

## INORGANIC AND ORGANIC CONTAMINATION IN SEDIMENT FROM IZMIR BAY (TURKEY) AND MYTILENE HARBOR (GREECE)

M. KOSTOPOULOU<sup>1</sup>

M. GUIDA<sup>2</sup>

A. NIKOLAOU<sup>1,\*</sup>

R. ORAL<sup>3</sup>

M. TRIFUOGGI<sup>5</sup>

I. BORRIELLO<sup>2</sup>

M. VAGI<sup>1</sup>

A. D'AMBRA<sup>4</sup>

S. MERIC<sup>6</sup>

G. PAGANO<sup>2</sup>

<sup>1</sup>Department of Marine Sciences, University of the Aegean  
GR-81100 Mytilene, Greece

<sup>2</sup>Federico II University, Department of Biological Sciences  
Section of Hygiene, I-80134 Naples, Italy

<sup>3</sup>Ege University, Faculty of Fisheries

TK-35100 Bornova, Izmir, Turkey

<sup>4</sup>Federico II University, Department of Mathematics & Statistics  
I-80126 Naples, Italy

<sup>5</sup>Federico II University, Department of Chemistry

I-80126 Naples, Italy

<sup>6</sup>Namık Kemal University, Çorlu Engineering Faculty  
Environmental Engineering Department, Çorlu, Tekirdağ, Turkey

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\*to whom all correspondence should be addressed:

e-mail: [nnikol@aegean.gr](mailto:nnikol@aegean.gr)

### ABSTRACT

Marine sediment contamination was evaluated in a set of sediment specimens collected from Izmir Bay (Turkey) and from Mytilene Harbor (Greece) in the Aegean Sea. Eight sediment specimens from Izmir (#IZ to #IZ8) and seven sediment specimens from Mytilene (#MYT1 to #MYT7) were analyzed for their content in different classes of contaminants, i.e. inorganics, organic carbon (OC), and seven polycyclic aromatic hydrocarbons (PAHs). Significantly higher levels of inorganic contaminants were detected in Izmir vs. Mytilene sediment, and the highest inorganic contamination was detected in the innermost sampling sites in Izmir Bay, namely sites #IZ1 to #IZ4. This was the case for Al, As, Cr, Cu, Fe, Li, Mn, Pb, Ti and Zn. Granulometric analysis, OC and individual PAH congeners failed to show any significant differences between total Mytilene and total Izmir Bay sediment samples. Nevertheless, the sum of PAHs in sites #IZ2 to #IZ4 displayed significantly higher levels both vs. the other Izmir sites and vs. all Mytilene sediment samples. The overall results point to higher pollution status in Izmir Bay, especially in the innermost sampling sites, compared to Mytilene Harbor, detected as inorganic contamination and as PAH contamination in some Izmir sampling sites.

**KEYWORDS:** marine sediment; harbor pollution; inorganics; polycyclic aromatic hydrocarbons.  
*Environmental Engineering Department, Çorlu, Tekirdağ, Turkey*

### 1. INTRODUCTION

The anthropogenic contamination of coastal sediments represents a major environmental threat both to marine biota and to human health, and requires thorough evaluation both under the analytical and the toxicological viewpoints in the prospect of appropriate risk assessment and of planning suitable amendment strategies (Chapman and Wang 2001; Chapman *et al.*, 2002; Chen and White 2004; Ho *et al.*, 2002; He and Morrison 2001; Pagano *et al.*, 2001, Kalantzi and Alcock, 2012; Thomaidis *et al.*, 2012; Petreas *et al.*, 2012).

Two major contaminant categories investigated in the marine environment worldwide are PAHs and heavy metals, due to their high toxicity and environmental persistence, and due to their inclusion as priority substances in the Water Framework Directive 2000/60/EC (EC 2000). Regarding the Mediterranean Sea, pollution studies of sediment contamination have been focused on several pollutant families throughout Mediterranean (Bertolotto *et al.*, 2003; De Luca *et al.*, 2005; Diez and

Bayona 2009; Esen *et al.*, 2010; Kanaki *et al.*, 2007; Khairy *et al.*, 2009; Kucukksezgin *et al.* 2006; Lipiatou *et al.*, 1997; Martin *et al.*, 2009; Bloutsos and Giannopoulos, 2011; Savvidis *et al.*, 2011).

The present study was aimed at evaluating the contamination status of marine surface sediments from two Mediterranean areas (Figure 1), namely Izmir Bay (Western Turkey) and Mytilene Harbor (NE Aegean, Lesbos Island, Greece). The selection of sampling sites was to examine sources of pollution as they were identified by means of previous data (Aksu *et al.*, 1998; Darilmaz and Kucuksezgin 2007; Kontas *et al.*, 2004; Kontas, 2006; Kucuksezgin *et al.*, 2006; Sunlu *et al.*, 2008) by a relatively broad spatial coverage of the studied areas thus allowing an assessment of their sediment quality (Casado-Martinez *et al.*, 2006). Analyses were carried out for the determination of conventional parameters (grain size, organic carbon), along with a set of inorganic (19 elements) and organic contaminants (7 PAH congeners) being analyzed for. The results showed different pollution patterns in Izmir and Mytilene sediment sampling sites, with highest pollution levels in the innermost Izmir sites and an overall worse pattern in Izmir vs. Mytilene sediment specimens.

