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A New Assessment of Heavy Metal Contaminations in an Eutrophicated Bay (Inner Izmir Bay, Turkey)

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Abstract

The distribution, controlling geochemical factors and contamination status of heavy metals in inner Izmir Bay (Eastern part of Aegean Sea) were investigated. 23 surface sediment samples were collected and analized for major elements (Al and Fe), heavy metals (Pb, Zn, Cd, Cu, Hg, Cr, Mn), organic matter, grain size composition, carbonate and Chl.-a. Metals controlling factors were elucidated based on statistical methods such as the Pearson product-moment linear correlation and Factor Analysis. The results illustrated that Pb, Zn, Cr and Cd are mainly controlled by organic matter and a lesser extent Fe. Pb also controlled by carbonate and Mn additionally. Other controlling factor on Cr and Cd are Chl.-a via uptake in water column and then sedimentation. Cu and Hg are mainly controlled by Chl.-a. Some evidences were found on changing of carrier phases. The results indicated that contamination of surface sediments in inner Izmir Bay is dominated Pb, Hg, Cd, Zn and to a lesser extent Mn, Cu, Cr and Fe. Igeo classification was consistent with the Enrichment Factor ans Contamination Factor classes generally. Geoaccumulation index values for Zn, Hg, Cr and Cd have decreased two contamination classes from 1994 to 2008, whereas Pb has remained the same and Cu has decreased only one class. Generally Cu, Zn, Pb, Hg and Cr contaminations were below effects range median values. The extent of heavy metal contamination and degree have been affected significantly by sedimentological parameters such as grain size, organic carbon, carbonate and chloropyll-a.

Keywords: Heavy metal, enrichment factor, contamination factor, geoaccumulation index, sediment quality guidelines.

Eutrofik Bir Körfezde (İzmir İç Körfez, Türkiye) Ağır Metal Kontaminasyonlarına Yeni Bir Yaklaşım

Özet

Bu çalışmada İzmir İç Körfezindeki (Doğu Ege Denizi) mevcut ağır metalleri etkileyen jeokimyasal faktörler, kontaminasyon durumları ve bu metallerin dağılımları araştırılmıştır. 23 istasyondan yüzey sediment örnekleri toplanarak, bu örneklerde majör elementlerin (Al ve Fe), ağır metallerin (Pb, Zn, Cd, Cu, Hg, Cr, Mn), organik karbon, karbonat, klorafil-a ve tane boyu dağılım analizleri yapılmıştır. Faktörleri kontrol eden metaller Pearson product-moment linear correlation ve Faktör analizi gibi istatistiksel metodlara dayalı olarak açıklanmaya çalışılmıştır. Sonuçlar Pb, Zn, Cr ve Cd un organik madde tarafından yüksek derecede, Fe in ise daha düşük derecede kontrol edildiğini göstermiştir. Pb un ayrıca organik karbonun yanısıra karbonat ve Mn tarafından da kontrol edildiği gözlemlenmiştir. Cr ve Cd u kontrol eden diğer faktörler su kolonundaki uptake yoluyla chl-a ve bunu takiben sedimantasyondur. Cu ve Hg ise başlıca chl-a tarafından kontrol edilmektedir. Taşıyıcı fazların değişimi üzerine de bazı sonuçlar bulunmuştur. Bu sonuçlar İzmir İç Körfezi yüzey sedimentlerindeki birikimin Pb, Hg, Cd ve Zn tarafından baskın olduğu; Mn, Cu, Cr ve Fe açısından ise daha az etkilendiğini göstermiştir. Jeoakümülasyon indexi sınıflaması genelliklezenginleşme ve kontaminasyon faktörü ile uyumluluk göstermiştir. Jeoakümülasyon indeks değerleri 1994 ten -2008 e doğru Zn, Hg, Cr ve Cd açsından hemen hemen iki kontaminasyon sınıfı azalma gösterirken; Pb aynı derecede kalıp, Cu ise bir sınıf azalma göstermiştir. Genellikle, Cu, Zn, Pb, Hg ve Cr kontaminasyonları medyan etki aralığı (ERM) değerlerinin altında bulunmuştur. Ağır metal kontaminasyonunun yayılımı ve derecesi tane boyu, organik karbon, karbonat ve klorifil-a gibi sedimentolojik parametrelerle önemli bir şekilde etkilenmektedir.

Anahtar Kelimeler: Ağır metal, Zenginleşme faktörü, Kontaminasyon faktörü, Jeoakümülasyon indeksi, Sediment kalite kılavuzu

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Introduction

Metals which discharged into near shore areas of marine environments is partitioned between the sediment and water column phases. Further partitioning of metals occurs within the sediment and water column with different ligands (Luoma, 1983; Korfali and Davies, 2004). This process of metal speciation may lead to the self-purification of aquatic environment from metal pollution (Korfali and Davies, 2004). Because of the metals are likely to be scavenged by particles and removed to the sediment, sediments become large repositories of toxic heavy metals. The distributions, bioavailability and mobility of heavy metals in marine sediments can change natural and anthropogenic impact (i.e., parent rock, weathering, transportation, soil erosion) and may be greatly different various aquatic ecosystems. Therefore, heavy metal pollution is one of the largest threats to marine environment and human health. In many coastal regions adjacent to industrial and urban areas where metals from both geological and man-made sources accumulate together, it can be difficult to determine the proportion of anthropogenic inputs (Ergin et al., 1993).

Marine sediments provide useful information for environmental and geochemical research about marine pollution (Uluturhan, 2009). Therefore, sediments are ecologically important components of the marine environment and have been contaminated by inorganic and organic materials. They are composite minerals consisting of inorganic components, mineral particulates and organic matter in various stages of decomposition (Küçüksezgin *et al*., 2006).

Development of industrial activities in coastal zones brought the risk of heavy metal contamination in marine environment (Esen *et al*., 2008). Since industrial revolution, tremendous amounts of the toxic pollutants have been discarded into coastal environment and sediments of bays and estuaries have huge sinks of heavy metals (Fukue *et al*., 1999; Turner, 2000; Billon *et al*., 2002; Fan *et al*., 2002; Wang *et al*., 2010).

Several studies have demonstrated that heavy metal pollution especially in marine environment increased over the last few decades at global scale; therefore, the evaluation of metal distribution in marine sediments is useful to assess the pollution status in coastal zones.

While general status is as it is described above, in this study, it could be found the detailed analysis of the situation in the inner Izmir Bay is now becoming increasingly polluted with organic and inorganic contaminant discharged into the Aegean Sea from various anthropogenic sources (Parizanganeh *et al*., 2007). The bay has a highly disturbed environment due to the rapid increase of the population and development industry (Atgin *et al*., 2000). Especially domestic and industrial waste water are the most important sources of pollution.

As it is known, there are so many studies on sedimentology and geochemistry of sediments in the Aegean Sea (Küçüksezgin, 2001; Dalman *et al*., 2006; Pekey, 2006; Uluturhan, 2009; Esen *et al*., 2010). Each of the scientist have been assessed one or two accumulation indexes and have been commented about that indexes results. Also it has been evaluated the geochemical approach using deviations of organic carbon normalized heavy metal values in the inner Izmir Bay. The geochemical approach is an effective strategy for distinguishing anthropogenic from naturally occuring metal concentrations, paticularly when it is used with the traditional quantitative statistical evaluations. The objective of this research are: (a) elucidate the distribution of a number heavy metals in the inner Izmir Bay sediment, (b) evaluate geochemical factors that control the distribution pattern of the studied heavy metals, (c) investigate biological effects of heavy metal concentrations in sediments of inner Izmir Bay.

In order to realize the objectives of this study, 21 core sediment samples were collected and analyzed according to the that criterias: grain size, organic carbon, carbonate, heavy metal. So, the asseessment of sediment contamination based on: (a) Enrichment factor (b) contamination factor and contamination degree (c) sediment quality guidelines used by US EPA.

