Analysis of Some Environmental Toxic Elements in Water Resources of Kosova

*Naser TRONI[1], Fatbardh GASHI[1], Tahir ARBNESHI[1] & Dario OMANOVIC[2]
[1]University of Prishtina, Faculty of Natural & Mathematical Sciences,
Prishtina, Kosovo
[2]Departament of Physical Chemistry "Rudjer Bosković"
Zagreb, Croatia

Abstract:

The aim of this paper was to analyse some environmental toxic elements in few water resources of Kosova using Differential Pulse Anodic Striping Voltammetry, DPASV, in universal cell in three electrode system with HDME. Considerable amounts of these environmental toxic elements are continuously emitted in environment from anthropogenic sources. Since the main source for the drinking water, are the rivers that flow within the territory of Kosova, it is of mayor priority the quality of water of these rivers and the water mineral sources.Concentration of Cd^{2+} ; Pb^{2+} and Cu^{2+} ions in all the samples were determined at pH = 1.40 – 2.30 while those of Zn^{2+} ions at pH 3.7 - 4.2. All the determined parameters with DPASV are compared with the results of ICP/MS method. The mass concentrations of lead and copper ions in the analyzed samples were evidently higher than their natural concentrations levels in these kinds of water, while the zinc and cadmium ions were generally in their natural concentrations levels. Toxic elements results of surface waters are compared with the results of underground waters, with those waters in where there are no anthropogenic effects.

***Key Words**: Water Resources, Environmental Toxic Elements, DPASV, ICP/MS, Kosova.*

Introduction

Determination of total quantitative and qualitative metals and distribution of all physical and chemical forms in traces (speciation) in natural water equilibrium resources today is to be considering as the main challenge for most of the scientists (Kester, 1977). Specified physical and chemical species of each metal in trace are solved and distributed in the natural aquatic systems in the ionic forms (hydrated), in the form of inorganic and organic complexes or adsorbed in the colloidal particles (Florence, 1986). As we know natural waters contain different species of ligands with wide extension of concentrations and with traces of metals create complexes. (Morgan & Stumm, 1991; Sigg et al., 1994). Most of metals in traces are not determinate yet and the distribution of all their species, but experimentally is proved that the influence of metal concentration in biologic processes dipends primary from the free ionic metal concentration. (Anderson & Morel, 1982; Sunda, et al, 1984). In natural equilibrium of water resources each of physical and chemical forms of metal in traces has the different toxicity. 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 by applying methods and very sensitive electrodes are used successfully to detect different chemical and physical forms of metal in traces and distribution of their ionic species in the champions of natural waters. (Branica, et al., 1977).
These methods are based on chemical-physical treatment of champions by transforming certain metal concentrations of all forms through displacement equilibrium into free ionic metal statements and, from analytic aspect easy can be determinate (Byrne, 1996). The main objective of this study also could be explained from the two important aspects: Application of several physical-chemical equipments for detection of environmental toxic elements in traces in work with extremily llow concentrations, and a study guide for our Country in transition about the quality of natural water resources in Kosova as human enrichment.
Even it is known that there are no branch of industry especially industry of food, that does not use the water, is one more fact that indirectly our anthrobiogeochemical cycle may be protected if we pay more attention about our concerns for degradation of environment. The wasted waters from the urban and industrial centers spills out in the river without any kind of treatment, and in the last decennia these rivers are conversed in a source of waste waters. Are monitoring some sampling points downstream the river were is evidented influence of wasted waters in the end main cities were still are not installed technology equpments for the treatment of waste waters (Arbneshi, et. al., 2007).

Study Field and Methodology

The point of this study was the quantity determination of environmental toxic elements in the two main rivers of Kosova: The Lepenci river Basin with Nerodime, located in south side of Kosova, The Drini i Bardhe river Basin located in west side of Kosova as surface waters and also as reference points two underground resources: Aqua mineral natural resource of Kllokoti and Thermal natural water resource of Peja. Extraction of champions and elaboration of samples were done according to standards methods for surface water [APHA, 1992; Dalmacija, 2000].

