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PAH Contamination Sources in the Sediments of the Strait of Istanbul (Bosphorus), Turkey

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The Strait of Istanbul (Bosphorus) is a narrow and shallow strait which builds a water passage between the Black Sea and the Sea of Marmara, placed at the northern part of the 300-km long Turkish Straits System (Figure 1). It is formed in the Quaternary by incision of a river valley into the older basement rocks. It twists and turns for 31 km, with a dozen course changes to be navigated, some as sharp as 90 degrees. It is one of the busiest straits in the world, boasting frequent variations in width (0.7 and 3.5 km with an average of 1.6 km), depth (30 and 110 meters with an average of 36 m) and current (Alpar and Yüce 1998).

Today, 56.000 commercial ships pass through the Strait of Istanbul annually, 5.500 of them oil tankers. In addition, 2.500 commuter ferries traverse the strait each day. Therefore, this rather important biological corridor is one of the most polluted water passages of the world. Its physical and chemical characteristics have attracted many researchers from different disciplines.

There is a two-layer flow through the Strait of Istanbul; brackish Black Sea water and underlying more saline and dense Mediterranean water. In normal conditions, the interface depth of these two layers is 10-15 m to the south and about 45 m to the north entrance. Their volume and density, however, change on the basis of the Black Sea's hydrologic budget, dominant wind systems and their seasonal variations. The distinguished morphology, constraint and sills at the southern and northern entrances, and hydrodynamics of this intricate strait make this flow more complicated. The northward flow, driven by thermohaline differences, carries the Mediterranean water to the Black Sea along the sea bottom. This flow, however, is found to be continuous, except for infrequent and short-duration interruptions (Yüce 1996; Özsoy et al. 1996).

Pollution occurring in the Strait of Istanbul is due to mass traffic and can be examined under two topics; air pollution caused by funnel gasses of vessels and marine pollution. Pollution deriving from marine traffic in the strait is much more important. Vessels passing through the strait pollute and cause a dense international marine traffic. This pollution reasons are varied; bilge piping, all kinds of garbage unloading, dirty oil unloading, waste water unloading resulting from deck cleaning and leakage.

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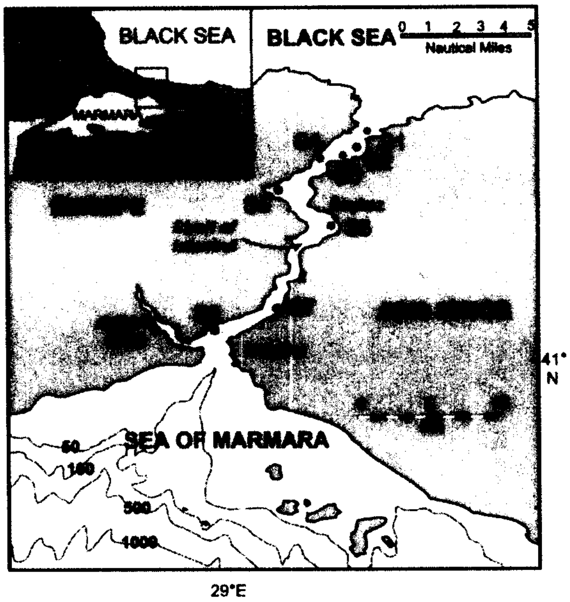


Figure 1. Location of the sampling stations in the Strait of Istanbul. See Table 1 for other details.

Polycyclic aromatic hydrocarbons (PAHs) form a widespread class of environmental chemical pollutants and can originate from many sources; incomplete combustion at higher temperatures of recent and fossil fuels (coal and oil; pyrolytic origin), slow maturation of organic matter under the geochemical gradient conditions (petrogenic origin) and short-term diagenetic degradation of biogenic precursors (biogenic origin).

It is very well know that oil products are the most typical kind of contamination of marine basins. Tanker traffic, oil transfer and ballast treatment facilities in the strait are likely to increase the level of hydrocarbons in the environment. In past, pollution monitoring activities in the Strait of Istanbul is concentrated mostly on vary pollutants, but unfortunately no previously published data have been found for PAHs origin.

