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Hydrocarbon Balance of Surface Sediments in Izmit Bay (Marmara Sea), Turkey

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Izmit Bay is a semi-enclosed basin; 49 km long, 2-10 km wide with a surface area of 310 square km (Figure 1). It is separated into three morphologic regions; western, central and eastern sub-basins with water depths of 200, 180 and 35 m, respectively. Active tectonism affects the actual basin-fill deposits (Yüksel et al. 2003). The region is important with its seaports, oil terminals, urban centers and industries located along shore. The total crude oil imported into the Tüpraş refinery, in the middle of the bay, is 27.6 mio t/a.

The intensive anthropogenic activity leads to the introduction of contaminants and the possibility of polluting the bay. The bay is subject to high anthropogenic pressure due to inputs from coasts, rivers, atmosphere, oil refineries and shipping activities. Another common anthropogenic source of PAHs is spillage of fossil fuels including unrefined (crude oil) and refined products (e.g. petrol). Over the years the bay has received very irregular quantity of hydrocarbons with variable compositions because of different origins of the crude oils treated in the refinery.

As industrialization processes speed up and demands for energy grow worldwide, oil spills have become a global problem, particularly in industrialized countries. The coastal area of this important industrial bay receives high inputs of organic matter, mostly anthropogenic. During the disastrous Eastern Marmara earthquake in 1999, several tanks and a cooling tower of the massive Tüpras refinery (Figure 1) burned out of control for three days when naptha spilled from a floating roof tank and ignited. The central and eastern basins of bay experienced a catastrophic oil spill (Güven and Ünlü 2000).

The fate and behaviour of spilled oil in the environment depends on a number of physicochemical and biological factors including evaporation, dissolution, microbial degradation, photooxidation and interaction between oil and sediments.

Hydrocarbons entering the aquatic environment, due to their hydrophobicity, rapidly become associated with sediments and suspended particles (Readman et al. 1984). Therefore, recent sediments can act as an indicator of the relationship between natural and anthropogenic variables (Salamons 1995).

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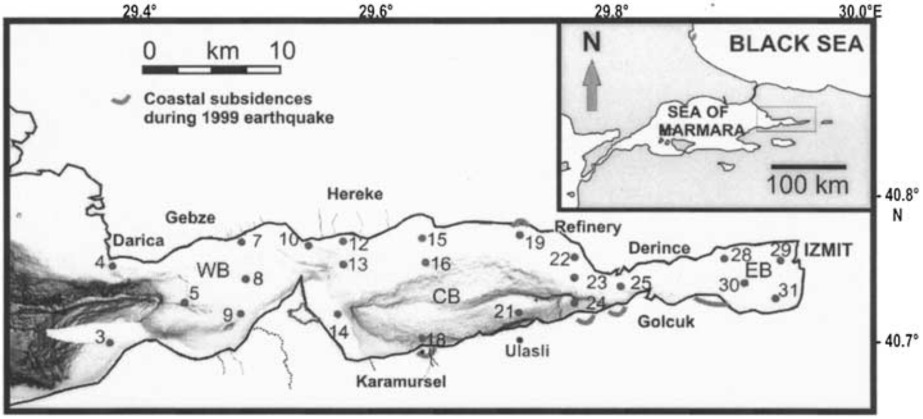


Figure 1. Location of Izmit Bay and sampling stations superimposed on the multibeam bathymetry. WB, CB, EB: western, central and eastern basins.

Sediment retention capacity may be related to physico-chemical properties such as grain size and organic matter. The polycyclic aromatic hydrocarbons (PAHs) are a class of organic priority pollutants, ubiquitous in the aquatic ecocystems, which show lipophilic character resistance to biodegradation depending on the molecular weight and structure.

The aim of this work was to determine the concentration of the PAHs in the surface sediments of Izmit Bay, to provide data for comparison by different reference materials (crude oils and chrysene) and assess the possible source of these compounds, whether pyrolytic or petrogenic input from anthropogenic processes.

