

Assessment of Marine Pollution in İzmir Bay: Heavy Metal and Organic Compound Concentrations in Surficial Sediments

Ali Engin AKSU

*Department of Earth Sciences, Centre for Earth Resources Research
Memorial University of Newfoundland, St. John's,
Newfoundland CANADA A1B 3X5*

Doğan YAŞAR, Orhan USLU

*Institute of Marine Sciences and Technology, Dokuz Eylül University
1884/8 Sokak, No:10, İnciraltı 35340, İzmir-TURKEY*

Received 06.03.1997

Abstract

The extent of marine pollution in İzmir Bay is investigated using inorganic and organic geochemical data from surface sediments. The concentrations of 42 elements in 84 samples established that surface sediments in Inner İzmir Bay display significant enrichments in Ag, As, Cd, Cr, Cu, Hg, Mo, P, Pb, Sb, Sn, V, and Zn, associated with notably high concentrations of total organic carbon and sulphur. Organic geochemical data in 14 samples from Inner İzmir Bay showed that these sediments also exhibit significant enrichments in polycyclic aromatic hydrocarbons and polychlorinated dibenzo-d-dioxins and dibenzofurans. Combined inorganic and organic geochemical data indicated that Inner İzmir Bay surface sediments are extremely polluted and probably pose high risk to the resident marine biological community.

Except for a few small regions, the Outer and Central İzmir Bays show low levels of heavy metal enrichments. Moderate enrichments in Ag, Cd, Hg, Mo, Sb and Sn in surface sediments east of Hekim and Çiçek Islands probably reflect continuous dumping of sediments excavated from the most polluted innermost İzmir Bay between 1976 and 1990. The zone of moderate enrichments in Cd, Cr, Cu, Hg, Pb and Zn south of the present-day mouth of Gediz River suggests that discharge from this river is one of the major sources of anthropogenic input into the Outer İzmir Bay and probably reflects the large quantities of industrial discharge into Gediz River along its course.

Key Words: İzmir Bay, Marine Pollution, Heavy Metals, Dioxins, Furans, Polycyclic Aromatic Hydrocarbons.

İzmir Körfezi'nde Deniz Kirliliğinin Değerlendirilmesi: Yüzey Sedimanlarında Ağır Metal ve Organik Madde Yoğunlukları

Özet

İzmir Körfezi'nde deniz kirliliğinin boyutları yüzey sedimanlarında inorganik ve organik jeokimyasal verilerle değerlendirilmiştir. Seksen dört örnek üzerinde belirlenen 42 elementin yoğunlukları İzmir Körfezi yüzey sedimanlarının toplam organik karbon ve sülfür ile bağlantılı olarak gelişen Ag, As, Cd, Cr, Cu, Hg, Mo, P, Pb, Sb, Sn, V, ve Zn gibi ağır metallerce belirgin bir zenginleşme gösterdiğini saptamıştır. İzmir İç Körfezi'nde 14 örnek üzerinde gerçekleştirilen organik jeokimyasal veriler ise bu sedimanların aynı zamanda poliklorlu dibenzo-p-dioksinler, poliklorlu dibenzofuranlar ve polisiklik aromatik hidrokarbonlarca da çok zengin olduğunu belgelemiştir. Bu inorganik ve organik veriler İzmir İç Körfezi'nin aşırı derecede kirliliği olduğunu ve denizsel çevrede yaşayan canlılara büyük ölçüde risk oluşturabileceğini belirtmektedir.

Birkaç küçük bölge dışında İzmir Orta ve Dış Körfezi düşük oranlarda ağır metal zenginleşmesi göstermektedir. Hekim ve Çiçek Adaları'nın doğu kesimlerinde görülen ve Ag, Cd, Hg, Mo, Sb and Sn yoğunluklarında gözlenen zenginleşmelerin 1976'dan 1990 yıllarına kadar süren, İzmir İç Körfezi'nin en kirli sedimanlarının tarama ve döküm işlemleri sonucunda oluştuğu düşünülmektedir. Gediz Nehri'nin güncel ağzının güney kesimlerinde görülen ve Cd, Cr, Cu, Hg, Pb ve Zn gibi ağır metallerle belirlenen zenginleşme ise Gediz Nehri'nin drenaj alanındaki büyük sanayileşmeyi yansıtmakta ve bu nehirin Orta Körfez'in önemli antropojenik kaynaklarından biri olduğunu belirtmektedir.

Anahtar Sözcükler: İzmir Körfezi, Deniz Kirliliği, Ağır Metaller, Dioksinler, Furanlar, Polisiklik Aromatik Hidrokarbonlar.

1. Introduction

İzmir Bay is a long embayment situated along the eastern Aegean Sea (Figure 1). It is naturally divided into three parts: Outer, Central and Inner İzmir Bays. The Outer İzmir Bay is ~20 km-wide between Karaburun and Foça and extends ~45 km in a northwest-southeast direction. Uzun Island divides the Outer İzmir Bay into a ~6 km-wide western and a ~12 km-wide eastern segments (Figure 1). The eastern segment is bounded in the northwest by the shores of the Holocene Gediz delta and in the southeast by the Uzun, Hekim, and Çiçek Islands (Figure 1). At the exit to Aegean Sea the water depth exceeds 72 m; the axis of Outer Bay becomes shallower towards the southeast to <50 m east of Çiçek Islands. The Central and Inner İzmir Bays extend in an east-west direction, and are collectively ~24 km-long and ~6 km-wide (Figure 1). The Central Bay (10 km-long) is separated from the Inner Bay by a 13 m-deep sill (Yenikale Entrance; Figures 1, 2) which is created by the rapid progradation of the now abandoned Karşıyaka and Pelikan lobes of the Gediz delta during the last few hundred years (Aksu and Piper, 1983). The water depth in Inner İzmir Bay is less than 20 m.

The water circulation in İzmir Bay is predominantly controlled by the prevailing winds in the region: semidiurnal tides of 20-40 cm have negligible effect (Akyarlı *et.al.*, 1988). During the summer and autumn, surface water is driven towards the southeast by the prevailing northwesterlies with speeds of ~40 cm s⁻¹. During the winter northerlies and northeasterlies drive the surface waters towards the south-southwest with speeds of <30 cm s⁻¹. There is no dominant surface current direction in the spring and measurements show significant reduction in current speeds to 6-20 cm s⁻¹. Although surface water moves with the prevailing winds, there is little water exchange between the Inner and Central İzmir Bays (Akyarlı *et.al.*, 1988).

2. Scientific Objectives

The city of İzmir is built around the perimeter of Inner İzmir Bay (Figure 1). The shallow sill depth at the Yenikale Entrance and the shallow water depths of the Inner Bay prevent large container ships to enter the İzmir harbour (Figure 1). Between 1930 and 1976 the innermost harbour region was dredged and ~ 2.8 × 10⁶ m³ of excavated sediments were dumped on the sea-bed at Göztepe Bay Dump Site (Figure 1; Uslu and Akyarlı, 1992). Subsequent excavations between 1976 and 1990 produced ~ 9.0 × 10⁶ m³ of sediments, which were also dumped on the sea-bed at the Hekim Island Dump Site (Figure 1). During the last ca.30 years a large number of studies have been carried out on the physical, chemical and biological oceanography of İzmir Bay (e.g. Demircanlı and Güçer, 1983; Güçer *et.al.*, 1983; Şengül, 1986; Yaramaz, 1983; Kestioğlu and Şengül, 1984; Büyükişık, 1988; Müezzinoğlu and Şengül, 1988; Türkoğlu, 1991; Mülazımoğlu, 1993; Cihangir, 1995; Bizsel, 1996). However, only a limited number of marine geological studies have been conducted during this period, mainly focussed on the sedimentology of a small region within İzmir Bay (e.g. Başoğlu, 1980; Eftelioğlu, 1983; Köken, 1985). Therefore, despite almost continuous dredging and dumping since the 1930's no systematic sediment sampling and studies were carried out in İzmir Bay. Consequently, there is little baseline data on the extent of pollution and the types of pollutants in İzmir Bay, thus, critical data for the assessment of the environmental pollution in this embayment is limited at best.

The primary scientific objectives of this paper are (1) to document the occurrence, abundance and distribution pattern of a large number of inorganic and organic pollutants and (2) to delineate the extent of the anthropogenic pollution in İzmir Bay surface sediments.

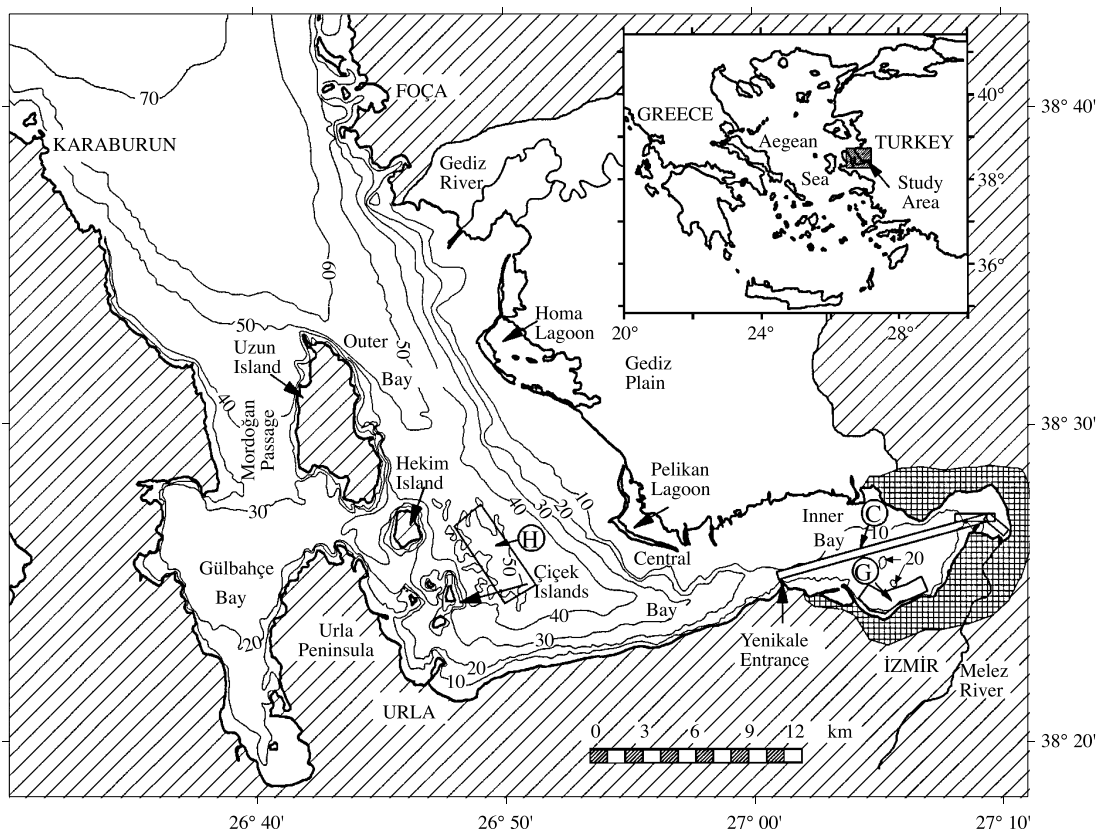


Figure 1. Location map of the study area, showing present-day bathymetry. C=Proposed Entry Canal; G=Göztepe Bay Dump Site; H=Hekim Island Dump Site (from Uslu and Akyarlı, 1992). Isobaths are in metres. Inset shows the location of İzmir Bay in eastern Aegean Sea.

3. Materials and Methods

During the summer of 1994 sediment samples were collected from 84 stations in İzmir Bay using a modified grab sampler/box corer and the RV *Koca Piri Reis* of the Institute of Marine Sciences and Technology (Figure 2). At each station the sediment water interface was carefully skimmed: these samples are referred to as “surface sediments”. A second sample was collected at each station from ~25 cm below the surface: these samples are referred to as “subsurface sediments”. All sediments were dried at 40°C immediately following recovery, and dry sediments were shipped to Memorial University of Newfoundland for analyses.

A combination of X-ray fluorescence spectrom-

eter (XRF), inductively coupled plasma emission spectrometer (ICP-ES) and atomic absorption spectrophotometry (AAS) were used to determine the total levels of the following elements in 84 surface and 50 subsurface samples: Ag, Al, As, Ba, Be, Ca, Ce, Cd, Cl, Co, Cr, Cu, Dy, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Si, Sn, Sr, Th, Ti, U, V, Y, Zn and Zr.

For major and trace element determinations using ICP-ES or AAS, except Ag, As, Cd, Hg, Rb and Sb, sediments were powdered, 5 g of powder was treated with 30% H₂O₂ to extract elements absorbed by organic matter and amorphous oxides. Samples were then digested by 15 ml HF, 5 ml concentrated HCl and 5 ml 1:1 HClO₄ at 200°C and subsequently by 50 ml 20% HCl at 100°C. Measure-

ments were made using an ARL ICP-ES. Samples for Cd were processed as above and Cd was measured using a Varian Model AA1275 AAS. For Ag samples were digested by 2 ml concentrated HNO₃ and left at room temperature over night, subsequently they were placed into a hot water bath at 90°C and were further digested for 2 hours. Measurements were made using an AAS. For As and Sb samples were partially digested by concentrated HNO₃, subsequently

1 ml concentrated HCl was added and samples were further digested for 90 minutes. As and Sb were measured using an ICP-ES. For Hg samples were digested by 10 ml concentrated HNO₃ and 1 ml concentrated HCl for 10 minutes. Samples were then placed in a hot water bath at 90°C and digested for an additional 2 hours. Hg was measured using an ICP-ES where four on-peak and four off-peak measurements were made.

