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ORIGINAL ARTICLE

Concentrations of cadmium and lead heavy metals in Dardanelles seawater

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Abstract Cadmium and lead were determined simultaneously in seawater by differential pulse stripping voltammetry (DPSV) preceded by adsoptive collection of complexes with 8-hydroxyquinoline (oxine) on to a hanging mercury drop electrode (HMDE). In preliminary experiments the optimal analytical condition for oxine concentration was found to be 2.10^{-5} M, at pH 7.7, the accumulation potential was -1.1 V, and the initial scannig potential was -0.8 V. The peak potentials were found -0.652 V for Cd and -0.463 V for Pb At the 60 s accumalation time. The limit of detection (LOD) and limit of quantitatification (LOQ) were found to be by voltammetry as 0.588 and 1.959 μg l^{-1} (RSD, 5.50%) for Cd and 0.931 and 3.104 μg l^{-1} (RSD, 4.10%) for Pb at 60 s stirred accumulation time respectively. In these conditions the most of the seawater samples are amenable for direct voltammetric determination of cadmium and lead using a HMDE. An adsorptive stripping mechanism of the electrode reaction was proposed. For the comparison, seawater samples were also analysed by ICP-atomic emission spectrometry method (ICP-AES). The applied voltammetric technique was validated and good recoveries were obtained.

Keywords Cadmium · Lead · Heavy metals · Oxine · Seawater · Waste water · Water pollution · Adsorptive stripping voltammetry · Inductively coupled plasma-atomic emission spectrometry

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1 Introduction

Heavy metal pollution is one of the most environmental problems in sea-water and sediment in the world. Discharge of sewage and industrial spoils increase heavy metal concentarations in aquatic area (Türkoğlu *et al.*, 1992; Balcı and Türkoğlu, 1993; Alonso *et al.*, 2004; Özmen *et al.*, 2004). However, dumping of balast waters, fuel-oil, sewage and other waste waters in ship cause addional pollution in sea-waters. The heavy pollution in industrial areas such as Gulfs and intercontinental seas is more important than open seas. Due to transition point between Sea of Marmara and Mediterranean, the pollution in the Dardanelles is effected by Black Sea and Mediterranean due to upper- and sub-flows. Especially, metal pollution in the upper flows of the Dardanelles is more important than sub flows. Recently, fast development of technology and industry on coastal areas of the Marmara Sea effects upper layer waters in the Dardanelles and also north Aegean Sea waters. The increase of trace elements and

heavy metals in the Dardanelles taht was caused by antrhopogenic waste waters, destroy the optimum stability of aquatic environment.

Generally, high metal acumulation of organisms and their consumption in food chain causes very important health problems. As a result, toxic metal accumulation in food causes serious healt problems (Türkoğlu and Parlak, 1999; Gündüz, 1999).

Especially, lead which was also takes place in bone effects that was needed for blood formation and nerve system (Doğan and Soylak, 2000).

It is known that the sea food chain is seriously affected by Cd and Pb in seawater. Therefore accurate determination of trace 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. Voltammetric method was firstly used to determine the concentration of Cd and Pb in seawater at 1959 (Neeb and Anal, 1959).

Recently anodic stripping voltammetry was also used for this purpose (Zirino *et al.*, 1973; Abdullah *et al.*, 1976; Gillain *et al.*, 1979; Van den Berg, 1986; Jurado-Gonzelez *et al.*, 2003).

In this study we aimed to determine the Cd and Pb pollution which were sourced from industrial waste and transportion in Black Sea, Marmara Sea and Umurbey Stream in Dardenelles. The different application of oxine to determine cadmium and lead by ASV in seawater is presented in this article (Van den Berg, 1986).

2 Materyal and methods

2.1 Instrumentation and operating conditions

Voltametric determinations of metals were performed with Metrohm 757 VA Computrace (Herisau, Switzerland); operating parameters are given in Table 1. HMDE (Hanging Mercury Drop Electrode) Multimode working, Ag/AgCl (3 M KCl) referans and platinum counter three electrode systems were used. Metrohm 744 and Hanna HI 8314 Models pH metres were used for pH measurements.

Spectroscopic determination of cadmium and lead were performed with a Varian Liberty Series II AX Sequential Model inductively coupled plasma-atomic emission spectrometer (ICP-AES) with a glass nebulizer and SPS 5 Autosampler; operating parameters are given in Table 2.