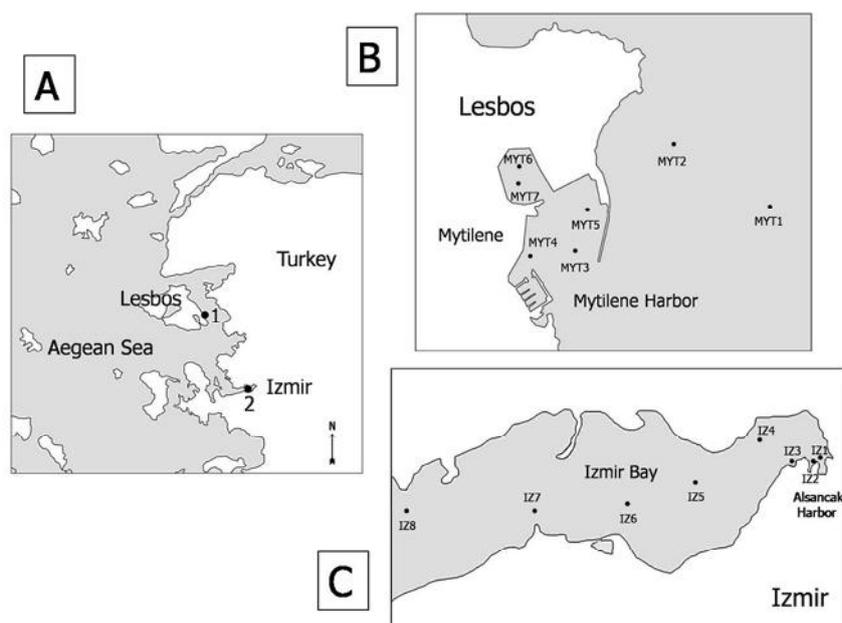


Figure 1. The study area. A. Aegean Sea; B. Mytilene Harbor; C. Izmir Bay

## 2. MATERIAL AND METHODS

### 2.1 Sediment sampling sites

#### *Mytilene harbour*

The harbor of the town of Mytilene (~ 36.000 inhabitants) is the main port of Lesbos island (Greece), the third largest island of the north-eastern Aegean (Figure 1B). It is located at the eastern part of the island and its surface covers an area of about 20 km<sup>2</sup>. It comprises two sections, the inner harbor and the outer harbor, the latter being exposed to the action of frequently prevailing N – NE winds and waves. Untreated residential and commercial effluents and town runoffs still discharged in the harbor are the main sources of water pollution in the studied area. As reported in previous studies, effluents contain important loads of organic matter, suspended solids and anthropogenic metals as it is the case for many Mediterranean towns of similar size (Aloupi and Angelidis, 2001). Although the uncontrolled discharge of untreated effluents has been decreased by a wastewater treatment plant (2001), sediments near Mytilene Harbor still carry increased loads of anthropogenic metals. The untreated sewage that still flows out in the harbor seems to affect water quality, since a higher mesotrophic character with eutrophic trends was observed in the area (Aloupi *et al.*, 2007). Industrial activity is limited to small scale traditional plants and manufacturing.

#### *Izmir Bay*

Izmir Bay is Turkey's second largest coastal municipal area and hosts a well preserved natural harbor, which is located on the west coast of the Anatolian peninsula (Figure 1C). Izmir Bay is

roughly 'L'-shaped with about 50 km in length, 2-10 km in width and with a surface of 310 km<sup>2</sup> (Sayin, 2003). The bay consists of three sections: the Inner Bay, where Izmir port is located and extends to Yenikale lighthouses, the Middle Bay, and the Outer Bay, the latter being open to the Aegean Sea. The inner part of Izmir Bay, where Alsancak Harbor is located, has been subjected to various pollution discharges since the 1960s and is considered to be one of the most polluted environments of the Mediterranean Sea over the last two decades. The main pollutants affecting the quality of the bay water are organic matter, nutrients, suspended matter, hydrocarbons, metals, and pathogenic organisms, all derived mainly from domestic and industrial wastes (50%), rainfall (15%), rivers and streams (10%), agricultural sources (10%) and others (15%) (UNEP 1993). The main industries in the region include food processing, oil, soap and paint production, chemical industries, paper and pulp factories, textile industries and metal processing. According to the statistical data maintained by the Alsancak Harbor Authority in 2003, a total of 3,640 vessels approached the harbor for loading/uploading. Due to the intensive pollution in the Bay, azoic conditions have been previously reported for Izmir Bay (Muezzinoglu *et al.*, 2000; Dogan *et al.*, 2005).

