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Polycyclic Aromatic Hydrocarbon Pollution in Sediments of the Çanakkale (Dardanelles) Strait, Turkey

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Sea pollution has become a major threat to the marine environment and ecological equilibrium of the Marmara Sea and her straits, known by the name of the Turkish Straits System (TSS). The Istanbul (Bosphorus) and Çanakkale (Dardanelles) straits are famed by their unmatched beauty, nature, history and cultures which rises from 3000 years of past. The straits, however, are the only connection for growing maritime trade and oil transportation by tankers between the Black Sea states and other flag states. In recent years the world tanker fleet has greatly expanded principally through major use of supertankers. The Turkish straits already now work by the maximum capacity. 140 vessels per a day pass through these most important biological corridors of the world and 50,000 ones per a year; 8,000 tankers transporting oil and petroleum derivatives more than 145 million tons and other potentially dangerous cargo (Akten 2003).

Pollution of polycyclic aromatic hydrocarbons (PAHs) in water column and surface sediment along the TSS, including their surrounding coastal areas, is mainly caused by dense navigation, maritime accidents and improper disposal of ballast and bilge waters (Güven et al. 1997; Ünlü et al. 2004; Ünlü and Alpar 2004). However, no previous pollution monitoring activities or published data have been found for petroleum hydrocarbon pollution in the sediment of the Çanakkale strait (Figure 1). This strait is a 62-km long, shallow and intricate seaway passage along the growing maritime trade and oil transportation route between the Aegean Sea and the Marmara Sea.

This paper describes a case study to identify and determine the polyaromatic structure and the total PAH concentration levels in the sea floor sediments recovered at the Marmara exit of the Çanakkale strait which has not been surveyed in the past.

MATERIALS AND METHODS

Twelve surface sediment samples (Figure 1) recovered in August 2003 are from the center of the Van Veen grab from top down to a depth of max 3 cm. The extraction method and associated recommendations were given in the Manuals and Guides of UNESCO (1982) in detail. 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). The non-saponificable fraction was obtained by extracting twice with 25ml of hexane.

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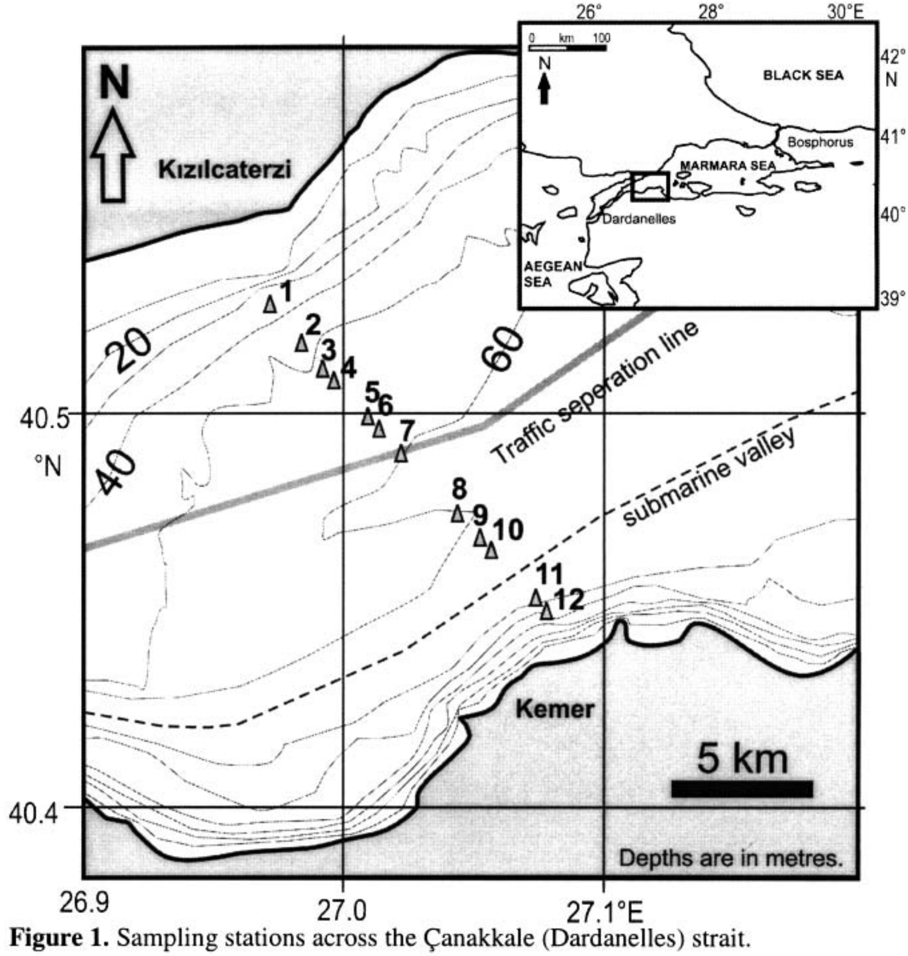