Table 1 Instrument operating parameters for voltammetry

Parameter	Description
Working electrode	(Hanging mercury drop electrode, HMDE)
Mode	(Differential Pulse, DP)
Calibration	Standard addition
Blank purge time (s)	300
Accumulation potential(V)	−1.10
Accumulation time (s)	60
Pulse amplitude (V)	0.05
Start potential (V)	−0.80
End potential (V)	−0.10
No of replication	3
Sweep rate (V/s)	0.015

2.2 Chemicals

All reagents used were of analytical reagent grade (Riedel and Merck). Double-distilled deionized water was used through all experiments.

Stock solutions of cadmium and lead were prepared by dilution of AccuTrace Reference Standard (MCS-01-1) solution for ICP-AES. A stock solutions of 0.1 M oxine (Riedel) was prepared in 0.2 M HCl (Riedel) and diluted with distilled water; this solution is stable for prolonged periods (months). Stock pH buffer solution of 1 M HEPES (4-(2-hydoxyethyl) piperazine-1-ethane sulphonic acid) (Fluka) was prepared in 0.5 M NaOH (Riedel). The initial studies were carried out in KCl (Merck) solutions prepared as seawater for voltammetry and in synthetic seawater samples for ICP-AES.

Table 2 Instrument operating parameters for ICP-AES

Parameter	Description
Rf power	1.20 Kw
Plasma gas flow rate	15.0 l/min
Auxilary gas flow rate	1.50 l/min
Argon gas (high purity)	99.996%
Troiach type	Axiel
Nebulizer type	Glass
Replicates	3
Wavelength	Cd 228.802 nm Pb 405.783 nm

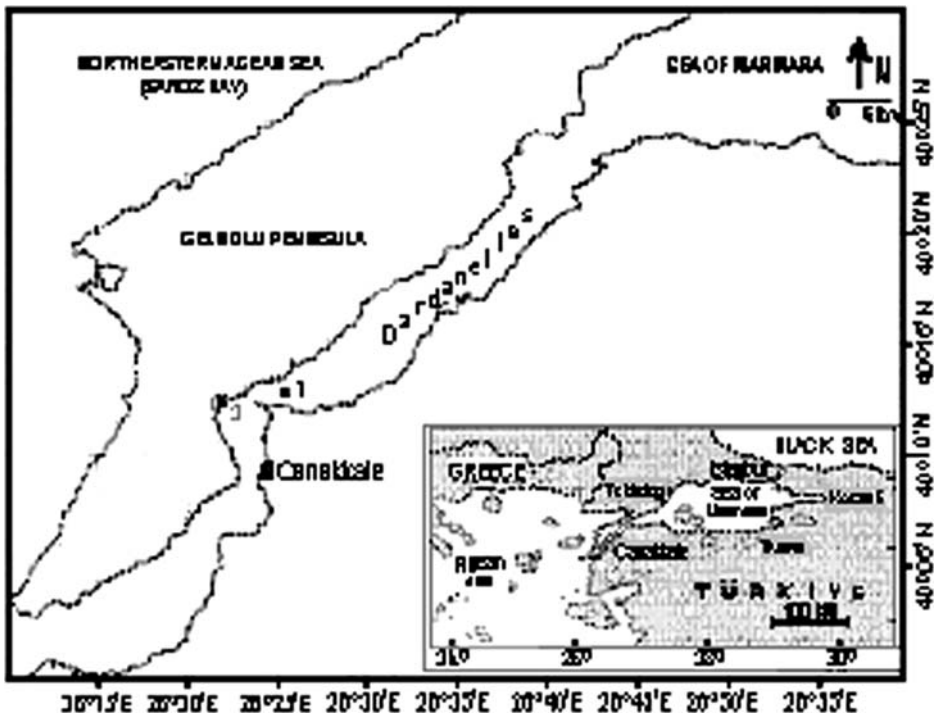


Fig. 1 Canakkale Straits (Dardanelles) and sampling stations: 1) Nara 2) Kilya.

2.3 Procedure of sampling

In this study, seawater samples collected from 2 sampling stations of Dardanelles (Fig. 1) in June and July 2003 and analysed.

Seawater samples taken by Nansen Sampling Bottle were filtered from 0.45 μm membran filtre by using glass milipore vacum apparatus on the ship and put into polyethylene bottles (500 ml volume). After the filtration, adjusted pH to 2 of the seawater samples with concentrated HNO_3 using Hanna HI 8314 model pH-meter and stored in the refrigerator at -20°C until the measurements.

