contaminating bottles Pyrex according to standards methods for surface water[11]. 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%)[12]. In natural rivers most of trace elements occur primarily as 'dissolved' including colloidal species less the 0.45 or 0.4 µm in these analyses filtration is avoided, to minimize contamination or losses due to adsorption. The chemical analysis of suspended particle matter itself is not done in this kind of determinations.

For determination of heavy metals is applied anodic stripping voltammetry using internal standards techniques Fig 2. (VA STAND 746 Trace Analyzer, Metrohm), with three electrodical sistem: working electrode (hang mercury drop electrode); referent electrode (Ag/AgCl) and auxiliary electrode (Pt) in acid nitric HNO_3 (s.p) as bazic electrolyte. The study area with the sampling locations is shown in **Figure 1.**

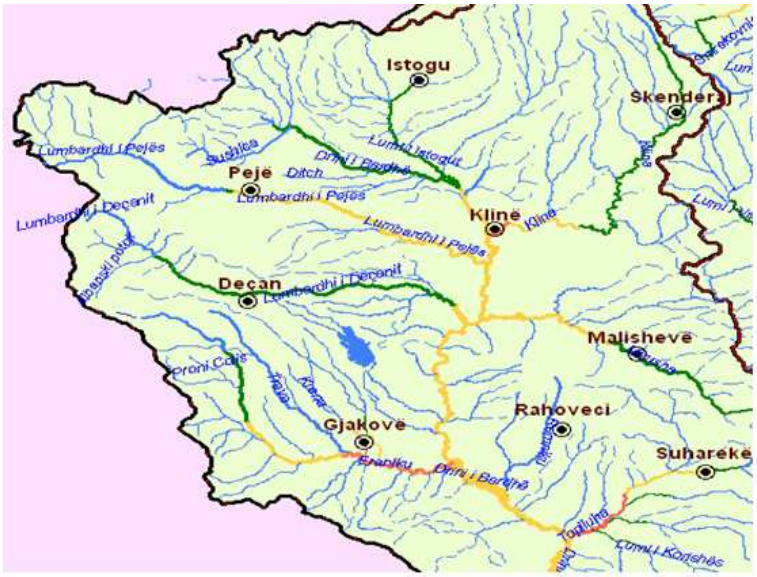

Fig.1: Hydrologic flow map of Lumbardhi river basin in the West side of Kosova

RESULTS

Unfortunately, saying in general the surface water in Kosova are under permanent pollution and is the matter of fact that our cities are without any program of industrial and waste water treatment plant. Because Kosova is on transition process and here are not established yet functional environmental institutions, they end up as natural recipients and this is our main focus of this study work. It is important to mention a fact that also the river Lumbardhi is permanent polluted from every kind of pollution from villages and urban centers, which are discharged in the river watercourses. The watercourse of river Lumbardhi basin is monitored for time period between March-July 2012 (winter-spring) and in this study we tent to gain many parameters of surface water quality. Lumbardhi River in the region of Peja in chemical aspects are used these chemical parameters: pH of samples (in situ), dissolved oxygen, total alkalinity, determination of major cation constituents, determination of major anion constituents, determination of trace elements. These chemical parameters are presented in the form of tables and will be a new data base for the Lumbardhi river.

Table -1: Water quality data: The ASV results of heavy metals compared with the results and the ICP\MS analyses presented in µg/dm^3

Sampling (II)	Zn (II)	Cd (II)	Pb (II)	Cu (II)	Zn (II)	Cd (II)	Pb (II)	Cu
Place	ASV	ASV	ASV	ASV	ICP\MS	ICP\MS	ICP\MS	ICP\MS
L_1	24.75	$1.9\ 10^{-2}$	0.300	0.90	12.30	2.86	6.70	20.10
L_2	38.50	$2.4\ 10^{-1}$	2.040	3.20	9.70	0.17	10.70	4.60
L_3	39.42	$2.3\ 10^{-1}$	2.510	7.15	59.20	0.27	8.74	3.40
L_4	55.45	$8.4\ 10^{-1}$	3.400	11.55	28.60	1.96	22.90	35.90
L_5	62.30	$2.8\ 10^{-2}$	4.400	12.50	23.90	0.32	5.82	9.90
L_6	67.40	$5.1\ 10^{-2}$	5.060	18.70	13.00	1.28	13.60	10.20

Table- 2: Water quality data: The ICP\MS analyses of chemical elements presented in µg/dm^3

Sampling	Tl	Mn	Rb	Co	Ni	As	Br	U
Place	ICP\MS	ICP\MS	ICP\MS	ICP\MS	ICP\MS	ICP\MS	ICP\MS	ICP/MS
L_1	<1.0	1.7	0.479	<0.05	<3.00	<0.3	<30	0.04
L_2	1.1	8.2	0.323	0.11	<3.00	<0.3	<30	0.12
L_3	<1.0	9.3	0.312	0.18	<3.00	<0.3	<30	0.16
L_4	1.5	51.4	0.375	0.65	3.50	<0.3	<30	0.24
L_5	<1.0	4.4	0.197	0.06	<3.00	<0.3	<30	0.11
L_6	<1.0	12.3	0.566	0.99	5.60	0.4	<30	<0.22