Figure 1. Sampling stations across the Çanakkale (Dardanelles) strait.

The combined extracts were dried with anhydrous sodium sulphate, and the volume was reduced to 2 ml by rotary evaporation. The total concentration of petroleum hydrocarbons was measured in the extracts using a *Jasco-6300* luminescence spectrometer. The calibration curve was plotted in concentrations of 0.25-1.5μg/ml. The cargo crude oils passing through the TSS (e.g. former Soviet Union, Iraqi, Iranian, Saudi Arabian, Libyan, Syrian and Egyptian) were used as reference materials. The correlation equation was calculated from the equations of standard curves of crude oils examined. The fluorescence was measured at excitation wavelength 310 nm, emission wavelength 360 nm according to Ehrhardt and Burns (1993).

Analysis of sediments by synchronous fluorescence has been currently used since Lloyd (1971) has developed this method. UV fluorescence in synchronous excitation-emission technique allows us to determine the polyaromatic structure of a compound. The technique of synchronous excitation-emission is of particular interest because it produces simplified emission spectra.

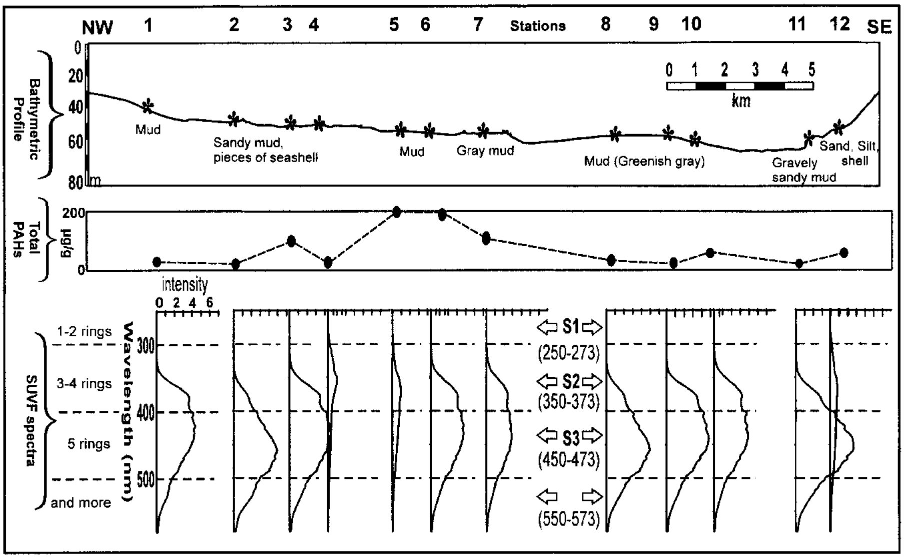

Figure 2. The spectra of the polycyclic aromatic hydrocarbons present in the sediment samples. Textural characteristics of the sediment are shown along the bathymetric profile.

This technique simplifies the emission of each component of a mixture and gives a better-resolved spectrum for the whole of the mixture components (Vo-Dinh et al. 1984). The $\triangle\lambda$ interval between λ_{ex} and λ_{em} was constant and equal to 23 nm. One-centimeter thick quartz cells were used.

