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Baseline

Comparison and origins of polycyclic aromatic hydrocarbons (PAHs) in the entrance and the exit of the Turkish Straits System (TSS)

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ABSTRACT

Investigations of total petroleum hydrocarbons (TPHs) in water and polycyclic aromatic hydrocarbons (PAHs) in sediments were performed in the entrance and the exit of the Turkish Straits System (TSS) in autumn of 2016 and spring of 2017. TPH and PAH values ranged from 1.7 to 11.6 μg/l and 120 to 2912 ng/g (dw), respectively. On the basis of the given surface fluxes of the TSS, average petroleum flows were calculated as 1631 t/y from the Black Sea to the Marmara Sea and 8484 t/y from the Marmara Sea to the Aegean Sea. Pollution by PAHs ranged from relatively moderate to high. The most polluted sediments were collected from regions affected by shipping, such as Riva and Seddülbahir located at the entrance and the exit of the TSS, respectively. Moreover, origins of PAHs were determined using the ratios of PAH congeners. The main origins of PAHs were found as both pyrolytic and petrogenic at most stations.

Polycyclic aromatic hydrocarbons (PAHs) are harmful pollutants in the marine environment, and they originate from anthropogenic activities, burning of biomass, and emission from vehicles (Simoneit, 1984). PAHs originating from incomplete combustion of organic matter enter into the marine environment through stormwater runoff and urban discharges (Hoffman et al., 1984). Sediments usually contain higher concentrations of contaminants than the water column.

The Black Sea is the site for fishing activities for not only Turkey but also other countries on the shore. For this reason, there is a great deal of interest and research on the economic importance of the Black Sea, its biological richness, and its location of strategic importance. Moreover, its historic importance as a part of the Silk Road, the significance of oil production, and transportation has increased in recent times (Jaoshvili, 2002).

Moreover, the Black Sea is exposed to various problems including overfishing, illegal fishing (Öztürk, 2013), ship-originated pollution, accidental introduction of alien species (Kıdeyş, 2002; Zaitsev and Öztürk, 2001), and marine litter (Topçu and Öztürk, 2010).

İğneada, located on the southwest continent of the Black Sea, is an important region for biodiversity and a habitat for many fauna and flora. Despite the low population density, chemical anthropogenic stress is high in this coastal region owing to its proximity to the Danube River. Similarly, Şile has a vital prospect owing to its proximity to the Istanbul Bosphorus, a unique marine corridor, and both coastal and marine biodiversity (Öztürk et al., 2013). These two areas are proposed by Öztürk et al. (2013) as marine protected areas (MPAs) in the Black Sea as part of the CoCoNet Project supported by the European Union (EU).

In spite of the fact that the entrance of the Bosphorus, a part of the TSS, is also among these regions, there is no detailed study on petroleum pollution, especially PAHs, except for studies conducted by a few researchers (Readman et al., 2002; Balkıs et al., 2012; Binark et al., 2000).

Similarly, the Aegean Sea is influenced by the current coming from the TSS. The Aegean Sea, with the coasts of Greece and Turkey (2833 km), is one of the eastern Mediterranean sub-basins between Crete and Rhodes Island.

There is no report on the comparison of petroleum hydrocarbons in the entrance and the exit of the TSS even though there are some studies on petroleum and PAH pollution inside of the TSS (Balcıoğlu et al., 2017; Balcıoğlu et al., 2014; Balcıoğlu, 2013), Marmara Sea (Ergül et al., 2010; Ünlü, 2007; Tolun et al., 2006; Telli-Karakoc et al., 2002; Okay et al., 2003), Istanbul Strait (Karacık et al., 2009), Çanakkale Strait (Güven et al., 2003; Güven et al., 2002), Black Sea (Readman et al., 2002; Güven et al., 2009), and Aegean Sea (Küçüksezgin et al., 2013; Balcıoğlu et al., 2010; Darılmaz and Küçüksezgin, 2007).

Surface water and sediment samples were collected from 14 stations in autumn of 2016 and spring of 2017 for total petroleum hydrocarbon