Figure 1. Samples Points in the Kosovo's Rivers Flow

For determination of heavy metals is applied anodic stripping voltammetry using internal standards techniques, figure 2. (VA STAND 746 Trace Analyzer, Metrohm), with three electrodical sistem in acid nitric HNO_3 (s.p) as bazic electrolyte:

1. Working electrode (Hang mercury drop electrode)
2. Referent electrode (Ag/AgCl)
3. Auxiliary electrode (Pt)

For extraction of metal ions from the different organic and inorganic complexes (mononuclear, binuclear or poly nuclear) we have prepared a 10 mmol/dm^3 HNO_3 water solution (Midorikawa & Tanoue, 1994). The determination of Cu(II), Pb(II), Cd(II) ions is done in pH interval between 1.40 – 2.30, whereas Zinc(II) was determined increasing pH from 1.40 – 2.30 until pH = 3.8 - 4.5 adding in the analyzed solution 25 μdm^3 3mol/dm^3 **(**s.pure**).** CH_3COONa (Buffer acetate).

Results and discussion

To determine the ion concentration of different metals we have used the method of internal and external standards. The results obtained using this procedure in the case of zinc ions are shown in the figure 1. From the graphs we can show that there exists a linear dependence of current from ion concentration. In conclusion we demonstrate that this method is correct for the determination of zinc ion concentration in the range of low concentrations.

From the table 1 and 2 we can see that the calculated results in many cases we observed a variability of metal ions depending from the region where the samples were taken. In the river Lepenci (monitoring place L_4) is evidently a high amount of mass concentration of zinc Zn (II) (figure 1) and that of copper (II) and we explain that discrepancy because in this place the river Nerodime is joining with the river Lepenci. The discharged waste waters in the river Nerodime are done without any physical chemical treatment from urban and industrial cities Kaçanik and Ferizaj with surroundings. Also the mass concentrations of lead Pb (II) in the analyzed samples downstream the river Lepenci were evidently higher than their natural concentrations levels in these kinds of waters, especially in the monitoring place L_2, while the element cadmium Cd (II) was generally slightly in his natural concentration levels.

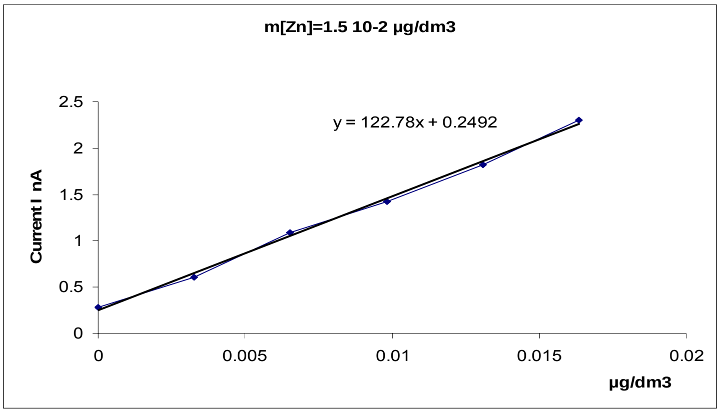

Figure 2. Determination of mass concentration with internal and external standards from the calibration curves.

In this work are investigated some parameters of surface water quality for time period December 2005 –February and March 2006, and these parameters are presented in the table 1.

Table 1. Water quality data

Samp place	γ Zn(II)/ µg/dm^3 ASV	γ Cd(II)/µg/ dm^3 ASV	γ Pb(II)/µg/ dm^3 ASV	γ Cu(II)/µ g/dm^3 ASV	γ Zn(II)/µg/ dm^3 ICP\MS	γ Cd(II)/µg/ dm^3 ICP\MS	γ Pb(II)/µg/ dm^3 ICP\MS	γ Cu(II)/µg/ dm^3 ICP\MS
L_1	21.55	$9.1\ 10^{-3}$	0.738	2.862	30.5	0.01	0.81	2.0
L_2	29. 10	$1.2\ 10^{-1}$	3.948	5.38	61.5	0.12	3.84	7.7
L_3	35.24	$1.95\ 10^{-1}$	2.152	4.48	37.8	0.17	1.45	6.6
L_4	54.45	$5.9\ 10^{-1}$	3.461	16.55	77.9	0.34	2.42	15.6
L_5	52.30	$8.2\ 10^{-3}$	6.405	17.50	57.9	0.39	3.61	20.3
L_6	65.70 [1]	$1.5\ 10^{-2}$	5.634	27.70	62,3	0.47	4.53	28,4
D_1	26.35[2]	$7.4\ 10^{-3}$	2.178	2.676	36.3	0.1	3.29	3.7
D_2	29.41	$9.8\ 10^{-2}$	1.810	6.48	38.9	0.17	1.23	7.6
D_3	72.15	$3.55\ 10^{-1}$	2.998	15.98	87.9	0.45	2.45	14.8
D_4	70.39	$3.13\ 10^{-1}$	2.457	19.23	67.4	0.59	2.65	23.4
D_5	98.22	$9.56\ 10^{-1}$	2.351	33.56	94.5	0.78	3.70	34.4
THWP	3.87	$1.90\ 10^{-2}$	0.574	1.074	3.34	0.09	0.3	1.7
MWK	3.75	$1.50\ 10^{-2}$	0.132	1.377	1.69	0.07	0,09	1.5