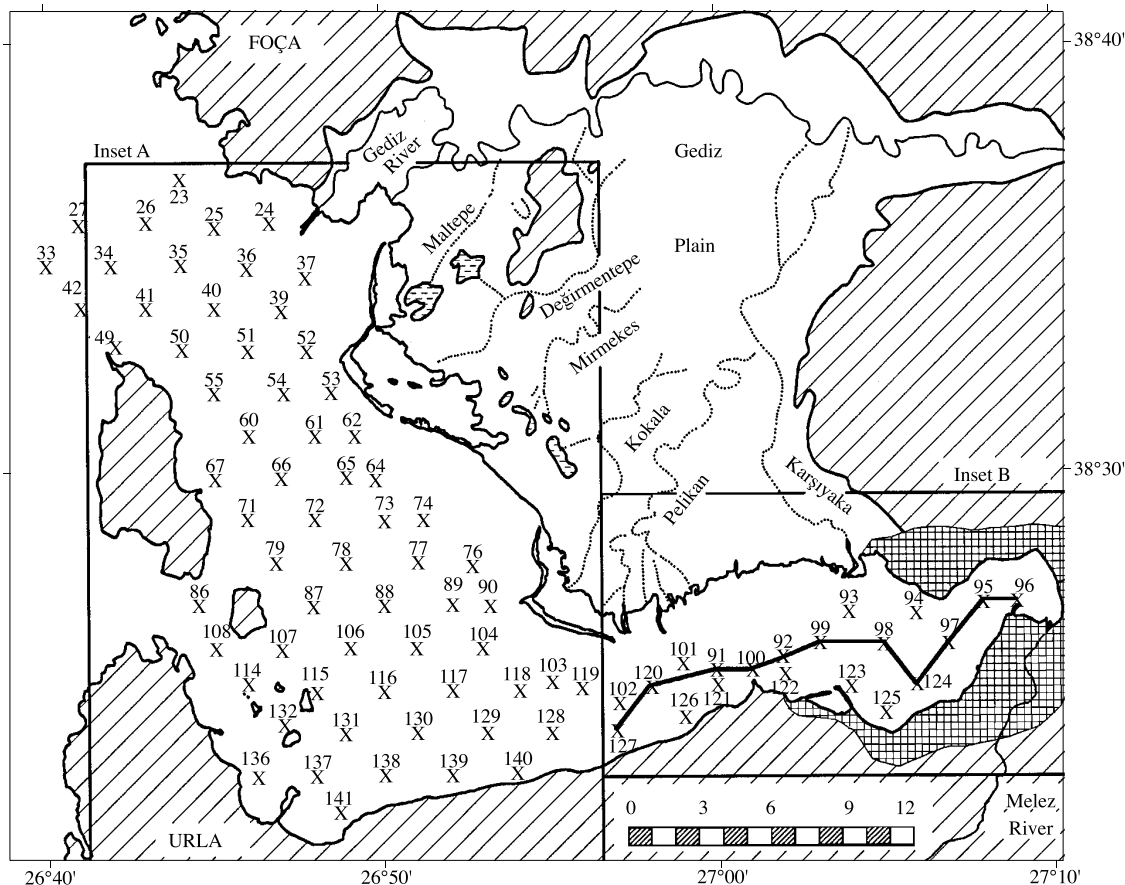


Figure 2. Map showing the location of samples used in this study, the positions of present-day Melez and Gediz Rivers and the abandoned channels of the Gediz River: Karşıyaka, Pelikan, Kokala, Mirmekes, Maltepe and Değirmentepe. Insets A and B show the position of Figures 7-8 and 9-10, respectively.

For XRF analyses sediments were powdered and 4 g of powder was mixed with 0.7 g of phenolic resin binder. After homogenization, XRF pellets were prepared and baked for 15 minutes at 200°C. Elements were determined using an XRF ARL 8420+ sequential wavelength-dispersive spectrometer, with a Rh

end-window X-ray tube and a LiF200 crystal, specially treated for enhanced heavy element sensitivity. For energies >7.471 keV (20° – 50°2θ) a scintillation detector was used with power settings at 75 kV and 40 mA. For energies <6.398 keV (50° – 150°2θ) a flow-proportional detector was used with power set-

tings at 30 kV and 100 Ma. Scan times were 4-6 seconds for the most abundant elements, 20 seconds for the trace elements and 100 seconds for Rb, Y and Nb. The intensities were then matrix corrected using Compton correction for elements with emission energies greater than Fe and using LaChance-Traill algorithm for elements with emission energies less than and including Fe.

For total organic carbon (TOC) samples were acidified with 30% HCl, and the carbonate-free residues were dried at 40°C to preserve all soluble organic matter. Total carbonate was determined as the percent of sample lost during acid digestion, where the evolved CO₂ was measured using a calibrated manometer in high-vacuum line. A portion of the dried sediment was transferred into quartz tubes; known amounts of purified cupric oxide and high purity copper were added. Quartz tubes are sealed in a vacuum line, then combusted for at 850°C for 1 hour. The evolved CO₂ was cryogenically isolated and TOC was determined using a calibrated manometer in high vacuum line.

Grain size distribution was determined using standard sieve technique for > 63µm and a Sedi-graph 5100 particle size analyzer for particles between 63µm and 0.1µm. The biogenic carbonate remains in the sand fractions were separated and the percentages of terrigenous sand, silt and clay fractions were recalculated. For clay mineralogy samples were disaggregated in distilled water with 10% H₂O₂ and 1% sodium metaphosphate. Clay-sized particles (> 2µm) were separated using the centrifuge technique described in Hardy and Tucker (1988). Clay minerals were treated with saturated CaCl₂ and oriented slides were prepared. Air-dried, ethylene glycol and glycerol saturated slides were run on a Rigaku R4-200 X-ray diffractometer (XRD), and semiquantitative abundances of illite, smectite, chlorite, kaolinite, vermiculite and mixed-layer clays were calculated following the methods described in Hardy and Tucker (1988) and Moore and Reynolds (1989).

The determinations of the priority organic pollutants, including polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polycyclic aromatic hydrocarbons (PAH), organochlorine pesticides (OP), phenoxyacid herbicides (PH) and polychlorinated biphenils (PCB) are carried out by Zenon Environmental Laboratories, Burlington Ontario. Keith (1992) provides the details of these methods, except for the determinations

of PAH where samples were spiked with isotopically labelled PAH (deuterium); and were analyzed by high resolution gas chromatography/low resolution mass spectrometry - selected ion monitoring technique. Quantification of various organic compounds were made by isotope dilution based on internal standards. All gas chromatography work was carried out using dual column capillary gas chromatography - electron capture detection method. Quality control involved a minimum of 1 blank in 14 and a replicate and matrix spike at a minimum of 1 blank in 20 samples. Fourteen samples from the Inner İzmir Bay were analyzed for these priority organic pollutants.

Results

Grain Size Distribution

Figure 3 illustrates the geographic distribution of sand, silt and clay in İzmir Bay surface sediments. The data show that medium-sorted terrigenous sands with 70-95% sand (> 63µm) are primarily confined to the shallow water pro-delta deposits encircling the shores of the present-day Gediz delta (Figure 3). Two large barrier islands encircling the Homa and Pelikan lagoons (Figure 1) and several smaller sand bars are also composed of medium-sorted sands, and are formed through winnowing and reworking of progradational channel mouth deposits by waves and long-shore currents following delta abandonment. Nineteenth century maps of İzmir Bay (Kiepert, 1887) show a narrow, elongate, birdfoot-type delta at the mouth of the Pelikan channel, with five major distributaries, but, no barrier island. Following the diversion of the Gediz River to its present-day channel in 1886, these progradational channel deposits appears to have formed the Pelikan barrier island. Similarly, the formation of the Homa barrier island system probably reflects the reworking of the delta mouth deposits of the former Değirmentepe and/or Mirmekes channels. These data clearly show that Gediz River exhibits a river-dominated delta front along delta mouths where active progradation occurs, but a wave-dominated delta front morphology predominates along the shores of abandoned channels.

Silty sands and sandy-silts with 40-70% sands also occur along the nearshore regions of western Outer İzmir Bay between the northern tip of Uzun Island and west of the Çiçek Islands (Figure 3).

ranges between 28 and 48% with highest values occurring along the shores of the Gediz delta plain, seawards of the Homa and Pelikan lagoons. Microscopic examination revealed that the sand fraction of these sediments contains 20-40% muscovite with lesser amounts of biotite. This positive relationship between illite and muscovite/biotite suggests that

most illites in İzmir Bay are probably clay-sized mica minerals. Poorly consolidated Neogene sedimentary successions and to a lesser extent the crystalline Palaeozoic metamorphic rocks (particularly the mica schists) outcropping along the drainage area of Gediz River probably provided the source for the illite minerals found in İzmir Bay sediments.

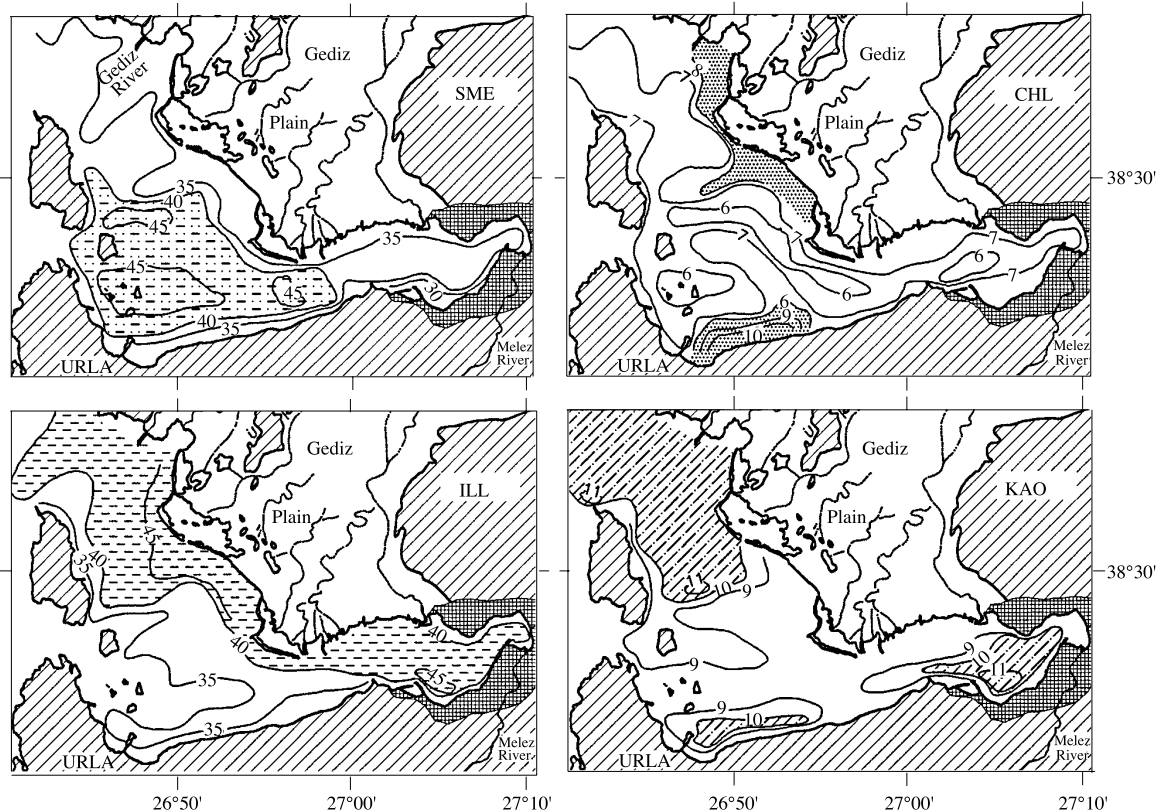


Figure 4. Geographic distribution of clay minerals illite, smectite, chlorite and kaolinite percentages in İzmir Bay surface sediments.

Smectite varies between 20 and 48% in İzmir Bay surface sediments with highest values occurring (a) in the southern segment of Outer İzmir Bay north of the Hekim Island, (b) in a large area, including the Çiçek Islands and extending eastwards and (c) a small area in Central Bay, south of the abandoned Pelikan mouth (Figure 4). Smectite shows a noticeable decline towards the Inner İzmir Bay, reaching values less than 30% over the Göztepe Bay Dump Site (Figure 4). Comparison between the regional distribution maps of illite and smectite shows the presence of an inverse relationship between these two

clay minerals (Figure 4). Smectite is also primarily supplied by the Gediz River. Smaller quantities of smectite may also be contributed from the Neogene sedimentary and volcanic rocks outcropping along the southern segment of İzmir Bay. Illite minerals are generally much bigger in size than smectite minerals (Moore and Reynolds, 1989); therefore, during sedimentation illites tend to concentrate closer to the shoreline, whereas the smectites are kept in suspension longer, thus transported into deeper basins. The strong inverse relationship observed between illite and smectite probably represents the differences

between the settling rates of these minerals, further accentuated by the percentage calculation in a closed data set.