Table 1. GPS coordinates of Izmir and Mytilene sediment sampling sites

Sampling Stations	depth (m)	Latitude	Longitude	
Izmir	IZ1	13	38° 26' 8.07" N	27° 9' 9.53" E
	IZ2	9.6	38° 26' 7.09" N	27° 9' 5.79" E
	IZ3	9	38° 26' 7.09" N	27° 9' 2.55" E
	IZ4	9.7	38° 27' 2.24" N	27° 8' 0.82" E
	IZ5	17.5	38° 26' 2.02" N	27° 6' 0.37" E
	IZ6	15.7	38° 25' 6.15" N	27° 4' 0.89" E
	IZ7	11	38° 25' 4.87" N	27° 0' 9.77" E
	IZ8	7.8	38° 25' 6.39" N	26° 57' 1.13" E
Mytilene	MYT1	29.8	39° 6' 8.40" N	26° 34' 36.00" E
	MYT2	20.5	39° 6' 22.80" N	26° 34' 10.20" E
	MYT3	10.5	39° 6' 0.00" N	26° 33' 40.80" E
	MYT4	5.5	39° 5' 59.40" N	26° 33' 28.80" E
	MYT5	13.7	39° 6' 9.00" N	26° 33' 44.40" E
	MYT6	7.8	39° 6' 19.20" N	26° 33' 25.90" E
	MYT7	7.5	39° 6' 15.60" N	26° 33' 26.30" E

## 2.2 Sediment sample handling

Surficial sediment was collected by van Veen grab samplers at the locations in Izmir Bay and Mytilene Harbor shown in Figure 1 and carried to the laboratory in refrigerated boxes. The sediment specimens were stored at +4°C, then mixed thoroughly and subdivided in aliquots for chemical analyses and bioassays. Sediment aliquots to be submitted to chemical analyses were dried at 60°C up to constant weight and then processed for inorganic or for organic analyses (see below).

## 2.3 Granulometric analysis

Grain size analysis was performed using standard sieves of  $\varnothing > 63 \mu\text{m}$  (coarse material) and pipette method analysis for fine material according to the procedures outlined by Folk (1980). Textural sedimentary information can be reliable information to establish the risk levels of increased water turbidity in the event of marine bottom removal as well as their potential capacity to adsorb hydrophobic contaminants (Carrasco *et al.*, 2003).

## 2.4 Inorganic analysis

The sediment samples were dried and ground to fine powder with a hardened steel mortar, thereafter a mild, non-destructive digestion procedure was carried out. One-gram powder aliquots were treated in an open flask with boiling 5% HNO<sub>3</sub> (ca. 10 mL) for 30 min, then filtered; solid residue was washed twice with 2-3 mL 5% HNO<sub>3</sub> and filtered; combined filtrates were treated with 1 mL 30% H<sub>2</sub>O<sub>2</sub> and boiled to a volume of 3 to 4mL; then filtrates were treated with 20 mL H<sub>2</sub>O, 1 mL 30% H<sub>2</sub>O<sub>2</sub>, 1 mL HNO<sub>3</sub> and boiled to a volume of 3-4 mL twice; finally it was treated with 20 mL H<sub>2</sub>O

and 1 mL HNO<sub>3</sub> and boiled up to a volume of 3–4 mL; after cooling, 20 mL H<sub>2</sub>O and 1 mL HNO<sub>3</sub> were added, then diluted to 50 mL with water. The solutions were analyzed using Agilent Technologies 7500A ICP-MS spectrometer (Santa Clara, CA, USA), equipped with a quadrupole mass analyzer, nebulizer Babington type, glass spray chamber, quartz monobloc torch and auto-sampler. The gas flow (99.99% Argon) used for the plasma was 15 L min<sup>-1</sup>; the auxiliary (cooling) gas flow was 1 L min<sup>-1</sup>; the transport gas flow used to introduce the sample was 1.12 L min<sup>-1</sup>. The radiofrequency generator worked at 1300 W; spray chamber was constantly kept at 2°C. The samples as well as the standards Romil® (Cambridge, UK) and Fluka® (Gillingham, Dorset, UK) ICP-MS multi-element standard solutions were analysed in a HNO<sub>3</sub> (1 to 10%) matrix to minimize the interferences and matrix effect. Before introducing the sample an auto-tuning sequence was implemented in order to optimize structural parameters, liquid and transport gas flows, to improve the sensitivity and mass resolution, and to limit the oxides formation and double charges, thus avoiding interferences (McCurdy and Potter 2001). The samples were fluxed in the system for a conditioning period of 2 min before the acquisition of each metal was performed (mean duration 0.5 sec); five repetitions were made and the final result was obtained as mean of readings. A good reproducibility was observed, within the range 3–5 % for measured elements. The accuracy (precision and trueness) of our results was calculated applying the Italian Rule UNI ISO 5725-1/2. The instrumental detection limit for ICP-MS is usually calculated as equivalent concentration corresponding to 3 times the standard deviation on the results of these measurements. (Giessmann and Greb 1994; Moens and Dams 1995). A precision of 0.5 – 1 % for major element oxides, 2 - 2.5 % for minor elements, 2 – 5 % for trace elements of 50 - 150 ppm, 2 - 10% for trace elements of 10 - 50 ppm and finally 5 – 25 % for trace elements of 0 - 5 ppm was found.

