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DETERMINATION OF LABILE CHEMICAL FORMS OF Cd AND Zn IN THE WATER OF «MODRAC» LAKE

Amra Odobašić,
Sead Ćatić,
Husejin Keran,
Amra Bratovčić
University of Tuzla, Faculty of Technology
Bosnia and Herzegovina

ABSTRACT
If we want to have satisfactory information about the behavior of metals in polluted water often it is not sufficient to know just the total concentration of the metals in polluted water. To a great extent their toxicity, biodegradability, bioacumulation, mobility, solubility, resistance and other critical features depend just on specific physical-chemical form in which certain heavy metals are present in water.
Metal fractions are classified by their relative lability: very labile, middle labile, low labile and inert. Their distribution mostly determined by their affinity for complexing with the organic ligands as well as with inorganic ligands and the change of the pH of water. In this work we have determined the total concentrations of Cd and Zn by DPASV and determined the presents labile chemical form Cd and Zn depending on the season using the software programs MINTEQ and HYDRA.
Key words: DPASV, natural water, cadmium, zinc.

1. INTRODUCTION

If we have information about the total concentration of the metals in a polluted environment often it is not sufficient to obtain the right information about their harmful efficiency. Toxicity biodegradability, bioacumulation, mobility, solubility and other important characteristics depend just on specific physical-chemical forms in which certain heavy metals are present.
In this work we used DPASV for determination of the total concentrations of Cd and Zn and combination with software programs MINTEQ, HYDRA and CHEAQS for determination of the labile chemical form Cd and Zn. Lability and chemical form Cd and Zn were examined during four seasons and four characteristic regions of Modrac lake (region of barrier – A, middle of lake – B, mouth of the river Turija – C and mouth of the river Spreča – D). The scheme of Modrac lake is shown in figure 1.

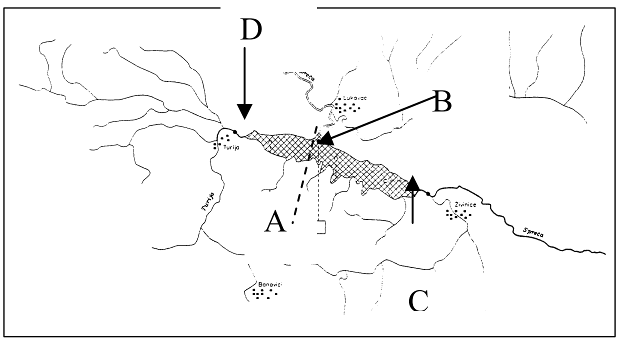

Fig 1. The scheme of Modrac lake

The concentration of trace metals and its mobility and lability are in direct connection with the beginning form of metal which depends on the kind of source and biogeochemical processes which occur in water. The water system of Modrac lake is characterized by the presence of traces of heavy metals, organic matter and suspended matters. Modrac lake is an artificial lake in the northeast of Bosnia about 15 kmilometers away from Tuzla. The lake takes 17 km^2 of surface with maximal depth of about 10 meters. When we take into cosideration the district where the lake is and the influx of polluted waters and the fact it's today used as a source of drinking water for the area of Tuzla it is very important to know the degree of pollution within the lake of heavy metals, but the degree of its toxicity which depends on the physical-chemical form.
Cd is one of the most toxic metal and takes the first place as the essential element such as Mn. Natural waters contain Cd in very low concentrations. Filled d and s – orbits insure stability in that element. Standard redox potential Cd has a negative value that means easy oxidizing in water solutions. Especially interesting are halogen complexes Cd whose forming is the result of an increase concentration of Cd and characterized by very low stability. Until now investigation showed that on bioavailability Cd influences other contents in water and food such as calcium, phosphorus and iron. The specification of Cd as a pollutant is in its long biologic life even about 30 years that means its concentration in the human body increases in proportion to age. For the protection of aquatic life, the maximal allowed concentration of Cd is about 0,001 μg/l at 200 mg/l $CaCO_3$ hardness of water according to the criterions of the EPA.
Zinc is from the same group as Cd. In its elementary state Zn is a strong reducing agent. It presents an essential element with an important role in biologic processes such as growth and development. The toxicity of some metal species toward aquatic organisms probably are linked by the ability to react with a biologic membrane. The transfer of O_2, Na, K i Cl_2 is interfered with by the building of metals in a morphologic chain. Just break through of the metal ion in a membrane directly depends on lipid solubility of metal and the rate of reaction of the metal ion with proteins from the membrane. Metal-protein reaction leads to the passing of metal through the membrane while covalence ions favor thermodynamics. Unpolluted and sweet and sea water contents are exceptionally low concentrations of the heavy metals like Cd and Zn, mostly soluble and adsorbtion of organic or inorganic colloid matters. Today inorganic compounds of the heavy metals of Cd, Zn, Pb and Cu are studied the most.