Kaolinite ranges between 8 and 13% in İzmir Bay surface sediments (Figure 4). This mineral is the by-product of chemical weathering in hot and humid climates (Moore and Reynolds, 1989). Low kaolinite abundances in İzmir Bay probably reflect the absence of this mineral and the predominance of illite and smectite in the source rocks. Chlorite varies between 5 and 12%, reaching values >8% only in the region encircling the Homa lagoon, and an elongate nearshore zone east of Urla (Figure 4). The source of chlorite is probably the metamorphic rocks along the Gediz River, and to a lesser extent the Neogene sedimentary rocks surrounding the study area. Mixed-layer clay mineral smectite-illite ranges between 3 and 9% in İzmir Bay surface sediments. Its highest values occur around the Hekim and Çiçek Islands. This regional distribution resembles that of the smectite, suggesting a similar source. Vermiculite varies between 3 and 11% in İzmir Bay, reaching its highest values in the innermost Inner İzmir Bay and is primarily supplied by the Melez River (Başoğlu, 1980).

3.2. Inorganic Geochemical Data

Elemental Associations

The inorganic geochemical data consist of measurements of 44 variables in 84 surface samples. This large data set does not immediately allow an unambiguous interpretation of elemental associations and potential sources in sediments. Factor analysis is a powerful tool in obtaining simple patterns from such complex data (Klován and Imbrie, 1971). The technique extracts a small number of hypothetical variables (R mode) or samples (Q mode), referred to as “factors”, which account for a given percentage of the total variance in the data set.

Both Q and R mode factor analyses are performed on the geochemical data from İzmir Bay. The results showed that three factors account for a total of 97.8% of the total variance, and that the remaining 2.2% is probably random (Figures 5, 6). Factor 1 accounts for 58.2% of the total variance and show high factor loadings in Al and Si, with statistically significant loadings (>0.3; Klován and Imbrie, 1971) in Be, Co, Dy, Fe, Ga, K, La, Li, Mg, Mn, Nb, Ni, Rb and Y (Figure 5).

This factor represents the most common constituent of siliciclastic marine sediments: aluminosilicates. High factor loadings in Fe, Mg, Ni, Rb, Y

and Nb probably reflect the distribution and variation in illite, chlorite and smectite in the area. Factor 2 accounts for 26.7% of the total variance and show high loadings in C, S, ignition loss (IL), but further show significant loadings in Ag, As, Cd, Cr, Cu, Hg, Mo, P, Pb, Sb, Sn, V, and Zn (Figure 5). This factor represents the organic matter and the associated metal enrichments. Factor 3 accounts for 12.9% of the total variance and show high factor loadings in Ca and total carbonate (Figure 5), with significant loadings in Sr and Sc. It represents the carbonates in the study area. The absence of any noticeable correlation between Ca and Mg suggests that most of the carbonate is stored as calcite and aragonite.

Figure 6 shows the geographical distribution of the normalized varimax components of each factor. Factor 1 (aluminosilicates) shows its highest loadings in deeper-water basinal suggesting that most of the Al and Si and the associated minor and trace elements are stored in silty-clays and sandy-silty-clays. Factor 2 (organic matter) is the dominant factor in Inner İzmir Bay, east of the Yenikale Entrance, however, small occurrence of this factor is also observed in the Outer İzmir Bay, west of the Çiçek and Hekim Islands (Figure 6). Factor 3 (carbonates) is concentrated along the western Outer İzmir Bay (Figure 6), where the Mesozoic carbonate rocks are well exposed (Dubertret, 1964).

Elemental Background Concentrations

Background level for each element is calculated as the mean value of that element in 50 subsurface samples collected from the Central and Outer İzmir Bays. The background concentrations, in ppm, of 12 elements associated with factor 2 are: Ag = 0.05, As = 10, Cd = 0.03, Cr = 175, Cu = 17, Hg = 0.05, Mo = 1, Pb = 8.5, Sb = 1, Sn = 2, V = 60 and Zn = 65. No chronological data is available from these samples. However, high-resolution seismic stratigraphy showed that away from the Gediz prodelta sequences the thickness of the post-glacial sediments vary between 5 m and 25 m (Aksu and Piper, 1983). Radiocarbon dates indicated that the base of Holocene sediments occurs at ~12500 years before present, suggesting overall sedimentation rates ranging between 40 and 200 cm per 1000 year (Aksu and Piper, 1983; Aksu *et al.*, 1987). This first order sedimentation rate estimate suggests that the subsurface sediments used for the heavy metal background concentrations were deposited between 125 and 625 years before present, clearly representing the pre-industrial period in the region.

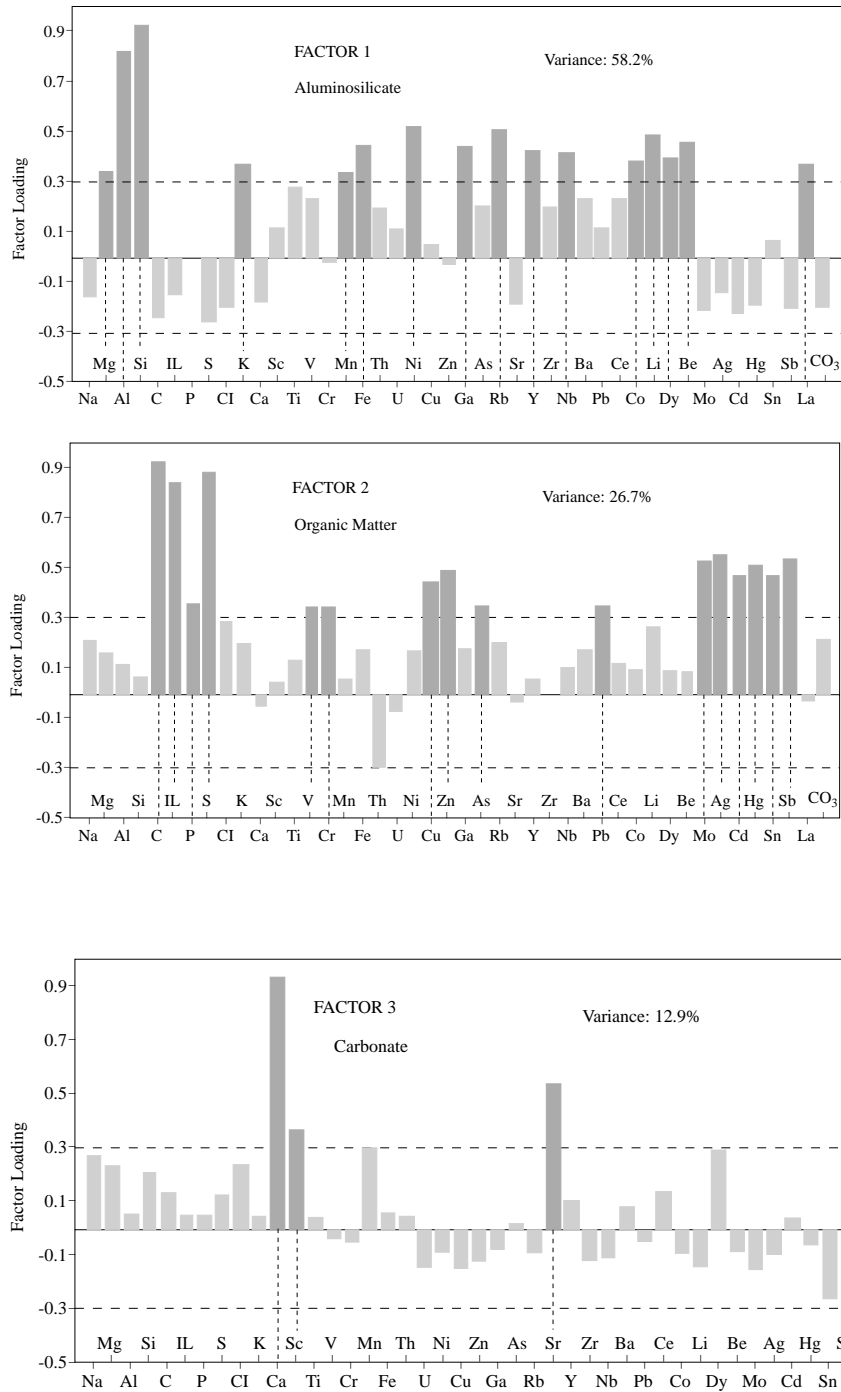


Figure 5. Results of factor analysis (R mode), showing the elemental composition of the three primary factors accounting 97.8% of the total variance. Factor loadings >0.3 are considered statistically significant (Klován and Imbrie, 1971).

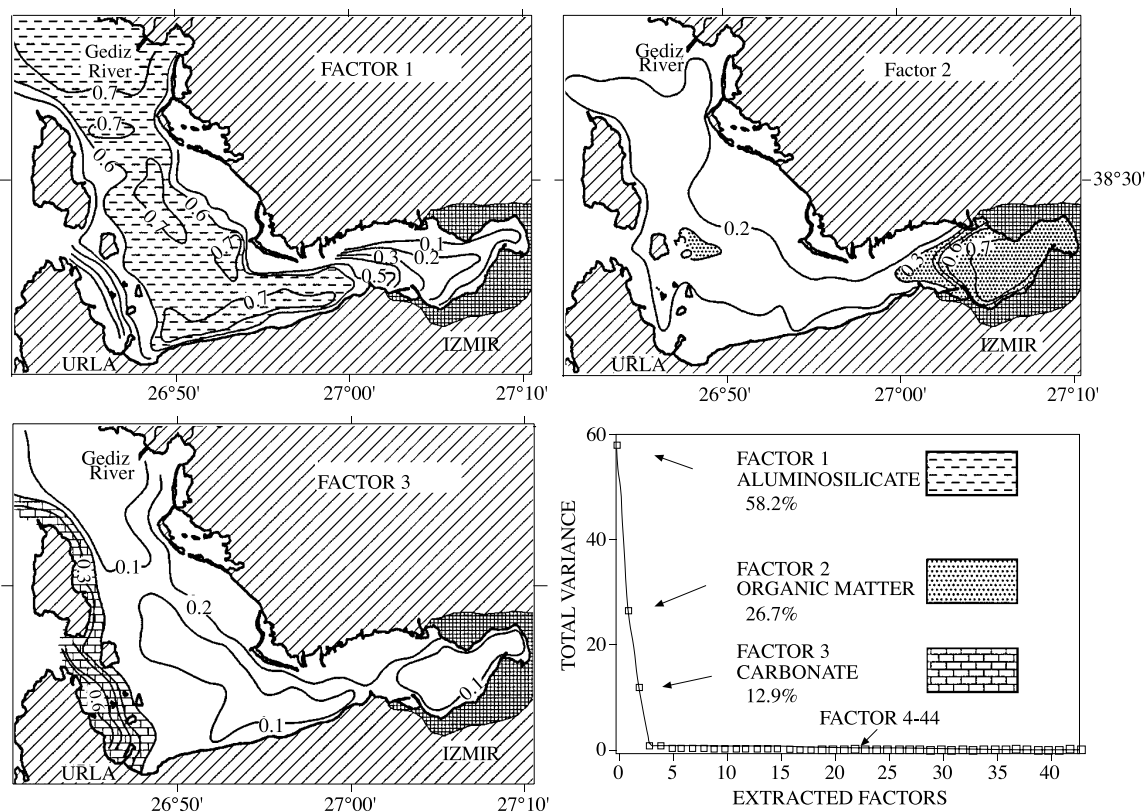


Figure 6. Geographical distribution of the normalized varimax factor components (Q-mode). Factors 1-3 are statistically significant, whereas straight line created by factors 4-44 represent random variance (**bottom right**).

Distribution of Heavy Metals in Outer İzmir Bay

Figures 7 and 8 illustrate the geographical distribution of 16 heavy metals and compounds associated with factor 2 in Outer İzmir Bay. Silver ranges between 0.2 and 0.5 ppm, with highest values occurring east of the Hekim and Çiçek Islands (Figure 7E). East of Uzun Island and east of Hekim and Çiçek Islands Cd concentrations are relatively high ranging between 0.2 and 0.6 ppm (Figure 7C); otherwise Cd concentration is below its detection limit of 0.1 ppm in Outer İzmir Bay. Arsenic ranges between 20 ppm along the southwestern shores of Gediz delta plain to >50 ppm around the mouth of the Gediz River (Figure 7F). Relatively high As concentrations are also observed west of the Hekim Island. Chromium is >300 ppm along the southwestern shores of the Gediz delta, decreasing to >150 ppm around the Çiçek Islands (Figure 7H). Copper ranges between 15 and 40 ppm, with highest concentrations occur-