Replicated measures of international reference materials (PACS2), reagent blanks, and duplicated sediment samples (about 20% of the total number of samples randomly selected from the set) were used to assess accuracy (estimated as >95%) and precision (estimated on triplicate samples >93%).

## 2.5 Organic carbon

Organic carbon was measured by Jackson-modified Walkley-Black method (Loring and Rantala, 1992). Aliquots (0.3 - 0.5 g) of homogenized, sieved ( $\varnothing < 2\text{mm}$ ), and dried (80°C) sediment were oxidized with 10 mL of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 1N and 20 mL of concentrated H<sub>2</sub>SO<sub>4</sub>. Solution was back titrated with Fe(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in the presence of diphenylamine indicator (Loring and Rantala, 1992). Each measurement was carried out in duplicate.

## 2.6 Polycyclic aromatic hydrocarbons (PAH)

PAHs were measured in marine sediment samples collected from Mytilene Harbor and Izmir Bay and the following seven PAHs, included in WFD 2000/60 were determined by GC-MS: anthracene [A], fluoranthene [Fluo], benzo(ghi)perylene [BPer], benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP] and indeno(1,2,3-cd)pyrene [IP] (Kostopoulou *et al.* 2007). Two grams of homogenized, dried (80°C) sediment was weighed directly in a centrifugation tube, where 2 mL CH<sub>3</sub>OH (Pestiscan grade), 1g sodium sulphate (200°C for 24 h) and 20 mL CH<sub>2</sub>Cl<sub>2</sub> (Pestiscan grade, Lab-Scan, Dublin, Ireland) were added and ultrasonicated (frequency 50–60 Hz, Branson 2200) (Branson Ultrasonic Co., Danbury, CT, USA) at room temperature for 15 min. The solution was left undisturbed for about 30 min and afterwards centrifuged at 2,500 rpm for 10 min. The supernatant was transferred to a round bottomed flask, where activated copper was added to desulphurize the extract, reduced to a small volume (at about 1 mL) using a rotary evaporator and then purified by using silica micro-columns chromatography. Elution was followed by using hexane and CH<sub>2</sub>Cl<sub>2</sub>, the purified extract was concentrated to a final volume of 0.5 mL and stored in a Teflon sealed vial at 4°C until analysis. The same sample preparation procedure was applied for sediments spiked with known concentrations of priority PAHs purchased from Supelco Co. (Park Bellefonte, PA, USA) and recoveries ranged from 65% to 100%. The analyses were performed with a Hewlett Packard 6890GC –5973MSD (EI 70 eV) (GMI, Ramsey, MN, USA), equipped with a HP-5MS fused silica capillary column 30m x 0.25mm x 0.20 $\mu\text{m}$ . Carrier gas was helium (purity 99.999%) with column flow of 0.6 mL min<sup>-1</sup>. Injection was made in the splitless mode (purge delay 1 min, purge flow 30 mL min<sup>-1</sup>). The oven temperature program was: 80°C for 1 min, rate 15°C min<sup>-1</sup> to 220°C (for 1 min) and then up to 290°C with rate 5°C min<sup>-1</sup> (for 15 min). MS source temperature was 180°C and transfer line 240°C. For higher sensitivity, the analysis was performed in Selected Ion Monitoring, (SIM) mode. For the instrument

calibration, a PAHs mixture solution (Supelco Co.) was used, from which secondary standard solutions were prepared, with concentrations ranging from 5 to 400  $\mu\text{g L}^{-1}$ . R2 values for the 7 PAHs ranged from 0.995 to 1.000. The detection limits (LOD) for each determined compound, as well as the quantitation limits (LOQ) were calculated on the basis of signal-to-noise ratios 3 and 10 respectively.

## 2.7 Statistical analysis

The data have been analyzed using two inferential techniques, i.e.: a) test of hypothesis on means of two normal distributions, with unknown variances, and b) test of hypothesis on the variance of two normal distributions, according to Hines and Montgomery (1980). The SPSS software was utilized.

## 3. RESULTS

### 3.1 Granulometric analysis

Grain analyses results of sediments collected from Izmir Bay and Mytilene Harbor in March 2007 are shown in Table 2, where sand (0.063 - 2 mm), silt (0.004 - 0.063 mm) and clay (< 0.004 mm) were determined.

