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RESEARCH ARTICLE

Assessment of heavy metal (Zn, Pb, Fe) contamination in surface sediments of creeks flowing to inner part of Izmir Bay (Eastern Aegean Sea)

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Abstract

The objective of this study is to evaluate the new environmental situation following the waste water treatment facility built in 2000 by determining Zn, Pb and Fe concentrations of samples obtained in 2007-2008 from surface sediments of seven creeks flowing into Izmir Bay. Zn concentrations ranged between 5.25-928.76 mg/kg, Pb between ND-265.92 mg/kg and Fe between 22700-141770 mg/kg. Enrichment factor (EF) values show that Zn and Pb mainly originated from anthropogenic sources. While average contamination factor (CF) values displayed a change from moderate contamination to considerable contamination for Zn, contamination level varied between considerable and high in terms of Pb. As Fe is an element originating from the natural structure of the earth, low-moderate contamination levels were detected in the sediments. Although the waste water treatment facility of the municipality started to operate partially in 2000 and in full capacity in 2002, the result of this study revealed the outstanding fact that high amounts of heavy metals were still found in the creeks which should have only included rain water in 2007-2008 when this study was conducted.

Key words: Izmir Bay, heavy metals, enrichment factor, contamination factor, sediment.

Introduction

Marine sediments provide useful information for environmental and geochemical pollution. Urban and industrial activities contribute to the introduction of significant amount of pollutants into the marine environment and affect directly the coastal ecosystem. At the same time, heavy metals, pesticides, and other toxic substances could be absorbed from the water column onto the surface of fine particles and usually move thereafter with sediments (Uluturhan

2010). Contaminated marine sediments have been recognized as a major repository for persistent toxic substances released to the aquatic environment from various sources (Zabetoglou *et al*. 2002). The heavy metal content of sediments comes from natural sources (rock weathering, soil erosion, dissolution of water-soluble salts) as well as anthropogenic sources such as municipal wastewater-treatment plants, manufacturing industries, and agricultural activities. In prevalent industries with heavy metal content in their wastewaters are: textile (on Manda and Sepetci Creeks), chemicals (on Melez and Sepetçi Creeks), metal (on Manda, Melez, Ilıca, and Bostanlı Creeks), automotive (on Manda Creek) industries, the tanneries (on Manda and Melez Creeks), and the industrial zones (on Melez and Old Gediz Creeks) (İZTO1995).

The Bay of Izmir is one of the most naturally productive coastal areas in the Aegean Sea (Figure 1). The bay is divided into an inner, middle and outer bay with respect to the topographical and hydrographical characteristics. The inner part of the bay had received domestic and industrial wastewaters mainly by sewage discharge and small creeks before the construction of a wastewater treatment plants. Because of the limited water exchange with the outer part of Izmir Bay and Aegean Sea, the pollution of the inner bay had reached unacceptable levels. For this reason, a wastewater treatment plant was built in 2000. The sewage system of the city was connected with the wastewater treatment plant. Thus it was expected that creeks should contain only rain water. The aims of this study are to determine both the heavy metal contamination in the surface sediments of seven creeks flowing to inner Izmir Bay after the construction of wastewater treatment plant. Although there are many studies to determine contamination levels of the bay, this study reflects the first results on heavy metal levels of seven creeks simultaneously after the treatment plant operation was started.

Materials and Methods

Within the scope of the study, sediment samples of seven creeks (Old Gediz outfall, Bostanlı, Bayraklı, Bornova, Manda, Meles and Balçova) flowing into Izmir Bay were collected seasonally by a TFO core sampler between September 2007 and July 2008 (Figure 1). Coordinates of the stations where samples were collected are given in the Table 1.

Samples were stored at -20 C°. After they were dried in a drying oven at 60 C°, they were prepared by being pestled in the mortar. For heavy metal analyses of sediment samples, 0.2 g dry sediment was extracted in a HCI, HNO_3 and $HClO_4$ acid mixture. Fe, Zn and Pb analyses were carried out with methods specified in Metrohm 797 VA Application Book (AWUK4-0134-042002) by 797 VA Computrance model Metrohm Voltameter with the use of Differential Puls Anodic Stripping Voltametry. Lower limit of measurements were 2 ng/g for Pb, 1.2 ng/g for Zn and 250 mg/g for Fe.

