

## **Heavy metals in shallow sediments from the Black Sea, Marmara Sea and Aegean Sea regions of Turkey**

### **Karadeniz, Marmara Denizi ve Ege Denizi sıđ sedimentlerinde ağır metalller**

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#### **Abstract**

In this work the total Cd, Co, Cr, Ni, Zn, Fe, Mn, Pb and Cu contents is measured in shallow sediments from the Bosphorus, Gökova, Marmara and Black Sea stations are measured. Generally Cd and Pb concentrations are lower than the detection limit (0.01µg/L) of the method in Yeşilırmak, Kızılırmak and Sakarya samples whereas Co, Cr, Ni, Zn, Fe and Mn contents are higher than the shale average. Cd is rather high in Bosphorus and Marmara sediments and Cd and Mn contents are rather high in Gökova sediments compared with shale average.

**Keywords:** Heavy metal, sediment, Black Sea, Marmara Sea

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#### **Introduction**

Many heavy metals concentrations in sediment are at least three orders of magnitude higher than the same metals in surrounding water. Especially the fine grained sediment which acts as a transport agent in the water column. The analysis of heavy metal levels in sediment samples helps in the

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interpretation of water quality (Heiny and Tate, 1997). The heavy metals are present in the river sediments as a result of urban discharge and industrial waste water beside of natural sources. The sediments are also used for determination of heavy metals when the concentrations in water are undetectable with present methods of analysis (Soares *et al.*, 1999).

Some papers have been published concerning heavy metal levels in sediment samples collected from the Turkish Black Sea and Aegean Sea coasts and Marmara Sea (Güven *et al.*, 1998; Algan *et al.*, 1999; Kut *et al.*, 2000; Balkis and Çağatay, 2001; Topcuoğlu *et al.*, 2002; 2004 a,b). No paper has been published on the heavy metal concentrations in polluted river mouth and shelf sediments in the Turkish marine environment.

In this work the heavy metal levels in sediment was determined at the Rivers of Sakarya, Kızılırmak and Yeşilırmak in the Black Sea and sediment samples were also collected from the Bosphorus, Marmara Sea and Aegean Sea.

## Materials and Methods



Figure 1. Sampling stations.

The sampling stations of sediment samples in the Turkish marine environment are shown in Figure 1. The surface sediment samples were taken by using a Van Veen type grab in November 1996, March 2001 April 2002, and June 2002 from the Bosphorus, Gökova, Marmara and Black Sea stations, respectively. The collected sediment samples were homogenized

and stored in plastic cups that were cleaned by 1:1 HCl and 1:1 HNO<sub>3</sub> before analysis.

About 100 g of sediment samples were dried at 85 °C for 48 h, crushed and homogenized prior to the analysis. Fe, Mn, Cu, Zn, Pb, Ni, Cd, and Cr contents were determined by atomic absorption spectrophotometer (Varian, Model Spectra AA 100/200 and Shimadzu 6701F). After a “total” digestion, involving HNO<sub>3</sub>+HClO<sub>4</sub>+HF acid mixture, Hg was analyzed by a flameless-AAS method following hot HNO<sub>3</sub> decomposition. The accuracy of the analysis was verified by analyzing the IAEA’s certified reference materials, SL-1 and lake sediment, by the same procedure. Values are expressed as the mean of three analyses for each sample.

## Results and Discussion

The heavy metal concentrations of sediments are shown in Table 1. The Cd and Pb concentrations in the rivers sediments were found to be below the limit of detection. However Cd level in sediments of Bosphorus, Marmara and Aegean Seas were found between 0.3-0.5 µg g<sup>-1</sup> and Pb content in the same stations determined 11.8-23.5 µg g<sup>-1</sup> dry wt. The Cr, Ni, Zn, Fe, Mn and Cu concentrations in the rivers sediment samples were generally higher than the other tested sediment samples.

The concentrations of Cd, Co, Cr, Ni, Zn, Fe, Mn, Pb and Cu in the sediment samples at the Turkish Black Sea were determined after collection in 1997, 1998 and 2001 (Topcuoğlu *et al.*, 2002, 2003, 2004a). The ranges of the metal concentrations were as follows (µg g<sup>-1</sup>): Cd, <0.02-0.9, Co, <0.05-86.2, Cr, 10.8-245; Ni, 2.2-79.2; Zn, 33.9-484.2; Fe %, 4.2-29.6; Mn, 206-2830; Pb, <0.05-84.2 and Cu, 11.5-528. Much higher concentrations of Cr and Ni were found at the stations in the Black Sea Rivers. On the contrary, Cd and Pb concentrations in the river sediment samples were lower than that found in present work. The Cr, Ni, Fe and Cu concentrations in the outside of the Yeşilirmak and Sakarya stations and inside the Kızılırmak station

indicated that regions were heavily polluted and approaching the “severe effect level” when compared with the Sediment Quality Guidelines of the Ontario Ministry (Persaud *et al.*, 1992).