Table 2. Organic carbon (OC, % dw) and sediment granulometry (%) in surface sediments of Izmir Bay and Mytilene Harbor

Sampling Sites	OC	Sand	Silt	Clay	Silt & Clay
<b>Location</b>					
<b>Izmir</b>					
IZ1	2.3 ± 0.5	2.6	36.8	60.6	97.4
IZ2	2.2 ± 0.1	19.9	38.2	41.9	80.1
IZ3	2.2 ± 0.0	22.9	36.7	40.4	77.1
IZ4	5.1 ± 0.1	42.6	25.6	31.7	57.3
IZ5	4.7 ± 0.3	24.5	34.1	41.4	75.5
IZ6	3.6 ± 0.0	17.3	46.4	36.2	82.6
IZ7	1.0 ± 0.1	61.7	23.2	15.0	38.2
IZ8	0.2 ± 0.1	44.2	33.5	22.3	55.8
<b>Mytilene</b>					
MYT1	3.0 ± 0.8	59.9	21.6	18.5	40.1
MYT2	3.5 ± 0.0	70	16.7	133	30.0
MYT3	4.1 ± 0.5	49.3	26.6	24.1	50.7
MYT4	2.8 ± 0.0	36.9	37.2	25.9	63.1
MYT5	3.8 ± 0.0	17.3	40.0	42.7	82.7
MYT6	2.5 ± 0.2	21.4	32.6	46.0	78.6
MYT7	2.8 ± 0.0	33.8	37.3	28.9	66.2

The percentage of silt and clay fraction of Izmir Bay ranged from 38.2 % to 97.4 %, with the greatest values being observed in the innermost locations. According to Folk classification (1980) the sediments were classified as sandy mud (sM) and as sandy silt (sZ) with the exception of IZ7 and IZ8 sites being classified as silty sand (zS).

In almost all sediment samples of the inner and the outer harbor of Mytilene the percentage of silt and clay was > 60%, showing relatively low variability being classified as sandy silt (sZ) and as sandy mud (sM). Locations at the outer area (MYT1, MYT2) and at the entrance of the harbor (MYT3) were classified as muddy sand (mS) due to the lower % of silt and clay.

### 3.2 Organic carbon

As shown in Table 2, % OC in sediment samples from Izmir Bay and Mytilene Harbor failed to display any significant differences with the exception of IZ7 and IZ8, which presented low values. Organic carbon content at Izmir Bay locations ranged between 0.24 to 5.08 % (dry wt) with a median value of 2.25 %. The highest values of organic carbon content are observed at the innermost locations, which are characterized by high % of silt and clay.

Correspondingly, organic carbon content at Mytilene Harbor locations showed values within a range of 2.5 to 4.1 % dw with a median value of 3.0. By comparing the data of the two areas, values of OC (% dw) were higher at locations subjected to human anthropogenic activities, such as waste discharges and/or urban runoffs. No statistically significant correlation between OC and grain size fractions was detected in both cases.

### 3.3 Inorganic analysis

The concentrations of a set of inorganic elements in sediment specimens from Izmir Bay and Mytilene Harbor are reported in Table 3. Concentrations of the most frequently determined metals (Zn, Cu, Cd, Ni, Cr, Pb, Zn) in Izmir Bay were higher in locations close to the head of the bay (IZ1 to IZ4) compared to the other locations IZ5 to IZ8. The highest values were observed for Zn (47.4 – 435.2  $\mu\text{g g}^{-1}$  dry wt), followed by Cr (40.9 - 189.5  $\mu\text{g g}^{-1}$  dry wt), Pb (8.9 – 105.2  $\mu\text{g g}^{-1}$  dry wt), Cu (13.1 – 95.7  $\mu\text{g g}^{-1}$  dry wt), Ti (3.6 – 88.1  $\mu\text{g g}^{-1}$  dry wt), Ni (43.7 – 59.8  $\mu\text{g g}^{-1}$  dry wt), V (13.7 - 34.2  $\mu\text{g g}^{-1}$  dry wt), As (13.6 – 28.8  $\mu\text{g g}^{-1}$  dry wt) and Co (5.9 – 11.6  $\mu\text{g g}^{-1}$  dry wt). Lower concentrations were found for Mo (0.4 – 5.8  $\mu\text{g g}^{-1}$  dry wt), Cd (0.1 – 1.1  $\mu\text{g g}^{-1}$  dry wt), and Hg (0.2 – 0.6  $\mu\text{g g}^{-1}$  dry wt).

By comparing the mean concentrations of trace metals in Izmir Bay vs. Mytilene Harbor, a significantly higher pollution status was detected in Izmir vs. Mytilene sediment. Iron and aluminum (Figure 2) displayed significantly higher levels in all sediment samples from Izmir vs. Mytilene samples ( $p = 0.01$  both for iron and for aluminum). Manganese and zinc also showed significantly higher levels in Izmir vs. Mytilene sediment (Figure 3). Trace elements As, Cr, Cu, Pb and Ti again showed significantly higher levels in Izmir vs. Mytilene sediment, displaying highest concentrations in sites #IZ1 to #IZ4, which are located at the head of the Bay (Figure 4).