The purpose of this paper is determine some of the PAHs origin and the levels of them in the sediments of the Strait of Istanbul and to compare these sources with hydrocarbons in sediment samples from the region.

MATERIALS AND METHODS

Our samples were taken from the top most 0-3 cm of the surface sediments recovered by van Veen grab sampler of 10 kg of capacity along the Strait of Istanbul during the water quality monitoring cruises in 1999 (Table 1). Most of the stations are close to the coasts and only the station S1 stays within the north-flowing lower-current layer. The station S2 is somewhere in the mixed waters between the two current layers while others are in the southward flowing upper Black Sea water. However, there exists coastal current instabilities and eddies accompanying the upper current at the stations S5, S6, S7 and S8. The thickness of surface sediments in the strait (Middle - Late Holocene) varies at areas that typically experience high marine current flows and erosion. These actual sediments mainly consist of interstratified coarse-to-fine shelly and clayey sands with shell-bearing green clays, arranged in fining and coarsening upwards sequences. Closer to the marginal parts, continental facies become dominant.

Table 1. Granulometry, total aromatic hydrocarbon concentrations in sediments.

Station No	Location		Depth (m)	Granulometry(%)			Hydrocarbons (µg/g)[a]
	Lat-N	Long-E		Fine	Sand	Gravel	
S1	41°12.32'	29°07.08'	70	46.5	53.4	0.1	205.6
S2	41°11.39'	29°06.46'	42	1.4	98.5	0.1	93.0
S3	41°11.14'	29°06.18'	25	1.4	98.5	0.1	144.9
S4	41°11.07'	29°04.44'	17	1.9	98.0	0.1	22.8
S5	41°09.24'	29°02.42'	20	35.2	64.7	0.1	140.5
S6	41°07.32'	29°05.38'	10	0.7	99.2	0.1	293.6
S7	41°03.02'	29°03.08'	20	1.8	98.1	0.1	427.9
S8	41°02.04'	28°59.42'	10	31.4	68.5	0.1	397.8

[a] : Aromatic hydrocarbon concentrations in µg/g (dry weight) as crude oil equivalents.

Surface sediments were carefully removed using a cleaned stainless steel spatula. These 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.

We followed the methods and recommendations suggested in UNESCO Manuals and Guides (1982). Frozen sediments were dried at 40°C to constant weight, and 50 g of the dry material was digested under reflux with 100 ml in a mixture isopropyl alcohol-hexane (80:20) and 3g 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. To isolation of hydrocarbon fractions were carried by column chromatography with activated alumina (activity grade I, acidic). Elution with hexane gave a fraction consisting of aliphatic hydrocarbons while elution with hexane-dichloromethane yielded a fraction containing aromatic hydrocarbons.

Elemental sulphur was removed from the extracts using activated copper and the total concentration of petroleum hydrocarbons was measured in the extracts using Ultraviolet fluorescence spectrophotometer (UVF, Shimadzu, RF-1501). Russian crude oil was used as the standard for expressing the results. The calibration curve was plotted in concentrations of 2.5, 5, 10 and 15 µg/ml in hexane. The fluorescence was measured at excitation wavelength 310 nm, emission wavelength 360 nm according to Ehrhardt and Burns (1993).

A Hewlett-Packard Model 6890 GC with Hewlett-Packard Model 5972 Mass Selective Detector was used for all analyses. The GC column was an HP PONA 50 m x 0.20 mm i.d. (film thickness 0.5µm) fused–methyl siloxane (Hewlett-

Packard). Injections (2µl) were conducted in the splitless mode with the column held at 40°C for 6 min, from 40-280°C for 10°C/min, 280°C at 10 min, from 280-290°C at 10°C/min, 290°C for 5 min; the carrier gas helium (1.0 ml min^{-1}). The injector temperature was held at 300°C. Mass spectral data were acquired in Selected Ion Monitoring (SIM) mode.

