Comparative Analytical Data in the Source Determination of Unknown Spilled Oil in the Haydarpaşa Port (Marmara Sea), Turkey

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The coasts of Marmara Sea are continually affected by heavy crude oil and heavy fuel oil pollution. In addition to the coastal pollution, some point sources such as ports and oil terminals have serious effects. The Haydarpaşa Port is the most important port situated on the Anatolian side of the Strait of Istanbul (Bosphorus) (Fig. 1). It has two breakwaters about 1,700 and 600 m long (Fig. 1). The pollution of the maritime, coastal and harbor environments continues to be an issue around the globe. In the Haydarpaşa Port, fuel oil spillage from ships and vehicles and conventional shipping activities such as tank cleaning and de-ballasting operations and bilge waste waters are the main sources of PAHs in the vicinity.

All crude oils and petroleum products, to some extent, have chemical compositions that differ from each other. This variability in chemical compositions results in unique chemical fingerprints for each oil and provides a basis for identifying the source(s) of the spilled oil (Wang 2003). In recent years, numerous studies concerned with the origin type, fate and behavior of spilled oils in various environments have been published. Great advances have been made on both interpretive and analytical methods for fingerprinting oil hydrocarbons. Flexible, tiered analytical approaches, which facilitate the detailed compositional analyses based primarily upon GC/MS has been developed in response to the oil spill identification (Wang 2003). An important discovery is that the diagnostic indices in a vessel's bilge contents and its discharges could also constitute fingerprints for the ships. In so that, by comparing the fingerprints of different spilled oils with the material

from the bilges of ships, it would be possible to determine the source of spill oil.

In this study SUVF and GC/MS analysis were used to characterize the chemical composition of the unknown oil spilled from the Haydarpaşa Port by using advanced fingerprinting techniques and diagnostic ratios.

Materials and Methods

Two different analytical equipments were used to identify the source of unknown oil spill on contaminated seawater of the Haydarpaşa Port and comparing it with the samples taken from two ships on September 23, 2004. The samples were collected from the ships which were anchored at the berths 13–17 at 9:10 and 9:20 a.m., respectively. On the other hand, three spill samples are taken from the surface sea water around the ships (less than 100 m) where pollution observed at 9:45 a.m.

Samples were stored at 4°C upon collection and all samples were analyzed on the same day. The methodology of any oil spill investigation begins with collection of appropriate samples. Protocols for the collection of the floating oil, mousse, tar balls, sheens, vessel tanks and port supplier tanks have been described adequately in the guidebook of Nordtest (1991).

Analysis for n-alkane distribution (nC_8 through nC_{33}, pristane and phytane) was performed on an HP 6890 gas chromatography (GC) equipped with HP5972 mass selective detector (MSD). The capillary column used was a HP-5MS (Hewlett-Packard, Palo Alto, CA, USA): 30 m × 0.25 mm, ID × 0.25 μm film thickness. GC/MS analysis was performed utilizing a selected ion monitoring (SIM) mode to improve detection limits. The ions moni-