RESULTS AND DISCUSSION

The study area shows a distinctive funnel shape in plan view, with the widths and depths increasing eastward towards the western part of the Marmara Sea (Figure 1). The strait channel extends to the deep basin through a canyon, which reaches a water depth of about 200 m.

Most of the surface sediments in the study area are fine-grained (Figure 2) and water content of the sediment column generally starts to decrease at about 25 cm below the surface (Alpar et al. 2004). Based on their depositional characteristics, the surface sediments are 0.5 to 3 m thick and overlay the coarse-grained sediments with varying amounts of biogenic material. The surface samples from the deepest stations (5 to 11) are composed of mainly fine-grained and trace amount of sand-sized material. In shallower water depths, sand-sized materials increase to 50-60% and the surface sediments consist of the coarse-grained shelly sediments. In addition close to the shores, muddy sediments with large and hard assemblages of algae form about 30 cm thick cover over relatively hard and coarse-grained sedimentary layers with shell fragments.

Even grain size has been shown to be important factors in sediment PAH distribution (Nishigima et al. 2001), our findings did not indicate a significant relationship between the total aromatic hydrocarbon concentrations in surface sediment and sediment textural properties (Table 1). The anomalies on the total PAH concentration distribution along the stations (Figure 2) may be related with other processes and factors such as seafloor morphology, currents, erosion and sediment control works. The higher values of the total PAH concentrations at stations 5, 6 and 7 may also be attributed to the atmospheric inputs of the transporting vessels along their specified traffic routes.

The total PAH concentrations (sum of two to six-ring aromatic hydrocarbons) in the sediment varied between 4 and 189 μg/g dry weight. Since no previous data on hydrocarbon pollution is available for the Çanakkale area, our results could only be compared with those found in the Bosphorus, Marmara and Black Seas (Table 2). In that way, hydrocarbon levels in the study area are somewhat lower.

Table 1. Sampling location, textural characteristics and total polycyclic aromatic hydrocarbon concentrations of the recovered surface sediment.

Station No	Location Lat. °N – Lon. °E	Depth (m)	Texture	Hydrocarbons (μg/g dry weight)
1	40.52729 - 26.97096	41	Mud	30.1
2	40.51756 - 26.98327	47	Muddy sand	15.1
3	40.51149 - 26.99195	50	Muddy sand	95.7
4	40.50837 - 26.99629	50	Clayey sand	4.0
5	40.49921 - 27.00922	54	Sandy mud	189.5
6	40.49609 - 27.01349	54	Clay	184.5
7	40.48996 - 27.02213	55	Mud	84.0
8	40.47467 - 27.04373	56	Mud	15.8
9	40.46851 - 27.05241	58	Mud	7.8
10	40.46543 - 40.46543	61	Mud	41.9
11	40.45316 - 27.07395	57	Sandy mud	8.2
12	40.44976 - 27.07798	52	Muddy sand	42.2

SUVF analysis was used to identify common patterns and possible sources of PAHs. In Synchronous spectra, compounds with different numbers of fused aromatic rings exhibit their maximum emissions at particular wave lengths (spectral region from 280-480 nm) (Kister et al. 1996). Benzenes unit most strongly in the 280-290 nm region, naphthalenes round 310-320 nm, 3 and 4 ring aromatics between 340 and 380 nm and compounds with 5 or more rings above 400nm.

Fluorescence intensity is related to the quality of aromatic compounds present in the samples. It appears likely that the more volatile 2-ring PAHs are rapidly lost in this environment, through evaporation and photo-decomposition. S1 (two rings) PAHs have not been encountered in the samples. Profiles are similar for the stations 1, 2, 3, 6, 7, 8, 9, 11 and their SUVF spectrums were shown in Figure 2.

Table 2. World-wide concentrations of the total polycyclic aromatic hydrocarbons in sediment (μg/g dry weight).