MATERIALS AND METHODS

The surface sediment samples were recovered from all of the basins along the bay (Figure 1) using Van Ven grab sampler of 10 kg of capacity. The topmost 0-3 cm was carefully removed using clean stainless steel spatula. The samples were placed in solvent-cleaned glass-jars with foil-lined seals and transferred in an ice box to the laboratory where they were frozen to -20 °C.

The methods and recommendations suggested in (UNESCO Manuals and Guides (1982)were used and only a brief description is presented here. Frozen sediments were dried at 40°C to constant weight, and 50 g of the dry material was extracted by Soxhlet with 100 ml in a mixture isopropyl alcohol-hexane (80:20) and 3 g of KOH. The non-saponificable fraction was obtained by extracting twice with 25ml of hexane. The combined extracts were dried with anhydrous sodium sulphate, and the volume was reduced to 2 ml by rotary evaporation. Elemental sulphur was eliminated using the method described by Blumer (1957). The total concentration of petroleum hydrocarbons was measured in the extracts using ultraviolet fluorescence spectrophotometer (UVF, Shimadzu, RF-1501) at excitation wavelength 310 nm, emission wavelength 360 nm according to Ehrhardt and Burns (1993). Crude oil and chrysene equivalents were used as the standard for expressing the results. Reference crude oils in this study were supplied by the Tüpras refinery (Figure 1). The calibration curves were plotted in concentrations of 0.25-1.5μg/ml for crude oils and 0.05-0.3μg/ml for chrysene in hexane (Ünlü and Güven 2001).

A Hewlett-Packard Model 6890 GC with Hewlett-Packard Model 5972 Mass Selective Detector were used for all analyses. For detailed chromatographic conditions, analysis quality control, and quantification methodology were described earlier (David et al. 1994).Identification of the compounds was based on comparison of retention indices and mass spectra.

RESULTS AND DISCUSSION

Resulting from their granulometry analysis, the surface sediments are composed of mud (clayey silt). The amount of oil pollution in the dry sediment samples were calculated by chrysene reference and also the correlation equation (Table 1). The correlation equation was calculated from the equations of standard curves of crude oils examined (Ünlü and Güven 2001).

The oil concentration in sediment was within a range of 4.5-443.7 μg/g for crude oil and 0.8-84.6 μg/g for chrysene references. From a comparison of the present results with the data obtained earlier in the same region (Tolun et al. 2001; Tellikarakoç et al. 2002), the concentration calculated from chrysene is much lower than that of crude oil references. As can be seen in the Table 1 the values of pollution based on crude oil are 3.0-8.3 times higher than those found by chrysene references. The data demonstrated that the measurements of oil pollution based on solely a chrysene reference had not given true results because chrysene is one of the many fluorescent compounds in crude oil with varying amount. Therefore using crude oil as the reference substance seems more suitable since a particular kind of oil is responsible for pollution of a specific area. Ehrhardt and Petrick (1989) suggested that the usual reference substance was a crude oil likely to be used or transported in the area under investigation. Our findings supported experimentally this opinion.

In this work, significant levels of hydrocarbons were recorded in the sediments of the central and eastern basin of Izmit Bay (Table 1). These data are important to understanding the potential sources of hydrocarbons in the surface sediments. The presence of high hydrocarbon concentrations at 0-3 cm could be the result of deposition from an older spill. The distribution of petroleum hydrocarbons in the sediments is not only governed by sediment types, but it may also be controlled by the prevailing currents in the area, bottom morphology and sediment disturbance (Figure 2). The low PAH concentrations observed at the stations 21 and 24 may be attributed to possible coseismic slumps occurred at the edge of the central depression (Figure 1) during the 1999 Izmit earthquake (Alpar et al. 2001).

The water column in Izmit Bay has two distinct layers; the upper Black Sea water and the lower Mediterranean Sea water. The interface layer takes place at 19-26 m water depths depending on the seasonal variations. The inflow of two different water masses has a profound effect on the sediment transportation and deposition in the bay. Therefore, we have reevaluated a series of observational studies of currents and water mass exchange processes performed by different institutions (Morkoç et al. 1996).

Table 1. The location, depth and total PAH concentrations (dry wt., µg/g) in the sediments of Izmit Bay.