Table 1. Coordinates of the stations

	North	East
Old Gediz	38° 28' 56,82"	27° 3' 28,48"
Bostanlı	38° 27' 23,38"	27° 5' 37,69"
Bayraklı	38° 28' 0,86"	27° 9' 31,40"
Bornova	38° 27' 36,65"	27° 10' 2,14"
Manda	38° 26' 52,55"	27° 10' 22,82"
Meles	38° 26' 29,39"	27° 10' 6,74"
Balçova	38° 24' 48,68"	27° 1' 56,72"

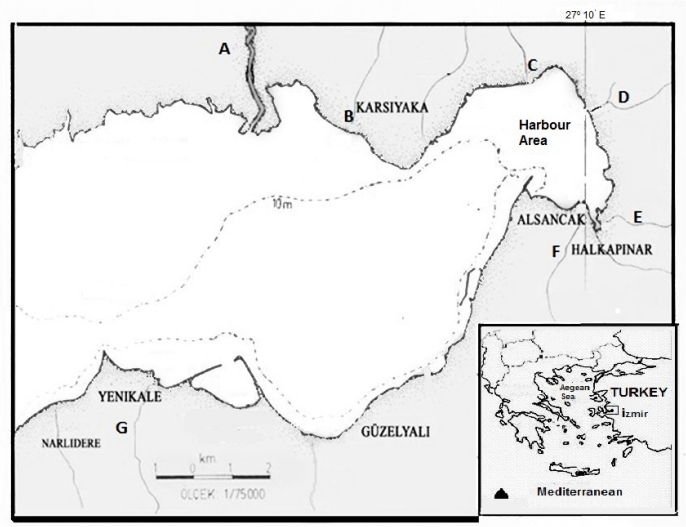

Figure 1. Location of sampling stations (A: Old Mouth of Gediz River, B: Bostanlı Creek, C: Bayraklı Creek, D: Bornova Creek, E: Manda Creek, F: Meles Creek, G: Balçova Creek)

Two techniques were used in order to evaluate the contamination. First of them was the enrichment factor (EF) to determine the anthropogenic contribution to the heavy metal concentration in the sediment (Zhang *et al*. 2007). This factor was obtained by dividing the measured metal/Al (or Fe) rate into the metal/Al (or Fe) rate belonging to the period before contamination. In these calculations, either Al or Fe was preferred as they were conservative and free from anthropogenic effect. Turekian and Wedepohl (1961) crustal average contamination of the trace metals for the background concentrations were used in this study.

Second of them was the contamination factor (CF), which was calculated as the ratio between the sediment metal content at a given station and the normal concentration levels, reflected the metal enrichment in the sediment. CF was classified into four groups in Hakanson (1980).

When ;

CF < 1, there is no metal enrichment by natural or anthropogenic inputs,
1 ≤ CF < 3, the sediment is moderately contaminated by the element,
3 ≤ CF < 6, the sediment considerable contaminated,
CF > 6, there is very high contamination for that metal.

Results and Discussion

Minimum, maximum and average values of the variables are given in Table 2.

Table 2. Minimum, maximum and mean values of heavy metal concentrations mg/kg for Zn and Pb, g/kg for Fe

	Zn	Pb	Fe
	Min-max mean	**Min-max mean**	**Min-max Mean**
Old Gediz	5.25-393.55 207.58	BDL*	52.37-71.18 61.17
Bostanlı	83.4-326.83 196.2	BDL	40.54-51.33 48.41
Bayraklı	81.2-384.67 192.91	BDL-129.32 44.46	32.15-42.81 38
Bornova	168.21-241.55 215.59	BDL-254.16 74.17	39.6-42.93 41.1
Manda	465.85-928.76 606.89	41.35-265.92 180.28	22.7-53.98 37.54
Meles	188.77-439.84 157.15	61.93-187.11 62.26	45.1-77.78 30.72
Balçova	166.0-296.59 223.55	BDL-83.39 30.65	67.18-141.77 90.35

*Below detection limit

Zn concentration reached at its highest level in Manda Creek in December 2007 and this value was considerably higher than the values observed in all creeks throughout the year. Manda Creek was followed by Balçova and Bornova creeks. The lowest Zn levels were observed in Bostanlı Creek (Figure 2).