The GC/MS was calibrated for the Priority Pollutant PAHs using the internal standard calibration procedure described in US EPA method 8000 (PAH calibration mixture purchased from Supelco, a part of Sigma-Aldrich Corporation). The mass spectrometer was operated in the electron impact ionization mode (70 eV) with continuos scan acquisition from m/z of 50 to 550 daltons at a cycling rate of 1 scan/s the mass spectrometer parameters were set up with the electron multiplier at 1050 V, source temperature of 200°C, and transfer line temperatures both at 290°C. The MS was tuned and calibrated with PTFA immediately before use. The ChemStation data system software was used to process the acquired spectral information. Grain size analysis was performed using the combined dry sieve and pipette method (Folk 1974).

RESULTS AND DISCUSSION

The results of both aliphatic and aromatic hydrocarbons are presented based on the dry weight of sediments. Table 1 shows the granulometry of the concentration total aromatic hydrocarbon in sediments. The granulometry analysis showed sediments with dominant fraction of sand. Concentrations of petroleum hydrocarbons in sediments from all stations varied from 22.8-427.9µg/g, dry wt.

The stations S1, S6, S7 and S8 show the highest total concentrations of PAHs while the lowest values were recorded in stations S2 and S4 which human activity is not directly related. Black Sea origin hydrocarbon pollution at the station S2 is lower because this sample location is occasionally under the effects of Mediterranean water. On the other hand, low pollution value at the station S4 is due to the high speed reverse currents nearby the sandbank where our sample is recovered. The higher concentrations were found at the stations S7 and S8 located at the southern part of the strait, near the domestic and international sea ports close to downtown.

Little is know about hydrocarbon pollution in the Strait of Istanbul; the only data is from a few stations recovered after the Nassia Tanker accident in 1994 (Güven et al. 1996). However, our results show higher hydrocarbon levels compared to this previous study. In addition, if we compare our results with those obtained at the Black Sea exit by Readman et al. (2002) and in the Sea of Marmara by Güven et al. (1998), our hydrocarbon levels are substantially higher (concentrations <100 µg / g dry wt).

Identification of n-alkanes was based on comparison of retention indices and mass spectra. The quantification of the compound classes was determined using the measurements of peak area in the total ion chromatograms.

The gas chrotomograms of the alkane + alkene hydrocarbon fractions of all sediment samples exhibited a more or less pronounced envelope of UCM unresolved components underlying a series of resolved peaks, mainly consisting of n-alkanes in the C11 to C26 range, the isoprenoids Pristane (Pr) and Phytane (Ph) and a number of biogenic alkanes, e.g. Perylene (Figure 2).

GC/MS analysis of the sediment samples (S1, S3, S5, S6, S7, S8) showed an unresolved complex mixture (UCM) of hydrocarbons, which is also typical of fossil fuels (Blumer and Youngblood 1975). Our results have shown varying UCM magnitude which is directly related to the degree of anthropogenic contribution.

The ratio of isoprenoid pristane and phytane concentrations were determined for each station. Two isoprenoid alkanes, Pr, and Ph were present in all sediment extracts, however, their relative abundances varied greatly. These are common constituents in coastal marine sediments and in most of the crude oils (Clark and Blumer 1967).

The predominance of a single isoprenoid (e.g. pristane) or a high ratio of pristane to phytane generally indicate a biogenic input possibly originating from algae and bacteria (Readman et al 2002). In our case, the pristane is dominant isoprenoid alkane in the station S3. However, the ratio of pristane and phytane was found low in most of sediment samples (except station S6), indicating low contribution from biogenic hydrocarbons.

The influence of microbial degradation could be verified by examining n-C17/Pr and n-C18/Ph ratios. It is known that the normal alkanes are more rapidly biodegraded than those with a branched carbon chain (Clark and Blumer 1967). The relative n-C18/Ph ratios at all stations are between 1.3 and 0.6, implying that microbial degradation processes are more effective (Table 2). In the station S8, C17/Pr and C18/Ph indices were greater than 1, corresponding to low degradation.

Table 2. Values of n-alkanes evaluation indices applied to the sediment samples.