Stations		Depth (m)	A(*)	Chrysene	Sediment Type
Western Basin	3	320	13.0	3.1 (4.2)	muddy sand
	4	320	4.5	0.8 (5.6)	mud
	5	81	11.5	2.7 (4.2)	muddy sand
	7	65	13.5	3.3 (4.0)	muddy sand
	8	55	24.9	3.2 (7.7)	gravel / muddy sand
	9	35	23.4	2.8 (8.3)	mud
	10	30	10.0	3.3 (3.0)	silt
Central Basin	12	25	138.3	28.4 (4.8)	sandy mud
	13	54	49.0	9.7 (5.0)	mud
	14	45	162.8	35.0 (4.6)	mud
	15	52	190.8	42.4 (4.5)	silt
	16	80	90.5	20.7 (4.4)	mud
	18	46	205.2	46.3 (4.1)	mud
	19	106	214.8	48.9 (4.6)	mud
	21	64	34.8	8.4 (5.2)	sandy mud
	22	23	335.6	72.7 (5.0)	clay
	23	43	443.7	84.6 (5.1)	mud/clay
	24	56	49.1	9.7 (5.3)	mud
	25	40	236.4	46.2 (4.1)	sandy mud
Eastern Basin	28	19	343.6	83.3 (4.1)	sandy mud
	29	19	124.5	29.8 (4.1)	mud
	30	29	274.9	64.9 (4.2)	sandy silt
	31	30	170.2	38.6 (4.4)	mud

A: Calculated from the correlation equation. (*) Crude oils (former Soviet Union, Iraqi, Iranian, Saudi Arabian, Libyan, Syrian and Egyptian). The ratio of oil pollution levels based on crude oil and chrysene references are given in parenthesis.

Regional surface and bottom water current patterns and general drift directions in the bay are shown in Figure 2. The hourly averaged upper-layer current speeds during the measurement period ranged from 10 to approximately 40 cm/s, increasing in spring. Mainly on the basis the wind direction and the flux of Black Sea water, the less-saline, fluvial, drainage and sewer inflows of surface water may circulate in two directions. Meanwhile, the average speed of bottom layer is almost half of that of the upper layer; increasing in fall. No or very little sediment transportation there are from the central to the eastern basin.

The different classes of phenanthrenic compound (parent, mono and dimethylated derivatives) are often measured as part of monitoring programme; so it is possible to understand the sources of the PAHs identified in a sample (Kennicutt et al. 1992).