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Fig. 1 The Haydarpaşa Port, Istanbul
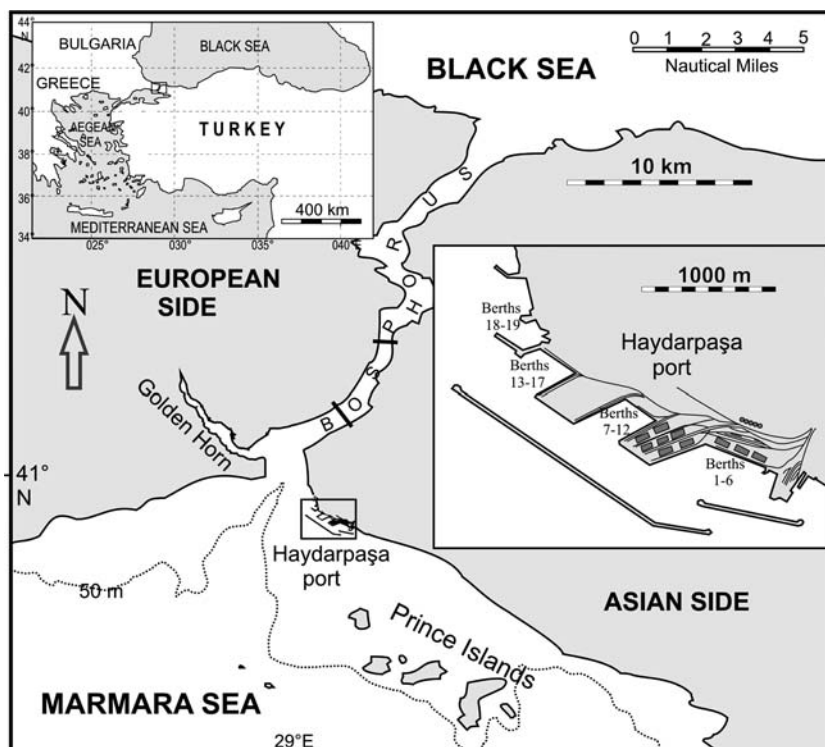
tored were 178, 192, 206 and 220 for alkylated phenanthrene homologous series; 184, 198, 212 and 226 for alkylated dibenzothiophene homologous series. A computer system interfaced with the MS continuously acquired and stored all mass-spectral data during the analysis. For detailed chromatographic conditions, analysis quality control and quantification methodology were described earlier by David et al. (1994). Response factors and retention times were determined based on the internal standards d14-terpenyl and phenanthrane-d10. On the basis of internal standards, the average recoveries for diagnostic indices were between 88% and 97%.

The polyaromatic structure of samples was determined in the extracts using a *Jasco-6300* luminescence spectrometer. The $\rho\lambda$ interval between λ_{ex} and λ_{em} was constant and equal to 23 nm. One-centimeter thick quartz cells were used.

Results and Discussion

In the case of the fuel oil spillage from ships, the main task is to correlate the samples collected from the ships with the spill sample. The problems to be questioned at this stage could be if the spill sample was really different from the samples taken from two ships on the basis of their chemical compositions?

The major chemical composition features of petroleum hydrocarbons in the samples are summarized as follows:

On the basis of the comparison of the extracted ion chromatograms at *m/z* 85 for the suspected spill sample and samples taken from the ships, the n-alkanes distribution in the Ship2 sample and the spill sample are rather similar (Fig. 2). The most noticeable difference between ship samples is that the Ship2 sample shows much higher abundance of n-alkanes in the diesel carbon range C_8 to C_{28} with the retention time in the range of 3–30 min and implying that the spilled oil collected from the spill sample may be contaminated by diesel (Wang 2003).

The ratios between or among normal alkanes and acyclic isoprenoids, e.g. n-C_{17}/Pristane, n-C_{18}/Phytane, Pristane/Phytane has been proposed by Didyk et al., (1978) in order to identify oil slicks in water and sediment. Samples Ship2 and Ship1 show nearly identical GC chromatographic profiles, implying these two samples were most likely oil. Source identification of spilled oils becomes increasingly difficult with the lapse of time due to changes in oil compositions caused by exposure to light, air, water and microorganisms. Comparing biodegradation indicators (such as n-C_{17}/pristane and n-C_{18}/phytane) for the spilled same oil with the some oil can be also used to monitor the effect of microbial degradation on the loss of hydrocarbons at the spill site for short time periods. It is known that the n-alkanes are more rapidly biodegraded than those with a branched carbon chain. Therefore, for fresh or mildly weathered on products, alkane and isoprenoid oil analysis may be used for oil source identification (Blumer et al. 1971).

Note that isoprenoid ratios (Table 1) were determined from GC/MS measurements at m/z 85 (Fig. 2). Comparison of differences between the Pr/Ph and $n\text{-}C_{18}$/Phytane ratios can be sufficient to establish if they are from the same source or not (Tibbetts and Large 1988). However, even if the ratios are similar a simple assessment using only these parameters may not be responsive or be sensitive enough to establish a final statement.