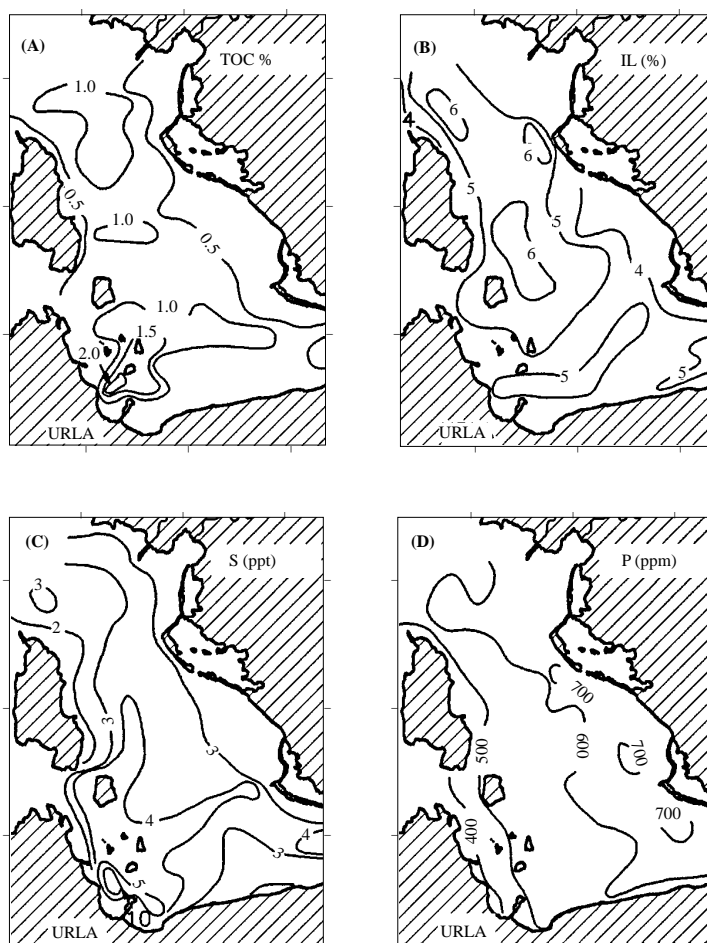
ring near the mouth of the Gediz River and northeast of Hekim and Çiçek Islands (Figure 7A). Mercury distribution shows two zones of relatively high Hg concentrations: a north-south trending belt extending from the present-day mouth of the Gediz River towards the northern Hekim Island and a higher concentration zone occupying the southern portion of the Outer İzmir Bay east of the Hekim and Çiçek Islands (Figure 8B). Except for a zone of 2-3 ppm east of the Hekim and Çiçek Islands, Mo is below its detection limit of 1 ppm in the Outer İzmir Bay (Figure 8C). Lead ranges between 15 ppm and 30 ppm, with highest concentrations occurring east of the Hekim and Çiçek Islands, and near the mouth of the Gediz River (Figure 8D). Antimony ranges between 0.5 and 3.0 ppm, with highest values occurring east of the Hekim and Çiçek Islands (Figure 8E). Tin shows a similar pattern to Sb with highest values of >4 ppm occurring east of the Hekim and Çiçek Islands (Figure 8F). Vanadium ranges from >130 ppm

along the southwestern shores of the Gediz delta and the shores of the Çiçek Islands to >160 ppm near the mouth of the present-day Gediz River (Figure 8G). Zinc distribution is similar to that of V, with values ranging between 50 ppm and 150 ppm (Figure 8H).

Distribution of Heavy Metals in Central and Inner İzmir Bays

Figures 9 and 10 illustrate the geographical distribution of these elements and compounds in Central and Inner İzmir Bays. TOC is generally less than 2% in Outer and Central Bays (Figure 7) and rapidly increases to >3% east of the Yenikale Entrance and to >7% in Inner İzmir Bay (Figure 9A). IL mimics the TOC with values of 8% in Central Bay, increasing to 18% in Inner Bay (Figure 9B). Sulphur ranges between 3 and 4‰ in Central Bay, rapidly increasing to >20‰ in Inner İzmir Bay (Figure 9C). Phospho-

rus ranges between 400 and 600 ppm in Outer İzmir Bay (Figure 7D), rapidly increasing to >900 ppm in Inner İzmir Bay (Figure 9D). The colour of surface sediments west of the Yenikale Entrance vary between grayish olive (10Y4/2) and olive gray (5Y4/1), whereas sediments in Inner İzmir Bay are grayish black (N2) to black (N1). The dissolved oxygen content of bottom waters show a strong inverse relationship with TOC and sulphur contents of surface sediments, ranging from 8.9 ml l⁻¹ near the Yenikale Entrance to 0.1 to 0.5 ml l⁻¹ in innermost Inner Bay (Yaşar, unpublished data). This inverse relationship, together with the distinctive black colour suggest that although bottom waters in Inner İzmir Bay may be periodically oxygenated during storms, sediments immediately below the sediment water interface are anoxic.



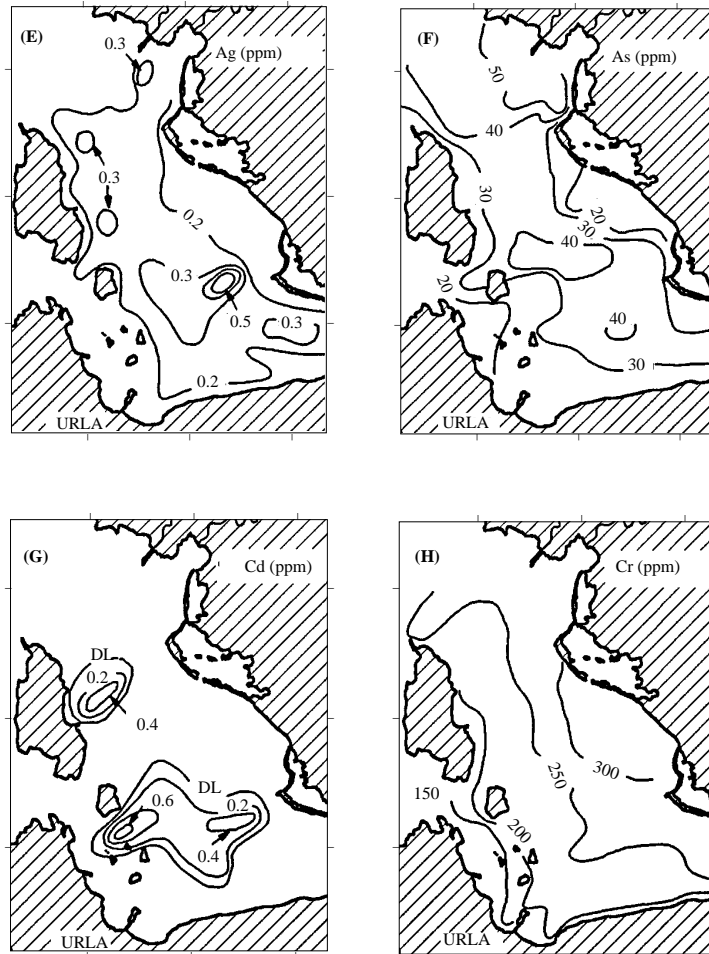


Figure 7. Distribution and abundance of TOC, IL, S, P, Ag, As, Cd and Cr in Outer İzmir Bay surface sediments. ppt=parts per thousand, ppm=parts per million, DL=detection limit.

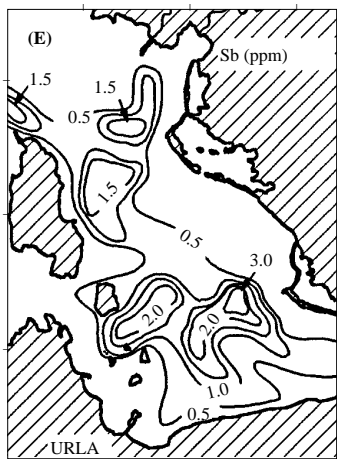
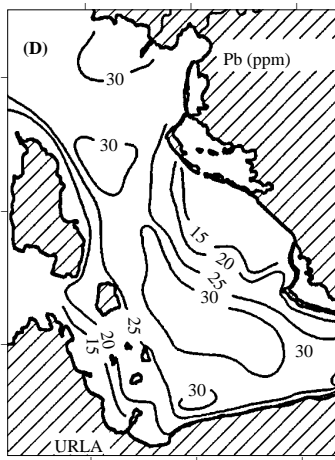
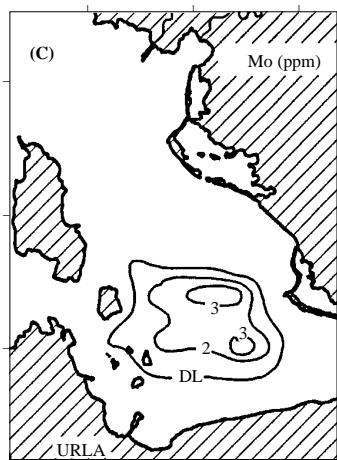
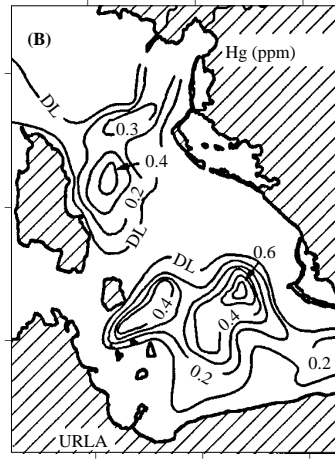
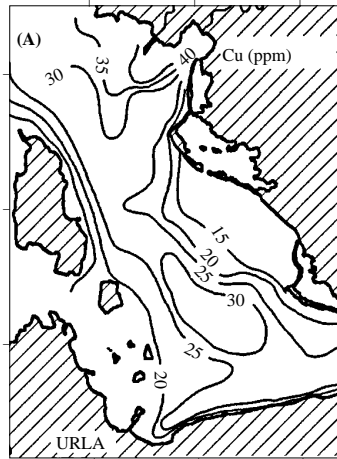
Regional distribution of the previously discussed 12 heavy metals in Central and Inner İzmir Bays show remarkable similarities to one another (Figures 9, 10). For example, all surface sediments in Central İzmir Bay generally have significantly lower elemental concentrations, showing notable increases east of the Yenikale Entrance, with highest elemental concentrations occurring in the Inner İzmir Bay. Of these elements Ag, As, Mo, V and Zn show maximum abundances in central Inner Bay, Cd, Cr, Cu, Pb, Sb and Sn show maximum abundances in innermost Inner Bay and Hg shows high values in both

regions (Figures 9, 10).

3.3. Organic Geochemical Data

Pesticides, Herbicides and Polychlorinated Biphenyls

The results of the analyses for organochlorine pesticides (OP), phenoxyacid herbicides (PH) and polychlorinated biphenyls (PCB) indicated that the concentrations of these compounds in the Inner and Central İzmir Bay are below the detection limits of $0.01 \mu\text{g/g}$ (OP), $0.05 \mu\text{g/g}$ (PH) and $0.02 \mu\text{g/g}$ (PCB).



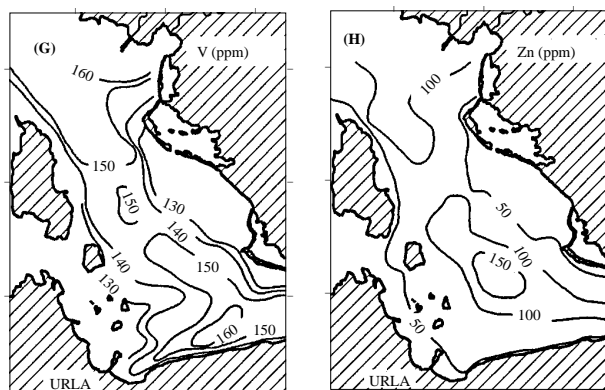


Figure 8. Distribution and abundance of Cu, Hg, Mo, Pb, Sb, Sn, V and Zn in Outer İzmir Bay surface sediments. ppm=parts per million, DL=detection limit.

Polychlorinated Dibenzop-dioxins (PCDD) and Dibenzofurans (PCDF)

Total amounts of tetra (T_4), penta (P_5), hexa (H_6), hepta (H_7) and octa (O_8) isomers of PCDD and PCDF are determined in 14 samples from the Inner and Central İzmir Bay surface sediments. The data show that dioxins and furans are ubiquitous in the surface sediments of Inner İzmir Bay. In all samples PCDD were dominated by the O_8 CDD congener (50-65%), with lesser quantities of H_7 CDD (15-25%) and T_4 CDD (3-12%); and that these samples showed very low quantities of P_5 CDD and H_6 CDD (Figure 11). PCDF were dominated either by O_8 CDF, H_6 CDF or T_4 CDF, but, in all cases the contribution of the P_5 CDF and H_7 CDF were significant (Figure 11).

Total PCDD in concentrations ranged from >0.95 ng/g (ppb) in the innermost harbour region of the Inner İzmir Bay, to 0.09-0.07 ng/g at the Yenikale Entrance to >0.04 ng/g in Central İzmir Bay (Figure 12). Total PCDF concentrations were notably less, ranging from 0.06 ng/g in Inner Bay to 0.04 ng/g at the Yenikale Entrance to 0.03 ng/g in Central İzmir Bay (Figure 12).

Various isomer ratios were calculated for each sample and were found to be constant. For example, the 1,2,3,4,6,7,8- H_7 CDF to 1,2,3,4,7,8,9- H_7 CDF was 0.884 ± 0.048 ; the ratio of 1,2,3,4,6,7,8,9- O_8 CDD to 1,2,3,4,6,7,8- H_7 CDD was 5.057 ± 0.945 ; the ratio of 1,2,3,6,7,8- H_6 CDD to 1,2,3,4,7,8- H_6 CDD was 0.989 ± 0.026 . These isomer ratios showed no trends between samples for any of the hexa-, hepta- or octa-dioxins and furans, suggesting no evidence for degra-

ation of the PCDD and PCDF in İzmir Bay sediments.