Materials and Methods

Study Area

Izmir Bay is located in the western Aegean Sea and is one of the great natural bays of the Mediterranean. It is an important semi-enclosed basin and has been increasingly polluted with massive loads of contaminants discharge from various anthropogenic sources. From the topographic and hydrographic points of view, the bay is divided into inner, middle outer regions (Guven and Akinci, 2008). Its' average depth is 15 meter and total area is 500 km^2.The exponential growth of Izmir on both sides of inner Izmir Bay has led to severe pollution. The quality of water and sediment in the inner Izmir Bay is seriously affected by pollutants which enter through drains that bring domestic as well as industrial effluents and discharge into the river and also from the sewage system that pumps untreated effluent into it during its journey through the city. These industrial and domestic waste waters, besides other pollutants also contain high concentration of heavy metals. The main industries in the city of Izmir include food processing, beverage manufacturing and bottling, tanneries, oil soap and paint production, chemical industries, paper and pulp factories, textile industries, metal processing and timber processing (Küçüksezgin, 2001). Most of the industries in Izmir are located edge and the catchment basins of the creeks which flow into the inner Bay. So, inner Izmir Bay is consequently one of the most important sources of heavy metal pollution in the western Mediterrenean.

Analytical Procedure

The sediment samples were taken from the 21 stations using a gravity corer. 14 samples were collected from the inner Bay and also 7 sediment samples were collected creeks (Melez, Manda, Bayrakli, Bostanlı, Bornova and Balcova) in August 2008.

The stations were selected considering heavy metal concentrations in sediments of the inner Bay. Coordinates were determined by Global Positioning System (GPS). The locations of sampling stations are shown in Figure 1.

After the cores collection, all of them were sliced as two cm intervals with the sediment extruding device. The sediment slices were stored in cleaned polyethlene bottles with on ice and transferred to the laboratory. They were frozen at -20 ºC in a deep freeze. The microwave digestion was carried out with a CEM Model Mars 5. 0,1 g of sediment samples which were placed in teflon vessels were digested with a mixture of concentrated HNO_3 (3mL), HF (1mL) and HCl (0,8 mL) for 30 minutes at 200 ºC using microwave oven (CEM Corp. MARS 5). Ultrapure water was used throughout the study. All glassware and other containers were throughly cleaned with ultrapure water several times prior to use. The average values of three replicates were analyzed for each determination. Heavy metal contents of the sediment samples were determined using metrohm voltammeter model 797 VA computrace. A voltammetric analyzer (VA 797, Metrohm, Switzerland) including a voltammetric cell with a HMDE as a working electrode (WE), a platinum rod electrode as an auxiliary electrode (AE), and a Ag/AgCl electrode (3M KCl) as a reference electrode (RE), was employed for differential pulse anodic stripping voltammetric analysis. The voltammetric analyzer was controlled by a personal computer, using a VA Computrace version 2.797.00X0, SR1 software (8.797.8013, 797 VA Computrace, Metrohm). All chemicals used were of analytical reagent grade. Deionized water was used throughout the experiment. Stock standard solution (1000 ppm) of heavy metals was purchased from Merck, Germany. The working standard solutions were prepared daily by diluting the stock standard solution of each metal with 0.025 M acetate buffer (pH 4.6). An oxygen free nitrogen (OFN) gas (99.9995%) was used for purging the solution to remove dissolved oxygen. An aliquot of 10 mL acetate buffer (pH 4.6) was placed in a voltammetric cell and the solution was purged with pure Nitrogen for 300 second. Then, a fixed potential of -1.15V was applied to the WE for a period of 90 s, while the solution was stirred at 2000 rpm (deposition step). After that the stirring was stopped and equilibrate for 5 s, followed by anodically scanning of the potential from −1.15 to 0.15 V, employing a square wave waveform with amplitude of 50 mV, step potential of 30 mV, and frequency of 50 Hz (stripping step). A

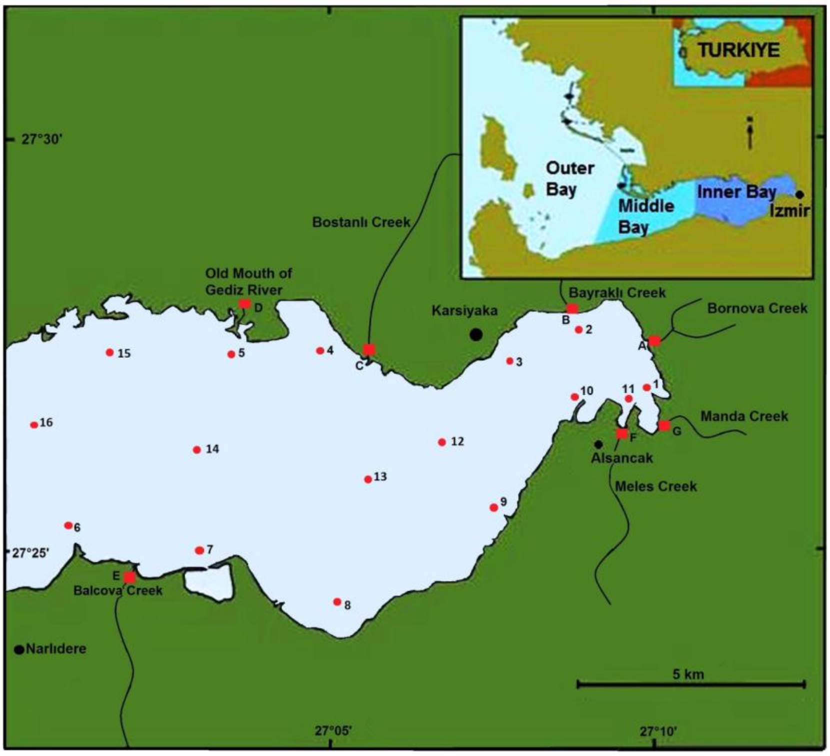

Figure 1. Map of Inner Izmir Bay and sampling sites.

voltammogram was recorded with a personal computer. Peak potential and peak current corresponding to each metal was calculated from the voltammogram. Amounts of the metal from sample were reported as µg/L. The metal contents were quantified by the standard addition method with four additions for each metal. The values obtained for the curve slopes were used to calculate the metal quantities in the sample solution and in the blank. Detection limits for 0.5 g sediment are: 0.005 ppm for Fe; 0.05 ppm for Al; 0.03 ppm for Mn; 0.02 ppm for Cu; 0.01 ppm for Hg; 0.02 ppm for Cr; 0.02 ppm for Cd; 0.01 ppm for Zn and 0.02 ppm for Pb.

Dried samples at 50-60 ºC were analyzed for carbonate and organic carbon contents. Before the organic carbon analysis, homogenized sediments were moistened with distilled water and exposed to concentrated HCl flumes for 48 hour to remove carbonates.

The amount of organic matter was measured by the Walkey-Black methods (Gaudette et al., 1974) which is based on remaining dichromate with back titration ferrous ammonium sulfate using phenylamine as an indicator. Total carbonate content was determined by a gasometric method. This method is based on the measurements of the partial pressure of CO_2 released by acidification with 10% HCl. Chlorophyll-a (Chl-a) were analyzed through acetone extraction and spectrophotometry (Lorenzen 1971).

For grain size analysis, initially the sediment samples were homogenized with 10% H_2O_2 to remove the organic matter. The granulometric composition was investigated by standard sieve and pipette analysis techniques (Folk, 1954). Textural classification of the samples were based on the sieves for four fractions: <0.002mm (clay), 0.002-0.063mm (silt), 0.063-2mm (sand) and the fraction more than 2mm (gravel) (Shepard, 1954).

Statistical Analysis

The data set has been subjected to correlation and factor analysis for elucidating the relationships between heavy metals and geochemical characteristics such as organic carbon (C_{org}), chloropyll-a (chl.-a), grain size, carbonate (CO_3^{-2}). Different modules of the statistical software statistica such as Pearson Product Moment linear correlation method and the Factor Analysis were used to elucidate the relationships between heavy metals. The correlation between coefficient is significant with p-value < 0.05.

