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Study of heavy metal pollution in seawater of Kepez harbor of Canakkale (Turkey)

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Abstract In this work, the heavy metals cadmium and lead in Kepez harbor were studied with regard to the determination of the environmental pollution levels. Seawater samples of the Dardanelles (Canakkale Strait) were collected from the nearest station to Kepez harbor in July 2007. Then, the concentrations of these metals were determined after simple pretreatment of samples by the proposed inductively coupled plasma–atomic emission spectrometry (ICP-AES) method. The analysis of a given sample is completed in about 15 min by the ICP-AES method, and the concentrations of Cd and Pb were found to be 73.80 mg L^{-1} (relative standard deviation [RSD], 1.07%) and 9.39 mg L^{-1} (RSD, 0.70%), respectively. The accuracy of the applied ICP technique was checked by recovery studies, and good recoveries were obtained. The pollution levels of Cd and Pb recorded in this study were compared with those in other studies to analyze the water sample in Kepez harbor.

Keywords Kepez harbor · Cadmium · Lead · ICP-AES

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Introduction

Water pollution of heavy metals has become a question of considerable public and scientific concern in the light of the evidence of their toxicity to human health and biological systems (Yayıntas et al. 2007a, b; Anazawa et al. 2004; Özmen et al. 2004; Alonsa et al. 2004). This pollution can cause serious problems on the environment (Süren 2004; Süren et al. 2007). Discharge of sewage, industrial spoil dumping of ballast water, ship cause and in harbor facilities increase heavy metal concentrations in aquatic media (Süren 2004; Süren et al. 2007; Doğan and Soylak 2000). Water quality and properties also change with physical, chemical, and biological pollution of water. The changes in the properties of the water affect organisms living in the area (Novotry et al. 2000).

Heavy pollution in industrial areas such as gulfs and intercontinental seas is more important than open seas. Due to its being the transition point between the Sea of Marmara and the Mediterranean, pollution in the Dardanelles is

affected by the Black Sea and the Mediterranean due to upper and subflows. Metal pollution in the upper flows of the Dardanelles is especially more important than subflows. Recently, the rapid development of technology and industry in the coastal areas of the Marmara Sea has affected the upper layer waters in the Dardanelles and also the north Aegean Sea waters (Süren 2004; Süren et al. 2007). The increase of the concentration of heavy metals in the Dardanelles caused by anthropogenic waste waters is destroying the optimum stability of the aquatic environment. It is known that food chain in the seawater is seriously affected by Cd and Pb in seawater (Süren 2004; Süren et al. 2007).

The above-indicated reasons, the determination of Pb and Cd, have special importance in seawater samples (Novotry et al. 2000; Abollino et al. 2000). Therefore, accurate determination of these metals in seawater systems is taking much more attention. The conventional electrochemical determination of the trace levels of cadmium and lead has been done by anodic stripping voltammetry. The voltammetric method was firstly used to determine the concentration of Cd and Pb in seawater (Neeb 1959). Recently, anodic stripping voltammetry was also used to this purpose (Zirino et al. 1973; Abdullah et al. 1976; Gillain et al. 1979; Jurado-Gonzelez et al. 2003; Van den Berg 1986).

According to literature investigations, there is no study about the determination of the pollution levels of the heavy metals Cd and Pb in seawater of Kepez harbor by the proposed ICP-AES technique. In this study, the ICP-AES technique was used to determine the pollution levels of the heavy metals Cd and Pb in seawater samples of Kepez harbor.

Experimental

Apparatus and operating conditions

Quantitative determination of heavy metals in seawater was performed with a Varian (Liberty AX sequential) inductively coupled plasma–atomic emission spectrometer with a concentric glass type nebulizer; operating parameters are given in Table 1.