The GC/MS-SIM analysis provides a means of extracting useful biomarker 'fingerprints' from the weathered or fresh oils.
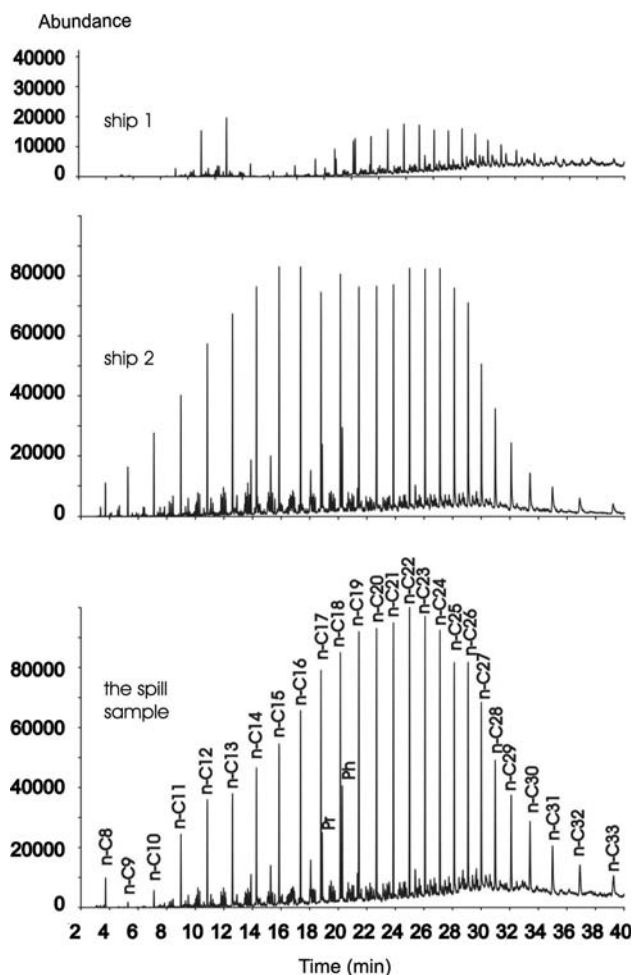

Fig. 2 Fragmentograms m/z 85, a characteristic ion for n-alkanes and isoprenoids

Numerous studies on the fingerprinting methods and source identification for the petroleum redisposed due to oil spill have been reported in literature (Prahl and Carpenter 1983; Readman et al. 1984; Kennicutt et al. 1992; Wang et al. 1999; Kennicutt 1998; Fayad and Overton 1995; Farran et al. 1987; Teal et al. 1992; Wang et al. 1997).

The detailed chemical fingerprinting results of samples highlight the followings:

The ratios of the $C_0\text{-}C_3$ m-Phenanthrene (Phe) isomers (m/z 178, 192, 206, 220) and $C_0\text{-}C_3$ m-Dibenzothiophene (DBT) isomers (m/z 184, 198, 212) have been used to successfully discriminate different oil samples (Wang et al. 1998a) and also unknown spilled oil samples (Wang et al. 1998b). This selectivity has been found to be very powerful fingerprinting technique for the differentiation of oils and petroleum products. GC/MS distribution chromatograms of the highly degredation-resistant Phe and DBT isomers are shown in Fig. 3. The interpretation of these comprehensive analysis results reveal that the suspected spill sample was chemically similar to the sample taken from ship 2.

The precision of the alkyl-PAH measurements was improved by performing manual individual peak integrations of computer-displayed ion chromatograms and integrations of isomer clusters. Ratios of C_3 m-DBT isomers (m/z 226) were used for source identification of unknown petroleum residues (Fayad and Overton 1995; Wang et al. 1997, 1999). The recognition and quantification of PAH isomer groups or patterns (Fig. 4) requires a systematic reproducible, manual application of baselines to the computer-derived GC/MS selected ion chromatograms, in order to obtain reproducible precise and accurate data.