Results

The contents of heavy metal in the inner Izmir Bay sediments from the 21 sites were evaluated. Analysis showed that the concentrations of metals were found very high in the inner part of the Bay due to intensive industrialization such as textile industries, metal processing, cement factories, iron, paperand pulp factories, antifouling paints, timber processing. Also, the heavy metal concentrations in sediments from the eastern stations are higher than those from the western stations. It is resonable assume that the pollution level in this area is much higher in industrial areas. The heavy metal concentrations in surface sediments varied from 2,48% to 6,95% for Fe, 1,1% to 3,98% for Al, 210,1 to 304,7 mg kg^{-1} for Mn, 31,6 to 81,6 mg kg^{-1} for Cu, 0,3 to 0,82 mg kg^{-1} for Hg, 154,9 to 385,4 mg kg^{-1} for Cr, 0,02 to 0,49 mg kg^{-1} for Cd, 105,4 to 265,3 mg kg^{-1} for Zn and 81,2 to 172,8 mg kg^{-1} for Pb. Especially the maximum heavy metal concentration were measured at harbour.

Enrichment Factor

Assessment of heavy metal pollution in marine sediments requires knowledge of pre-industrial metal concentrations to act as a reference against which measured values can be compared (Abrahim and Parker, 2007). So in order to better understand the sediment quality in the inner Bay, levels of metal pollution were evaluated different techniques for environmental assessment should be considered. One of them is “enrichment factor (EF)” which is a powerful tool to distinguish between anthropogenic and naturally occuring sources of heavy metals. EF technique is used in the area of atmospheric aerosols, sediments, soil and solid wastes to determine the degree of modification in the composition (Pekey, 2006).

The EF of metal is defined as follows using Aluminium as a reference element.

$$EF = \frac{(C_x/C_{Al})_{sample}}{(C_x/C_{Al})_{background}}$$

where $(C_x/C_{Al})_{sample}$ is the ratio of metal and Al concentrations of the sample and $(C_x/C_{Al})_{background}$ is the ratio of metal and Al concentrations of background. The background concentrations of Fe, Mn, Cu, Zn, Pb, Hg, Cr, Cd and Al in the average shale obtained from Turekian and Wedepohl (1961) are used in this study (Table 1).

Birch (2003) divided contamination into different categories based on EF values. EF<1 demonstrates “no enrichment”, EF<3 is “minor enrichment”, EF=3-5 is “moderate enrichment”, EF=5-10 is “moderately severe enrichment”, EF=10-25 is “severe enrichment”, EF=25-50 is “very severe enrichment” and EF>50 is “extremely severe enrichment”. In this study, EF values are 2.56 for Fe (minor enrichment), 0.958 for Mn (no enrichment), 3.324 for Cu (moderate enrichment), 20.372 for Pb (severe enrichment), 5.854 for Zn (moderately severe

Table1. Average, min and max metal values of Enrichment factor and geoaccumulation index values

		Fe	Mn	Cu	Zn	Pb	Hg	Cr	Cd
EF	max	4,711	2,205	11,954	16,049	57,303	15,655	32,701	15,836
	min	1,305	0,519	1,723	2,499	9,797	1,722	4,277	1,721
	average	2,566	0,958	3,324	5,854	20,372	3,994	9,537	3,821
	std sapma	0,094	0,046	0,276	0,325	1,38	0,322	0,602	0,301
□*geo*	max	-0,038	-0,336	0,712	0,450	0,230	0,820	0,380	1,327
	min	-1,115	-0,872	-0,656	-0,880	-0,860	-0,630	-0,935	-3,977
	average	0,431	-0,583	-0,115	-0,130	-0,200	0,002	-0,191	0,147
	std sapma	-0,820	-2,296	0,910	0,812	3,317	2,734	-0,001	3,011

enrichment), 9.537 for Cr (moderately severe enrichment) and 3.821 for Cd (moderate enrichment). The Ef values of Fe, Mn, Cu, Hg and Cd are especially less than 5 (moderate enrichment and minor enrichment), because such small enrichment may arise from differences in the composition of local soil material.

Elements Zn, Pb and Cr are very heavily enriched in the inner Izmir Bay. Although the high enrichment factor is a first indication of a potential anthropogenic contribution for an element, some natural sources can also cause for the observed enrichments (Atgin *et al*., 2000).

Especially the maximum EF values of heavy metal were measured at harbor. All antifouling paints applied to commercial, naval and recreational vessels in the inner bay contain significant quantities Cu and lesser quantities of Pb and Hg (Aksu *et al*., 1998). Also these metals come from the effects of ships gasoline combustion, catodic protection of ship's body (there are some block of Pb on the vessel's hull), metal coating and metal smelters industries (especially Bornova and Melez Creek).

The EF of Pb in the inner parts of the Bay is quite high because of the automobile traffic. The automobile exhaust emissions have significantly accentuated Pb accumulations in the air and soils (Sutherland, 1999). Also Pb and Zn derive from the Izmir domestic and industrial sewage. Fly ash constitutes a major pollutant of the coal burning process and is known to contribute notable quantities of Cd, Cu, Pb and Zn into the environment (Natusch *et al*., 1975; Aksu *et al*., 1998).

Elevated Cr, Pb and Zn values indicate to some anthropogenic pollution by the Bostanli, Manda and Melez Creek discharges. These Creeks for long years carried the untreated discharges of leather manufacturers to the inner Bay. But now, the leather indusrty has moved away and their discharges are minimized by effective measures. Even so, the Cr originated from manufacturing for a long years is accumulated in the sediments.

Enrichment for the element Pb ann Zn in the inner Bay should be identified in order to assess a possible human influence. Especially, the harbor in the inner Izmir Bay, where the higher enrichment Pb and Cu are observed. High Zn and Pb enrichments come from gasoline combustion from ship and boats. On the other hand, Pb and Cd are bound to the ferro-manganese oxides and/or organic matter fraction, suggesting anthropogenic sources (Karageorgis *et al*., 2003). Cr and Zn pigments and compounds are used in metal plating and probably contributing some quantities on these metals into the inner Bay (Küçüksezgin, 2001). Cd and Zn originate primarily from anthropogenic sources, whereas the major part of the Fe and Al seem to come from natural sources. The labile Mn should not be attributed to possible anthropogenic source, because Mn tends to be present in less thermodinamically stable in sediment phases, such as Mn^{+2}, easily reducible Mn oxides and Mn enclosed in carbonate minerals (Angelidis and Aloupi, 2000).

High Hg values may ocur natural and anthropogenic riverine inputs. The effluent from large chlor-alkali and chlorine plants probably supply most of the mercury found in the inner Izmir Bay surface sediments (Aksu *et al*., 1998).

Contamination Factor

A contamination was described the contamination of a given toxic substance in a basin by Hakanson (1980). Contamintion factor (C_f) is ratio of the concentration of the element in samples to pre-industrial reference value for the element.

$$C_f^{\ i} = {C_e}/{C_{pi}}$$

According to Hakanson (1980), C_f has been classified into four groups: Cf <1 low contamination factor, 1≤ Cf<3 moderate contamination factor, 3≤ Cf <6 considerable cotamination factor and Cf>6 very high contamination factor. In the calculation of Cf, is commonly used the average shale values (Turekian and Wedepohl, 1961) and/or average crustal abundance (Taylor, 1972). In this study, it was used to the average shale values (Turekian and Wedepohl, 1961) as reference baselines. It was calculated the Cf values of Mn, Cu, Zn, Pb, Hg, Cr, Cd and Fe using the raw elemental data. Accordingly, metal levels existed in order of Pb > Cr > Zn > Cd > Hg > Cu > Mn in the inner Bay (Table 2). The Cf values Cu, Cd, Cr, Hg and Zn are moderate contamination, Pb and Mn are low contamination. The maximum Cf value was found for Pb.