Manda Creek was also the only creek whose sediments revealed Pb concentrations during four seasons and the highest Pb level was observed in this creek. None of the samples taken from Old Gediz Outfall and Bostanlı Creek displayed Pb content. Manda Creek was followed by Meles and Bornova creeks in terms of Pb concentration. The lowest Pb level was observed in Balçova Creek (Figure 2).

When they were examined in terms of Fe concentration, the highest level was found in Balçova Creek while the lowest Fe concentration on average was

detected in Meles Creek. It was also determined that Fe levels did not change significantly in the other creeks throughout the year (Figure 2).

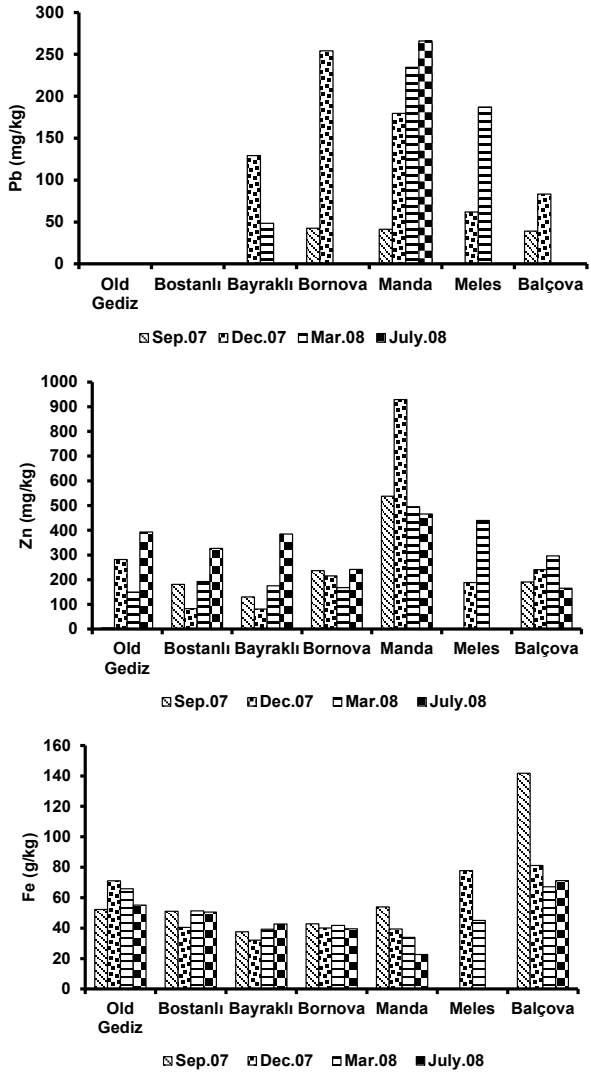

Figure 2. Spatio-temporal variations of heavy metals

Results obtained with the samples of sediments belonging to seven creeks flowing into Izmir Bay were compared to the studies previously conducted in Izmir Bay and in other areas of both Turkish and Greek regions of the Aegean

Sea (Table 3). It was observed that Zn values obtained in this study were higher than many values measured in other regions. The maximum value detected in this study was only exceeded by the studies carried out in Theassoloniki and Izmir Bay. The maximum value reached with the samples containing Pb in the sediment (in Manda Creek) was highly above the values observed in many bays situated in the Aegean Sea. However, when Pb values of the other stations in the study were examined, highly significant differences were not detected between them and the values obtained in the aforementioned bays (except for Saros and Gökova Bay). The closest value to the calculated maximum value was detected in Thermoikos Bay of Greece. Fe content in the sediment generally was not anthropogenic. CF values also confirmed this finding. It was found that Fe concentration measured in the creek sediments was higher than that found in other bays. However, it is close to the values belonging to Izmir Bay.

