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Simultaneous Determination of Some Heavy Metals in Water, Sediments and Aquatic Macrophytes of Marmara Lake (in Turkey) by Using Differential Puls Polarography (DPP)

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ABSTRACT

In this study, cadmium (II), copper (II), lead (II) and zinc (II) levels of Marmara lake are determined by Differential Puls Polarographic (DPP) Method. These metal ions were measured in water, bottom sediments and plants taken from Marmara Lake in Aegean Region of Turkey. The collected plants were *Phragmites australis, Carex otrubue, Ceratophyllum sp., Valisneria sp., Ranunculus sphaerospermus, Myriophyllum sp.* All of the samples were measured polarographically after preparation of samples by different techniques. Experimental results obtained on five replicate samples. It was applied Pearson correlation between water-plants, sediments-plants and sediment–water systems. The results compared with old papers concerning Turkish river samples.

Keywords: *Heavy metals, sediment, water pollution, aquatic plant.*

INTRODUCTION

In recent years, the danger of the extinction in living forms have also started in Turkey, as it was in all over the world, due to the pollution caused by the factory and city wastes. This situation necessitates investigation on the pollution level in the rivers and lakes (Ozmen, 2004; Varol 2011; Varol, 2012).

The need for regular monitoring of toxic elements like cadmium (II), lead (II),copper (II), zinc(II) in aquatic plants adequately sensitive and selective multielement determination, high sensitive neutron activation techniques, atomic emission spectrometry with inductively coupled plasma excitation (ICP–AES), X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS) (Ozmen, 2004, Fossi, 2013) are very expensive any need any apparatus, time–consuming and often do not offer adequate sensitivity for reproducible determination at trace to ultra-trace concentration of multi elements in salty biological materials (Williams, 1995; Koçak, 2002, Tokusoglu, 2004). Voltammetric techniques such as differential Pulse Polarography (DPP), anodic stripping voltammetry (ASV) (İnam, 1999), cathodic stripping voltametry (CSV) (Plavšić, 2011) , amperometry (Lesven, 2010) and adsorption voltametry (AV) require relatively inexpensive instrumental analysis methods, are capable of multielement determining accurately at trace to ultratrace levels (İnam, 1999; Reichart, 1998; Koçak, 2002; Tokusoglu, 2004).

This investigation was carried out in Marmara Lake in Turkey. Zinc, lead, cadmium and copper pollution is a very serious environmental problem. There are a number of studies on the metal pollution in river and lake sediment aquatic plant and water (Yang, 2014; Xua, 2013; Bing, 2013; Wang, 2012; Hou, 2013, Roo, 2001, Jha, 2002, Multer, 2002, Karadede, 2000, Akçay, 2003). The papers consist of values obtained from different techniques like (AAS) and ICP

In our study, we used polarographic technic. Polarography was discovered by Czechoslovakian chemist Jaroslav Heyrovsky in the early 1920's. Most polarographic analyses are performed for metal ions and also organic functional groups. Polarographic data are obtained by measuring current as a function of the potential applied to a special type of electrolytic cell. A pilot of the data gives current-voltage curves. In recent years, many modifications of the original polarographic method have been developed like as differential pulsed polarography, rapid scan polarography, stripping voltammetry Differential Pulse Polarography (DPP) has become accepted as one the most powerful electroanalytical tool for trace element analysis of some materials due to its extreme sensitivity and selectivity (Qiong, 1999; Rodriques, 1999, Rodriques, 1997). In addition it is possible simultaneous determinations with this method.

MATERIALS AND METHODS

A polarographic analyzer (Metrohm 746 VA Trace Analyzer) together with a capillary hanging mercury drop electrode (HMDE) and lenseis LY 1600 Model recorder was used for all electroanalytical measurements. A platinum wire was used as the auxilary electrode and a Ag/AgCl (sat. KCl) electrode used as reference electrode.

Sediment, water and aquatic macrophyt samples were taken from five stations of differing characteristics at seasonally intervals for a one year period (Fig. 1).