Table 1 Instrument operating parameters for ICP-AES

Parameter	Description
Radiofrequency power	1.20 Kw
Plasma gas flow rate	15.0 L/min
Auxiliary gas flow rate	1.50 L/min
Argon gas (high purity)	99.996%
Troiach type	Axiel
Nebulizer type	Glass
Replicates	3
Wavelength	Cd 226.50 nm
	Pb 220.35 nm

Reagents and solutions

All reagents used were of analytical reagent grade (Merck, Germany). Ultrapure water was used throughout all the experiments. A stock standard solution was prepared daily by appropriate dilution of AccuTrace, the reference standard (item number ICP-07W-1, USA) in ultrapure water with one to five drops of concentrated nitric acid. This solution was appropriately diluted in ultrapure water for prepared metal standard calibration solutions between 10 and 100 mg/L. Furthermore, the blank was prepared with ultrapure water containing one to five drops of concentrated nitric acid.

Study area and sampling station

Kepez harbor is located in the southwest part of Marmara Region of Turkey (Fig. 1). The surface water samples were collected by a polyethylene bottle at the station, shown in Fig. 1. The sampling station was the nearest to Kepez harbor on the Dardanelles.

Procedure of sampling

In this study, seawater samples collected from the nearest sampling station to Kepez harbor on the Dardanelles (Fig. 1) in July 2007 were analyzed for the concentrations of Cd and Pb.

For this aim, seawater samples were taken into polyethylene bottles (volume of 250 mL) and immediately transported to the laboratory for ICP-AES analysis. The pH of the samples was adjusted to about 2 by adding 3-mL concentrated HNO_3

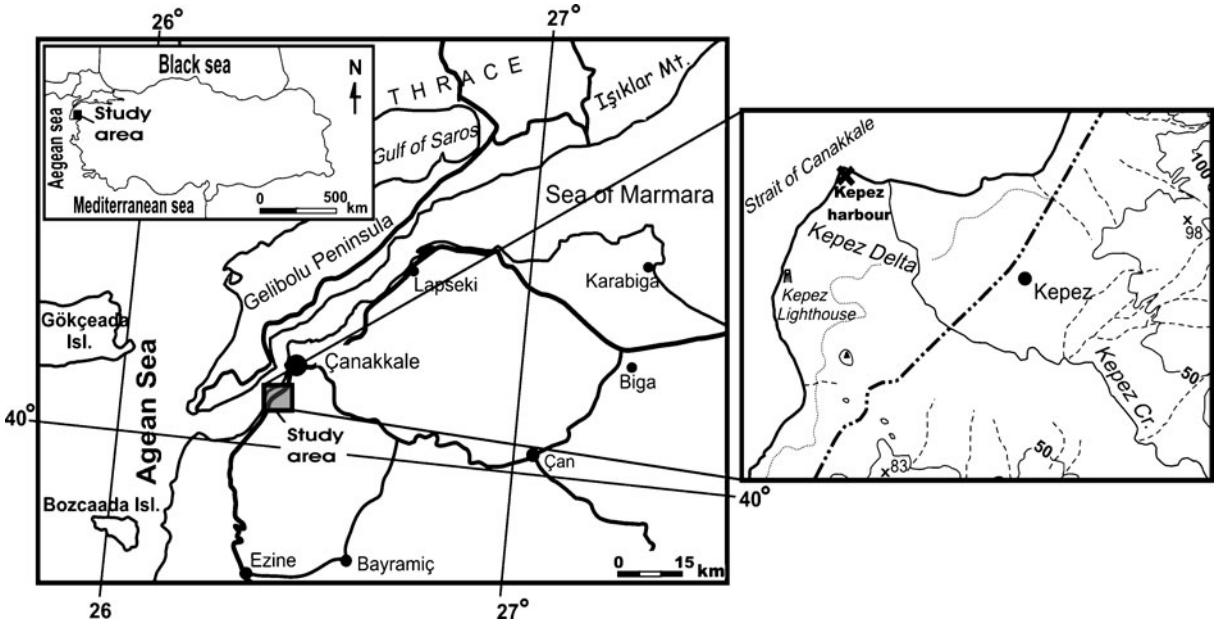

Fig. 1 Area of study with indication of sampling station

using a Hanna HI 8314 model pH-meter and these solutions stored in a refrigerator until the measurement process.