Station No	n-C17/Pr	n-C18/Ph	Pr/Ph
S1	0.85	0.69	0.64
S2	0.78	0.63	0.71
S3	1.25	ND	ND
S4	0.30	1.18	0.52
S5	0.83	0.64	0.67
S6	0.67	1.36	1.52
S7	0.67	0.92	0.78
S8	2.05	1.17	0.34

Pr : Pristane, Ph : Phytane ND : not determined.

Several methods can be used to determine the probable sources of PAH. A common method is the calculation of the specific alkylated PAH/parent PAH or parent PAH/PAH ratios (Blumer and Youngblood 1975). In the present study, the ratios of methylpyrene / pyrene (MPy/Py), methylphenanthrene / phenanthrene (MPhe/Phe), Fluoranthene / Pyrene (Flt/Py), Chrysene/Benz(a)anthracene (Chr/B(a)An) and Phenanthrene / Anthracene (Phe/An) were examined.

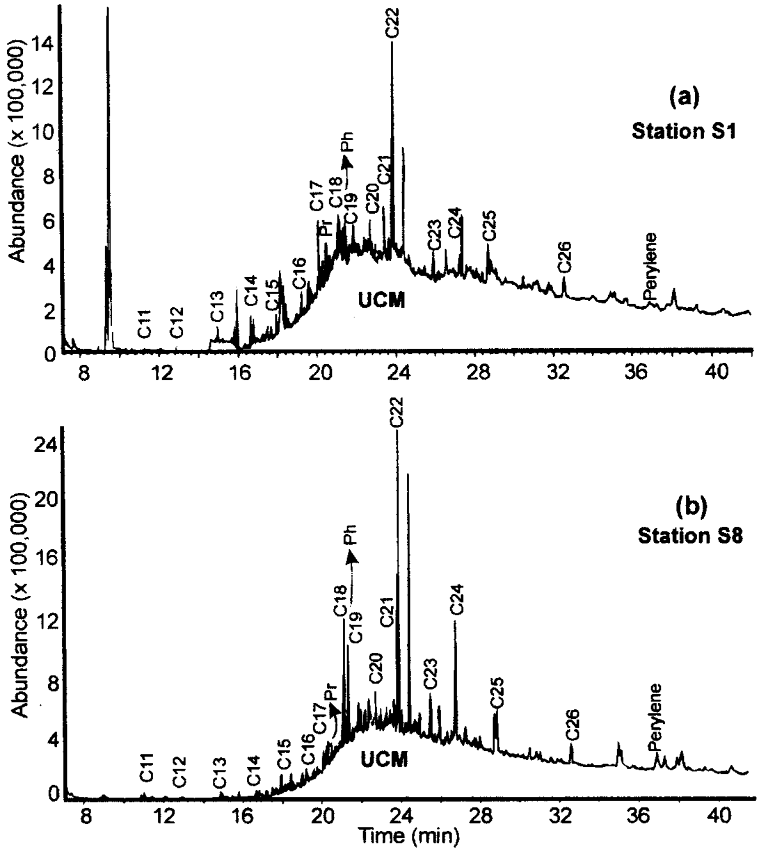
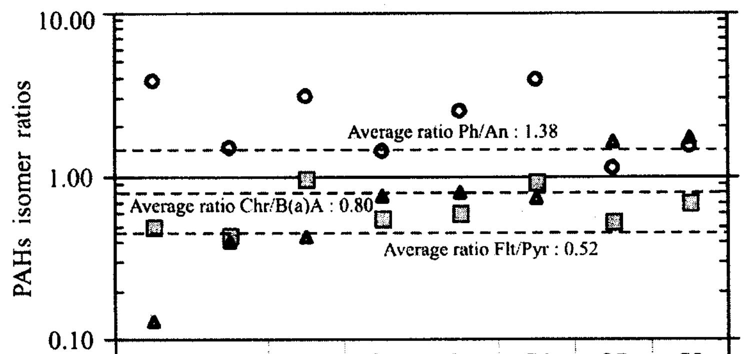


Figure 2. GC / MS Chromatograms of surface sediments taken from stations a) S1 and b) S8. Pr: Pristane, Ph: Phytane. UCM: Unresolved Complex Mixture.