2. MATERIAL AND METHODS

We analyzed samples from four characteristic regions of Modrac lake through four seasons. The samples were taken from the depth of 2,5 m. We took two samples from every region. One sample was acidified immediately by concentrated hydrochloric acid to pH 2 to determine the total concentration of Cd and Zn while the second sample was frozen and it was used after for determining labile chemical forms. Today several methods are used for determining different forms of metals in natural waters. DPASV and CSV are often used. With those technics it is possible to separate species on the basis of their redox potentials and determined labile or electroactive complexes and free ions. In this work we used DPASV. The experimental work was done on potentiostat PAR 263 A in electrochemical cell Princenton Applied Research (EG&G) model 303A. There are the following instrumenatal parameters during work:

- working electrode, HMDE
- auxiliary electrode, Pt-wire
- reference electrode, Ag/AgCl (E = 0,222 V)
- purge time (deaeration by nitrogen) 150 sec
- equal time 20 sec
- scan rate 2 mV/sec
- deposition time 300 sec

Halfwaves potentials of Cd and Zn are given in table 1.

Table 1.

Metal	Start potential (mV)	End potential (mV)
Cd	-0,9	-0,6
Zn	-1,2	-0,9

In this experimental work we used standard solution of Cd and Zn the concentration 1 mg/l, supra pure HNO_3 i KNO_3.

3. RESULTS

In figure 2-3 voltammograms are given for Cd for summer and Zn for winter at characteristic regions.

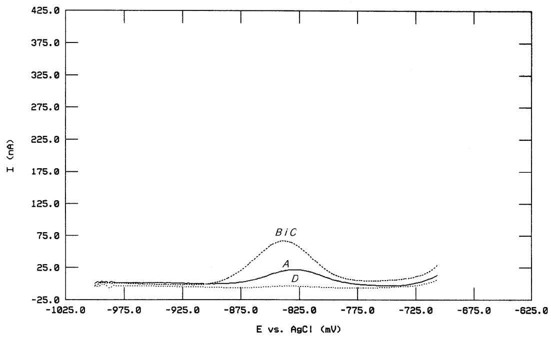

Figure 2. Cd in summer at regions A, B, C and D

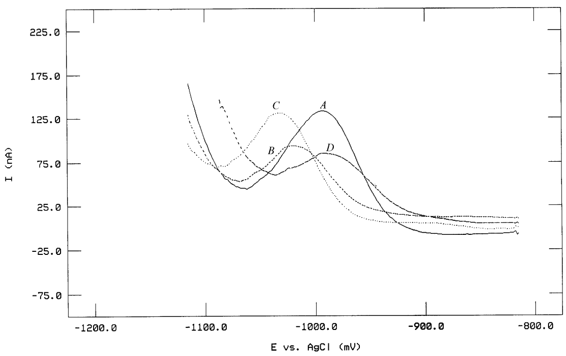

Figure 3. Zn in winter at regions A, B, C and D

In table 2 calculated average concentrations of Cd in Modrac lake are given.

Table 2.

Region	Summer (mol/l)	Autumn (mol/l)	Winter (mol/l)	Spring (mol/l)
A	$3{,}4688\cdot10^{-8}$	$3{,}7000\cdot10^{-11}$	$< 10^{-12}$	$6{,}5560\cdot10^{-10}$
B	$9{,}2638\cdot10^{-9}$	$2{,}2917\cdot10^{-8}$	$< 10^{-12}$	$1{,}0078\cdot10^{-10}$
C	$1{,}0000\cdot10^{-11}$	$3{,}3456\cdot10^{-8}$	$<10^{-12}$	$7{,}9106\cdot10^{-9}$
D	$1{,}526710^{-8}$	$1{,}1100\cdot10^{-11}$	$1{,}0\cdot10^{-11}$	$1{,}0078\cdot10^{-8}$

In table 3 calculated average concentrations of Zn in Modrac lake are given.

Table 3.