Polycyclic Aromatic Hydrocarbons (PAH)

The signature of the PAHs in İzmir Bay surface sediments is dominated by the 4- and 5-ring PAH, with lesser contributions from the 2- and 3-ring compounds (Figure 13). The individual concentrations of PAH are normalized to total PAH concentrations in each sample. This process allowed inter-sample comparisons to be made between samples with significantly different absolute PAH concentrations. Normalized concentrations showed that in all İzmir Bay surface samples, except one, either benz(a)anthracene or pyrene dominate the PAH assemblages (Figure 13). One samples from the deeper central regions of the Inner Bay is dominated by anthracene. Samples from the innermost harbour region contained major quantities of benzo(b)fluoranthene, benzo(a)pyrene and benzo(ghi)perylene (Figure 13). Total PAH concentrations are highest in İzmir Bay ($9.27 \mu\text{g/g}$ or ppm), dramatically decreasing to $1.25 \mu\text{g/g}$ at the Yenikale Entrance and to $0.42 \mu\text{g/g}$ in Central İzmir Bay (Figure 13).

3.4. Levels of Marine Pollution

Levels of heavy metal pollution in İzmir Bay are evaluated using three different techniques: (1) normalization (Calvert, 1990), (2) the degree of sediment contamination by heavy metals (Hakanson, 1980), and (3) index of geo-accumulation (I_{geo}) of heavy metals in sediments (Müller, 1979).

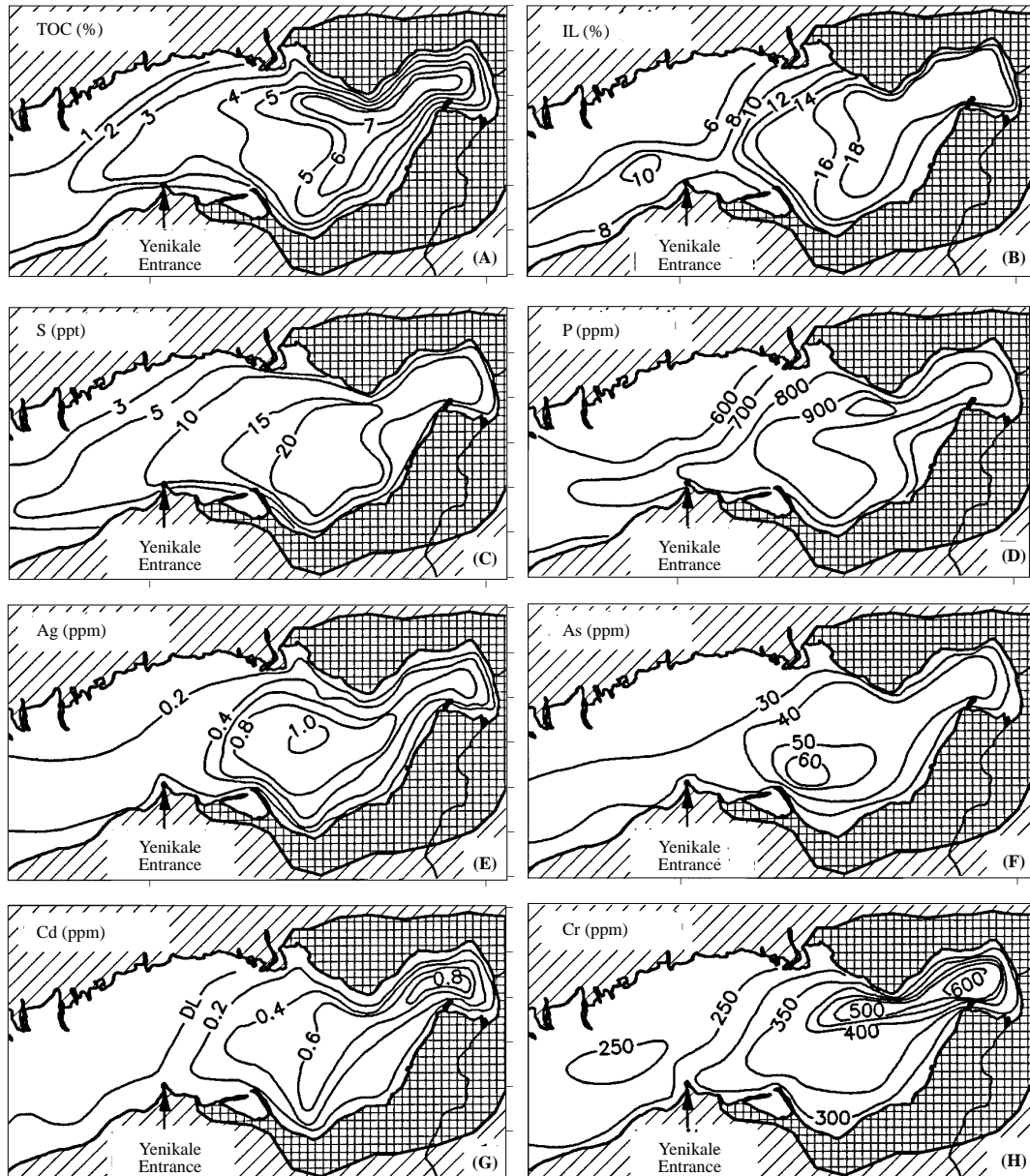


Figure 9. Distribution and abundance of TOC, IL, S, P, Ag, As, Cd and Cr in Central and Inner İzmir Bay surface sediments. ppt=parts per thousand, ppm=parts per million, DL=detection limit.

(1) The technique of normalizing elemental concentrations to grain size (Ackerman *et.al.*, 1983) and/or compositional characteristics (Calvert, 1990) improves the sensitivity of comparisons in elemental concentrations and provides a first order account of

elemental enrichments in sediments. The geochemical data of each surface sample is normalized to the percent weight of the $<63 \mu\text{m}$ fraction of that sample. The data are further normalized to aluminium, where the element/Al ratios (Calvert, 1990) elimi-

nate potential enrichments due to variations in the aluminosilicates in sediments; thereby, highlighting only those variations caused by environmental factors (e.g. anoxia, anthropogenic inputs etc.). The grain-size normalized element to Al ratios showed

significant enrichments in heavy metals above the background levels in Inner İzmir Bay; these are: Ag*18, As*5, Cd*27, Cr*3, Cu*5, Hg*38, Mo*11, Pb*8, Sn*5, Sb*9, V*3 and Zn*5.

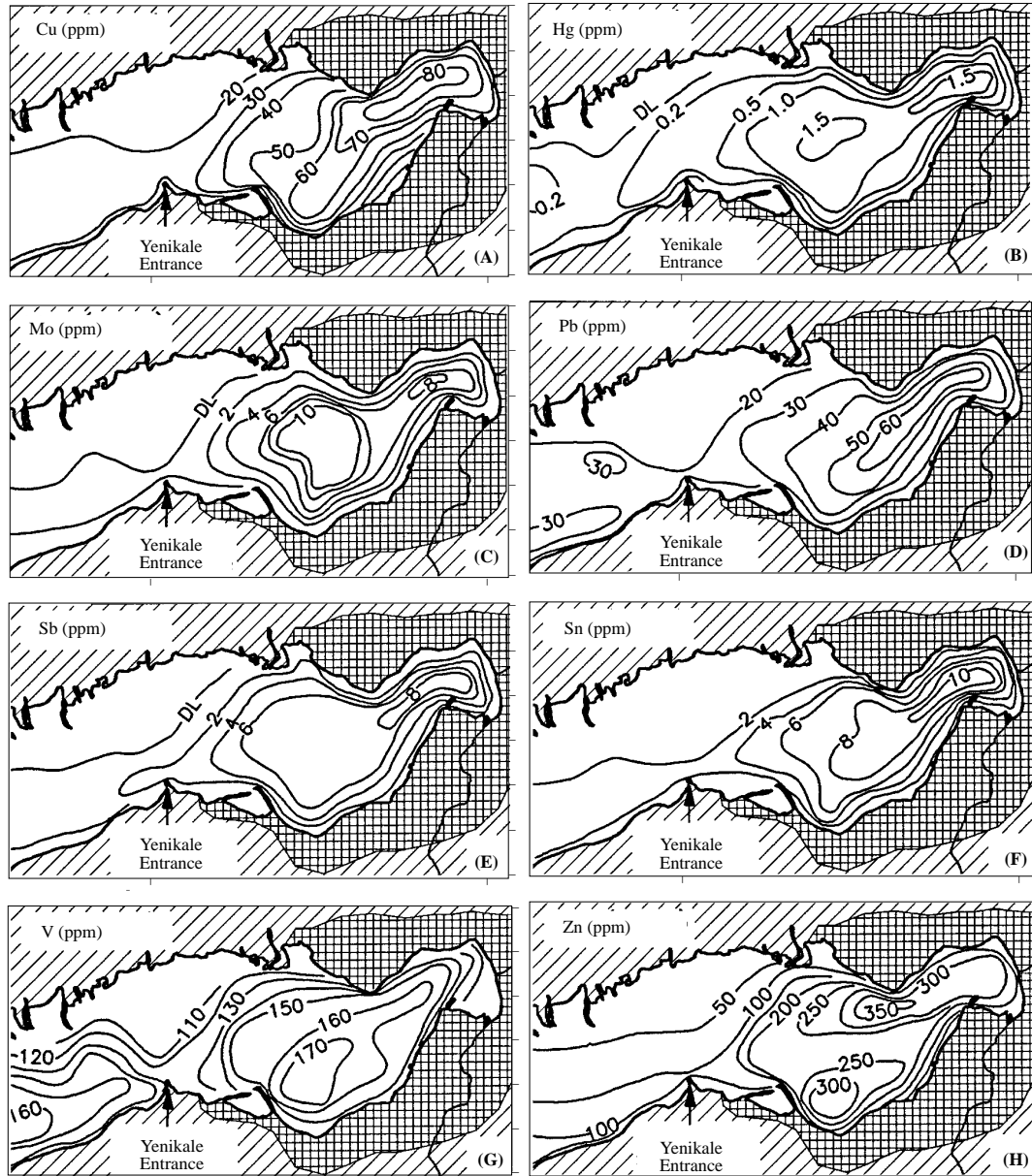


Figure 10. Distribution and abundance of Cu, Hg, Mo, Pb, Sb, Sn, V and Zn in Central and Inner İzmir Bay surface sediments. ppm=parts per million, DL=detection limit.

(2) Hakanson (1980) introduced the term “contamination factor, C_f ” to describe the contamination of a given toxic substance in a basin:

$$C_f = C_e/C_{pi}$$

where C_e = concentration of the element in samples, and C_{pi} = pre-industrial reference value for the element. The “degree of contamination, C_d ” in a de-pocentre is defined as the sum of all contamination factors for various heavy metals.

Contamination factors for 12 heavy metals (Ag, As, Cd, Cr, Cu, Hg, Mo, Pb, Sb, Sn, V, and Zn) in surface sediments and the degree of contamination in İzmir Bay were calculated, using the raw elemental

data (C_e) and the following background concentrations (C_{pi}) values in ppm: Ag = 0.05, As = 10, Cd = 0.03, Cr = 175, Cu = 17, Hg = 0.05, Mo = 1, Pb = 8.5, Sb = 1, Sn = 2, V = 60 and Zn = 65. Figure 14 illustrates the degree of contamination (C_d) caused by these 12 heavy metals. The following terminology is used to describe the C_d values:

- $C_d < 12$ low degree of contamination
- $12 \leq C_d < 24$ moderate degree of contamination
- $24 \leq C_d < 48$ high degree of contamination
- $48 \leq C_d < 96$ very high degree of contamination
- $C_d \geq 96$ extremely high degree of contamination

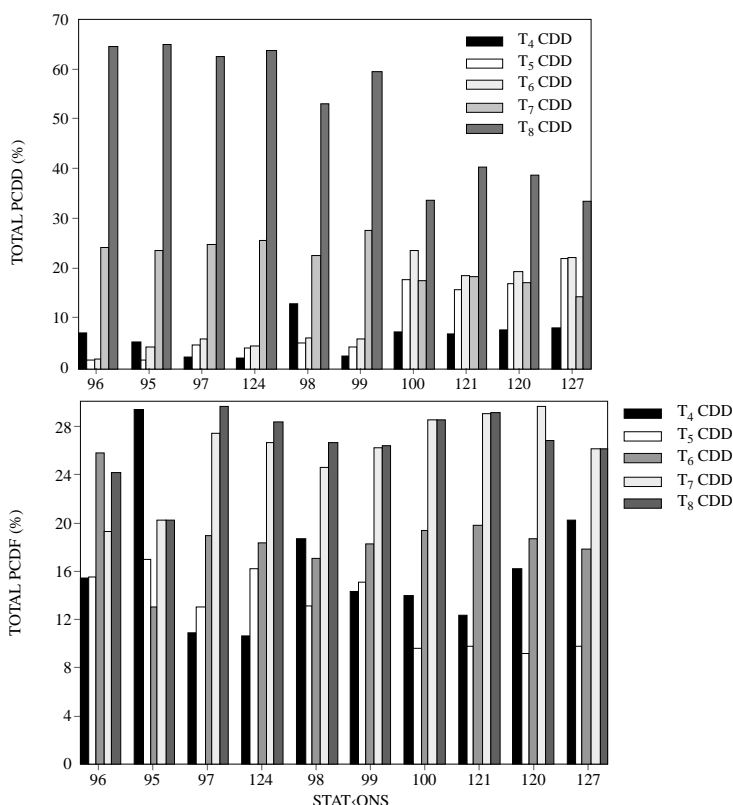


Figure 11. Congener profiles of PCDD and PCDF in surface sediments from Central and Inner İzmir Bays. Abundances are given as percent of total PCDD or PCDF.