Güven and Akıncı (2008) reported that the highest metal concentrations (except for Pb) were found at the port section of the bay and the underlying reason of these high values was Manda, Meles, Bornova and Sepetçi Creeks flowing into this section. Our study covering Manda, Meles and Bornova creeks flowing into this area also supports this finding as the maximum Zn concentration values were observed in the creeks flowing into the port. However, in contrast to Pb concentrations reported in the above mentioned study for the bay, the maximum values for this element were also observed in the creeks flowing into this region in our study. The same study emphasized that the bay could be enriched in Zn by the Old Gediz and Manda creeks due to the existence of metal and automotive factories along them. High Zn concentrations in the sediments of these creeks confirmed this point.

In the studies conducted before the water treatment facility was opened at Izmir Bay, the highest metal concentrations were found at discharge points of creeks and at the bay (Atgın *et al*. 2000). Detection of high amount of metal in the creek sediments in spite of the water treatment facility demonstrates that there are still waste water inputs which are not treated at these points.

Enrichment Factor

Minimum, maximum and average EF values were given in Table 4 while spatio-temporal alteration of EF was given in Figure 3. The highest EF values for Pb were calculated at Manda Creek. In the other stations, values were also above 1.5 except for September 2007 sampling of Balçova Creek. This shows that Pb enrichment in the sediment was anthropogenic.

Two stations where EF exceeded 1.5 in all samples for Zn were Bornova and Manda. The biggest enrichment amount of Zn was calculated in these stations. Although it was observed that EF values sometimes fell below 1.5 in the other stations, average values were above 1.5 at all stations except for Balçova Creek. This also points out a significant, anthropogenic enrichment in the creeks.

Table 3. Comparison of the ranges of heavy metal concentrations (mg/kg) found in this study with previous studies in Izmir Bay and different parts of the Aegean Sea

	Zn	**Pb**	**Fe**	**References**
Saros Gulf	48.7-121	3.9-48.2		Uluturhan 2010
Gökova Gulf	47.9-90.9	10-21.8		Uluturhan 2010
Güllük Gulf	0.34-9.05		692-6785	Başaran *et al.* 2010
Çandarlı Gulf	55-358	14.5-137.8		Pazı 2011
Çandarlı Gulf	63.23-105.1	2-35.5	12199-30340	Taş *et al.* 2007
Nemrut Bay	75-271	22.3-89.4	10507-45828	Esen *et al.* 2010
East Cost of Greece (polluted area mean)	152.5		39200	Nicolaidou and Nott 1998
Thessaloniki Bay (mean)	28-1014	3.1-77	6300-19000	Zabetoglou *et al.* 2002
Thermaikos Bay	96-429	42-264		Karageorgis *et al.*2003
Norteastern Aegean Sea	69.9-136	26-80.5		Kanellopoulos *et al.* 2006
Izmir inner Bay (avg)	260	62	46000	Atgın *et al.* 2000
Izmir Bay	14-311	6.7-103		Küçüksezgin 2001
Middle and Inner İzmir Bay		44-113		Küçüksezgin *et al.* 2006
Izmir Inner Bay	242.3-254.6	71.3-85.3		Gündoğdu *et al.* 2007
Izmir Inner Bay	217-1031	18-203		Güven and Akıncı 2008
Izmir Inner Bay	93.5-295		42109-68901	Kontaş 2008
This Study	5.25-928.76 257.12 (mean)	ND-265.92 55.97 (mean)	22700-141770 49610 (mean)	