The relative distribution of parent homologues and their alkylated derivatives is characteristic of pyrolytic (natural and / or anthropogenic) sources. The uniformly high abundance of phenanthranes and methyl phenanthranes calls for a diagenetic origin. The presence of polycylic aromatic hydrocarbons in marine sediments corresponds either to concentrations of residues from high temperature processes like fossil combustions (fluoranthanes, pyrenes, chrysenes and benzopyrenes) or oil activities such as direct discharges, tanker operations, refinery processes, and accidental spills (mostly methyl derivatives and dimethyl substituted naphthalenes and phenanthrenes). According to Maher and Aislabie (1992), the MPy/Py ratio is less than 1 for PAHs derived from combustion sources, while the same ratio is less than 2 for a petroleum source. Our results calculated for all sediments are found to be less than 1, between 0.18 and 0.74. Considering this result the PAH in the samples investigated in our study originate from combustion sources.

Prahl and Carpenter (1983) reported that MPhe/Phe ratio is between 0.5 and 1 for phenanthrenes originating from combustion processes, while it is between 2 and 6 for the sediments dominated by fossil-fuel phenanthrenes.



Stations	S1	S2	S3	S4	S5	S6	S7	S8
○ Ph/An	3.80	1.48	3.08	1.42	2.49	3.88	1.12	1.50
▨ Flt/Pyr	0.50	0.44	0.97	0.56	0.60	0.92	0.53	0.70
▲ Chr/B(a)A	0.13	0.40	0.43	0.77	0.79	0.75	1.64	1.61

Figure 3. PAHs isomer ratios of the samples.

The ratios of MPhe/Phe could only be determined at the stations of S3, S4, S6, S7, S8, with values between 1.1 and 2.8. In fact, phenanthrene and anthracene are two structural isomers. Because of their physico-chemical properties, they could have behave differently in the environment and could lead to different values for their Phe/An ratio that would give useful information on the PAH origin (Gscweng and Hites 1981). Because the phenanthrene is more stable than anthracene in thermodynamical sense, the Ph/An ratio is observed to be very high in PAH petrogenic pollution, but lower in pyrolytic contamination cases. Anthracene is generally attributed to pyrolytic sources, i.e. petroleum products and/or forest fires (Soclo et al. 1986). Similarly, fluoranthene and pyrene were often associated during natural matrices analyses and were considered as typical pyrogenic products derived from high-temperature condensation of lower molecular weight aromatic compounds.

The plot of Phe/An (phenanthrene concentration versus anthracene concentration) against Flt/Py (fluoranthene concentration versus pyrene concentration) shows pyrolytic PAH contamination in the sampling stations of S1, S2, S3, S4, S5 and S6 (Figure 3). The pyrolytic PAH inputs in the Strait of Istanbul are confirmed by the Chr/B(a)A ratio values which are lower than 1. The stations S1, S2, S3, S4, S5 and S6 were characterised by Phe/An values < 10, Flt/Py values ≤ 1 and Chr/B(a)A < 1; characteristic of pyrolytic and petrogenic contamination with strong pyrolytic input. This would be originated from the fossil fuel combustion particles emitted by commercial vessels. On the other hand, the stations S7 and S8 were characterised by Flt/Py values lower than 1 and Chr/B(a)A higher than 1. These stations appear to be contaminated by petrogenic PAH and probably a slightly pyrolytic PAH contamination possibly due to the shipping traffic in the strait. A mixture of pyrolytic and petrogenic PAHs were observed in most of the sediments, usually with strong pyrolytic predominance. This was most notable at all localities placed to the north of station S6. On the other hand, the diagenetic origin of perylene, a common breakdown product of natural organic matter, was most notable in our samples.

In conclusion, our analysis, which provide a useful tool in assessing PAH contamination levels and their possible sources, have shown that the pollution from petroleum derived hydrocarbons are in variable levels in the strait, especially on the coastal area. It is due to the pyrolytic activity which is a potential threat to the environment and to growing economic activities, such as ecotourism and fisheries. These results suggest indispensable needs for improvement in transport conditions, reduction of ballast and bilge waste discharges and minimising fuel spills.

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