2.4 Procedure of sample minerilazition

Ship wastes cause serious polution in sampling area so, acid digestion (wet digestion) method was used to destroy the natural organic surfactants or complexing material in samples from polluted seawater before the the voltammetric and ICP-AES measurements (UV-digestion is only recommended for slightly poluted samples and as a post-treatment step wet digestion solutions; Metrohm 757 VA Computrace Software Manual.: 2001 Computrace). After adding 3 ml concentrated HNO_3 to each samples, they were evaporated on magnetic stirrer to dryness and then cooled to room temparature and degisted with 5 ml concentrate HNO_3. Samples were put in to closed beaker and heated to dryness, then 10 ml dilute HCl and 15 ml deionized water added to each sample. Sample were filtered and diluted to 25 ml deionized water (EPA, Method 200.7, 1994).

Standards and blank were prepared according to sertificated artificial seawater (25.40 g NaCl, 5.08 g $MgCl_2$, 1.10 g $CaCl_2$, 0.72 g KCl, 0.03 g H_3BO_3 and 0.20 $SrCl_2$ were dissolved in 1 l deionized water (Parker,1972; Tran, 1992; Süren 2004).

Analysis conditions were optimizated after some experimental studies. The initial studies were carried out in KCl solutions prepared as seawater for voltammetry and in synthetic seawater samples for ICP-AES. At least three analysis were performed under optimal conditions.

2.5 Voltammetric measurements

10 ml of the sample is pipetted into the voltammetric cell, the pH is adjusted to 7.7 by addition of 0.01 M

(0.1 ml of the 1 M stock solution) HEPES and 2.10^{-5} M (0.2 ml of the 0.1 M stock solution) oxine (Gündüz, 2005) is added the solution is deaerated by purging with argon. At the −1.1 V accumulation potential, the strirrer is started and a new mercury drop is extruded, which signifies the beginning of the adsorption priod which is carried out for 60 s accumulation time depending on the metal cocentrations; the strirrer was turned off, and after a 10 s waiting period the potential scan is started in the positive direction, using the differential pulse mode; given other paremeters in Table 1. The procedure is repeated after a standard addition of metal ions. The peak potentials cadmium and lead were found −0.652 V and −0.463 V respectively.

2.6 Spectroscopic measurements by ICP-AES method

A 20-ml seawater samples were diluted with double-distilled deionized water and added 1–5 drops concentrated nitric acid. Then, spectroscopic measurement was made under optimal instrumental parameters (Table 2). The standard addition method was used for the determination.

3 Results and discussion

3.1 Adsorptive stripping mechanism of the electrode reaction

In the DPAdASV determination of Cd (II) and Pb(II) form a complex with oxine (Scheme 1; Gündüz, 2005), step (1), which subssequently adsorbed on the mercury drop electrode during the accumulation (deposition; surface solution or adsoption) step (2). Thus reduce to metal form during the accumulation step (3). Finally, metals in the complex are oxidised to initial ionic form of metals, which contributes to the oxidation current during the stripping step (4) (Jurada-Gonzolez *et al.*, 2003). These steps may be proposed as follows (Constant, 1984; Paneli and Volugaropoulos, 1993; Aycan, 1994; Sander, 1999; Yıldız and Genç, 1993; Yılmaz, 2001; Huang and Zhang, 2002; Vanysek).

$$M^{m+} + L_n \rightarrow (ML_n)^{m+}{}_{soln} \text{ complex form step} \quad (1)$$

$$(ML_n)^{m+}{}_{soln} + Hg \rightarrow (ML_n)^{m+}{}_{surf\ soln}\,(Hg) \quad \text{accumulation step} \quad (2)$$

$$(ML_n)^{m+}{}_{surf\ soln}\,(Hg) + m^- \rightarrow \left(M^{(0)}L_n\right)_{surf\ soln}(Hg) \quad \text{accumulation step} \quad (3)$$

$$\left(M^{(0)}L_n\right)_{surf\ soln}(Hg) \rightarrow M^{n+} + L_n + me^- + Hg \quad \text{stripping step} \quad (4)$$

in where; accumulation (deposition) step: (surface solution or adsorption); (M: Cd and Pb metals); (L: oxine as ligand); (m: charge of metal and number of electron transferred; (surf soln: surface solution) (Hg: Hanging mercury drop electrode).

3.2 Determination of Cd and Pb in seawater samples and validation of proposed method

Both methods were applied to the seawater samples succesfully. Cadmium and lead were determined by diferential pulse adsorptive anodic stripping voltammetry (DPAdASV) in seawater using an oxine concentration 2×10^{-5} M. Adsoption was carried out at −1.1 V for 60 s for both metals. The simultaneous adsorptive stripping voltamograms of Cd and Pb were given Fig. 2. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation.