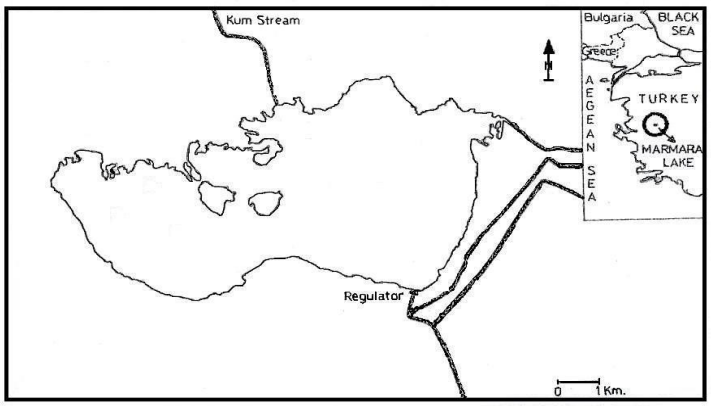

Figure 1. Working area and sampling point for Marmara Lake

Reagents

All the reagents were used analytical grade (Merck). The mercury used in the HMDE was obtained from Merck (Darmstadt Germany). In all measurements ultrapure water was used. A 0.1 M stock matrix standard solution including cadmium (II), lead (II), copper (II) and zinc (II) was prepared by dissolving Cd $(NO_3)_2$, $Pb(NO_3)_2$, Cu $(NO_3)_2$ and $ZnCl_2$ in water respectively. In this stock solution individual concentrations of elements were shown below: Zn^{2+}: 139,1 mgL^{-1} ,Cd^{2+} (II): 108,7 mgL^{-1}, Pb^{2+}: 122,5 mgL^{-1} and Cu^{2+}: 161,2 mgL^{-1}. Dilute solutions were prepared as daily from above mentioned standard stock solutions

Electroanalytical determination

For quantitative determination of cadmium, lead, copper and zinc in sediments, water, aquatic macrophytes; the polarogram of the individual metal ions in the standard mix solution was obtained using standard addition procedure. For the sample analysis, the 0.1 M (pH 4.64) acetic acit/acetate buffer was used

Water analysis

Water samples taken by Nansen bottle have been put placed into polyethylene bottles by filtration with whatman paper and added 1 ml HCI. All samples have been kept in the refrigerator for analyses (Bernhard, 1976).

Sediment analysis

Sediment samples in polyethylene bags in the cooling device have been prepared in the laboratory. Samples have been kept in the furnace at 100 °C for 24 hours and then reduced to powder using a mortar. Samples were sieved (100µ) and prepared as 1 g and then were digested using by acid mixture which contains HCI, HF, $HClO_4$ (1:1:6) of 10 ml were added to the samples of 1 g in the flask of 100 ml then it is filled up to 100 ml with ultrapure water (Bernhard, 1976).

Preparation of plant samples for analysis

The collected plants were *Phragmites australis, Carex otrubue, Ceratophyllum sp., Valisneria sp., Ranunculus sphaerospermus, Myriophyllum sp*.The plants have been dried at the air after being washed with tap water and pure water and then became dry with grinding and at 105 °C for 20 hours. HNO_3 which is ratio of 5:1 and $HCIO_4$ of 10 ml were added to the samples of 1 g in the flask of 100 ml. Then it is filled up 100 ml with ultrapure water).

RESULTS AND DISCUSSION

Marmara Lake has basic pH values and its water doesn't chance according to the seasons (Table 1). Oxygen amount temperature, conductivity and salinity also given Table 1.

A Differential Pulse Polarographic (DPP) method has been suggested for the simultaneous determination of heavy metals (cadmium, copper, lead and zinc) in samples.

Table 1. Physico-chemical parameters of Marmara Lake

	° C	pH	DO mg/L	ECμs/cm	Salinity %0
February	7	7.4	5,9	477	0,16
April	19	8.2	6,7	465	0,22
July	29	8.	6,7	650	0,29
October	22	8.1	7,9	852	0,28

The standard solution was scanned anodic direction from -1.15 V to +0.1 V versus a Ag/ACI(sat. KCl) electrode. Using the differential pulse mode peak potentials as E_p were -0.98 V; - 0.58 V; 0.40 V and 0.07 V for zinc, cadmium, lead and cupper respectively. The polarogram of the individual metal ions in the standard mix solution as shown in Figure 2.