Non-lithogenic metal values were calculated following as:

$$M_{NL}(\%)=[Me_{total}-(Me/Al)_{crustal}*Al_{total}]*100 \quad / \quad Me_{total}$$

Non-lithogenic Mn values were found as except stations 1, 11, 14, 16 and E. Negative values explain metal concentrations of sediment are lower than that of the values come from crustal. Indicating that the sediment condition of inner Bay have been changed to reducing condition. Matthiesen (1998) emphasized that Fe and Mn mobilization in sediment at the reducing condition Fe^{+2} rapidly precipitated on the sediment but reduced and dissolved Mn diffuses overlying oxic water.

The degree of contamination (C*d*) in a depocentre is defined as the sum of all contaminants factor various heavy metals (Aksu et al., 1998).

$$Cd = \sum_{i=1}^{n=8}(Cf_i)$$

The C*d* values therminology is used to: C*d* < 8 low degree of contamination, 8 ≤C*d* < 24 moderate degree of contamination, 24 ≤C*d* < 48 considerable degree of contamination and C*d* > 48 very high degree of contamination. The degree of contamination values are between the 8-24. All of them is moderate degree of contamination.

Comparison between the C*d* and C*f* shows that the contamination of the surface sediments in the inner Izmir Bay is dominated Pb, Hg, Cd, Zn and to a lesser extent Mn, Cu, Cr and Fe. Also, compared with the literature values reported for the heavy metal in sediments, the values of heavy metal concentrations lowers than that reported by previous studies. Acomparision of metal values in sediments have shown in different localities of Aegean Sea (Table 3). Cu, Zn, Cr inner Izmir Bay are two times; Pb and Hg five times; Cd is ten times more and Mn ten times less than Eastern Aegean Sea. Fe is similar with all localities.

Geoaccumulation Index

A common approach to estimating the enrichment of metal concentrations above background or baseline concentrations is to calculate the geoaccumulation index (I*geo*) as proposed by Müller, 1969 (Abrahim and Parker, 2007). Sediment I*geo* is the quantitative measure of heavy metal pollution in aquatic sediments. This index is basically a single metal approach to quantify metal pollution in sediments when the concentration of toxic heavy metal is 1.5 or more times greater than their lithogenic background values (Gaur *et al*., 2005).

$$Igeo = log_2[Cn/1.5Bn]$$

where C*n* is the measured concentration of the element *n* and B*n* is the geochemical background value element *n* in average crust (Wedepohl, 1995). The factor 1.5 is used to compansate possible variations which may be attributed to lithologic variations in the sediment. Geochemical background values of Fe and Mn were taken from Turekian and Wedepohl (1961). The others were taken from Aksu et al., (1998) as: Cu: 17 ppm, Zn: 65 ppm

Pb: 8.5 ppm Hg: 0.005 ppm, Cr: 1.75 ppm Cd: 0.003 ppm Al: 84000 ppm

According to this classification, the inner Izmir Bay can be categorized unpolluted to strongly polluted. The I*geo* shows the general tendency proven

Table 2. Contamination factors (C*f*) and degree of contamination (C*d*) of surface sediments in the inner Bay

Station	***Cf***								***Cd***
	Mn	Cu	Zn	Pb	Hg	Cr	Cd	Fe	
1	0,31	0,72	1,43	4,06	0,75	1,72	0,77	0,63	10,39
2	0,30	1,64	2,20	7,84	2,05	4,28	2,17	1,46	21,93
3	0,34	0,93	2,26	8,64	1,15	4,20	2,63	1,48	21,63
4	0,29	0,86	2,12	7,63	1,08	2,85	1,87	0,53	17,22
5	0,25	0,75	1,33	7,43	0,88	2,50	0,70	0,76	14,59
6	0,30	0,80	1,28	6,91	0,75	2,06	0,60	0,64	13,33
7	0,25	0,70	1,25	6,09	0,95	1,80	0,63	1,11	12,79
8	0,34	0,96	1,11	4,67	0,78	2,19	0,83	0,66	11,54
9	0,28	0,71	2,79	4,41	0,83	2,89	1,53	0,77	14,20
10	0,35	1,03	2,09	4,81	1,28	3,13	0,93	0,68	14,30
11	0,29	1,26	1,79	8,51	1,58	3,63	1,20	0,69	18,94
12	0,36	1,81	1,81	8,47	2,20	3,72	1,63	0,91	20,92
13	0,29	0,97	2,77	7,59	1,03	2,71	1,37	0,78	17,49
14	0,28	0,73	2,72	8,18	0,80	3,27	1,00	0,94	17,92
15	0,30	0,80	1,97	6,27	0,75	2,73	0,73	0,72	14,27
16	0,28	0,77	1,16	5,55	0,78	2,21	0,67	0,73	12,12
A	0,35	1,37	2,11	8,38	1,73	3,52	0,70	0,98	19,15
B	0,35	1,02	2,03	6,37	1,23	3,27	1,53	0,78	16,57
C	0,32	0,72	1,96	6,83	0,98	2,06	1,13	1,06	15,05
D	0,31	0,98	1,36	5,72	0,78	1,92	0,87	0,90	12,82
E	0,30	0,96	1,56	4,77	0,95	1,98	1,13	0,76	12,42
F	0,27	1,49	1,93	4,16	1,83	3,62	1,20	0,68	15,17
G	0,25	1,54	1,81	5,03	1,98	4,01	1,60	0,85	17,07

by the EF and C*f* (Table 4). In Table 4, EF, C*f* and I*geo* indexes for all metals consistent with each other except I*geo* values of Cr. In the fact that I*geo* values of Cr are different from the classes of EF and C*f* is expected situation because of the precautions on the leather tanning plant. Also the values of I*geo* for Zn, Hg, Cr and Cd have decreased two contamination classes from 1994 to 2008, whereas Pb has remained the same and Cu has decreased only one class.

Sediment Quality Guidelines

Numerical sediment quality guidelines (SQGs) have been developed using a variety of approaches, typically involving statistical comparisons of chemical concentrations and measures of adverse biological effects upon exposure to sediments (Long and MacDonald, 1998).This guidline was used correctly classifying sediments as either toxic or non-toxic. Two sets of SQGs developed for marine and estuarine ecosystems (MacDonald *et al*., 1996; Long and MacDonald, 1998). One set of SQGs (the effect range low (ERL)/effect range median (ERM)) was applied in this study, to assess the ecotoxicological sense of trace element concentrations in sediments. Generally Cu, Zn Pb, Hg and Cr contaminations were below ERM values, whereas only Cd contaminations had below ERL values. Expected adverse biological effects for all of the stations in Cd were found only 6.6%, in contradiction with I*geo* classification (moderate to strongly polluted), indicating that the pre-industrial background value is well below the crustal value. There is a strong accumulation of this metal but it does not reach to highly toxic levels. In the inner most part of inner Bay, 95%, 42% toxic effects will be able to expected for Cr and Hg respectively. In other stations it maybe uncountered with the toxic effects greater than 20% (Table 5). Pb values of all stations correspond to between ERL-ERM, indicating 35.8% incidence of adverse effects. 47% toxicity of Zn in 15 satations and 29% toxicity of Cu in 17 stations are expected. Toxicity of Zn decreased to 6.1% in old Gediz River mouth, Balcova Creek, northwestern and southwestern stations. In western stations, toxicity for Cu decreases also 9.4%.

Grain Size, Organic Carbon and Carbonate

The grain size distribution in the study area are given in Figure 2. Fine grianed sediments with 14-79% silt (sandy silt and silty sand) ocur in inner Izmir Bay. The sand content is higher southwest and northwest in the inner Bay. In the east of the study area, silt is major companent of the sediment. The surface sediments of inner bay are composed of from silty sand to sandy silt with range of grain size.