Procedure of sample mineralization

Ship wastes and harbor facilities cause serious pollution in the sampling area. Therefore, the acid digestion method was used to destroy the natural organic surfactants, and the complexing material in samples of polluted seawater before the ICP-AES measurements was taken. However, ultraviolet digestion is only recommended for slightly polluted samples (Metrohm 757 VA Computrace Software Manual, 2001 Computrace). After adding 3-mL concentrated HNO_3 to each sample, they were evaporated on a magnetic stirrer to dryness and then cooled to room temperature and digested with 5-mL concentrate HNO_3. Samples were put into a closed beaker and heated to dryness, then 10-mL dilute HCl and 15-mL ultrapure water were added to each sample. The samples were filtered and diluted to 25-mL deionized water (Yayıntas et al. 2007a, b; Süren 2004; Süren et al. 2007).

Determination of Cd and Pb in seawater by ICP-AES technique

After the mineralization procedure, seawater samples of 20 mL were diluted with ultrapure water, and then, these solutions were put into the ICP-AES apparatus sampling tubes, following which spectroscopic measurement was made under optimal instrumental parameters (Table 1) using the standard addition method for the determination.

Table 2 Analytical parameters for the determination of heavy metal levels in seawater sample at the nearest station to Kepez harbor by ICP-AES

Parameters	Cd	Pb
Linear concentration range (mg L^{-1})	1–100	1–100
Slope (s/M)	14,596.60	943.09
SD of slope	0.050	0.061
Intercept (s)	406.20	45.17
SD of intercept	0.050	0.050
Correlation coefficient (r)	0.999	0.999
Number of measurements (n)	5	5
LOQ (mg L^{-1})	73.80	9.39
RSD (%)	1.07	0.70

Table 3 Mean recoveries values of Cd and Pb obtained in seawater samples by ICP-AES technique

Added (mg L^{-1})	Cd Found (mg L^{-1})	Recovery %	Added (mg L^{-1})	Pb Found (mg L^{-1})	Recovery %
0[a]	73.80 ± 0.040	(RSD, 1.07%)	0[a]	9.39 ± 0.030	(RSD, 0.70%)
10[b]	83.70 ± 0.060	99.00	10[b]	19.09 ± 0.045	97.00
20[c]	93.50 ± 0.100	98.50	20[c]	29.08 ± 0.075	98.45

Each value is the mean (± standard deviation) of five experiments
[a]Sample (seawater)
[b,c]Added standard solution of Cd and Pb metals
RSD relative standard deviation

Results and discussion

Determination and validation

We performed direct quantitative determination of cadmium and lead in seawater samples by the ICP-AES technique. The sensitivity was calibrated by standard additions to the sample, and the initial metal concentrations were calculated by extrapolation.

Analytical parameters for the determination and the validation were evaluated for the ICP-AES methods using the proposed suitable set of experimental conditions (Tables 2, 3).

The limit of quantitation (LOQ) is given in Table 2, which was calculated from the intensity for the ICP-AES technique using the following equations (Riley and Rosanske 1996; Swartz and Krull 1997):

$$\mathrm{LOD} = 3s/m; \mathrm{LOQ} = 10s/m$$

where s, the noise estimate, is the standard deviation of the intensity for the ICP-AES (five runs) of the sample, and m is the slope of the calibration curve.