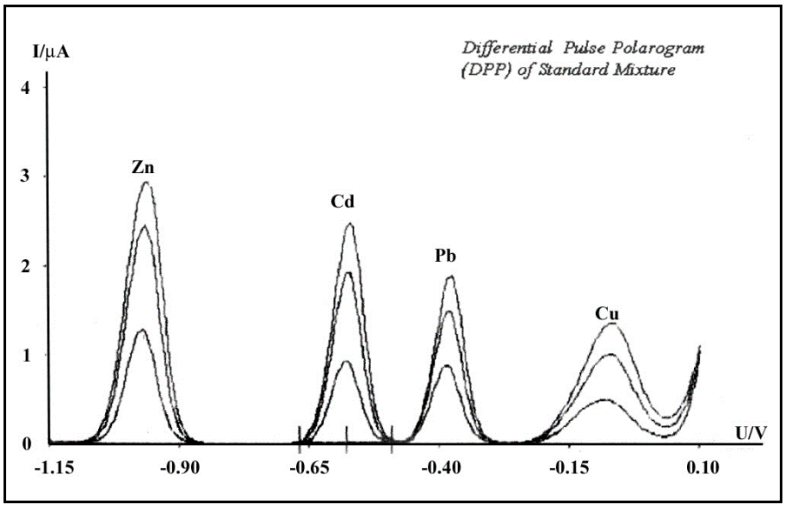

Figure 2. Differantial pulse voltammograms of simultaneous heavy metal ions

The Marmara lake is enriched by Gediz river. Trace element concentrations river basins depend on not only city waste inputs but also on the geochemical composition of the area (Akçay, 2003).

Table 2. Heavy metal ions values of samples according to seasons

	Zn mg/L	Cd mg/L	Pb mg/L	Cu mg/L
February	7.828	0.070	1.301	1.396
April	1.421	0.049	0.557	0.116
July	1.181	0.032	0.475	0.282
October	1.263	0.044	0.495	0.380
February	5.580	0.105	2.505	0.605
April	18.070	0.145	2.605	0.790
July	5.920	0.217	2.647	0.807
October	11.530	0.097	2.185	0.744
February	20.95	0.056	1.250	6.21
April	4.155	0.027	1.485	0.513
July	13.636	0.043	0.708	0.350

The standard deviation and mean values were given at Table 3.

The experimental results show that Zn mostly occurs in lake water, plant and sediments. These findings are compatible with other literature data obtained from other rivers and lake (Ure, 1993, Akçay, 2003, Somecka, 2001)

The Pb content Marmara lake sediments, water and plants are between 3,66-2.03 mgL^{-1},1.34-0.30 mgL^{-1} and 2.58-0.530 mgL^{-1}. The Zn content lake Marmara sediments, water and plant are between 3,45-.0 mgL^{-1}, 13.63-1.09 mgL^{-1} and 34.0-1.28 mgL^{-1}. While the Cd concentration of Marmara Lake sediments, water and plant ranges between 0,50 -0.09 mgL^{-1},0.084-0.02 mgL^{-1} and 0.021-0.093 mgL^{-1}. The Cu content lake Marmara sediments, water and plant are between 1,87-0.05 mgL^{-1}, 4.75-0.07 mgL^{-1} and 12.00-0.02 mgL^{-1}.

Table 3. Standard deviation and mean values of heavy metals in samples

	Zn mgL^{-1} Mean SD	Cd mgL^{-1} Mean SD	Pb mgL^{-1} Mean SD	Cu mgL^{-1} Mean SD
Water	2,86 ± 3,53	0.048 ± 0,018	0,43 ± 0,19	0,25 ± 0,20
Sediment	8,40 ± 7,33	0,14 ± 0,10	2,48 ± 0,48	0,73 ± 0,49
Plant	11,76 ± 9,85	0,05 ± 0,05	0,48 ± 0,35	0,28 ±0,23

Speciation data indicates that although there is no pollution risk the values are greater in the lake sediments. The fractionation pattern is in correlation with other literature data (Ure, 1993, Bougriet 1992, Akçay, 2003).

Strong positive correlations were found between concentrations of Zn in water and in plants and between Zn (Table 4).

Table 4. Statistically significant relations (Pearson Correlations, r) between chemical characteristic of water, sediments and plants*

Relations	P	r
Cd in water and Cd in plants	0.652	0.122
Pb in water and Pb in plants	0.587	- 0.147
Cu in water and Cu in plants	0.328	- 0.261
Zn in sediments and Zn in plants	0.680	- 0.112
Cd in sediments and Cd in plants	0.717	- 0.098
Pb in sediments and Pb in plants	0.050	- 0.497
Cu in sediments and Cu in plants	0.774	0.078
Zn in sediments and Zn in water	0.444	- 0.206
Cd in sediments and Cd in water	0.329	- 0.261
Pb in sediments and Pb in water	0.660	0.119
Cu in sediments and Cu in water	0.564	-0.156

* P = significance level

Marmara lake especially the region where Leuciperca leuciperca and Cyrinus carpio consumer has an importance as an economical resource for people. The factores which were located an the shores at the Gediz river that feeds this lake have a threat an people healt. As a result of this study, there is no danger now this time, but in the future the potential danger facts must be make disappear

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