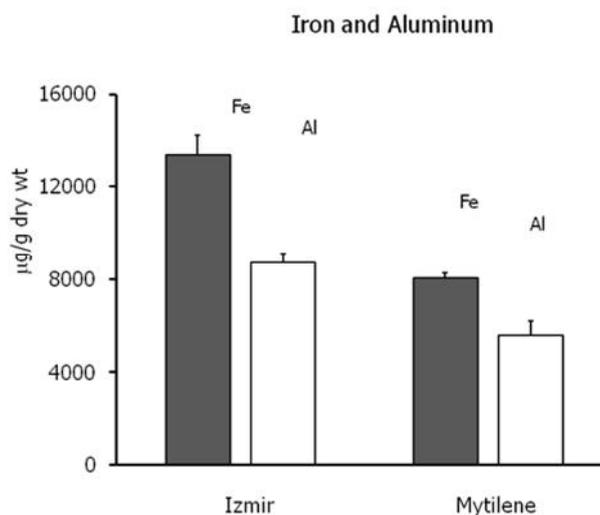


Figure 2. Concentrations of aluminum and iron ( $\mu\text{g g}^{-1}$  dry wt) in sediment samples from Izmir and Mytilene

In Mytilene Harbor sediment, Zn had the highest values (59.1 – 285.4  $\mu\text{g g}^{-1}$  dry wt), followed by Cr (29.5 – 125.3  $\mu\text{g g}^{-1}$  dry wt), Pb (39.4 – 69.0  $\mu\text{g g}^{-1}$  dry wt), Ni (30.4 – 56.6  $\mu\text{g g}^{-1}$  dry wt), Cu (19.0 – 53.4  $\mu\text{g g}^{-1}$  dry wt), V (13.8 – 35.8  $\mu\text{g g}^{-1}$  dry wt), Ti (2.3 – 35.5  $\mu\text{g g}^{-1}$  dry wt), As (9.1 – 20.7  $\mu\text{g g}^{-1}$  dry wt) and Co (4.4 – 11.8  $\mu\text{g g}^{-1}$  dry wt). Lower concentrations were found for Mo (0.7 – 5.7  $\mu\text{g g}^{-1}$  dry wt), Cd (0.2 – 0.7  $\mu\text{g g}^{-1}$  dry wt), and Hg (0.3 – 0.4  $\mu\text{g g}^{-1}$  dry wt).

*Table 3.* Concentrations ( $\mu\text{g g}^{-1}$  dry wt) of some selected inorganics in sediment specimens collected in Izmir (IZ) Bay and in Mytilene (MYT) Harbor. Means of quintuplicate measurements. Measurements detected the following variation ranges: 0.5 – 1 % for major elements, 2 - 2.5 % for minor elements, 2 – 5 % for trace elements of 50 - 150 ppm, 2 - 10% for trace elements of 10 - 50 ppm, and 5 – 25 % for trace elements of 0 - 5 ppm

Elements	Isotopes	IZ1	IZ2	IZ3	IZ4	IZ5	IZ6	IZ7	IZ8	MYT2	MYT3	MYT4	MYT5	MYT6	MYT7
<b>Al</b>	Al / 27	8433	7843	7396	8269	5642	9626	8068	9066	5901	4186	4581	8607	4889	5313
<b>As</b>	As / 75	24.0	28.8	28.4	25.8	14.6	15.5	13.6	14.1	9.1	13.7	14.4	20.7	11.4	15.1
<b>Be</b>	Be / 9	0.72	0.76	0.67	0.85	0.50	0.67	0.57	0.68	0.45	0.32	0.45	0.77	0.37	0.44
<b>Cd</b>	Cd / 111	0.70	0.51	0.45	1.07	0.06	0.40	0.26	ND	0.43	0.42	0.29	0.72	0.17	0.44
<b>Co</b>	Co / 59	9.3	10.5	9.9	10.3	5.9	11.2	11.6	10.1	5.9	4.4	4.5	11.8	5.3	4.5
<b>Cr</b>	Cr / 53	82.3	115.1	78.1	189.5	44.0	65.6	40.9	41.3	36.7	29.5	32.5	125.3	33.2	37.3
<b>Cu</b>	Cu / 63	66.6	50.8	49.4	95.7	13.1	38.5	21.3	22.4	19.0	48.9	29.7	52.0	19.5	53.4
<b>Fe</b>	Fe / 57	14030	12940	13370	13770	8210	16860	13920	13850	7097	7014	7899	15090	6683	8516
<b>Hg</b>	Hg / 202	0.31	0.30	0.35	0.56	0.17	0.28	0.25	0.17	0.29	0.29	0.28	0.41	0.33	0.31
<b>Li</b>	Li / 7	29.0	33.1	29.8	24.1	12.3	22.8	20.0	20.9	11.9	7.4	8.2	22.5	9.6	9.4
<b>Mg</b>	Mg / 24	14270	14500	13410	15180	17240	15670	15260	17710	18420	11900	16130	16700	16400	14860
<b>Mn</b>	Mn / 55	316.9	384.9	400.9	306.3	160.9	331.7	414.5	367.1	150.3	136.8	145.0	305.4	138.3	141.4
<b>Mo</b>	Mo / 95	1.5	1.0	0.8	5.8	9.7	2.8	0.5	0.4	0.7	4.5	4.7	5.7	3.0	3.2
<b>Ni</b>	Ni / 60	49.8	48.4	43.7	51.3	55.2	59.8	58.0	56.9	46.7	30.4	38.3	56.6	42.5	37.0
<b>Pb</b>	Pb / 208	105.2	53.41	46.19	83.92	8.937	32.73	22.36	17.15	43.96	68.96	39.43	55.43	42.39	56.12
<b>Sr</b>	Sr / 88	212.8	237.4	241.8	189.7	610.5	149.5	183.9	163.2	581.3	314.7	606.7	186	690.2	381.9
<b>Ti</b>	Ti / 47	14.09	7.571	8.202	18.44	3.622	39.53	55.81	88.15	4.432	10.21	2.321	35.51	2.64	4.058
<b>V</b>	V / 51	18.15	14.54	13.71	31.22	34.24	28.28	20.09	22.71	25.23	13.85	14.04	35.8	23.17	15.09
<b>Zn</b>	Zn / 66	314.6	244.3	171.5	435.2	47.43	159.1	84.73	75.44	59.09	172.6	93.09	285.4	67.16	160.7