Analytical prameters for the determination and validation were evaluted for both methods using the proposed suitable set of experimental conditions (Tables 3 and 4).

The limit of detection (LOD) and the limit of quantitation (LOQ) of the the procedure are shown in Tables 3 and 4. which was calculated for the peak current for voltammetry and the intensity for ICP-AES using the following equations (Riley and Rosanske 1996; Swartz and Krull 1997):

$$LOD = 3\,s/m \quad LOQ = 10\,s/m$$

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

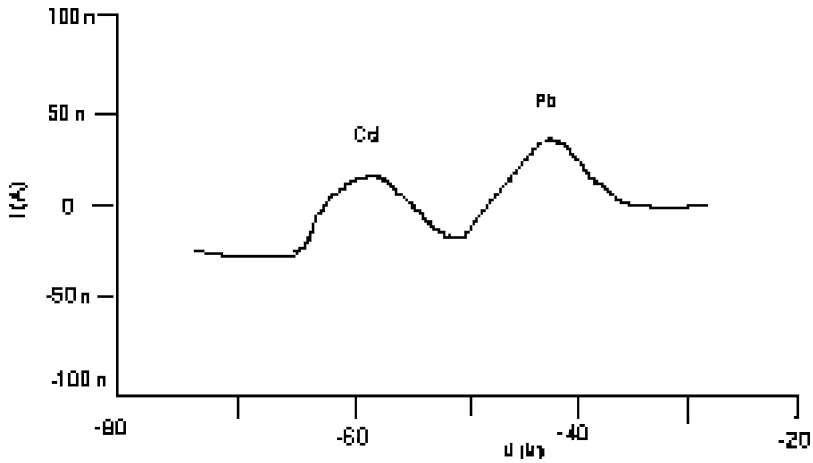


Fig. 2 Diferential pulse anodic stripping voltammetric (DPASV) peaks for cadmium and lead at 60 s accumulation time. The solution contained seawater (from Dardanells, Canakkale.

The vertical distribution of cadmium and lead concentration in the Dardanelles was given in Fig. 3. As seen from Fig. 3 the lowest concentrations were founded by voltammetry as 1.959 μg l^{-1} Cd (RSD, 5.50%) and 3.104 μg l^{-1} (RSD, 4.10%) Pb while 2.075 μg l^{-1} (RSD, 5.54%) Cd and 3.009 μg l^{-1} (RSD, 4.12%) Pb for ICP-AES.

The comparison of the results obtained by both methods suggest that the agreement between the two methods is satisfactory. According to the student's t-test (Table 5), the calculated t values did not exceed the theoretical value for significance level of 0.05. This result indicates that there is no significant difference between the proposed adsorptive differential pulse anodic voltametric technique and ICP-AES technique as regards to accuracy and precision. As can be seen from Table 5, good recoveries were obtained after the addition of known amount Cd and Pb standard solutions. So, applied voltammetric method validated with these good results.

Table 3 Analytical prameters for the determination of Cd and Pb metals in seawater by voltammetry

Prameters	Supporting electrolyte	
	Cd	Pb
Measuremed potential (V)	−0.652	−0.463
Linear concentration range (μg l^{-1})	2–10	3.5–10
Slope (nA M^{-1})	0.5513	0.4124
S.D. of slope	0.4313	0.3114
Intercept (nA)	0.1213	0.1124
S.D. of intercept	0.0120	0.0110
Correlation coefficent, r	0.999	0.999
Number of measurements (n)	5	5
LOD (μg l^{-1})	0.588	0.931
LOQ (μg l^{-1})	1.959	3.104
RSD %	5.50	4.10
Repeatibilty of peak current (R.S.D %)	1.10 for 1.50 (μg l^{-1})	1.98 for 1.50 (μg l^{-1})

Table 4 Analytical prameters for the determination of Cd and Pb metals in seawater by ICP-AES

Prameters	Cd	Pb
Linear concentration range (μg l^{-1})	2.5–10	3.5–10
Slope (s M^{-1})	9430	4286
S.D. of slope	0.010	0.010
Intercept (s)	94.96	99.02
S.D. of intercept	0.050	0.050
Correlation coefficent, r	0.998	0.999
Number of measurements (n)	5	5
LOD (μg l^{-1})	1.018	2.170
LOQ (μg l^{-1})	2.075	3.009
RSD,%	5.54	4.12
Repeatibilty of intensity (R.S.D %)	2.14 for 1.50 (μg l^{-1})	2.02 for 1.50 (μg l^{-1})

The advantages of the voltammetric method over ICP-AES was observed on samples preparation, sensitivity, rapidity and especially cost. Also there is no interferences in voltammetric method (Yılmaz, 2001).