The highest amounts of Co, Cr, Zn, Fe, Mn were found at the outside (a) than inside (b) of the Yeşilirmak and Sakarya Rivers. However, the lower concentrations on all the metals were observed at the outside zone of Kızılırmak River. The result showed that Kızılırmak mount and shelf zones were less polluted than the Yeşilirmak and Sakarya sediment samples.

**Table 1.** Heavy metal concentrations (mean and Standard Deviation) ( $\mu\text{g g}^{-1}$  dry wt) in sediment samples

Stations	Cd	Co	Cr	Ni	Zn	Fe %	Mn	Pb	Cu
Yesilirmak a	<0.02	63.7±2.3	1276.5±	128.1±1.	325.3±0.	4.7±0.01	2915±5	<0.01	59.9±1.0
Yesilirmak b	<0.02	33.6±1.9	370.8±1.	129.9±1.	119.8±0.	8.5±3.87	864±3	<0.01	43.7±2.1
Kızılırmak a	<0.02	22.7±1.2	231.9±1.	104.6±1.	91.4±0.5	4.9±0.01	989±4	<0.01	23.0±0.3
Kızılırmak b	<0.02	27.4±1.2	720.6±1.	120.0±2.	119.5±0.	7.8±0.03	1206±1	<0.01	27.6±0.7
Sakarva a	<0.02	79.2±1.3	2496.8±	134.3±4.	456.6±0.	48.1±0.2	3696±18	<0.01	39.1±1.9
Sakarva b	<0.02	22.2±0.5	135.3±1.	144.3±3.	106.4±0.	4.1±0.01	896±3	<0.01	42.8±1.1
		Hg							
Marmara	0.4±0.1	0.03±0.0	57.9±15.	31.6±14.	40.8±9.5	4.9±0.5	548±67	17.2±5.2	27.8±9.9
Bosphorus	0.5±0.2	0.48±0.2	19.2±6.5	99.6±48.	17.8±5.8	1.98±	202±50	23.5±5.2	12.0±3.5
Gökova	0.3±0.1	0.05±0.0	99.8±66.	8.0±4.1	17.0±5.2	4.1±0.8	1759±98	11.8±5.4	22.4±7.7

(a) Outside of the river, (b) Inside the river

The polluted streams or rivers transfer their heavy metal load to the coastal marine environment. Kızılırmak River is a pollution source for the coastal waters of the Black Sea (Yücesoy, 1991). The concentrations of the heavy metals in estuarine zone (a) of the Yeşilirmak and Sakarya Rivers were higher than at the station (b) in the same rivers.

A fertilizer plant and copper smelter located near the Yeşilirmak River and iron and steel complex industry and thermal power plant in the eastern coastal site of the Sakarya River are important sources of particularly heavy metals. In addition, the secondary sources of high metal levels are the erosion products of mineralized zones in the drainage basin of these rivers.

The Cd concentration in the Bosphorus, Marmara and Gökova sediment samples were similar. However, high concentrations of Hg, Ni, Pb and Cr, Mn and Zn, Fe, Cu in sediment samples were found in the Bosphorus, Gökova and Marmara sediments.

A comparison of the present results in the Bosphorus and Marmara Sea sediment samples with the data reported by Bodur and Ergin, 1994; Algan *et al.*, 1999 and 2004; Balkıs and Çağatay, 2001; Topcuoğlu *et al.*, 2004b; suggested that the concentrations of Cd, Co, Cr and Pb are not higher than in the surface sediments of the same sea. However, Fe and Mn in Marmara and Ni in the Bosphorus sediments are high. The concentrations of Zn and Cu have similar level.

The concentration being of Hg, Cd, Pb, Cr, Ni and Zn in sediment samples were determined after collected from the İzmir Bay and Kavala Gulfs at the Aegean Sea (Kamidis *et al.*, 2004). When comparing their results with the presented data in Gökova station, the Cr, Ni, Zn and Pb content have significantly decreased, but Cd and Hg concentrations did not changed in the same sea sediments.

## Özet

Bu çalışmada Kasım 1996, Mart 2001, Nisan 2002 ve Haziran 2002 yıllarında İstanbul Boğazı, Gökova, Marmara Denizi ve Karadeniz'den alınan yüzey sedimentlerinde toplam Cd, Co, Cr, Ni, Zn, Fe, Mn, Pb ve Cu içerikleri incelendi. Yeşilirmak, Kızılırmak ve Sakarya örneklerinde Cd ve Pb miktarı ölçüm limitlerinin altındadır (0.01 µg/l). Co, Cr, Ni, Zn, Fe ve Mn içerikleri ise şeyl ortalamasının üzerindedir. İstanbul Boğazı ve Marmara sedimentlerinde Cd, Gökova sedimentlerinde ise Cd ve Mn şeyl ortalamalarından oldukça yüksektir.

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