Where L_1- L_6 : represents monitoring places of river Lepenci, D_1- D_5 : monitoring places of river Drini i Bardhe, THWP: Thermal water of Peja, MWK:mineral water of Kllokoti.

In the river Drini i bardhë (monitoring place D_5) is evidently a high amount of mass concentration of zinc Zn (II) and copper Cu (II). Also the mass concentrations of lead Pb (II) in the analyzed samples in the water courses of the river Drini i bardhë were evidently higher than their natural concentrations levels in tendency of increasing, especially in the monitoring place D_3, D_4 and D_5 while the other element cadmium Cd (II) was generally slightly in his natural concentrations levels excepts in the monitoring place D_3. This situation is created by pollution of river by waste waters coming from urban centers as are Peja, Gjakova, Prizreni, Klina, and Rahoveci. The concern's are growing up because also this river is permanent polluted from the waste and industrial waters which are discharged in watercourses without any physical chemical treatment.
According to the results of mass concentration of heavy metals results in The Aqua mineral natural resource of Kllokoti and Thermal natural water resource of Peja it could be concluded that the mass concentration of Lead and Copper are in 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).etc.

Table 2. Water quality data : The ICP\MS analyses of chemical elements developed with in commercial Laboratories. "Act Labs" Ontario, Canada.

Sampling place	γAl µg/dm³ ICP\MS	γCr µg/dm³ ICP\MS	γFe µg/dm³ ICP\MS	γCo µg/dm³ ICP\MS	γNi µg/dm³ ICP\MS	γAs µg/dm³ ICP\MS	γBr µg/dm³ ICP\MS	γHg ng/dm³ FIMS
L_1	< 2	0.7	40	0.173	2.1	0.84	0.81	12
L_2	20	0.7	10	0.147	4	0.56	3.84	16
L_3	34	1	20	0.217	3	0.96	1.45	8
L_4	40	1.4	20	0.323	10.9	2.17	2.42	*149
L_5	17	1.2	20	0.373	9.4	1.24	3.61	7
L_6	21	1.5	< 10	0.412	12.6	1.39	4.53	9
D_1	34	1	< 10	< 0.05	0.6	0.43	54	16
D_2	14	0.8	12	6.48	7	0.56	79	18
D_3	34	1.2	21	15.98	5	0.96	130	6
D_4	43	1.6	19	19.23	12	1.15	110	24
D_5	18	1.2	32	33.56	15	1.26	149	19
THWP	< 20	< 5	< 10	< 0.05	< 3	< 0.3	0.3	< 6
MWK	< 20	< 5	< 10	< 0.05	< 3	4.7	0,09	6

Where L_1- L_6 : represents monitoring places of river Lepenci, D_1- D_5 : monitoring places of river Drini i Bardhe, THWP: Thermal water of Peja, MWK:mineral water of Kllokoti.

Generally, the surface waters in our country are under permanent pollution and the matter of fact that our cities aren't without any treating equipment program yet of urban and industrial wastewaters let us understanding that they end up as natural recipients.
Experimental results (table 1) show that some parameters of water quality as are heavy metals in rivers Lepenci, and Drini i Bardhe indicate tendency of increasing, comparing with former experimental results. (Jusufi et al 2002, Bacaj et. al., 2003 and Arbneshi et. al., 2003). Water with high quality (I category and I/II) in Kosova is rarely and mainly can be find only in the mountains where are *the sources of Kosova's rivers.*
It is important to point the fact that also these rivers are permanent polluted from every kind of trash yard from urban centers, which are discharged in the river watercourses (Bacaj et. al., 2003).