With the exception of three localized regions of moderate degree of heavy metal contamination, the Outer and Central İzmir Bays display low degree of

contamination (Figure 14). These three regions are: a narrow north-south trending belt extending from the present-day mouth of the Gediz River, a broad

zone east of Hekim and Çiçek Islands and a localized small anomaly at the entrance to Central Bay. Comparison between the degree of sediment contamination and the contamination factors shows that the

contamination of the surface sediments is dominated by Ag, Cd, Hg, Mo, Sb and Sn, and to a lesser extent Zn, Cu, Pb, As, V and Cr.

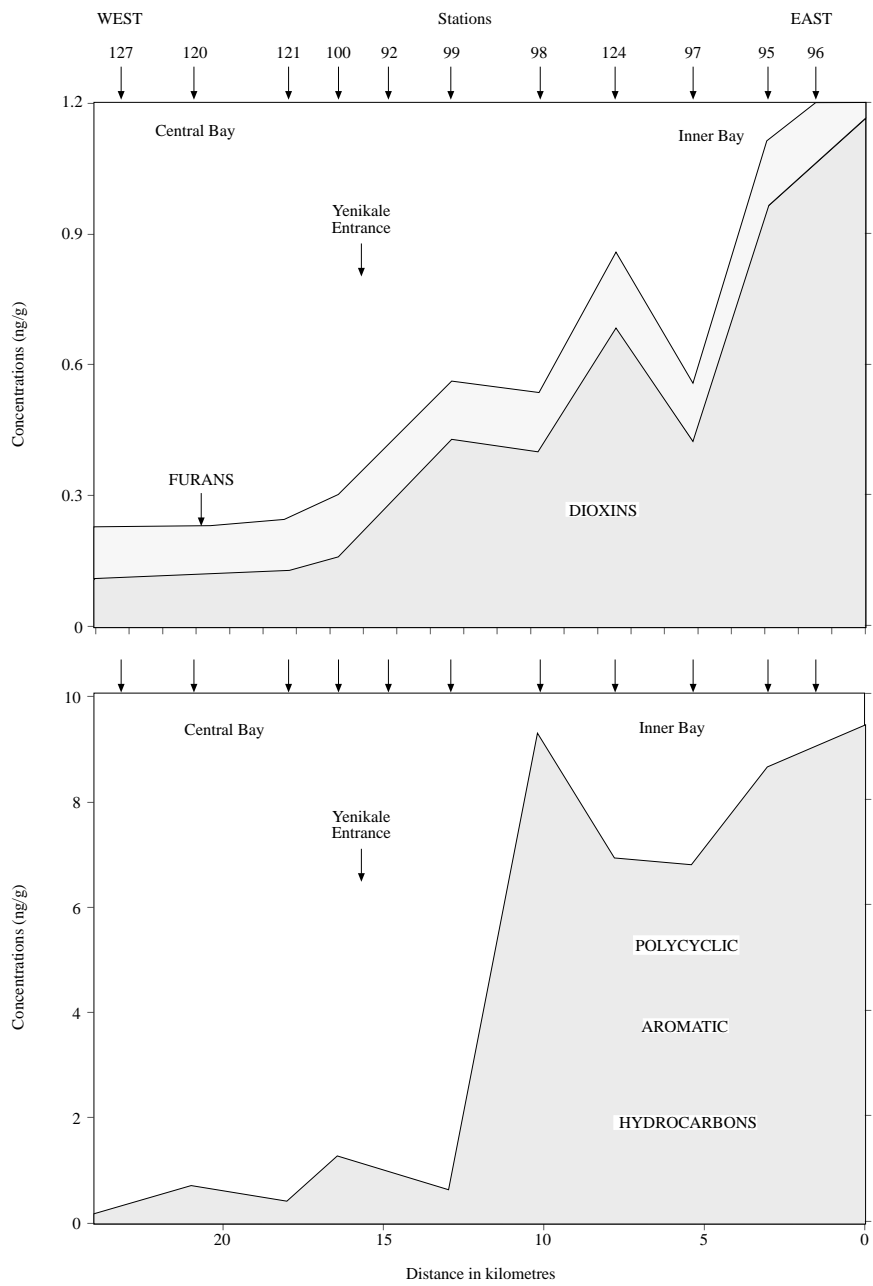


Figure 12. Cross-section showing the distribution of total PCDD and PCDF (**top**) and PAH (**bottom**) in Inner İzmir Bays. Location of profile is shown in Figure 2.

Inner İzmir Bay, east of the Yenikale Entrance, show very high degree of sediment contamination (Figure 14), where all 12 elements significantly contribute to the levels of pollution.

(3) Another quantitative measure of heavy metal and organic compound pollution in aquatic sediments has been introduced by Müller (1979):

$$I_{geo} = \log_2 C_n / 1.5 \times B_n$$

where I_{geo} = index of geo-accumulation, C_n = measured concentration of the heavy metal in the pelitic sediment fraction and B_n = geochemical background value in fossil argillaceous sediments (average shale); the factor 1.5 is used to compensate possible variations of the background data due to lithogenic effects (Müller, 1979).

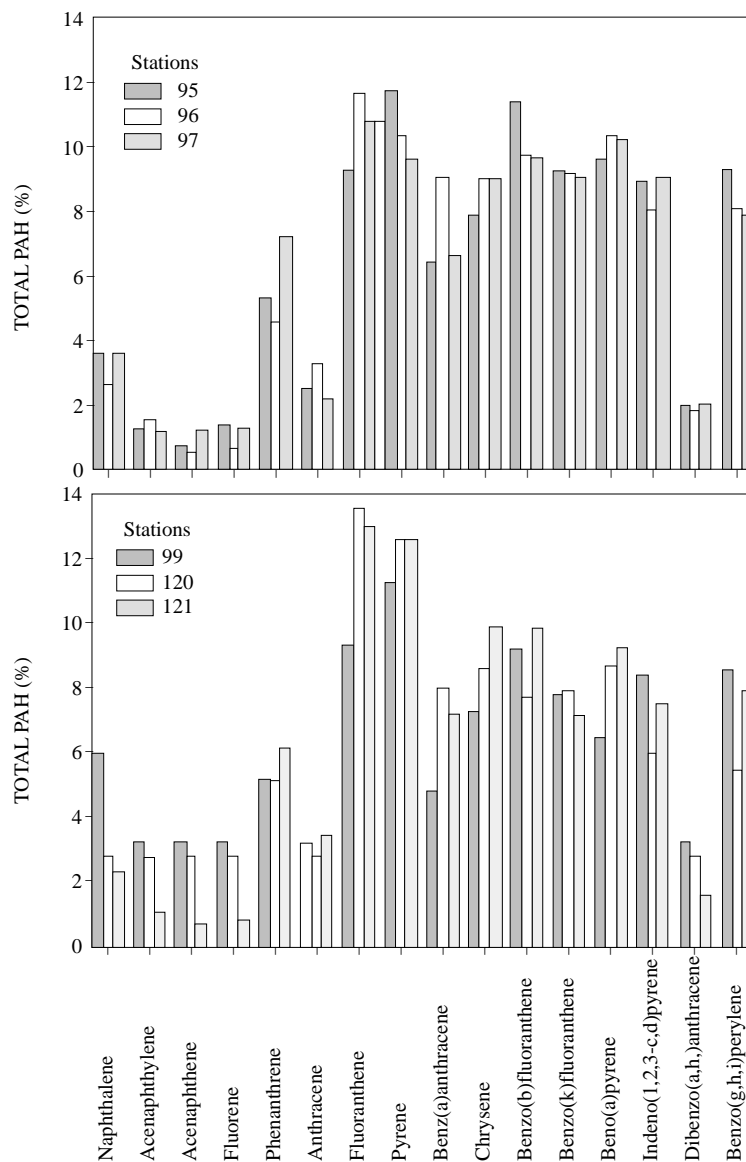
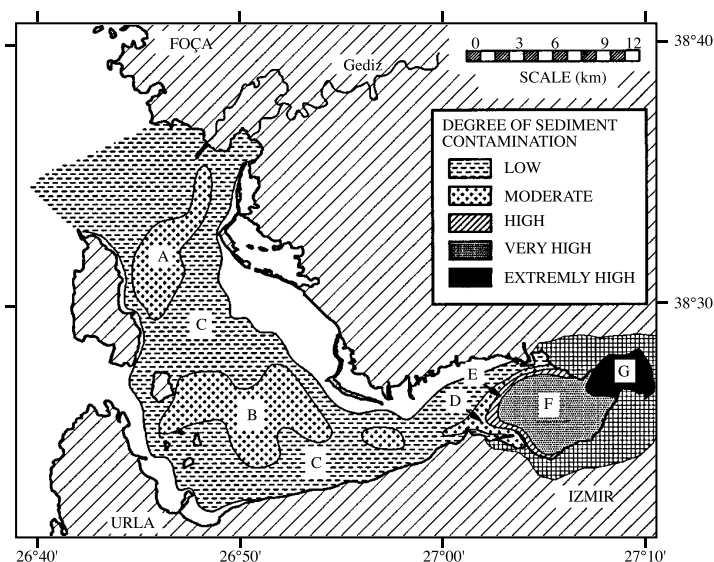


Figure 13. Congener profiles of PAH in surface sediments from Inner İzmir Bay. Abundances are given as percent of total PAH.

I_{geo} is calculated for the above 12 heavy metal in all İzmir Bay surface sediments (Figure 14), using the raw geochemical data (C_n) and the elemental background concentrations discussed earlier as (B_n). PCDD, PCDF and PAH data are also included where possible, and their background concentrations are assumed to be similar to that of Hg. The data show that the innermost Inner İzmir Bay (Zone G) display greater than 96-fold enrichments ($2^6 \times 1.5$; $I_{geo} = 6$) above background values in PAH, PCDD and PCDF, 48-fold enrichments ($2^5 \times 1.5$; $I_{geo} = 5$) in Hg and Cd

and 24-fold increase ($2^4 \times 1.5$; $I_{geo} = 4$) in Ag and Pb. A trend of decreasing I_{geo} values is clearly visible from the Inner İzmir Bay towards the Central İzmir Bay (Zone G through Zone C). Zone B, east of the Hekim and Çiçek Islands in Outer İzmir Bay, shows 12-fold enrichments in Ag, Cd, Hg and Mo ($I_{geo} = 3$), and 6-fold enrichments in As, Cu, Pb and Sb ($I_{geo} = 2$). Zone A, in northern Outer İzmir Bay south of the present-day mouth of the Gediz River (Figure 14) show moderate pollution in Cu, Cd, Cr, Hg, Pb and Zn.



POLLUTION INTENSITY	I_{geo}	I_{geo}	POLLUTERS							
			A	B	C	D	E	F	G	
very strongly polluted	>6	6								ORG1
strongly to very strongly polluted	>4-5	5							ORG1	Hg Cd
strongly polluted	>3-4	4						ORG1	Hg Cd	Pb Ag
moderately to strongly polluted	>2-3	3		Hg Cd			ORG1	Hg Cd	Ag Mo Pb	Zn Mo Sb
moderately polluted	>1-2	2	Cu Cd Cr Zn Hg Pb	Sb Pb As Cu			Hg Cd	Ag Mo	Cu Sb Zn Sn	Sn Cu Cr As V
unpolluted to moderately polluted	>0-1	1	Sb As Ag Sn Mo V	Cr Zn Sn V	Cu Cd Cr Zn Hg Pb	Cu Cr Zn Pb	Cu Sb Cr Zn Pb	Cr As V		
unpolluted	<0	0			Sb As Ag Sn Mo V	Sb As Ag Sn Mo V	As Sn V ORG2	ORG2		ORG2

Figure 14. Degree of contamination, C_d in İzmir Bay surface sediments caused by the following 12 metals: Ag, As, Cd, Cr, Cu, Hg, Mo, Pb, Sb, Sn, V, and Zn (top) and index of geo-accumulation (I_{geo}) in İzmir Bay surface sediments calculated using 12 heavy metal and PCDD, PCDF and PAN (bottom). ORG1 includes PAH, PCDD and PCDF, ORG2 includes OP, PH and PCB.

4. Discussion

4.1. Sources of Pollution in Inner İzmir Bay

The city of İzmir experienced a population explosion during the last 3 decades, from 450000 people in 1965 to 750000 in 1975, to 1500000 in 1985 and to approximately 3000000 in 1997. This growth coincided with a major proliferation of various size manufacturing, automotive, chemical, petro-chemical and food industries. İzmir is one of the largest, most industrial, but also one of the most polluted cities in the eastern Mediterranean. The following general sources can be identified for the pollution observed in Inner İzmir Bay surface sediments:

- (1) **Domestic pollution:** untreated liquid and solid waste by ~3 million inhabitants, supplied into the bay by the sewage network;
- (2) **Industrial pollution:** untreated liquid and solid waste produced by various industries, also supplied into the bay by the sewage network, and few small rivers;
- (3) **Atmospheric pollution:** particulate emission produced by vehicles, trains and vessels; fly ash emission from coal and fuel oil burning plants, by-products of open-air burning of municipal and industrial solid waste and garbage all of which are eventually transported into Inner İzmir Bay by precipitation and drainage.

Source of Heavy Metals in Inner İzmir Bay

There are over 100 major raw sewage outlets around the periphery of Inner İzmir Bay, actively discharging 500000-900000 m³/day of waste water into the bay, including untreated sewage (Uslu and Akyarlı, 1992). Nearly all industrial waste is also untreated and is either discharged through the domestic sewage network or few small rivers. There is no data on the chemical composition of the sewage discharge into İzmir Bay. However, high TOC in Inner İzmir Bay surface sediments can be correlated with the organic waste input into the bay. Similarly, high phosphorus can be related to the use of detergents and the discharge of phosphate through the sewage system. Fly ash from coal and petroleum burning plants is probably the major source of sulphur in Inner İzmir Bay sediments. Oxidation of the organic waste must account for the low dissolved oxygen observed in Inner Bay bottom waters.