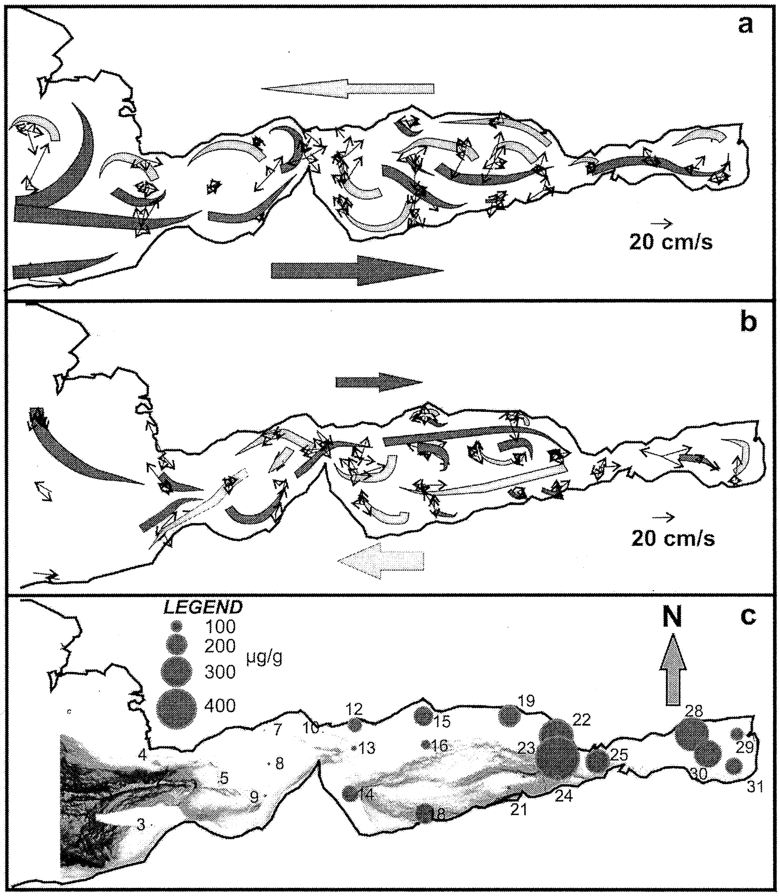
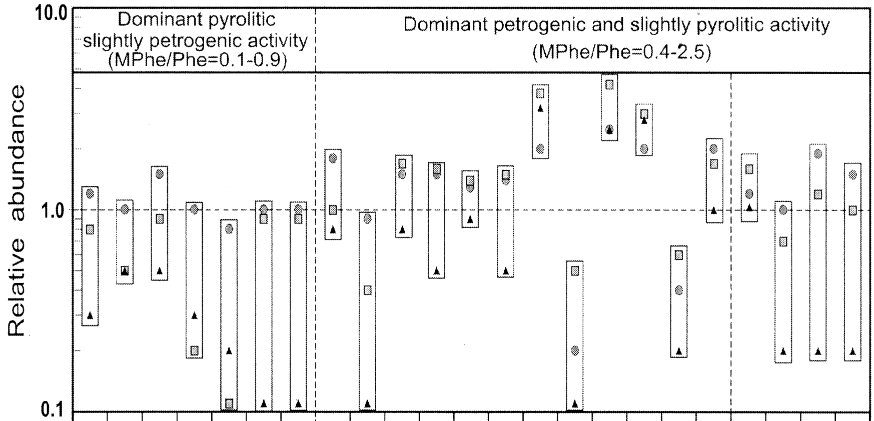


Figure 2. Surface (a) and bottom currents (b) are effective on the sediment transportation and sediment pollution (c) in the bay.

In the present work the relative abundances of different classes of phenanthrenic compound were observed and their alkylated derivatives is characteristic of pyrolitic (natural and/ or anthropogenic sources). The uniformly high abundance of phenanthrenes and methyl phenanthrenes calls for a diagenic origin. The presence of PAHs in marine sediments corresponds either to concentrations of residues from high temperature processes like fossil combustions (phenanthrene, fluorenthene, pyrene, chrysene and benzopyrene) or oil activities such as direct discharges, tanker operations, refinery processes and accidental spills mostly methyl derivatives and dimethyl substituted phenanthrenes).

Phenanthrene and anthracene are two structural isomers. Phenanthrene is more termodinamically stable than anthracene. This slight difference between the two series of sediment samples concerning the phenanthrene and anthracene abundance could be explained by their tendency to degrade (e.g. Fig 3.-station 28).



	3	4	5	7	8	9	10	12	13	14	15	16	18	19	21	22	23	24	25	28	29	30	31
● Phe	1.2	1.0	1.5	1.0	0.8	1.0	1.0	1.8	0.9	1.5	2.0	1.3	1.4	2.0	0.2	2.5	2.0	0.4	2.0	1.2	1.0	1.9	1.5
▨ MPhe	0.8	0.5	0.9	0.2	0.1	0.9	0.9	1.0	0.4	1.7	1.6	1.4	1.5	3.8	0.5	4.2	3.0	0.6	1.7	1.6	0.7	1.2	1.0
▲ DMPhe	0.3	0.5	0.5	0.3	0.2	0.1	0.1	0.8	0.1	0.8	0.4	0.5	0.5	3.2	0.1	2.5	2.8	0.2	1.0	1.0	0.2	0.2	0.2
Basin	WESTERN							CENTRAL												EASTERN			

Figure 3. Distribution of parent and their alkylated derivatives in the GC/MS chromotograms of sediment samples.