Survey Area	Period	Concentrations	References
Ukraine coastline	1995	49 - 310	Readman et al. (1999)
Bosphorus, Black Sea	1995	12 - 76	Readman et al. (1999)
Black Sea, Russia	1995	8 - 170	Readman et al. (1999)
Bosphorus	1999	93 - 428	Ünlü et al. (2004)
Izmit Bay, Marmara Sea	1999	5 - 444	Ünlü and Alpar (2004)
Çanakkale Strait	2003	4 - 189	This study

It is generally accepted that pyrogenic PAHs are characterized by the dominance of high molecular mass 4-5 and more ring PAHs over the low molecular mass 2-3 ring compounds. In contrast, petroleum hydrocarbons in crude oil and light refined products are dominated by the lowest molecular weight PAHs with only trace levels of the penta- and hexa- aromatics present (Baumard et al. 1999).

In this study, the SUVF spectra show the predominance of 5 and more ring PAHs such as Benzopyrene derivatives. This indicates pyrolytic origins in all samples with some exceptions at the stations 4, 5 and 12 where the 3-4 ring PAHs such as pyrene derivatives are dominant (Table 3). The dominant sources of PAH appear to be the combustion processes through run-off, sewage discharges and atmospheric input, rather than oil spill. Even not so large, an increment in emission between 370-400 nm on the synchronous scan for the station 10, is consistent with a slightly increased content of 3-to-5 and more ringed PAH series and/or fuel oil oxidation products (Table 3).

Some samples also contained further peaks at 403, 440, 468 nm; that indicates the presence of 5 and higher ringed aromatics. These peaks have also been observed in the spectra of our sediment samples (Figure 2). They were believed to come primarily from atmospheric dust fall (Wakeham et al. 1980). These hydrocarbons are usually thought to be generated by pyrolysis reactions during combustion of fossil fuels.

The oil pollution along this water passage is generally from normal tanker operations, such as tank cleaning, de-ballasting, and other operational reasons for periodically discharging oil overboard. Even though the risk of marine accidents in this strait may be somewhat higher due to its intricate morphological and oceanographic features, no important marine accident involving a public and a nonpublic vessel has occurred since the World War II. In that way, oil pollution in sediment, if encountered, would be based on the normal tanker operations.

Despite the environmental and safety threat posed by increased oil tanker traffic along the Çanakkale strait, the results in this study indicate that the study area is not greatly impacted by oil pollution. Therefore these results can be used as a reference for any comparison in future.

Table 3. Wavelength and relative abundance of each group of aromatic hydrocarbons from synchronous excitation emission spectra.

Station	Relative Abundance		Identified wavelength
no	3-4 rings	5 and more rings	(nm)
1	ND	4.2-4.0-4.4	403-408-421
2	ND	4.9-4.6-4.8	459-468-471
3	ND	4.7	432
4	1.0	ND	352
5	1.0	ND	373
6	ND	3.8	421
7	ND	2.9-3.8	421-440
8	ND	4.9-4.5-4.6	457-468-471
9	ND	4.3-4.1-4.6-4.5-4.8	403-408-422-427-440
10	3.2-3.1	3.8-3.6-3.8-3.7-3.9	377-385 / 404-409-422-427-440
11	ND	6.6-5.8-5.9	449-468-471
12	0.8	ND	370

ND: not detected.

Environmentally, the Çanakkale strait poses challenges for spill responders because fast surface currents can carry pollutants through the system due to its interesting internal hydraulic characteristics. Hydrodynamics of the Çanakkale strait are driven by two layers of water masses; the Black Sea and the Mediterranean. Typically the upper layer, which is infused with brackish water coming from the Marmara Sea, is about 10-20 m thick depending on the seasonal water budget. The lower layer, containing the great bulk of Mediterranean water, occupies the remaining zone between the upper layer and the bottom. In general, the water of this layer is very homogeneous and it discharges into the Marmara Sea. The dense lower layer may show somewhat complicated current velocity distribution. Relatively, the warmer and more saline undercurrent has higher intensity near the sides of the channel (Alpar et al. 2004).

The SUVF findings from sediment samples show that the dominating PAH group was composed from 4-to-5 and more ring aromatic hydrocarbons, indicating pyrogenic origin. The pyrolytic contamination of the strait could be attributed to fossil fuel oil particulates emission by commercial ship. Therefore, SUVF technique constitutes a promising tool to be used in geochemistry studies. Beyond its reduced cost, short time spent in this analytical procedure provides additional important advantages.

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