Fly ash constitutes a major pollutant of the coal burning process and is known to contribute notable quantities of As, Cd, Cu, Mo, Pb, Sb, and Zn into the environment (Natusch *et.al.*, 1975). Since the mid 70's world oil crises many former fuel-oil burning domestic heating systems have been converted to coal burning plants. Nearly all of the large number of smelters in the city also use coal as their primary fuel. The fly ash emanating from these plants initially precipitates over the greater city of İzmir and it is probably quickly washed by rain into the sewage network or into smaller rivers, all of which eventually drain into the Inner İzmir Bay. Until 1994 the leather tanning plants which use large quantities of arsenic and chromium salts in the tanning procedure discharged their untreated waste products directly into the Inner İzmir Bay via the Melez River. In a local study Müezzinoğlu and Şengül (1987) reported notable enrichments of Cr in bottom sediments of several small rivers entering Inner İzmir Bay. Nearly all antifouling paints applied to commercial, naval and recreational vessels in the greater İzmir Bay area contain significant quantities of copper and lesser quantities of antimony, lead and mercury. It is reasonable to assume that a large portion of these heavy metals will be released into İzmir Bay each year.

The main source of lead in the study area is probably the automobile traffic, since the great majority of the cars in Turkey have no catalytic converters and burn leaded gasoline. There are two major cement factories and numerous small to medium size marble processing plants in the greater İzmir area which, depending on the composition of the marbles are capable of delivering Pb, Zn and other trace metals into İzmir Bay. The effluent from large chlor-alkali plants probably supply most of the mercury found in the Inner İzmir Bay surface sediments. It is estimated that appreciable quantities of elemental mercury and mercury salts are also supplied by the various size chlorine plants as well as industries which use bleaching. Until recently, mercury-bearing compounds have been used in the prevention and control of industrial slime, and these compounds eventually ended up in Inner İzmir Bay. Battery recycling plants are known for their potential for delivering mercury and lead compounds into the environment. Kestioğlu and Şengül (1984) also suggested that mercury in İzmir Bay is largely supplied from industrial sources. In the process of chromium- and nickel-plating and galvanizing the surfaces to be plated are often cleaned using strong acids. This process

leaches a number of heavy metals, which are released into Inner İzmir Bay by the sewage network. Various chromium, nickel and zinc pigments and compounds are also used in metal plating, probably contributing some undeterminable quantities of these heavy metals into the bay.

In the greater city of İzmir cadmium is extensively used by various industries in the production of copper, lead, silver and aluminium alloys and in various pigments. Cadmium salts are also widely used by the ceramic industries, and may also be contributed by the zinc, lead and copper smelters and their wastes. Potential source for silver in Inner İzmir Bay surface sediments is more enigmatic. Major uses of silver includes silver alloys, such as sterling silver and jewelry and in the form of silver nitrate in the photographic industry, with lesser uses in silver-zinc and silver-cadmium batteries. Most of the smelting and refining is done in the city by the jewelry industry, and thus may contribute some undeterminable quantities of silver into İzmir Bay. Photographic processing industry is another potential source, although most of the silver is probably recovered. Molybdenum is frequently found in municipal sludges at levels that are above the background concentrations (Adriano, 1986). The primary sources of vanadium in the study area are probably combustion byproducts of coal-burning plants and the fly ash from petroleum-fired plants in the form of vanadium pentoxide. The major use of tin is as protective coating agent and as an alloying metal in bronze and solder. Until about mid 1950's all copper and aluminium cooking utensils were tin-plated. Today most of the tin usage is in tin-plating of cans and food packaging. Zinc-tin and cadmium-tin alloys are also used by the automotive and aircraft industries as protective coating in brake parts. Antimony is used in paints, lacquers, ceramic enamels and glass and pottery industries. It is also commonly used alloyed with lead by the manufacturing industries. Some antimony is potentially released into the environment through wear and tear of paints and the effluent of various industries which use antimony compounds.

Source of Organic Polluters in Inner İzmir Bay

No direct source data is available for the dioxins and furans found in the surface sediments of İzmir Bay; however, several general sources can be identified. Open air burning of municipal waste has been a routine practice of reducing waste in disposal sites. Since the 1970's this waste includes consider-

able quantities of house-hold and industrial plastic, nylon and PVC products. During open-air burning these products produce extremely high quantities of all congeners of PCDD and PCDF (Lao *et.al.*, 1985). Combustion of mainly petrochemical and chemical waste products is also known to yield various mixtures of PCDD and PCDF congeners (Rappe *et.al.*, 1987). Combustion byproducts associated with burning of fuel-oil/diesel mixtures in residential furnaces (following coal, the primary source of home heating), as well as commercial vessels produce significant amounts of dioxins and furans (Hellou and Payne, 1993). Similarly, automobiles with no catalytic converter burning leaded gasoline produce ~30-540 pg/km of 2,3,7,8-T₄CDD equivalent PCDD and PCDF (Ballschmiter *et.al.*, 1986). All automobiles in Turkey fit this category. The copper and pick iron/steel smelters in the greater İzmir area which use industrial scrap materials containing PVC-coated wires and cables and/or material contaminated with polychlorinated paraffins probably contribute significant quantities of PCDD and PCDF (Marklund *et.al.*, 1986). Once emitted particles containing PCDD and PCDF travel through atmosphere, quickly concentrating into sedimentological depocentres, such as İzmir Bay.

There is also no direct source data available for the PAH found in İzmir Bay surface sediments. In order to relate the observed PAH assemblages to potential primary and secondary sources the compositional ratios of several PAH were calculated. Phenanthrene to anthracene and fluoranthene to pyrene ratios of 2.278 ± 0.944 and 1.067 ± 0.169 are comparable to those reported from Australia (Maher and Aislabie, 1992) and eastern Newfoundland (O'Malley *et.al.*, 1996) and suggest significant contribution from combustion-related sources. Benz(a)anthracene to chrystene ratio of 0.823 ± 0.122 in the study area is nearly identical to that reported from St. John's harbour (O'Malley *et.al.*, 1996), Chesapeake Bay, (Foster and Wright, 1988), and indicate that these two compounds are also of combustion origin. Relatively higher benz(a)anthracene to chrystene ratios can also be attributed to soots from emissions from combustion engines.

PCDD, PCDF and PAH can propagate over long distances, absorbed onto airborne and waterborne particulate matter. Eventually these particles are transported into basins, such as Inner İzmir Bay, accumulating in sediments. In marine environment absorption by and adsorption onto clays and sus-

pended organic matter quickly removes the PCDD, PCDF and PAH from the water column, accelerating their incorporation into bottom sediments. Although this process clears the water from these compounds, quick sedimentation reduces the chance for their photodecomposition. Continued introduction of pollutants from industrial effluents and shipping activities in Inner İzmir Bay and subsequent accumulation of PCDD, PCDF and PAH on bottom sediments probably constitute a chronic source of these compounds to benthic organisms. Because organisms living on the sea bottom depends exclusively on marine sediments for their food source, bottom sediments in Inner İzmir Bay may result in long-term public health hazards through the incorporation of these compounds into the food chain. It is therefore, extremely important to immediately initiate multidisciplinary studies to conduct exposure assessments of PCDD, PCDF and PAH in locally consumed seafood products, such as fish, mussels, shrimps etc. These exposure assessments must then be used to determine whether detected levels of these mostly carcinogenic and mutagenic compounds are sufficiently high to warrant a more comprehensive risk assessment around the city of İzmir.

4.2. Sources of Pollution in Outer İzmir Bay

The abundance maps for various heavy metals (Figures 9-10) illustrate that a region in Outer İzmir Bay east of the Hekim and Çiçek Islands shows moderate degrees of heavy metal contamination. The correlation between the observed pollution and the boundaries of the Hekim Island Dump Site (Figure 1) is remarkable. This dump site received $\sim 9.0 \times 10^6 \text{ m}^3$ of contaminated sediments dredged from the most polluted segment of the innermost Inner İzmir Bay between 1976 and 1990. The presence of anthropogenic pollutants, primarily Ag, Cd, Hg, Mo, Sb and Sn, but, also Cu, Pb and Zn in surface sediments at levels notably above the pre-industrial background levels over the dump site strongly suggests that this area has been recently contaminated. Recent proposals for a deepened "Entry Canal" between the Yenikale Entrance and the innermost İzmir harbour (Figure 1) poses further difficulties regarding the disposal of these clearly contaminated sediments.

There is a narrow north-south trending belt in Outer İzmir Bay, extending from the present-day mouth of the Gediz River which shows moderate degree of pollution in Cd, Cr, Cu, Hg, Pb and Zn, and to a lesser extent in Ag, As, Mo, Sb, Sn and

V. Similar heavy metal enrichments, including Cr, Zn, Cu, Pb and Fe) are also reported from shallow water sediments off the Gediz River (Mülazımoğlu, 1983). Gediz River drains a basin of 15616 km², with an annual discharge ranging from 40 to 70 m³ s⁻¹ (EIE, 1984). Nearly 400 km-long course of the Gediz River is densely populated and include extensive agricultural lands and numerous manufacturing, food and chemical industries. The river is largely used for irrigation, and as a recipient of the municipal and industrial waste water. The narrow zone of moderate pollution observed in Outer İzmir Bay surface sediments is tentatively correlated with the pollution associated with the discharge of the Gediz River.

4.3. Sediment Toxicity and Ecological Risk

High concentrations of heavy metals in sediments enhances the importance of sediments as a direct source of potential toxins in the nearshore marine and estuarine environments. However, sedimentary geochemistry data, such as those presented in this paper, provide no evidence for biological damage in a marine environment. A comprehensive assessment of marine pollution should ideally include coupled studies linking the levels of pollutants in the seawater with those in the surface sediments, and the sea-water/sediment with those in tissues of various biota (cf. Chapman and Long, 1983). Furthermore, short- and long-term experiments are necessary to determine the effects of pollutants on the resident biological community, which will lead to better understanding of the well-being of the ecosystem.

This study does not have the biological and experimental data necessary to fully evaluate the İzmir Bay ecosystem. However, it is possible to obtain first order estimates of heavy metal sediment toxicities and the potential risk to the biological community using the technique developed by Hakanson (1980). This technique begins with the calculation of "sedimentological toxic factor, S_t " for each pollutant based on the assumption that in nature a proportionality exists between toxicity and rarity of elements and their affinity to solid substances. Heavy metals enter a marine depocentre as dissolved load, such as industrial effluent and/or as suspended load sorbed (absorbed + adsorbed) or organic matter or clay minerals. Therefore, the abundance of a heavy metal in marine sediments is a function of both the chemical composition of the source rock and the aqueous input (rivers plus sewage). S_t describes the concentrations

of a given heavy metal above the natural background values, accounting for these source characteristics. For example, Hg, Cd and Ag are very rare on most rocks and uncontaminated soils, so that they are not expected to form large concentrations in a given marine basin. However, by comparison, Cr or Zn are much more abundant and therefore are more likely to occur in larger concentrations than Hg, Cd or Ag.

The following S_t values are calculated for 12 heavy metals associated with factor 2: Zn=1 < Cr=2 < Cu=Pb=Sb=Sn=V=5 < Mo=15 < Cd=40 < Ag=50 < Hg = 75. This exercise indicated that in İzmir Bay sediments Hg is potentially ~75 times more unlikely to occur than Zn, and that Cu, Pb, Sb, Sn and V have similar likelihood of occurring in marine sediments. The S_t for PCDD, PCDF and PAH are expected in the same order of magnitude as that of Hg.

The sensitivity of fauna and flora to toxic substances in a basin is largely controlled by the bioproductivity of that basin (Hakanson 1980), where the negative effects of heavy metals increase with decreasing bioproductivity (Bowen, 1966) and those of organic compounds, such as PCB, PCDD, PCDF and PAH increase with increasing bioproductivity (Olsson, 1977). Therefore, the next step towards quantifying pollution in İzmir Bay is to determine the toxic response factor, T_r . This variable is analogous to C_f , and determines the potential toxic response of a particular heavy metal in a given marine setting with a describable bioproductivity. The following T_r values are calculated for 12 heavy metals: Zn=0.9, Cr=1.8, Cu=Sb=Sn=Pb=V=4.4, As=10.0, Mo=13.3, Ag=17.5, Cd=35.4, Hg=58.8.

Heavy Metal Toxicities

Heavy metal toxicity values are calculated as the sum of the 12 heavy metal abundances multiplied by their corresponding sedimentological toxic factors and toxic response factors. The data show that Inner İzmir Bay surface sediments contain very high heavy metal toxicities, with values dramatically decreasing at the Yenikale Entrance (Figure 15).

PCDD and PCDF Toxicities

PCDD and PCDF congeners have varying degrees of toxicities, of which 2,3,7,8-T4CDD is the most toxic anthropogenic compound yet known (Keith *et.al.*, 1985). Toxicity values are normally reported as equivalent of this compound. Total 2,3,7,8-T4CDD toxic equivalence of the PCDD and PCDF compounds is calculated using the International Toxicity Equivalence Factors following the procedures

described in NATO (1988 a,b), and found to range from 0.025 ng/g in the most polluted inner harbour region of the Inner Bay to 0.08 pg/g at the Yenikale Entrance to 0.04 pg/g at the Central İzmir Bay (Figure 15). There are no established criteria in Turkey for sites contaminated with dioxins and furans. Following the Times Beach dioxin incident in USA, the lifetime risk on exposure to soils contaminated with 1 ng/g 2,3,7,8-T4CDD is estimated to be one cancer case in one million people (Kleopfer, 1985).