Conclusions

The experimental results of chemical elements with ICPMS technique are used as a reference for our results obtained in our laboratories with Anodic Striping Voltammetry.
According to the results of Zinc(II) concentrations in the places where samples are taken, these places are categorized as follows: first category [sampling place L_1]; second category [sampling places D_1 and L_2] ; Third category [sampling places L_3, L_4, L_5, D_2, D_3, D_4] and fourth category [sampling places L_5 and L_6]
Based to the results of Cadmium (II) concentrations in the places where samples are taken, these places are categorized as follows: first category [sampling place L_1, L_2, L_3, L_4, L_5, D_1 D_2, D_3, D_4, D_5]; second category [sampling places L_6 and Mineral water of Kllokoti] and fourth category [sampling places L_5, L_6, D_4, D_5]
According to the results of Lead(II) concentrations in the places where samples are taken, these places are categorized as follows: Second category [sampling places L_1 and D_1] ; Third category [sampling places L_2, L_3, L_4, D_2, D_3 and Mineral water in Kllokoti] and fourth category [sampling places L_5, L_6, D_4, D_5 and Thermal water in Peja]
From the concentration of Copper in the monitoring places were the samples were taken, these sampling places are categorized as follows:
First category [sampling place D_1]; Second category [sampling places L_1,L_2,L_3 and D_2]; Third category [sampling places L_4, L_5, D_3 and mineral water in Kllokoti]; Fourth category [sampling places L_6, L_5, D_5 and Mineral water in Peja]; Fifth category [sampling place D_4]
In Kosova we don't have yet any legislative convent for allowed concentrations of toxic metals for natural water resources and the results from this paper are a small contribution to gain a clear picture of the situation in this field of environmental quality assurance.

References

Anderson M.A. &. Morel F.M.M., (1982). The influence of aqueous iron chemistry on the uptake of iron by the coastal diatom THALASSIOSIRA WEISFLOGII. Limnol. Oceanogr., 27 789.

APHA, American Public Health Association, 1992: Standard Methods for the Examination of Water and Wastewater. 18 th Edition Washington D.C.

Arbneshi T. Troni N. & Berisha L, (2007). The surface water quality in Kosova, Croatian Water and European Union pg. 61-67.

Bacaj, M, Jusufi S; Shehdula, M., Shala A. & Arbneshi T. (2003). Phenol Concentration in Sitnica River. II Congrees of Ecologist of the Republic Macedonia with International Participation, Abstracts, pg.123, Ohrid, Macedonia.

Branica M. Novak D.M & Bubić S., (1977). Application of anodic stripping voltammetry to determination of the state of complexation of traces of metal ions at low concentration levels. Croat. Chem. Acta, 49 539.

Byrne R. H., (1996). Specific problems in the measurement and interpretation of complexation phenomena in sea water. Pure & Appl. Chem., 69 (8) 1639.

Dalmacija, B., 2000: Water Quality Control in Towards of Quality Management.

Florence T. M., (1986). Electrochemical Approaches to trace element speciation in sea waters. A. Review. Analyst, 111. 489.

Kester D.R., (1975). Chemical speciation in sea water, in: E. D. Goldberg (Ur.), the nature of sea water, Dahlem konfernzen, Berlin.

Korça, B.; Jusufi, S.; Shehdula, M.& Bacaj, M. (2002). *Surface Water Pollution in Kosovo*, Conference: Technical-Technological Sustainable Development and Environment. p. 197-202.

Midorikawa T. & Tanoue E., (1994). Detection of a strong ligand for copper in sea water and determination of its stability constant. Anal. Chim. Acta, 284. 605.

Morgan J.J. & Stumm W. (1991). Metals and their compounds in the environment. E. Merian (Ur.),VCH Publ.Co., Cambridge.

Sigg L. & Xue H., (1994). in: G. Bidoglio i W. Stumm (Ur.), Chemistry of Aquatic Systems: Local and Global Perspectives. Kluwer Acad. Pubi., 153.

Sunda W.G., Klaveness D.. and Palumbo A.V., (1984). Bioassays of cupric ion activity and copper complexation. in: C.J.M. Kramer I J.C. Duinker (Ur.), complexation of Trace Metals in natural Waters. Martinus Nijhoff / Dr W. Junk Publishers, The Hague.