Cd and Pb concentrations were found in between limit values of WHO, TSE and EPA (Table 6.) But, concentrations of cadmium (2.215–3.380 μg l^{-1}) and lead (3.290–4.432 μg l^{-1}) in the upper flow effected by Black Sea surface water were higher than cocentrations of cadmium (1.959–2.977 μg l^{-1}) and lead

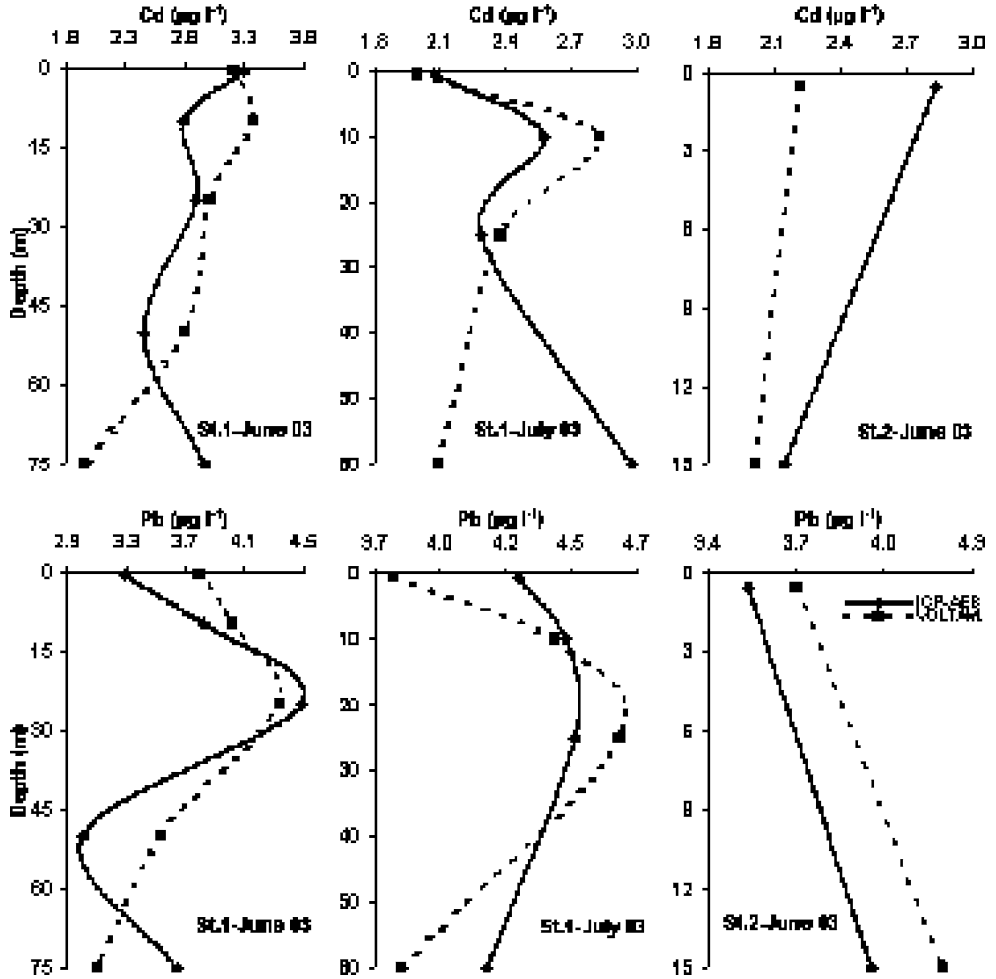


Fig. 3 Vertical distribution of cadmium and lead concentration in the Dardanelles in June and July 2003.