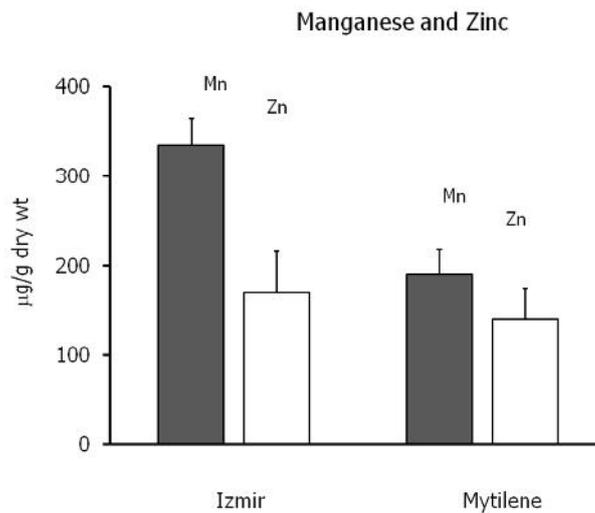


Figure 3. Concentrations of manganese and zinc ( $\mu\text{g g}^{-1}$  dry wt) in sediment samples from Izmir and Mytilene

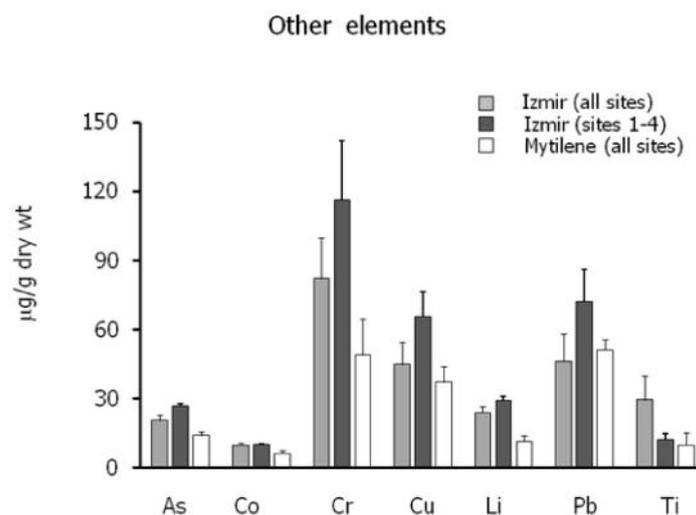


Figure 4. Concentrations of As, Co, Cr, Cu, Li, Pb and Ti ( $\mu\text{g g}^{-1}$  dry wt) in sediment samples from Izmir and Mytilene

### 3.4 Polycyclic aromatic hydrocarbons

Concentrations values of PAHs examined ( $\Sigma 7\text{PAHs}$ ) varied for Izmir Bay sampling sites from  $158 \text{ ng g}^{-1}$  to  $1,575 \text{ ng g}^{-1}$  (dry wt) with a mean value of  $599 \text{ ng g}^{-1}$ . Among the eight considered sites the obtained values of concentrations of ( $\Sigma 7\text{PAHs}$ ) at IZ1, IZ2, IZ3, IZ4 and IZ5 exceeded the effect range low concentration (ERL,  $552 \text{ ng g}^{-1}$ ) reported by Long *et al.* (1995), which is proposed as a first warning for biological effects. Correspondingly for Mytilene Harbor values of ( $\Sigma 7\text{PAHs}$ ) varied from  $110 \text{ ng g}^{-1}$  to  $615 \text{ ng g}^{-1}$  (dry wt) with a mean value of  $387 \text{ ng g}^{-1}$ . Values of concentrations of ( $\Sigma 7\text{PAHs}$ ) exceeding or close to the effect range low concentration (ERL,  $552 \text{ ng g}^{-1}$ ) were found for harbor locations where heavy traffic of commercial and large vessels takes place.