Region	Summer (mol/l)	Autumn (mol/l)	Winter (mol/l)	Spring (mol/l)
A	$3{,}6238\cdot10^{-8}$	$1{,}2265\cdot10^{-7}$	$2{,}5076\ 10^{-7}$	$4{,}7273\cdot10^{-8}$
B	$3{,}2334\cdot10^{-8}$	$6{,}8923\cdot10^{-8}$	$7{,}374010^{-8}$	$4{,}7848\cdot10^{-8}$
C	$3{,}1698\cdot10^{-8}$	$1{,}0823\cdot10^{-7}$	$2{,}3105\ 10^{-7}$	$2{,}7690\cdot10^{-8}$
D	$4{,}054510^{-8}$	$1{,}0312\cdot10^{-7}$	$5{,}0967\cdot10^{-8}$	$6{,}3712\ 10^{-8}$

On the basis of obtained data about total concentrations of Cd and Zn and chemical contents of the lake and taking into consideration ionic strength and pH of water of the lake and we used the software programs MINTEQ, HIDRA i CHEAQES to determine the inorganic speciations of Cd and Zn.

Table 4. Chemical contents of water of Modrac lake.

Chemical contents (mg/l)	**A**	**B**	**C**	**D**
carbonate	12	6	6	12
bicarbonate	149	155	161	152
nitrogen	0,11	0,17	0,2	0,17
nitrate	0,4	0,41	0,36	0,38
chloride	4,2	4,2	5,6	4,2
sulfate	63,8	56	64,8	60,7
calcium	52,1	20	49,1	18,8
magnesium	53	15,2	55,1	18,8
Ionic strength I (mol/l)	$5{,}990\cdot10^{-3}$	$5{,}990\cdot10^{-3}$	$5{,}990\cdot10^{-3}$	$5{,}990\cdot10^{-3}$

Table 5. Labile chemical forms of Cd and Zn in the water of Modrac lake.

Chemical compound	Summer, pH=6,5; T=26^0	Autumn, pH=7,5; T=20^0	Winter, pH=7,5;T=20^0	Spring, pH=7 ;T=22^0
Cd^{2+}	85,75%	**95%**	-	90%
$Cd(SO_4)_{aq}$	7,6%	5%	-	8,1%
CdCl+	6,6%	-	-	1,9%
Zn^{2+}	90%	92,7%	**93 %**	92%
$Zn(SO_4)_{aq}$	7,5%	7,3%	7%	7%
$ZnHCO_3$	2,5%	-	-	1%

In figures 4 and 5 labile chemical forms of Zn in winter and Cd in autumn are given.

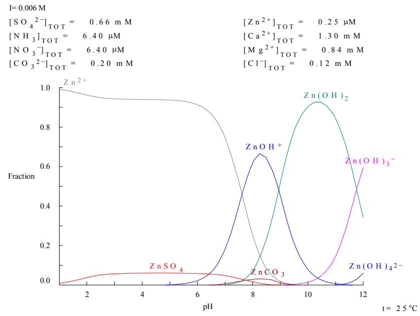

Figure 4. Labile chemical forms of Zn

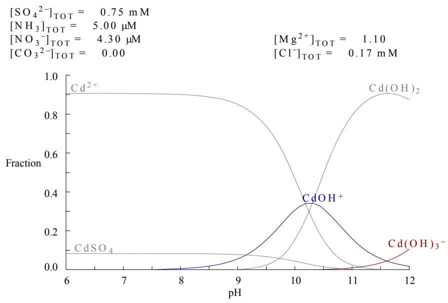

Figure 5. Labile chemical forms of Cd

4. DISCUSSION

The experimental results show that Zn is through four seasons at all selected regions found to be almost totally dissasociated ie. at ion form. Just one small part was found in the form $ZnSO_4$ whose determined equilibrium constant (K = 2,3) indicated that it is a very labile complex of zinc. Experimental results for Cd showed that there were very low concentrations of Cd and during that Cd wasn't found in samples of water in winter in any region, so the hypothesis is that concentrations are less than 10^{-12} mol/L.

5. CONCLUSION

The total concentration of labile fractions of cadmium is the highest in region A, which is explained with the demotion of organic matter and fastly changing physical chemical parameters because of the mixture of courses and high degrees of turbulence in this region. The total concentration of labile fractions of zinc is the highest in winter also in region A. And zinc and cadmium are most present in the form as free metal ions while zinc at pH 8 showed the tendency to form from free ion to easy labile complex of sulfate. The results showed that the use of selected DPASV technique is able to determine traces of heavy metals and in combination with suitable software programs it is able to determine chemical speciations with exceptionally good accuracy.

6. REFERENCE

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