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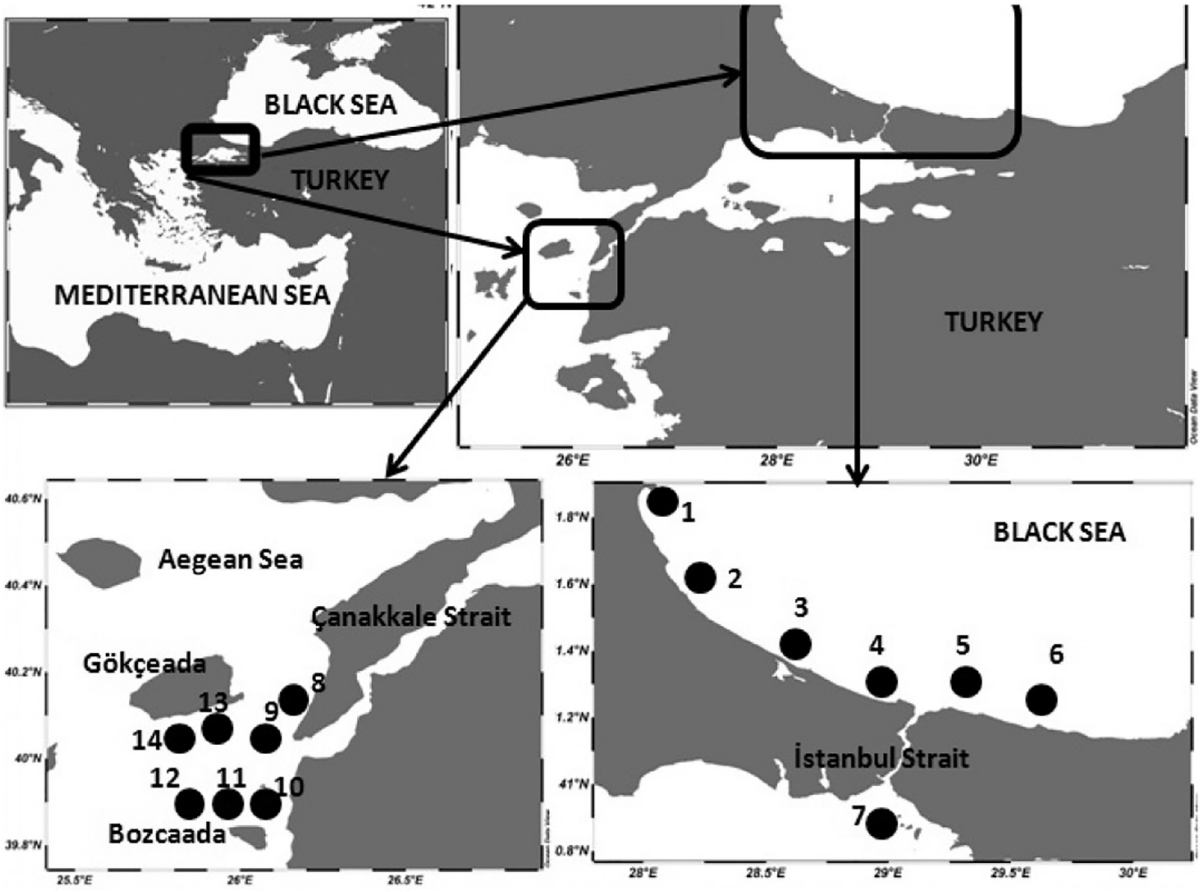

Fig. 1. Sampling stations.

(TPH) and PAH determinations, respectively. Sampling stations are demonstrated in Fig. 1.

In each station, surface water samples were collected in amber glass and extracted three times with 30 ml of dichloromethane (DCM). The extracts were combined, dried over anhydrous sodium sulfate, and evaporated using a rotary evaporator. The residue was dissolved in 1 ml of hexane. Clean up procedures were performed using a column that contains glass fiber, Florisil (deactivated with 3% water), and anhydrous sodium sulfate. The eluates were evaporated to dryness under a gentle flow of nitrogen and dissolved in 1 ml of hexane before the analysis (Kelly et al., 2000). Water samples were analyzed using an ultraviolet fluorescence spectrophotometer (UVF; JASCO FP 6200) to determine the TPHs.

Surface sediments were collected from the sampling stations shown in Fig. 1 using a grab sampler (Van Veen type) in autumn of 2016 and spring of 2017. All sampling methods were performed in accordance with internationally identified guidelines (UNEP, 1991). Sediments from individual stations were mixed well and stored at −20 °C in precleaned glass jars until subsequent analysis. Sediment samples were freeze-dried and homogenized before extraction. Sediments were extracted for 8 h using the Soxhlet apparatus with 200 ml of dichloromethane/hexane (1:1). The extract was evaporated using a rotary evaporator, and the residue was dissolved in 1 ml of hexane and cleaned up. The resulting extract was analyzed by HPLC.

PAHs were separated at ambient temperature using a column with C18, 250 × 6 mm i.d., 5 µm properties, and a gradient elution program with a flow rate of 1.3 ml min^{-1}. The initial mobile phase was 80% acetonitrile and 20% HPLC water for the first 4 min and was then modified to 100% acetonitrile and 0% water. Identification of PAHs was done on the basis of retention time, and quantification was performed by an external standard method. Recovery % for each component was found to be 84, 78, 84, 85, 85, 93, 80, 79, 100, 89, 85, 88, 89, 100, 75, and 100 for naphthalene (NAP), acenaphthylene (ACL), fluorine (FL), acenaphthene (AC), phenanthrene (PHE), anthracene (AN), fluoranthene (FA), pyrene (PY), chrysene (CHR), benzo(a)anthracene (BaA), benzo(b + k)fluoranthene (B(b + k)FA), perylene (PR), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DBahA), indeno(1,2,3-cd)pyrene (IP), and benzo(ghi)perylene (BghiP), respectively.

TPH concentrations in water samples are shown in Table 1. TPAH indicates the total concentrations of 16 PAH congeners (see Tables 2 and 3).

The highest TPH concentration was found to be 11.603 µg/l at station 9, and the lowest value was found to be 1.712 µg/l at station 2. It is known that İğneada and Kıyıköy areas are under the influence of

Table 1
TPH concentrations at the entrance and the exit of the TSS (µg/L).

	Stations		Sampling 1	Sampling 2
1	İğneada	Entrance	2.322	3.343
2	Kıyıköy		3.072	1.712
3	Karaburun		2.936	3.696
4	Rumeli Feneri		–	2.728
5	Riva		2.142	2.246
6	Şile		2.087	3.582
7	Kınalıada		2.406	5.304
8	Seddülbahir	Exit	9.484	9.586
9	Kumkale		11.603	7.656
10	Bozcaada 1		6.389	7.906
11	Bozcaada 2		3.807	9.646
12	Bozcaada 3		7.189	8.032
13	Aydıncık		6.507	2.327
14	Yüzen Taşlar		3.756	4.066