Prahl and Carpenter (1983) reported that MPhe/Phe ratio is between 0.5 and 1 for phenanthrenes originating from combustion processes, while it varies between 2 and 6 for the sediments dominated by fossil-fuel phenanthrenes. At almost all stations of the western basin where the relative partitions of MPhe's to Phe vary between 0.1-0.9, the phenanthrene predominates if compared with methylated and dimethylated derivatives. This view implies pyrolytic PAHs resulting from atmospheric combustion residues (forest fires and fossil fuels) and confirms the lower petroleum influence (Figure 4). The relative partition of MPhe's in comparison with phenanthrene is similar for the stations 14, 16 and 18 even if monomethylated derivatives are more abundant (0.4-2.5) in the stations of central basin than the others. These findings correspond to a petrogenic origin of these compounds (Garrigues et al. 1988) but confirm the lower pyrolytic activity. Accidental spilling of fuel into the sea during the loading operations might be the cause of petrogenic contamination. Likewise, this result is similar for the eastern basin (between 0.6 and 2.0).

We observed an important decrease of dimethyl phenanthrenes (DMPhe's) in the stations 13 and 21 compared to the others in the central basin. DMPhe's have a slighter abundance relatively to MPhe's in the western basin stations (Figure 4). This work shows a dramatic change in the spatial distribution in the concentration of PAHs of surface sediments. The high PAH concentrations in the central basin and adjacent areas originates mainly from municipal effluents, discharges from the local refinery, spillages from vessels, port operations and presumably atmospheric transport as well. These results suggest the need for improvements in loading and transport conditions, the reduction of ballast and bilge waste discharges and minimizing fuel spills. The western basin has much lesser anthropogenic activities leading to lower values of PAHs in sediments.

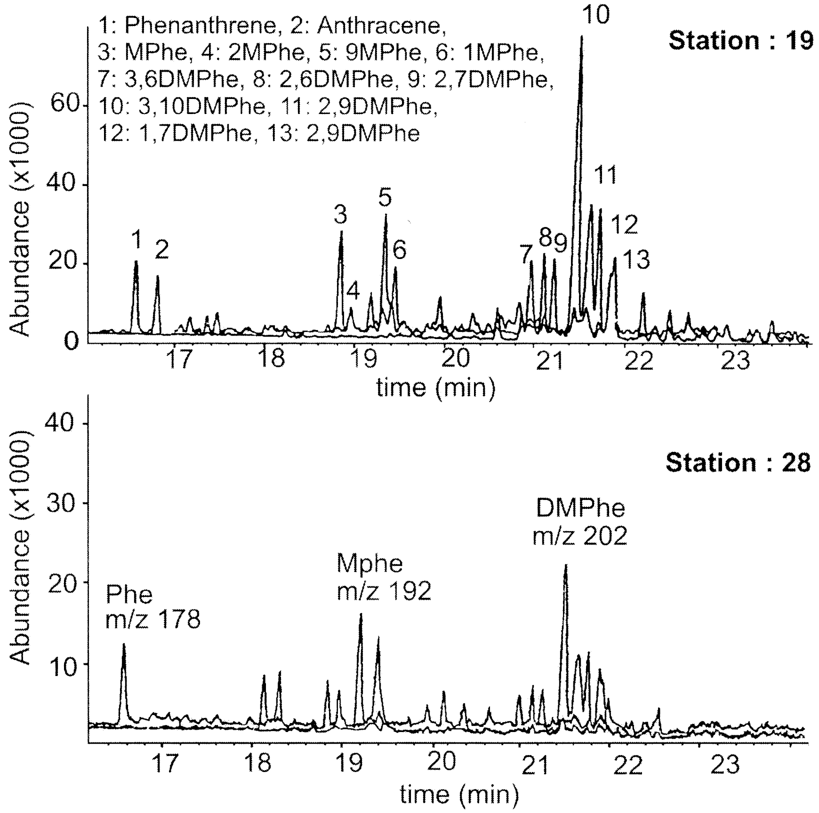


Figure 4. Mass chromatograms (Σm/z 178, 192, 202) of phenanthrene and mono and dimethylated derivatives

These results allow us to consider that important changes in the PAHs accumulation in sediments take place depending on the direct influence of anthropogenic activities, mainly combustion processes of traffic and industrial activities. The level of contamination detected, even if not comparable with that found in highly industrialized areas, is relatively high suggesting the indispensable need for an increasing effort in controlling sources of pollution in this specific area.

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