The carbonate content (CO_3^{-2}) varies between 4.07%-8.79% by dry weight. The total carbonate concentrations are generally high in the southwest and northwest part of he bay. This may be related to derived from skelatal parts and benthic organisms. There is no significant correlation between the total carbonate and grain size fraction (Table 6). On the other hand high carbonate contents also occur due to the presence of calcareous lithoclastics and bioclastics from the terrigenous sources (Ergin *et al.,* 1993) and riverine input of calcareous rocks.

Total organic carbon (Corg) concentrations of the surface sediment ranging from 1.98%-6.03% by dry weight are generally higher values in silt sized

Table 3. Average of heavy metal concentrations in sediment from different areas

Regions	Fe (%)	Mn mg kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}	Pb mg kg^{-1}	Hg mg kg^{-1}	Cr mg kg^{-1}	Cd mg kg^{-1}
This study[a]	3.41	256.75	45.98	177.03	128.92	0.47	259.43	0.35
Candarli B[b]	-	798.0	37.5	206.5	76.15	0.815	86.9	-
Nemrut B[c]	2.82	282.5	26.6	173.0	55.9	4.8	67.25	0.13
Güllük B[d]	-	-	25.0	81.0	20.0	-	-	0.56
Eastern Aegean Sea[e]	2.68	2534.0	27.15	82.85	26.05	0.098	117.4	0.025
Izmit Bay[f]	-	-	99.8	850.0	100.9	-	87.0	0.5
Milos Bay[g]	3.4	1985.0	51.0	325.0	151.0	-	119.0	-

[a]This study, [b]Pazi *et al.* (2010), [c]Esen *et al.* (2008), [d]Dalman *et al.* (2006), [e]Uluturhan (2009), [f]Pekey(2006), [g]Karageorgis *et al.* (1998)

Table 4. Comparison of enrichment factor, contamination factor and geoaccumulation index of metals

Heavy Metals	EF	*Cf*	*Igeo*
Mn	no enrichment	low contamination	unpolluted
Cu	moderate enrichment	moderate contamination	unpolluted to moderately polluted
Zn	moderately severe enr.	moderate contamination	unpolluted to moderately polluted
Pb	severe enrichment	very high contamination	strongly polluted
Hg	moderate enrichment	moderate contamination	moderate to strongly polluted
Cr	moderately severe enr.	moderate contamination	unpolluted
Cd	moderate enrichment	moderate contamination	moderate to strongly polluted
Fe	minor enrichment	low contamination	unpolluted

feaction. The high values of Corg were observed in the vicinity of stations (1, 10, 11, F and G). Relatively high Corg percentage in the inner bay may indicate the effect of terrestrial and anthropogenic inputs in addition to the relative proximity of creeks. The low Corg contents reflect variations in degree of dilution by the coarse grained biogenic components. The relatively high concentrations of Corg at stations 1, 2, 3, 9, 10, 11, 12, 13, A, B, F and G reflect high organic matter flux to sediments due to the eutrophication. The correlation of Corg against sand (%) was inversely correlated, because most of the stations contain low level clay component. From Pearson product correlation between each pair of variables (Corg, CO_3^{-2}, sand, silt, clay), the relationships of Corg/silt, Corg/sand exhibit statistically significant non-zero correlations at 95% confidence level. R^2 statistic indicates that linear model for Corg/silt (Figure 3) explains 76% of the variability in Corg. Sand content of sediment increases toward southwest and northwest stations whereas metal contents and toxicity decrease.

Al/OC, Fe/OC, Mn/OC, Cu/OC, Zn/OC, Pb/OC, Hg/OC, Cr/OC and Cd/OC ratios in Inner Izmir Bay sediments vary inversely with OC concentrations. Figure 4 indicating the differential addition of freshly produced organic carbon. Changing of natural organic matter (NOM) can also affect trace metal partitioning. Ships traffic may also causes resuspention of sediments because of the maximum 15 meters of depth as encountered in Galveston Bay (Wen *et al.*, 2008)

Me (metal) to Al ratios exhibit inverse linear relationships (Figure 5), likely due to particle fractionation processes such as differential sedimentation, resuspension and flocculation, allowing fine suspended matter to become enriched in secondary carrier phases such as organic matter or Fe, Mn oxyhydroxides. Wen *et al.*, (2008) reported that in Galveston Bay water column, decrease in Fe/Al ratios of particulate matter was consistent with a coupling of sediment resuspension by wind and wave action, with Fe diagenesis in sediments.

The regressions of Me/Al ratios vs. Al contents of sediments have negative slopes, indicating main sources of metals not pertaning to crustal material and/or adsorbing of freshly formed organic matter as carriers of trace metals via resuspension of sediments by winds, waves, turbulence of ships traffic. Therefore a dilution effect due to the Al comes out. Another possibility is the reducing conditions in sediment in relation to decreasing sediment permeability (clay fraction) and organic carbon accumulation as seen in Mn mobilization.

Factor Analysis

A R- factor analysis was performed. On raw geochemical data in an attempt to further clarify the major controling factors that determine the distribution of heavy metals in the sediment. Four of the factors which account for most of the variability in the 12 variables was obtained. 4 factors have been extracted, since 4 factors had eigenvalues greater than or equal to 1. Together they account for 79,467% of the variability in the original data (Table 7).

Table 5. ERM and ERL guideline values for trace elements[a,b]

	Cu	Zn	Pb	Hg	Cr	Cd
1	73,6	208,6	156,8	0,8	385,4	0,7
2	41,8	214,8	172,8	0,5	378,4	0,8
3	38,7	201,6	152,5	0,4	256,9	0,6
4	33,6	126,4	148,6	0,4	225,3	0,2
5	35,8	121,7	138,2	0,3	185,2	0,2
6	31,6	118,6	121,7	0,4	162,4	0,2
7	43,2	105,4	93,4	0,3	197,5	0,3
8	31,9	265,3	88,1	0,3	259,7	0,5
9	46,3	198,5	96,2	0,5	281,8	0,3
10	56,7	169,7	170,2	0,6	326,4	0,4
11	81,6	172,3	169,4	0,9	335,2	0,5
12	43,7	263,1	151,7	0,4	243,6	0,4
13	32,8	258,6	163,5	0,3	294,3	0,3
14	35,9	187,1	125,3	0,3	245,7	0,2
15	34,7	109,8	110,9	0,3	198,7	0,2
16	32,2	136,2	81,2	0,3	154,9	0
A	61,8	200,9	167,5	0,7	317,2	0,2
B	45,9	193,2	127,3	0,5	294,1	0,5
C	32,4	186,4	136,5	0,4	185,4	0,3
D	43,9	129,3	114,3	0,3	173,2	0,3
E	43,2	148,6	95,4	0,4	178,6	0,3
F	66,9	183,5	83,1	0,7	325,7	0,4
G	69,3	172,1	100,6	0,8	361,3	0,5
ERL[a]	34	150	46,7	0,15	81	1,2
ERM[a]	270	410	218	0,71	370	9,6

[a]Long et al., (1995, [b]Concentrations are in mg kg^{-1}

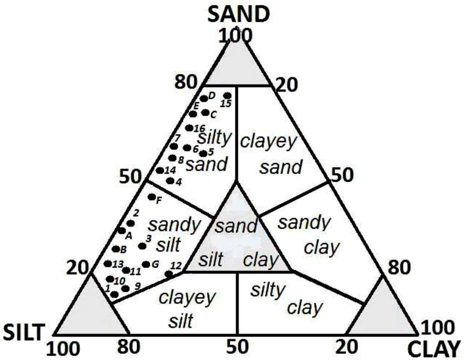

Figure 2. Grain size distribution and sediment type of Inner Izmir Bay.