The found concentrations and the recovery values of the cadmium and lead in the seawater to nearest station of Kepez harbor are given in Table 3. As can be seen from Table 3, the concentrations of Cd and Pb were found in the upper layer of the seawater (0–10 m) as 73.80 mg L^{-1} (relative standard deviation [RSD], 1.07%) and 9.39 mg L^{-1} (RSD, 0.70%), respectively. These values indicated that both metal concentrations exceeded the limit values according to the Turkish Standards Institute (TSE), the World Health Organization (WHO), the Environment Protection Agency (EPA; Table 4), and the inland water quality classification (Table 5). In addition, good recoveries were obtained after the addition of known amounts of standard solutions of Cd and Pb (Table 3). Therefore, the applied ICP-AES technique was validated with these satisfactory results.

There are few published data on heavy metals in the Turkish Strait System (Bosphorus, Sea of Marmara, and the Dardanelles) and the Black Sea, and those data reflect a low concentration and very variable concentrations. This is probably due to analytical difficulties caused by their being in high seawater (Süren 2004; Süren et al. 2007). As results of this analysis, important pollution levels of cadmium and lead in the upper layer of the seawater of the Dardanelles were found and compared with open-sea levels (Table 3; Yayıntas

Table 4 Limit values according to the TSE, the WHO, and the EPA and found values in the seawater samples of the nearest station to Kepez harbor by the ICP-AES (Yayıntas et al. 2007a, b; Süren 2004; Süren et al. 2007)

	Limit values			Found values in seawater	
				Preconstruction Kepez harbor	After the construction of Kepez harbor
Heavy metals	TSE 266 (mg L^{-1})	WHO (mg L^{-1})	EPA (mg L^{-1})	Upper layer water (0–10 m; mg L^{-1})	Upper layer water (0–10 m; mg L^{-1})
Cd	0.010	0.010	0.010	0.019 ± 0.030	73.80 ± 0.040
Pb	0.050	0.050	0.050	0.049 ± 0.124	9.39 ± 0.030

Table 5 Limit values of some heavy metals (micrograms per liter) according to inland water quality classification (Yayıntas et al. 2007a, b; Süren 2004; Süren et al. 2007)

Heavy metals	Water quality classes			
	Class 1	Class 2	Class 3	Class 4
Cd	3	5	10	>10
Pb	10	20	50	>50
Cu	20	50	200	>200
Zn	200	500	2,000	>2,000
Cr^{+6}	<20	20	50	>50
Cr (total)	20	50	200	>200
Fe	300	100	5,000	>5,000
Ni	20	50	200	>200

et al. 2007a, b; Süren 2004; Süren et al. 2007). The high heavy metal concentration indicated that seawater near the Kepez harbor was so polluted that all living organism may be adversely affected by this pollution. One of the sources of this pollution may be Danube River discharges annually of about 280 tons of cadmium and 4,500 tons of lead, which reach to the seawater of the Dardanells (Süren et al. 2007; Balcı and Türkoğlu 1993; Turkoğlu et al. 1992; Mee 1992). Others may be discharge of sewage, industrial spoils duping of ballast water, ship cause and in harbor facilities.

In addition, in this study, we found that the pollution levels of Cd and Pb were compared with those of preconstruction of Kepez harbor (Table 4). As can be seen from this table, the pollution levels of the heavy metals Cd and Pb in a seawater sample collected in July 2007 are so higher than those (in July 2005) preconstruction of Kepez harbor. This indicated that seawater is so polluted because of the Kepez harbor facilities.

Conclusions

In this study, pollution of the heavy metals Cd and Pb was determined successfully in seawater samples collected from the nearest station to Kepez harbor by the ICP-AES technique. The concentration values of studied heavy metals were found to be high; these may have a toxic effect on sensitive plants and living organisms in seawater. In addition, no effective measures have yet been taken to prevent heavy metal pollution in the study area. Therefore, especially heavy metal pollution must be taken under control in here. To prevent health risks, it is necessary to clean wastewaters in purification plants to control the pollution sources and maintain water quality. Full purification systems should be established to remove the risk in the studied area (Yayıntas et al. 2007a, b; Süren 2004, Süren et al. 2007).

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