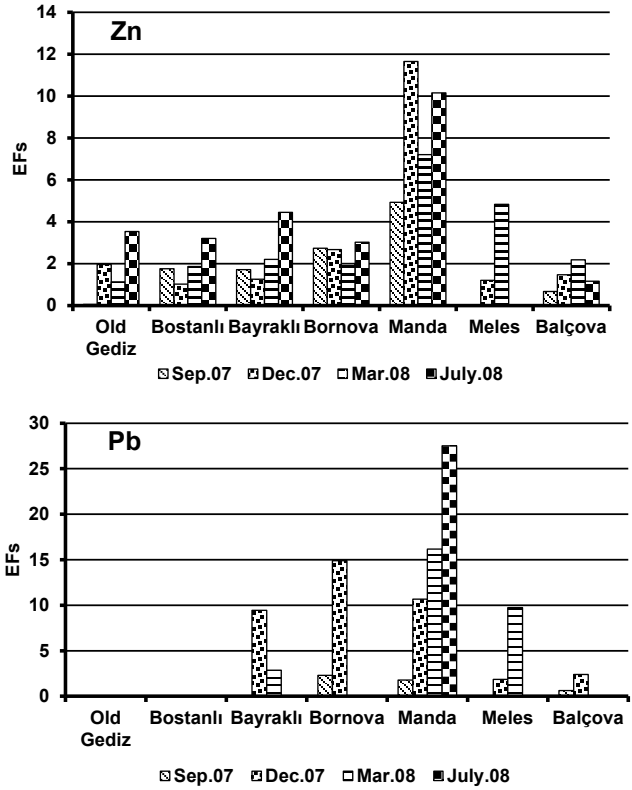

Figure 3. Enrichment factors at samling stations

Contamination Factor

Minimum, maximum and average CF values were given in Table 4 while spatio-temporal alteration of CF was given in Figure 4. The highest CF values for Pb were detected at Bornova and Manda creeks. In these stations, sediment was specified as "highly contaminated". For the other stations, considerable contamination was observed.

Table 4. Range (top) and mean values (bottom) of EF and CF

	EFs Zn	EFs Pb	CF Zn	CF Pb	CF Fe
Old Gediz	0.05-3.53 1.67	-	0.06-4.14 2.19	-	1.11-1.51 1.3
Bostanlı	1.02-3.20 1.96	-	0.88-3.44 2.07	-	0.86-1.09 1.03
Bayraklı	1.25-4.45 2.4	2.90-9.45 6.17	0.85-4.05 2.03	2.43-6.47 4.45	0.68-0.91 0.81
Bornova	1.99-3.02 2.6	2.33-14.91 8.62	1.77-2.54 2.27	2.13-12.71 7.42	0.84-0.91 0.87
Manda	4.93-11.65 8.48	1.80-27.53 14.05	4.90-9.78 6.39	2.07-13.30 9.01	0.48-1.15 0.8
Meles	1.20-4.82 3.01	1.87-9.75 5.81	1.99-4.63 3.31	1.20-4.82 3.01	0.96-1.65 1.31
Balçova	0.67-2.18 1.37	0.65-2.41 1.53	1.75-3.12 2.35	1.96-4.17 3.06	1.43-3.02 1.92

The highest CF for Zn was calculated at Manda Creek. While high contamination was observed in this station in the measurement of December 2007, the other measurements revealed considerable contamination. When average CF values were taken into consideration, sediments were found moderately contaminated at all stations except for Manda and Meles and these two stations were reported as considerably contaminated.

The highest CF for Fe was calculated at Balçova Creek. Even though this value indicates that the sediment was considerably contaminated, according to the average CF value, Balçova Creek had a moderate contamination level together with Old Gediz outfall and Bostanlı Creek. The other stations displayed low contamination.