The mass fregmantograms of spill sample and the samples taken from ships were compared by using C_3 m-DBT isomers. The ratios of C_3 m-DBT isomers (m/z 226) are 1.0, 0.65 and 1.0 for samples of suspected petroleum residue from sea water and samples from ships 1 and 2, respectively.

UV fluorescence in synchronous excitation-emission technique (Lloyd 1971) allows us to determine the polyaromatic structure of a compound while GC/MS technique is used to characterize both aliphatic and aromatic com-

Table 1 The isoprenoid ratios for the ships and 3 spill samples collected in the spillage area. If the ship-to-spill ratio is close to 1.0, it represents better correlation

Isoprenoid Ratios	Ship1	Ship2	Spill 1	Spill 2	Spill 3	Average spill	Ship1/spill	Ship2/spill
$n\text{-}C_{17}$/pristane	0.80 ± 0.01	1.53 ± 0.03	1.25	1.22	1.24	1.24 ± 0.02	0.65	1.23
$n\text{-}C_{18}$/phytane	0.72 ± 0.02	1.93 ± 0.03	1.79	1.77	1.82	1.79 ± 0.03	0.40	1.07
Pristane/phytane	0.61 ± 0.01	1.04 ± 0.03	1.01	1.00	1.00	1.00 ± 0.01	0.60	1.04
(Pristane+Phytane)/nC_{17}	3.35 ± 0.01	1.22 ± 0.02	1.58	1.56	1.59	1.58 ± 0.02	2.12	0.77

Fig. 3 a m/z 178+ 192+ 206+ 220, **b** m/z 184+ 198+ 212 summed mass chromatograms showing the dibenzothiophenes in samples, using GC/MS
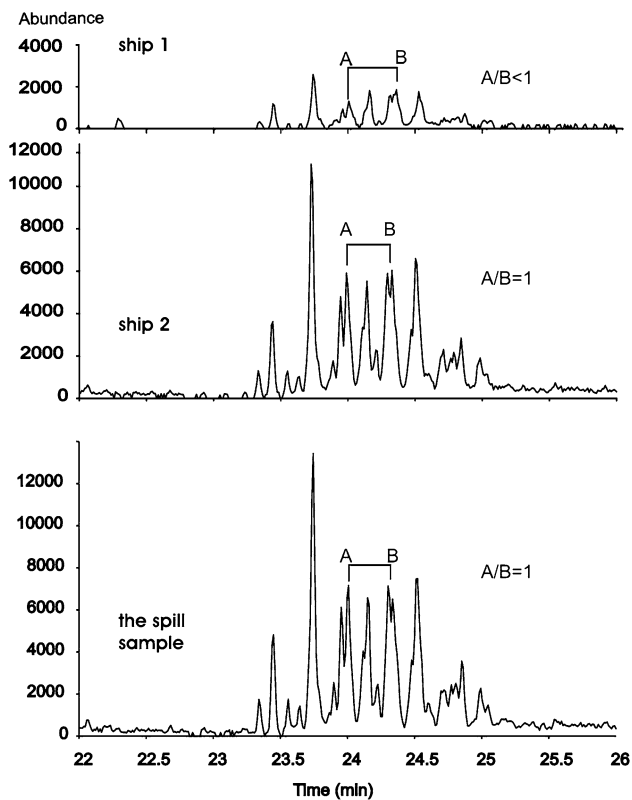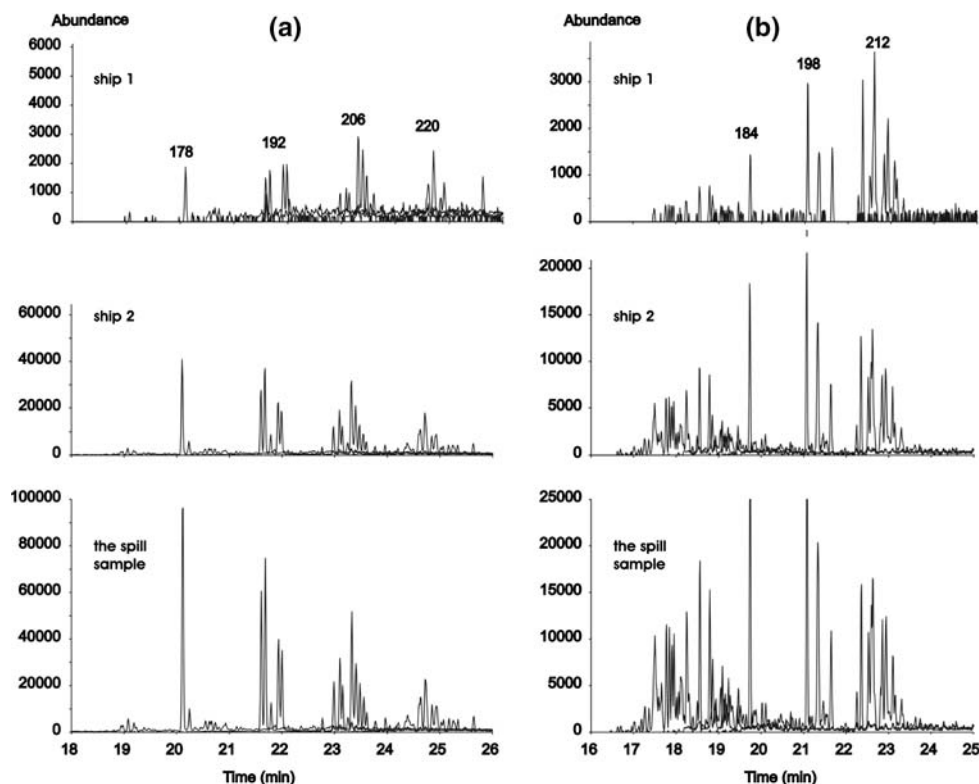