Table 5 Recoveries and comparison of Cd and Pb in seawater samples by voltammetry and ICP-AES methods[a]

Technique	Cd Added (μg l^{-1})	Cd Found (μg l^{-1})	Cd Recovery %	Pb Added (μg l^{-1})	Pb Found (μg l^{-1})	Pb Recovery %	t-test of ($p = 0.05$)
Voltammetry	0[b]	1.959 ± 0.108	(RSD, 5.50 %)	0[b]	3.104 ± 0.128	(RSD, 4.10 %)	Cd: 0.814*
	1.50[c]	3.339 ± 0.190	98.66	1.50[c]	4.577 ± 0.190	98.86	Pb: 0.377*
	2.50[d]	4.450 ± 0.245	98.19	2.50[d]	5.571 ± 0.231	98.68	
ICP-EAS	0[b]	2.075 ± 0.115	(RSD, 5.54 %)	0[b]	3.009 ± 0.124	(RSD, 4.12 %)	
	1.50[c]	3.525 ± 0.195	96.67	1.50[c]	4.485 ± 0.185	96.87	
	2.50[d]	4.475 ± 0.248	96.00	2.50[d]	5.447 ± 0.225	96.49	

[a] Each value is the mean (± standard deviation) of five experiments.
[b] Sample (seawater).
[c,d] Added standard solution of Cd and Pb metals.
* $t_{\text{theoritical}}$: 2.306 (95 % confidence limit).
RSD; relative standard deviation.

Table 6 Limit values of cadmium and lead according to TSE, WHO, EPA and founded sea-water values in the Dardanelles

	Limit values of cadmium and lead			Founded values in Dardanelles (Canakkale Strait) by voltammetry and ICP-EAS methods		
Heavy metals	TSE 266 (mg l^{-1})	WHO (mg l^{-1})	EPA (mg l^{-1})	Upper Layer Water (0–10 m) (μg l^{-1})	Interface Layer Water (25 m) (μg l^{-1})	Lower Layer Water (50–75 m) (μg l^{-1})
Cd	0.010	0.010	0.010	2.215–3.380	2.378–3.013	1.959–2.977
Pb	0.050	0.050	0.050	3.290–4.432	3.009–4.491	3.009–4.128

(3.009–4.128 μg l^{-1}) in the lower flow effected by salty Mediterranean deep water in summer period (June and July) in Dardanelles (Table 6, Fig. 3) (Anonymous, 1991). There were high concentrations of cadmium (2.378–3.013 μg l^{-1}) and lead (3.009–4.491 μg l^{-1}) in interface layer (25 m) of the Dardanelles according to the vertical distrubution (Fig. 3). However, Cd and Pb concentration increases with depth in Dardanelles. It is known that many contaminants are adsorbed onto particulate matter and may become trapped in the sediment. The sediment however is subject to resuspension and bioturbation, leading to the potential remobilisation of contaminants or their burial in deeper layers (Türkoğlu, 1992; Balcı and Türkoğlu, 1993; Türkoğlu and Parlak, 1999). Biological activity in surface waters incorporates the elements into particulate material, depleting concentrations in the dissolved phase. The decomposition of the particulate material as it sinks leads to a regeneration of the incorporated elements, and a consequent increase in dissolved phase concentrations with depth. By contrast the depth profile for lead (with a dominant atmospheric source and petrol) exhibits a surface maximum in concentration, followed by a decrease with depth associated with dilution and scavenging by particles.

There are a few published data on heavy metals in the Turkish Strait System (Bosphorus, Sea of Marmara and Dardanelles) and Black Sea, and those deta reflect low concentration and very variable concentrations. This is probably due to analytical difficulties caused by their in high sea water. Concentrations of metals in sea water are generally higher in the nearshore zones than further offshore and in the open sea. In particular, high levels of cadmium were found in the upper (2.215–3.380 μg l^{-1}) and lower layer (1.959–2.977 μg l^{-1}) of the Dardanelles compared with open sea levels of 0.01–0.05 μg l^{-1} (Table 6, Fig. 3). High levels of lead were also found in the upper (3.290–4.432 μg l^{-1}) and lower layer (3.009–4.128 μg l^{-1}) of the Dardanelles compared with open sea levels of 0.05 μg l^{-1}. Not only there were high levels in upper flow (Black Sea fresh water origin) but also in lower flow (Mediterranean salty water origin) levels of cadmium and lead in Dardanelles. High level of Pb concentration was originated from the lead mine which is located near Dardenells. It is known that high levels of cadmium are found along the coastline of Romania (up to 1.6 μg l^{-1}) (Dechev, 1990).

Concentrations of heavy metal are highly variable, and are generally higher in coastal waters, and lower in the open sea. Heavy metal concentrations generally are close to known values on the open sea, on average. However, elevated levels occur in the Turkish Strait System and in the Black Sea, especially Danube River discharges annually about 280 tons of cadmium and 4,500 tons of lead (Mee, 1992).

It is known that marine currents such as Turkish Strait System flux are important in the transport and distribution of contaminants.

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