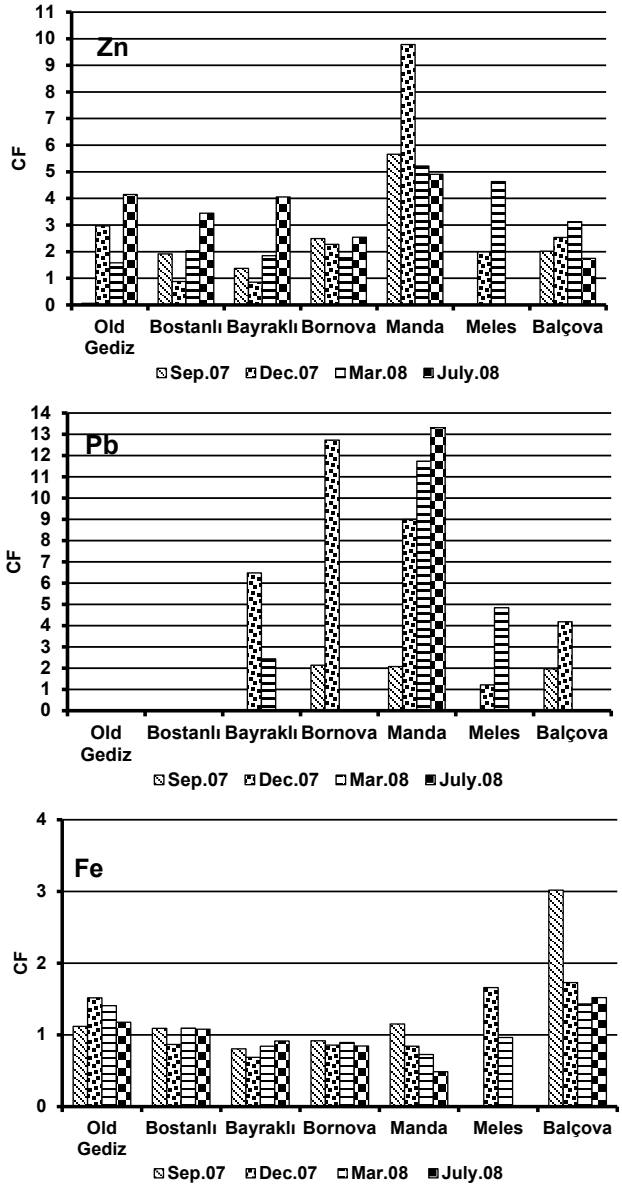

Figure 4. Contamination factors at sampling stations

Conclusion

At the end of Zn, Pb and Fe measurements performed with sediment samples collected from seven creeks flowing into Izmir Bay, it was determined that particularly Zn and Pb levels were significantly high. The calculated EF values demonstrated that the enrichment in the sediment largely resulted from anthropogenic factors. While average CF values show a change from moderate contamination to considerable contamination for Zn, contamination level varies between considerable and high in terms of Pb. As Fe is an element originating from the natural structure of the earth, low-moderate contamination levels are detected in the sediments. Although the waste water treatment facility of the municipality started to operate partially in 2000 and in full capacity in 2002, it was an outstanding result that high amounts of heavy metals were still found in the creeks which should have only included rain water in 2007-2008 when this study was conducted.

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İzmir iç Körfezi'ne (Doğu Ege Denizi) akan derelerin yüzey sedimentlerinde ağır metal (Zn, Pb, Fe) kontaminasyonlarının değerlendirilmesi

Özet

Bu çalışmanın amacı İzmir Körfezi'ne akan yedi derenin sedimentinden elde edilen örneklerde Zn, Pb ve Fe konsantrasyonlarının belirlenerek, 2000 yılında devreye giren atık su arıtma tesisi sonrası oluşan yeni çevresel durumun değerlendirmesinin yapılmasıdır. Zn konsantrasyonları 5.25-928.76 mg/kg, Pb ND-265.92 mg/kg ve Fe 22700-141770 mg/kg aralığındadır. EF değerleri Zn ve Pb'nin ağırlıklı olarak antropojenik kaynaklardan geldiğini göstermektedir Ortalama CF değerleri; çinko için "kısmı" kontaminasyondan "dikkate değer" kontaminasyona değişim gösterirken, Pb için kontaminasyon düzeyi "dikkate değer" ve "yüksek" seviye arasında dağılmaktadır. Fe yerin doğal yapısından kaynaklanan bir element olduğundan, "düşük-kısmi" seviyede kontamine sediment düzeyleri saptanmıştır. Belediyeye ait atık su arıtma tesisi 2000 yılında kısmi kapasiteyle, 2002 yılında ise tam kapasiteyle çalışmaya başlamış olmasına rağmen, bu çalışmanın sonuçları çalışmanın yapıldığı 2007-2008 yıllarında sadece yağmur suyu taşıması gereken derelerde yüksek miktarlarda ağır metal bulunduğunu dikkate değer bir durum olarak ortaya koymaktadır.

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