Table -3: Water quality data: The ICP\MS analyses of chemical elements presented in µg/dm^3

Sampling place	Ca ICP\MS	Na ICP\MS	Mg ICP\MS	Al ICP\MS	K ICP\MS	Fe ICP\MS	Sr ICP\MS	Ba ICP/MS
L_1	12400	927	1560	<20	640	<100	152	10.30
L_2	39500	806	3810	55	550	130	140	16.60
L_3	39800	1370	3600	62	530	100	169	13.10
L_4	51200	2110	4740	248	630	490	209	24.90
L_5	32300	730	2770	57	330	<100	142	17.80
L_6	56600	2180	3990	240	710	<100	171	48.55

Table- 4: Water quality data: The analyses of chemical parameters presented in mg/dm^3

Sampling place	CaO PO_4^{3-}	MgO	$KMnO_4$	Cl^-	SO_4^{2-}	NO_2^-	NO_3^-	PO_4^{3-}
L_1	16.80	5.500	3.08	3.45	7.070	0.020	0.00	0.051
L_2	57.68	7.280	6.17	1.41	3.680	0.020	0.00	0.002
L_3	56.95	5.900	6.17	1.43	1.760	0.032	0.10	0.009
L_4	54.32	15.22	7.71	2.12	7.940	0.030	2.90	0.017
L_5	66.08	5.600	7.71	2.13	9.976	0.065	1.40	0.011
L_6	66.09	5.400	9.26	2.18	10.03	0.089	1.20	0.010

DISCUSSION

The determination of Cu(II), Pb(II), Cd(II) ions is done in pH interval between 1.40-2.30, (with 10 mmol/dm^3 HNO_3) whereas Zinc(II) was determined increasing pH from 1.50-2.20 until pH = 3.9-4.2 adding in the analyzed solution 25 µdm^3 3mol/dm^3 CH_3COONa (s.pure) forming buffer acetate. An example of registration of voltammetric waves (intensity of current) by anodic stripping Voltametry using internal standards is shown in the Fig. 2. The calculation of mass ion concentration of copper is presented as the procedure in the **Fig. 3.**

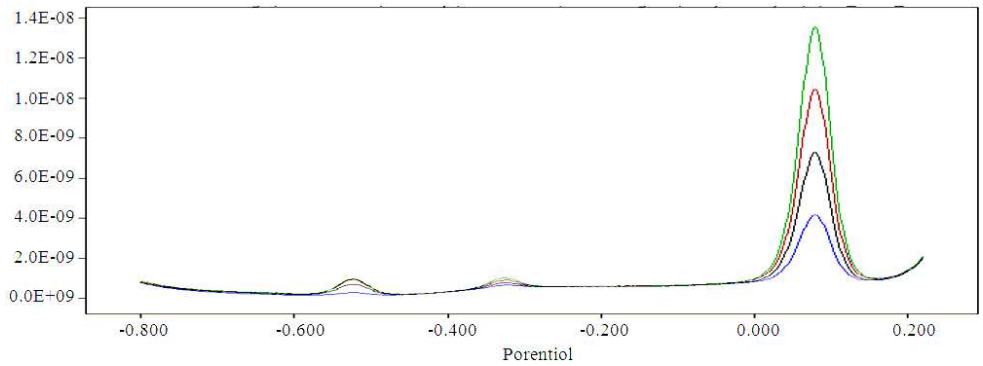

Fig. 2: Determination of mass concentration of heavy metals with internal standards

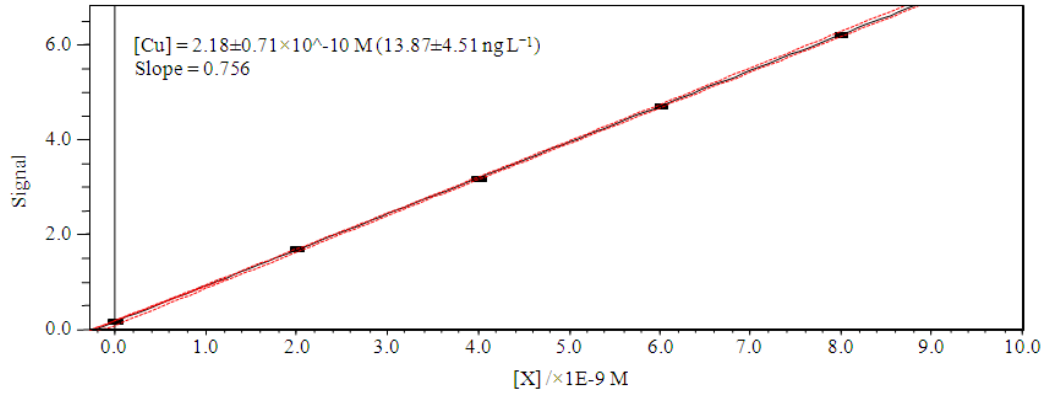

Fig. 3: Determination of mass concentration with internal and external standards from the calibration curves

From the graphs, we can see that there exists a linear dependence of intensity of current from ion concentration in constant potential. In fact, we concluded that this method is correct and useful tool for determination of heavy metals ion concentration in traces in the range of very low concentrations[13]. From all tables we can see that from the calculated results in many cases is observed a variability of metal ions depending from the region where the samples are taken.