Table 6. Pearson's product moment correlations between each pair of variables (Corg, CO_3^{-2}, sand, silt, clay)

	Corg (%)	CO_3^{-2} (%)	sand(%)	silt(%)	clay(%)
		0.0139	-0.8863	0.8726	0.1977
CO_3^{-2} (%)			0.1064	-0.1276	0.0774
sand(%)				-0.9761	-0.2604
silt(%)					0.0443
clay(%)					

The type of factoring have been selected as principal components. Metal loadings of the factors have been given in Table 8.

Factor1 accounts for 35,457% of the variability in the original data. The first group of variables can be described as an anthropogenic assemblage composed of mainly Zn, Pb, Cr, Cd and C_{org} . This factor reflects the binding of heavy metals to organic matter.

Factor 2 accounts for 21,974% of the variability in the original data. The second group of anthropogenic variables composed of mainly Cu Hg, Cr, Cd to some extent Fe with stations 1, 10, 11 are the main pollution sources for Cu Hg and Cr. Only the sediments of Melez and Bornova creeks contain lower levels of Cd. Also harbour (station 10) contain the effects of ship traffic and antifouling paints Cr and Cd have higher values in stations 2, 3, 8 and the sediment of Bayraklı creek. Cu with Hg and Cr with Cd can be discriminated as seen three dimensional factor loadings in Figure 6. The major carrier phase is likely ferric oxyhydroxides and to some extent organic matter for this anthropogenic assemblage.

Factor 3 accounts for 13.099% of the variability in the original data and explains metal sorbtion pools: carbonates, alumino silicates (clay minerals), ferric oxyhidroxides and algal biomass. The first two of them result from terrestrial sources. Both of them are conservative components and they lose some trace metal contents via resuspension by the winds, wave effects and ship traffic's turbulence. Iron accumulation in sediment surface derives from the oxidation and sedimentation of dissolved species, atmospheric dust, terrestrial sources and mobilization of reduced iron from deeper sediment layers (including past times) to surface of sediment. The last pool stems from eutrophication.

Factor 4 accounts for 8.936% of the variability in the original data and is composed of mainly Mn, Pb and Fe. This factor includes the effects of harbor traffic, shipyard, catodic protection of ship's body (there are some block of Pb on the vessel's hull) and metal coating and metal smelters industries (especially in Bornova creek and Melez creek).

Conclusions

The results illustrated that Zn, Pb, Cr, Cd are mainly controlled by organic matter and to some extent ferric oxyhydroxides. The second anthropogenic assemblage Cu, Hg, Cr, Cd mainly controlled by Chl.-a and organic matter. Metal sorbtion pools also distinguished as carbonate, aluminosilicates, ferric oxyhydroxides and algal biomass. Mn, Fe and lesser carbonate seem to extent some control on the Pb.

Comparison of heavy metal concentrations with different localities in Aegean Sea emphasized that Cu, Zn, Cr are two times, Pb, Hg five times, Cd ten times more and Mn ten times less than Eastern Aegean Sea. Fe is similar with all localities.

An established way to dedect anthropogenic contamination and to become comparable of different sediment samples is by normalization of contaminant concentrations to Al and/or organic carbon. Me/Al and Me/Corg ratios did not constant among stations and decreased with increasing Al and Corg values, indicating changing of carrier phases via resuspension by wind, wave, ships traffic and freshly formed autochthonous organic matter by eutrophication.

The contamination status by heavy metals was assessed based on comparison with Sediment Quality Guidelines, geoaccumulation index, Enrichment

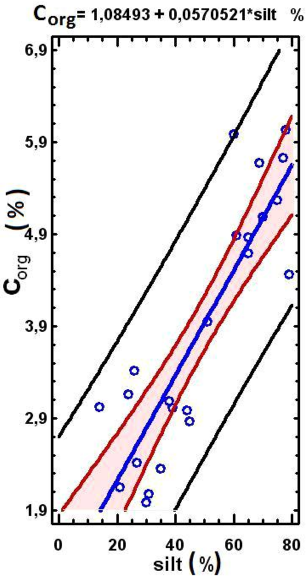

Figure 3. Statistically significant linear regression of Corg vs. silt content (P<0.05). Corg (%) = 0.057 [silt] + 1.085

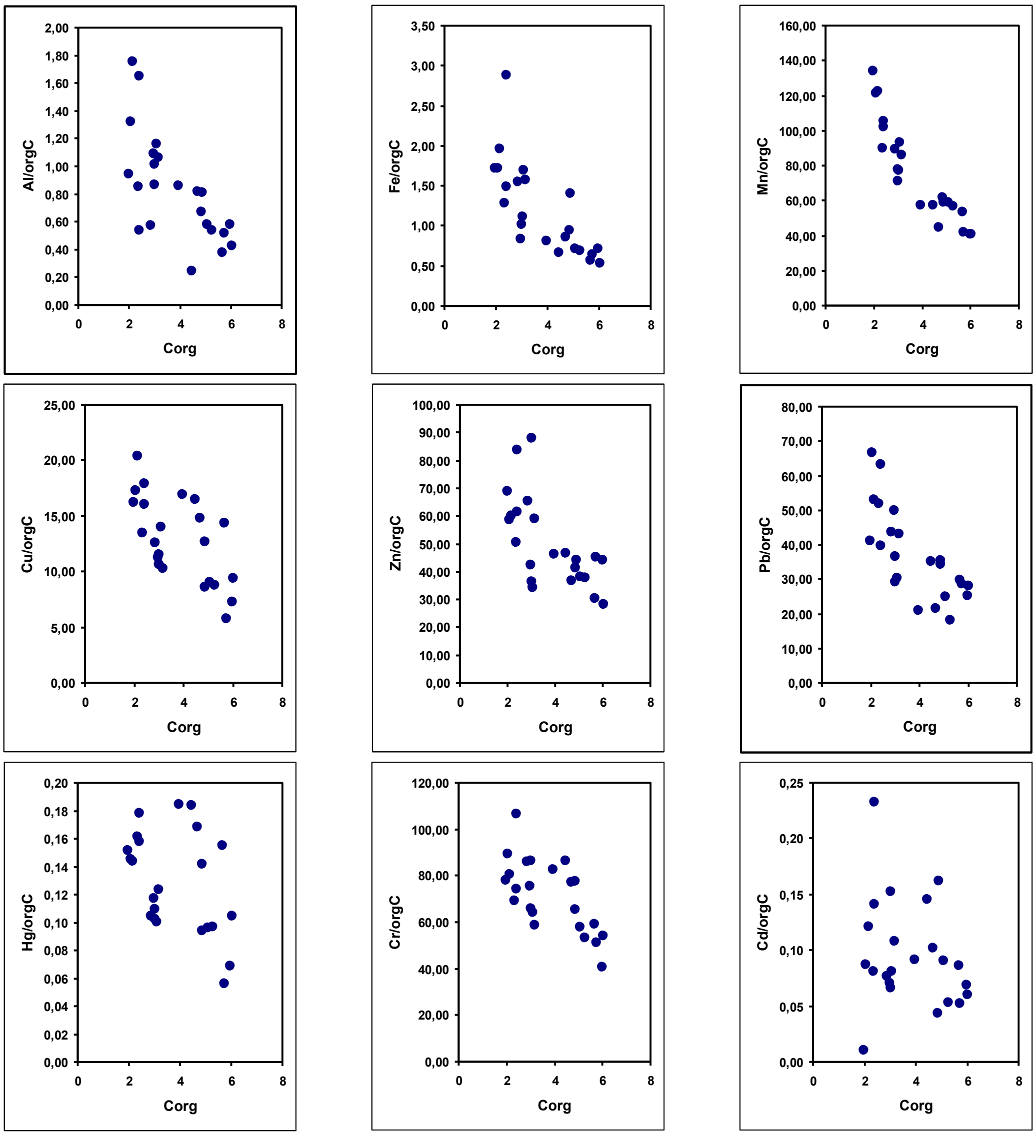

Figure 4. Scatter plot of Metal/C_{org} ratios against C_{org}.