Fig. 4 The mass fragmentograms of the spill sample, Ship1 and Ship2 samples were compared by using ratios of C_3 m-DBT isomers (m/z 226)

pounds. The technique of synchronous excitation-emission is of particular interest because it produces simplified emission spectra. 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).

In synchronous spectra, compounds with different numbers of fused aromatic rings exhibit their maximum emissions at particular wave lengths, namely spectral region from 280 to 480 nm (Kister et al. 1996). Benzene units place most strongly in the 280–290 nm region, naphthalenes around 310–320 nm, 3 and 4 ring aromatics between 340 and 380 nm and compounds with five or more rings above 400 nm.

The SUVF findings from the spill sample and Ship 2 sample show that the dominating PAH group was composed from 4 to 5 and more ring aromatic hydrocarbons. The SUVF spectrums for the spill sample and the sample taken from ship 2 are similar (Fig. 5).

Characterization of spilled oils and subsequent monitoring of the affected ecosystems have been found to be an important tool for environmental damage assessment. In addition, successful forensic investigation and analysis of oil and refined product hydrocarbons in contaminated sites and receptors yield a wealth of chemical fingerprinting data. It is hoped that the present data would provide a reference to similar environmental researches.
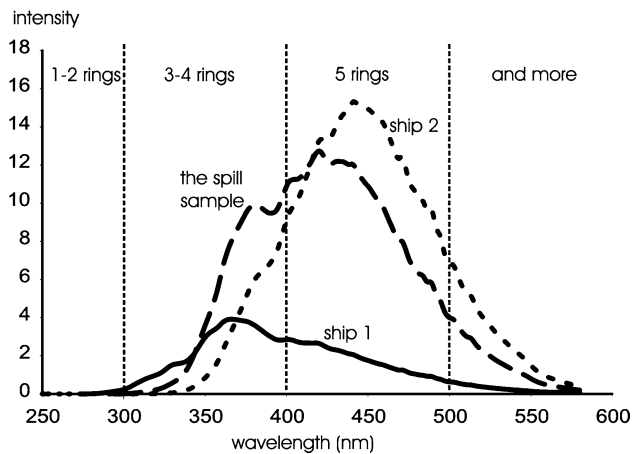
Fig. 5 The spectra of the polycyclic aromatic hydrocarbons present in the samples

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