PAH Toxicities

PAH compounds also show varying degrees of toxicities: 2- and 3-ring compounds are relatively non-toxic, whereas many of the higher molecular weight 4- and 5-ring compounds are carcinogenic and/or mutagenic (Saeed *et al.*, 1995). In this study total PAH toxicities are calculated as benzo(a)pyrene (BaP) equivalents. The data showed that BaP equivalent toxicities are very low (<0.15 ppm) in Central İzmir Bay, but rapidly increase to >1.0 ppm in the innermost harbour region of Inner İzmir Bay (Figure 16).

Ecological Risk Index

To quantify the potential ecological risk of the 12 heavy metals in İzmir Bay surface sediments the risk factor (E_r) for each of these heavy metals is calculated as $T_r * C_f$ (Hakanson, 1980). Final potential ecological risk index, RI, is calculated as the sum of all 12 risk factors in İzmir Bay (Figure 16), which describes the sensitivity of the biological community to the toxic substances and illustrates the potential ecological risk caused by the overall pollution. The following terminology is used to describe the RI values:

$RI < 600$	low ecological risk
$600 \leq RI < 1200$	moderate ecological risk
$1200 \leq RI < 2400$	high ecological risk
$RI \geq 2400$	very high ecological risk

The data discussed in this paper conclusively show that the heavy anthropogenic pollution observed in Inner İzmir Bay is almost exclusively confined to the Inner Bay by the shallow sill at the Yenikale Entrance. Low tidal range and very restricted water circulation between the Inner and Central Bays intensify this trend, preventing the contamination of the Central Bay, but also preventing the flushing of Inner Bay. The ecological risk index which accounts for the pollution caused by 12 heavy metals as well as PCDD, PCDF and PAH clearly illustrate that the Inner İzmir Bay is extremely polluted and potentially poses very high risk for the

resident biological community (Figure 16). There is a sharp boundary at the Yenikale Entrance where

the RI values decrease from very high ecological risk in Inner Bay to low ecological risk in Central Bay.

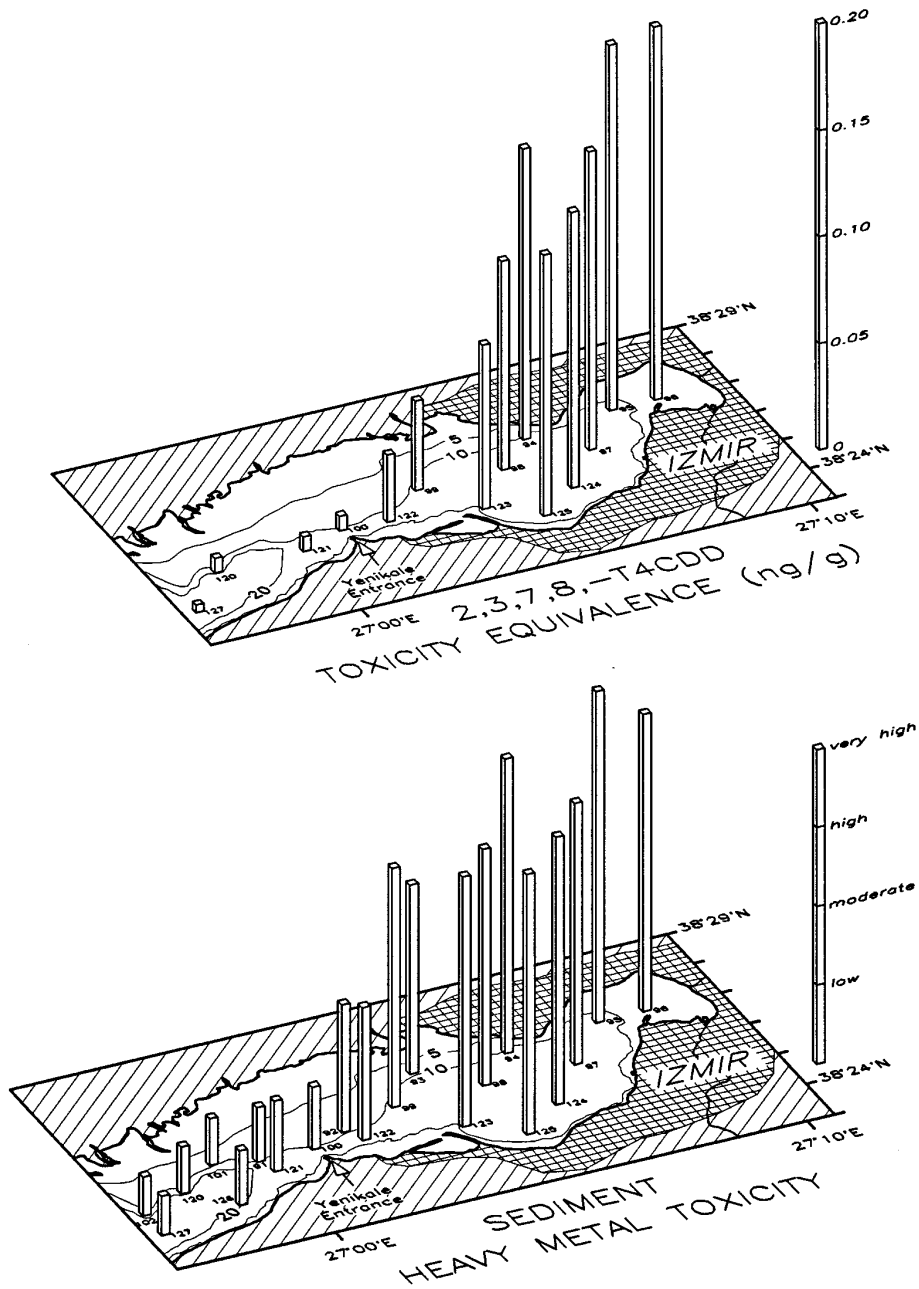


Figure 15. (Top) Total 2,3,7,8,-T4CDD toxic equivalence of the PCDD and PCDF in Central and Inner İzmir Bay surface sediments calculated using the International Toxicity Equivalence Factors (I-TEF; NATO, 1988 a,b). (Bottom) Heavy metal toxicity values in the Central and Inner İzmir Bay surface sediments calculated as the sum of 12 heavy metal abundances multiplied by their corresponding sedimentological toxic factors and toxic response factors.

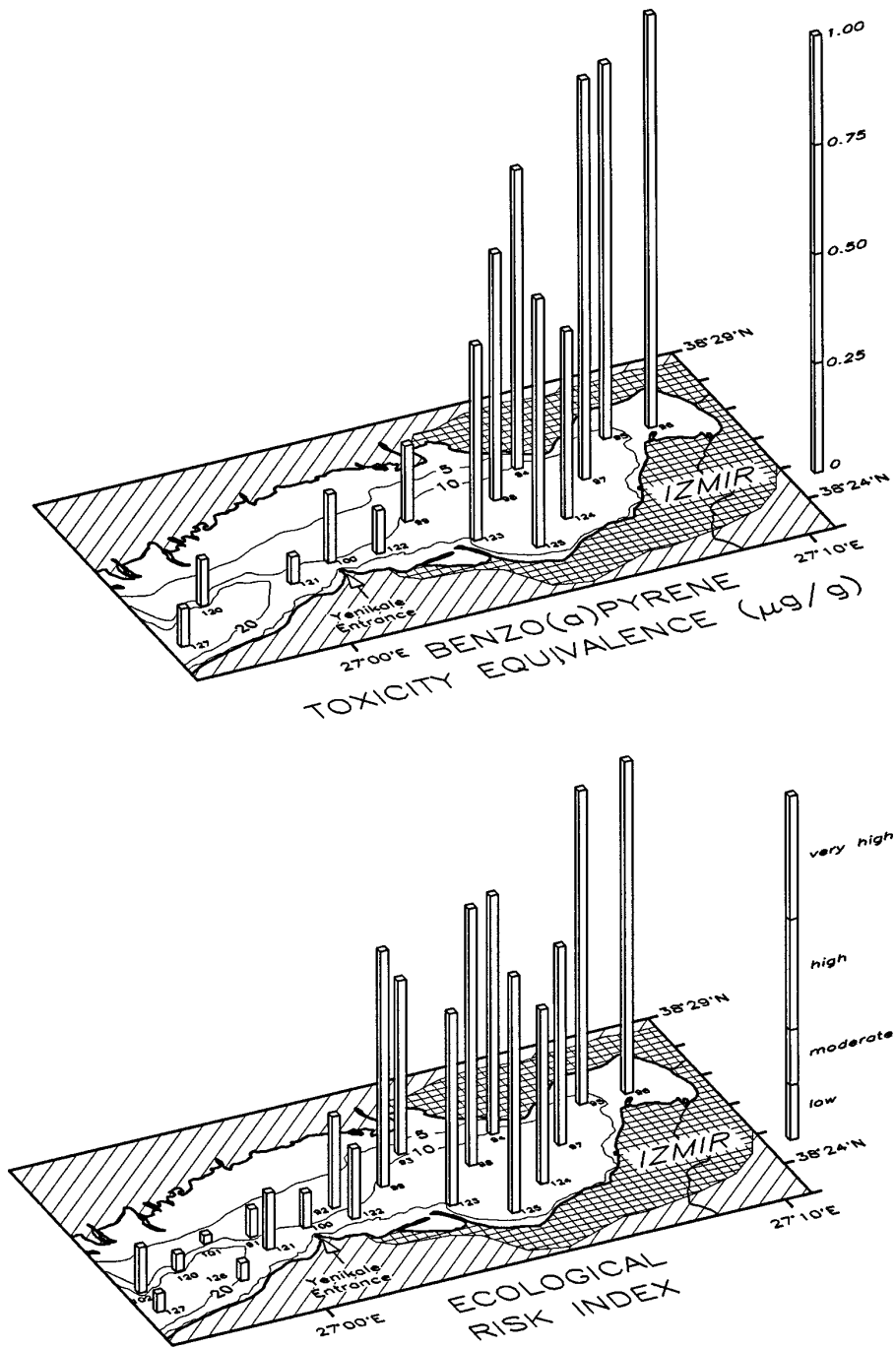


Figure 16. (Top) Benzo(a)pyrene (BaP) equivalence of the PAH in Central and Inner İzmir Bay surface sediments calculated using the equivalences given in Saeed *et.al.* (1995). (Bottom) Ecological Risk Index, RI, calculated using the technique described in Hakanson (1980).

5. Conclusions

The data discussed in this paper reveal the following conclusions:

1. Inner İzmir Bay surface sediments are extremely polluted and contain significant enrichments in Ag, As, Cd, Cr, Cu, Hg, Mo, Pb, Sb, Sn, V, and Zn, well above their pre-industrial background levels, as well as notable quantities of PCDD, PCDF and PAH. These enrichments are ascribed to anthropogenic input into Inner İzmir Bay. Heavy metal and organic compound concentrations are highest in the innermost harbour region of Inner İzmir Bay and sharply decrease near the Yenikale Entrance.
2. Except for two regions of moderate pollution the Outer and Central İzmir Bays show low levels of anthropogenic pollution. Moderate levels of heavy metal contamination observed around the Hekim Island Dump Site, is probably caused by the continuous dumping of sediments excavated from the most polluted innermost Inner İzmir Bay between 1976 and 1990. The zone of moderate pollution south of the mouth of the present-day Gediz River suggests that discharge from this river is one of the major sources of anthropogenic input into the Outer İzmir Bay and reflects the large quantities of industrial discharge into Gediz River along its course.
3. Total heavy metal toxicities, 2,3,7,8-T4CDD equivalent total PCDD and PCDF toxicities and BaP equivalent total PAH toxicities are highest in the innermost harbour region of In-

ner İzmir Bay and show notable declines towards the Yenikale Entrance.

4. The ecological risk index, accounting for the pollution caused by 12 heavy metals as well as PCDD, PCDF and PAH illustrate that surface sediments in Inner İzmir Bay potentially pose very high risk for the resident marine biological community.

Acknowledgements

We extend our special thanks to Prof.Dr. Erol Izdar for his continued support and encouragements. We thank the officers and crew of the RV *Koca Piri Reis* for their assistance in data acquisition, in particular Captain Mehmet Özsaygılı, Chief Engineer Ömer Çubuk. We acknowledge research funds from the Natural Sciences and Engineering Research Council of Canada to Aksu (OGP0042760) and special grants from the VP Research, Dean of Science and the Centre for Earth Resources Research of Memorial University of Newfoundland. Special thanks are extended to 1) Güzin Aksu, Emine Dişli, Feride Saçaklıoğlu and Nicole Aksu for their assistance in sample preparation in Turkey, 2) Erkan Fidan and Mike Tubrett of the Department of Earth Sciences for their assistance in general laboratory procedures and XRF analyses, 3) Chris Finch of the Department of Natural Resources, Government of Newfoundland for his assistance in the ICP-ES and AAS analyses, and 4) Zenon Environmental Laboratories for their assistance in the analysis priority organic pollutants. Jun Abrajano of the Department of Earth Sciences, and Murray Colbo of the Department of Biology at Memorial University of Newfoundland read the manuscript and provided many valuable comments.

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