The experimental results obtained from anodic stripping voltammtry are compared with the results from ICP/MS as reference results. In many cases, results of anodic stripping voltammtry are little bit lower then ICP/MS results, but saying other words these applied methods are complementary. We flagged in red the mass concentrations of zinc Zn (II) in the analyzed samples downstream the river Lumbardhi L_3 and L_6 were are evidently higher than their normal natural concentrations. The level of mass concentrations of lead Pb (II) in these kinds of waters is higher, especially in the monitoring place L_2, L_4 and L_6, while the element copper Cu (II) was in monitoring samples L_4, L_5 and L_6. We flagged also in red the higher level natural mass concentration of lead Pb (II) in his resource near the village Haxhaj.

We described the normal good quality of river Lumbardhi all away down to sampling points L_4, but in Peja city, in the river are many differences caused from pollution effected by human race.

In the river Lumbardhi from the table 2 we flagged in red monitoring place L_4 is evidently a high amount of mass concentration of manganese Mn (II) and nickel Ni (II) in the L_6. In addition, the mass concentrations of lead Co (II) in the analyzed samples in the watercourses of the river were evidently higher than their natural concentrations levels in tendency of increasing, especially in the monitoring place L_6 while the other elements thallium, rubidium and bromide are normally slightly in their natural concentrations. From the table 2, we must pay attention about arsenic in the monitoring place L_6 and uranium as radioactive pollutant indicator. The situation created by pollution of river with waste waters coming from urban centers as are Peja and Klina it is visible and from water eutrophication process which is present downstream the river Lumbardhi. This can be explained if we compare dissolved oxygen results of sampling waters between 9.60 mg/dm^3 in L_4 and 11.3 mg/dm^3 in L_6.

The preoccupations are growing up because also this river is less populated with some biological species of fish. The table 3 shows situation of mass concentration of major constituents in the river and we pointed here concentration of iron, barium, aluminum and strontium. According to the results of mass concentration of anions presented in the table 4 it could be concluded that the mass concentration are in little higher amounts.

These kind of waters before being used for human utilization 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). The vulnerability of water quality is followed by serious changes of its properties, resulting undesirable effects, like: lack of oxygen, reduction in pH value, increase of heavy metal complexion 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 excepting of some artificial accumulation lakes.

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

Utilization of several very sensitive laboratory equipments and new methods for detection of pollutants as a new technology with high costs and high efforts in work must be used while working with extremely very low mass concentrations. Kosovo's water territory is formed with around of three milliards m^3 of surface water per year and this entire water amount through four catchments areas flows into three seas: Adriatic Sea, Black Sea and Aegean Sea. Periodically these catchments are supported with monitoring teams from our department within our opportunities.

CONCLUSION

To compare the surface water quality in our country exactly in Lumbardhi river basin in the region of Peja, from chemical aspects are picked out some of main indicators pollution as are: pH value (in situ), dissolved oxygen, lead (Pb), Cadmium (Cd), Copper (Cu), zinc (Zn), arsenic (As), Cobalt (Co), nickel Ni(II), uranium (U), bromine, nitrites etc. Our special conclusion is that AS Votammetry successfully could be used as techniques for chemical characterization of heavy metals in traces. In some monitoring places alongside watercourses Lumbardhi river basin we "met" some of permanent top toxicants in very high level mass concentrations and we highlighted these places in red in our database.

During our experimental determinations we had allowed shifted curves (good reproducibility of methods used for this purposes.) Applied nitric acid HNO_3 (s.pure), is shown in the enjoyable priority during our investigations with anodic stripping voltammetry in the range of other mineral acids as are: $HClO_4$, hydrochloric acid HCl, fluoric acid, HF etc. Nitric acid almost played a role of electrolytic medium. Applied buffer acetate CH_3COOH/CH_3COON (s.pure), during investigations of Zn (II) with anodic stripping voltammetry, is shown in the enjoyable priority during our investigations in the range of other acidic buffers. (Citrate, phthalate, borate) The experimental results of chemical elements with ICP/MS techniques are used as a reference results obtained in our laboratories with anodic stripping voltammetry with the intention to practice and establish these last methods in our laboratories.

Even that in Kosova 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. We have concluded that water resources of Kosovo's are endangered by the pollution caused from human bean. As first step further, surface water pollution has to be stopped and to improve the existing condition. It is necessary prevention, monitoring and reduce of scale pollution, to ensure the quality level, biological equilibrium and these water ecosystem and at those places where quality rehabilitation is possible. We are very concerned about these facts but we hope that is still time to prevent the quality of Kosovo's

surface waters. According to this issue in the region, we are looking for practical and cheaper alternatives, which should be proceeded by serious projects that are intensively done in most of the countries in European Community.

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