Sampling sites IZ2 to IZ4 showed peak values in PAH content (totaling  $1,032 \pm 480 \text{ ng g}^{-1}$ ) that was significantly higher than either the remaining six Izmir sites ( $311 \pm 122 \text{ ng g}^{-1}$ ) ( $p = 0.03$ ) or vs. a total of seven Mytilene sites ( $387 \pm 172 \text{ ng g}^{-1}$ ) ( $p = 0.012$ ), as shown in Figure 5. However, the mean concentrations of PAHs from all Izmir sites were higher, yet did not differ significantly from all Mytilene sites ( $599 \pm 451$  vs.  $387 \pm 172 \text{ ng g}^{-1}$ , respectively).

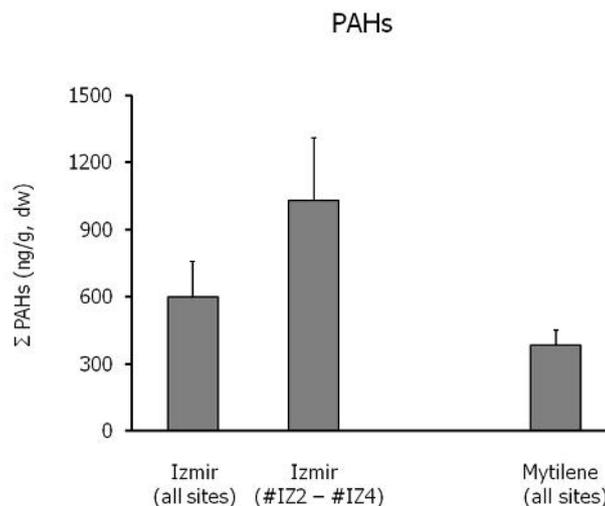


Figure 5. Concentrations of total PAHs ( $\Sigma$ PAHs,  $\text{ng g}^{-1}$  dry wt) in sediment samples from Izmir and Mytilene

Among the 7 examined PAHs in Izmir sediments, fluoranthene [Fluo] and benzo(a)pyrene [BaP] were the only compounds found in all sediments at a percentage ranging from 20.2 to 21.0 % and 14.8 to 17.3 % of ( $\Sigma$ 7PAHs) respectively. Benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF] were found in all sediment samples from Izmir Bay accounting for 30.7 % of ( $\Sigma$ 7PAHs), while for Mytilene Harbor sediments they were detected in locations subjected to navigation pollution.

#### 4. DISCUSSION

The results provided evidence for significant differences in the pollution status between Mytilene Harbor and Izmir Bay. The differences were particularly clear-cut by considering the data from inorganic analysis and, namely, the measured levels of some anthropogenic inorganics including aluminum, iron, manganese and zinc. These findings were in agreement with other studies conducted in the bay and is attributed to the heavily industrialized and urbanized coastal area as well as to the intense marine traffic in the Alsancak Harbor (Kucuksezgin *et al.*, 2006). In the case of chromium, copper, lead and titanium, a further difference was detected when the innermost sampling sites in Izmir Bay (#IZ1 to #IZ4) were considered, which displayed higher concentrations of these contaminants vs. Mytilene Harbor, in agreement with the anoxic conditions occurring in inner Izmir Bay (Ozkan *et al.*, 2008; Bizsel and Uslu 2000). The same distinction applied to total PAHs, displaying significantly higher levels in samples from sites #IZ2 to #IZ4, both compared to Mytilene and to the remaining Izmir sites.

Marine sediment contamination has been investigated in Izmir Bay and other coastal areas in Turkey by a number of previous studies (UNEP, 1993; Bizsel and Uslu 2000; Kontas *et al.*, 2004; Kucuksezgin *et al.*, 2006; Oral *et al.*, 2007; Esen *et al.*, 2008; Okay *et al.*, 2008; Guven and Akinci 2008; Ozkan *et al.*, 2008), providing evidence for extensive anthropogenic pollution. On the other hand, sediment from Mytilene Harbor has been evaluated for metal contamination only in one report (Aloupi and Angelidis 2001), whereas no published data are available on PAH contamination in Mytilene sediment, to the best our knowledge.

Along with the topographic features and the presence of several outlets of industrial and domestic effluents, the sediment from Izmir Bay displays a clear-cut gradient of anthropogenic pollution both in terms of inorganic and of PAHs levels, from the innermost to the outer sampling sites. Unlike Izmir Bay, Mytilene Harbor failed to show any evidence for topographic differences in the levels of either inorganics or PAHs; thus we could not confirm the data by Aloupi and Angelidis (2001), who reported different lead levels in Mytilene Harbor sediment between inner and outer harbor sites. All measured levels in Mytilene sediment were invariably lower than those measured in Izmir Bay and, especially, the innermost Izmir sampling sites. The values indicate that the area at the head of Izmir

Bay is affected by PAH contamination and the fine sediment texture, composed of high content of silt and clay facilitates the sorption of those hydrophobic contaminants (De Luca *et al.*, 2005).

The overall contamination levels detected in sediment from Izmir Bay overlapped with the data from several polluted coastal areas and lagoons (He and Morrison, 2001; Rodríguez-Barroso *et al.*, 2008; Accornero *et al.*, 2008; Skoog and Arias-Esquivel 2009), whereas anthropogenic pollution in Mytilene Harbor may be regarded as a relatively marginal phenomenon.

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