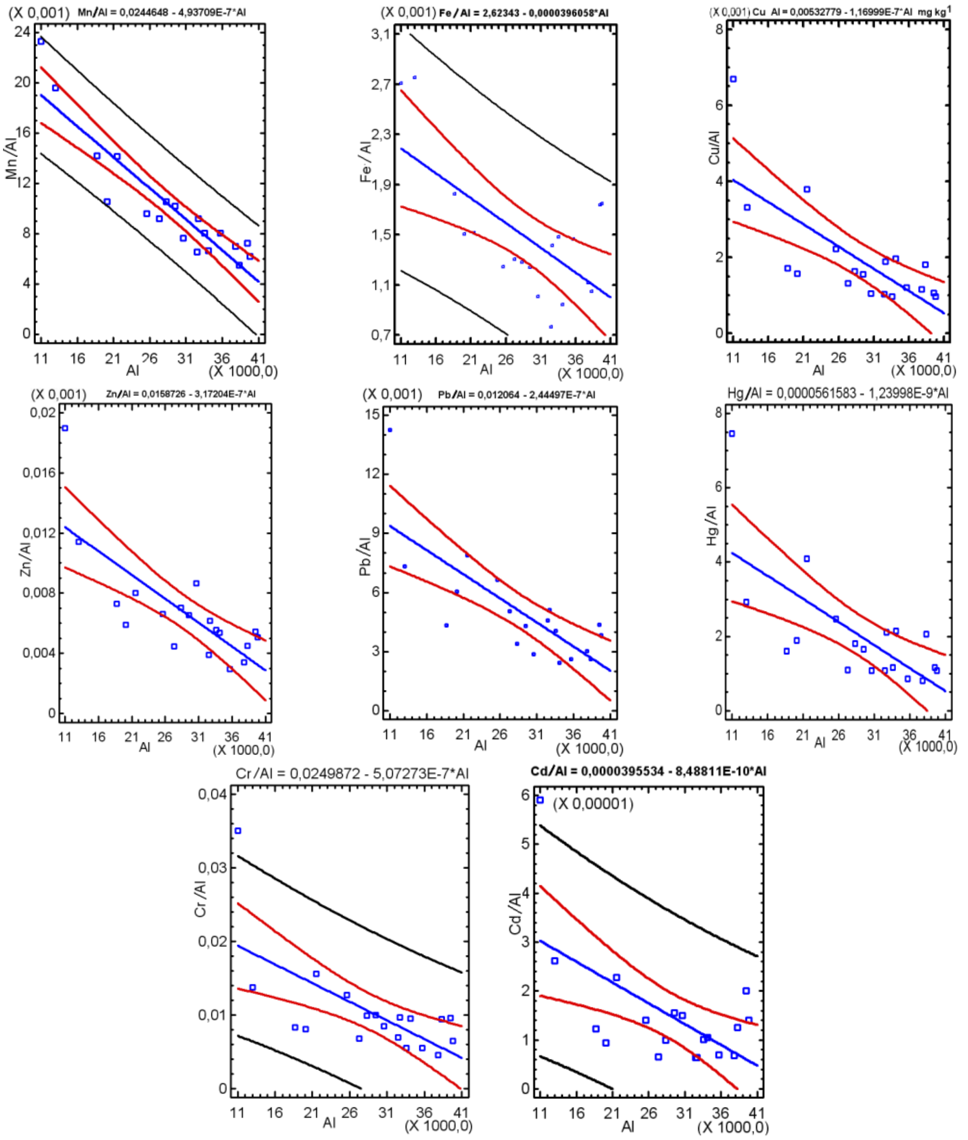

Figure 5. Linear relationships of Me/Al ratios vs. Al content (mg/kg) of Inner Izmir Bay.

Table 7. The results of R- Mod Factor analysis on the raw data. Four factor has been extracted (bold)

Factor Number	Eigenvalue	Percent of Variance	Cumulative Percentage
1	4,25487	35,457	35,457
2	2,63692	21,974	57,432
3	1,57191	13,099	70,531
4	1,07238	8,936	79,467
5	0,830242	6,919	86,386
6	0,57282	4,774	91,159
7	0,409095	3,409	94,569
8	0,250004	2,083	96,652
9	0,193446	1,612	98,264
10	0,122788	1,023	99,287
11	0,0548908	0,457	99,745
12	0,030643	0,255	100

Factor (EF) and Contamination Factor (Cf). The results indicated that contamination of surface sediments in inner Izmir Bay is dominated Pb, Hg, Cd, Zn and to a lesser extent Mn, Cu, Cr and Fe. I_{geo} values shows the general tendency proven by the EF and Cf, but the classes of I_{geo} for Cr are different from EF's and Cf's, indicating the precautions on the leather tanning plants. I_{geo} values for Zn, Hg, Cr and Cd have decreased two contamination classes from 1994 to 2008, whereas Pb has remained the same and Cu has decreased only one class.

Generally Cu, Zn, Pb, Hg and Cr contaminations

Table 8. Factor Loading Matrix After Varimax Rotation (Bold numbers indicates significant loadings on the factors)

	Factor 1	Factor 2	Factor 3	Factor 4
Mn	0,03094	0,15595	0,10359	0,8543
Cu	0,06932	0,96105	-0,018	0,13466
Zn	0,86129	0,06971	0,01742	-0,1339
Pb	0,63429	0,09194	-0,0971	0,45447
Hg	0,20117	0,95059	-0,032	0,0692
Cr	0,59841	0,7305	0,0947	0,02447
Cd	0,59393	0,43801	0,31873	0,02651
Al	0,23139	-0,1367	0,80572	-0,0803
Fe	0,3134	-0,2286	0,72462	0,42019
Corg	0,84446	0,21136	0,10098	0,16009
CO_3^{-2}	-0,0582	0,08096	0,89756	0,25099
Chl.-a	-0,1104	0,21408	0,77831	-0,1331

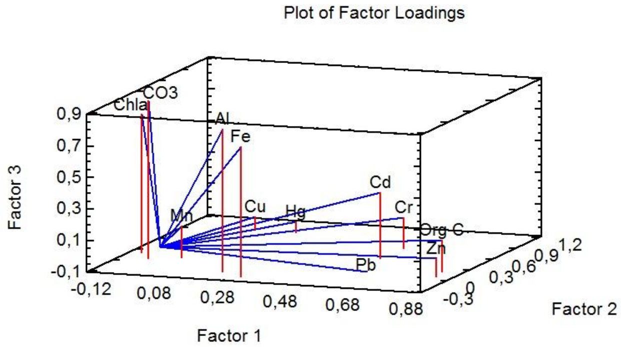

Figure 6. 3D plot of the factor loadings after Varimax rotation.

were below ERM values, whereas only Cd contaminations had below ERL values indicating that the preindustrial background value in Izmir Bay sediments is well below the crustal value. There is a strong accumulation of this metal but it does not reach to highly toxic levels.

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References

Abrahim, G.M.S. and Parker, R.J. 2008. Assessment of heavy metal enrihment factors and degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environmental Monitoring and Assessment, 136: 227-238. doi: 10.1007/s10661-007-9678-2

Aksu, A.E., Yaşar, D. and Uslu, O. 1998. Assessment of marine pollution in Izmir Bay: Heavy metal and organic compound concentrations in surficial sediments. Translations and Journal of Engineering and Environmental Science, 22:387-415.

Angelidis, M.O. and Aloupi, M. 2000. Geochemical study of coastal sediments influenced by river –transported pollution: Southern Evoikos Gulf, Greece. Marine Pollution Bulletin, 40(1): 77-82. doi: 10.1016/S0025-326X(99)00174-5

Atgin, R.S., El-Agha, O., Zararsız, A., Kocataş, A., Parlak, H. and Tuncel, G. 2000. Investigation of the sediment pollution in Izmir Bay: trace elements. Spectrochimica Acta Part B, 55: 1151-1164. doi: 10.1016/S0584-8547(00)00231-7

Billon, G., Ouddane, B., Recourt, P. and Boughriet A. 2002. Depth variability and some geochemical characteristics of Fe, Mn, ca, Mg, Sr, P, Cd and Zn in anoxic sediments from Authie Bay. Estuarine Coastal and Shelf Science, 22: 805-815.

Birch, G., ed. C.D.a. Woodroffe, F. 2003. Coastal GIS 2003, Wollongong University Papers in Center of Maritime Policy, 14, Australia, Edition edn.

Dalman, O., Demirak, A. and Balci, A. 2006. Determination of heavy metals (Cd, Pb) and trace elements (Cu, Zn) in sediments and fish of the Southeastern Aegean Sea (Turkey) by atomic adsorption spectrometry. Food Chemistry, 95: 157-162. doi: 10.1016/j.foodchem.2005.02.009

Ergin, M., Bodur, M.N., Ediger, V., Yemenicioğlu, S., Okyar, M. and Kubilay, N.N. 1993. Sources and dispersal of heavy metals in surface sediments along the Eastern Aegean Shelf. Boletino Di Oceanologia Teorica Applicata, 11(1): 27-43.

Esen, E., Küçüksezgin, F. and Uluturhan, E. 2010. Assessment of trace metal pollution in surface sediments of Nemrut Bay, Aegean Sea. Environmental Monitoring and Assessment, 160: 257-266.doi: 10.1007/s10661-008-0692-9

Fan, W.H., Wang, W.X. and Chen J.S. 2002. Geochemistry of Cd, Cr and Zn in highly contaminated sediments and its influences on assimilation by marine bivalves. Environmental Science and Technology, 36: 5164-

5171. doi: 10.1021/es020122m

Folk, R.L. 1974. Petrology of Sedimentary Rocks. Hemphill pres, Texas, 182 pp.

Fukue, M., Nakamura T., Kato, Y. and Yamasaki S. 1999. Degree of pollution for marine sediments. Engineering Geology, 53: 131-137. doi: 10.1016/S0013-7952(99)00026-5

Gaudette, H.E., Fligh, W.R., Tonner, L. and Folger, D.W. 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. Jornal of sedimentary petrology, 44: 249-253.

Gaur, V.K., Sanjay, K.G., Pandey, S.D., Gopal, K. and Mısra, V. 2005. Distribution of heavy metals in sediment and water of River Gomti. Environmental Monitoring and Assessment, 102: 419-433. doi: 10.1007/s10661-005-6395-6

Güven, D. and Akıncı, G. 2008. Heavy metals partitioning in the sediments of Izmir inner Bay. Journal of Environmental Sciences, 20: 413-418. doi: 10.1016/S1001-0742(08)62072-0

Hakanson, L. 1980. Ecological risk index for aquatic pollution control, a sedimetological approach. Water Research, 14: 975-1001. doi: 10.1016/0043-1354(80)90143-8

Karageorgis, A.P., Nikolaidis, N.P., Karamanos, H. and Skoulikidis, N. 2003. Water and sediment quality assessment of the Axios River and its coastal environment. Continental Shelf Research, 23: 1929-1944. doi: 10.1016/j.csr.2003.06.009

Korfali, S.I. and Davies, B.E. 2004. Speciation of metals in sediment and water in a river underline by limestone: role of carbonate species for purification capacity of rivers. Advances in Environmental Research, 8: 599-612. doi: 10.1016/S1093-0191(03)00033-9

Küçüksezgin, F. 2001. Distribution of heavy metals in the surficial sediments of Izmir Bay (Turkey). Toxicological and Environmental Chemistry, 80: 203-207. doi: 10.1080/02772240109359010

Küçüksezgin, F., Kontaş, A.,Altay, O. Uluturhan, E. and Darılmaz, E. 2006. Assessment of marine pollution in Izmir Bay: Nutrient, heavy metal and total hydrocarbon concentrations. Environment International, 32: 41-51. doi: 10.1016/j.envint.2005.04.007

Long, E.R. and MacDonald, D.D. 1998. Recomended uses of emprically derived, sediment quality guidelines for marine and estuarine ecosystems. Human and Ecological Risk Assessment, 4 (5): 1019-1039 doi: 10.1080/10807039891284956

Lorenzen, C. J. 1971. Chlorophyll-degradation products in sediments of Black Sea. Woods Hole Oceanographic Institution Contribution No. 2828: 426-428.

Luoma, S.N. 1983. Bioavailability of trace metals to aquatic organism – a review. Sci. Total Environ., 28: 1-22. doi: 10.1016/S0048-9697(83)80004-7

MacDonald, D.D., Car, R.S., Calder, F.D., Long, E.R. and Ingersoll C.R. 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology, 5: 253-278. doi: 10.1007/BF00118995

Matthiesen, H. 1998. Phosphate release from marine sediments: by diffusion, advection and resuspension. Ph.D. Thesis, Department of Chemistry University of Aarhus, Denmark, 131pp.

Müller, G. 1969. Index of geoaccumulation in the sediments of the Rhine River. Geojournal, 2: 108-118.

Natusch, D.F.S., Bauer, C.F., Matusiewicz, H., Evans, C.A., Baker J., Loh, A., Linton, R.W. and Hopke, P.K. 1975. Characterization of trace elements in fly ash. International conference on Heavy Metals in the Environment, Symposium Proceedings, October 27-31, Ontario, Canada, vol. 2. Part 2, 553-575pp.

Uluturhan, E. 2009. Heavy metal concentrations in surface sediments from two regions (Saros and Gökova Gulfs) of the Eastern Aegean Sea. Environ Monit Assess, 165:675-684.doi: 10.1007/s10661-009-0978-6

Parizanganeh, A., Lokhan, V.C. and Jalalian, H. 2007. A geochemical and statistical approach for assessing heavy metal pollution in sediments from the southern Caspian coast. International Journal of Environmental Science Technique, 4(3): 351-358.

Pekey, H. 2006. The distribution and sources of heavy metals in İzmit Bay surface sediments affected by a polluted stream. Marine Pollution Bulletin, 52: 1197-1208.
doi: 10.1016/j.marpolbul.2006.02.012

Shepard, F.P. 1954. Nomenclature based on sand-silt-clay ratios. Journal of Sedimentary Petrology, 24: 151-15.

Sutherland, R.A. 1999. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environmental Geology, 39(6): 615-627.

Taylor, S. R. 1972. Abundance of chemical elements in the continental crust: A new table. Geochimica et Cosmochimica Acta, 28: 1273-1286. doi: 10.1016/0016-7037(64)90129-2

Turekian, K.K. and Wedepohl, D.H. 1961. Distribution of the elements in some major units of the earth’s crust. Bulletin Geological Society of America, 72: 175-192. doi: 10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2

Turner, A. 2000. Trace metal contamination in sediment from U.K. estuaries: An empricial evaluation of the role of hydrous iron and manganese oxides. Estuarine, Coastal and Shelf Science, 50: 355-371. doi: 10.1006/ecss.1999.0573

Wang, S., Jia, Y., Wang, S., Wang, X., Wang, H., Zhao, Z. and Liu, B. 2010. Fractionation of heavy metals in shallow marine sediments from Jinzhou Bay, China. Journal of Environmental Sciences, 22: 23-31. doi: 10.1016/S1001-0742(09)60070-X

Wedepohl, K. 1995. The composition of the continental crust. Geochimica et Cosmocheimica Acta, 59: 1217-1232. doi: 10.1016/0016-7037(95)00038-2

Wen, L.S., Warnken, K.W. and Santschi, P.H. 2008. The role of organic carbon, iron, and aluminium oxyhydroxides as trace metal carriers: Comparison between the Trinity river and Trinity river estuary (Galveston Bay, Texas). Marine Chemistry 112:20-37. doi: 10.1016/j.marchem.2008.06.003