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Oil Pollution in Bosphorus, Golden Horn and Sea of Marmara after M/V GOTIA Ship Accident

M/V Gotia Gemi Kazası Sonrası İstanbul Boğazı, Haliç ve Marmara Denizindeki Petrol Kirliliği

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Abstract

The GOTIA ship accident occured on 06 Oct 2002 at Emirgan quay, in Bosphorus, 25 ton fuel was spilled into the sea. In this study the 279 samples of sea water, 6 mussel, 1 alg and GOTIA fuel oil were analysed by UVF and 287 samples by GC/MS and 200 samples by fingerprinting technique. The oil contamination was spread out at Istinye, northern part of Bosphorus at Golden Horn and at Yenikapı (near south end of Bosphorus).

The maximum oil levels found after the accident were 813.5 mg/L in Bosphorus is 7.3 mg/L in Golden Horn and 27.4 mg/L at Yenikapı.The oil pollution area related to GOTIA fuel oil was proved by using fingerprinting technique.

Keywords: Oil pollution, GOTIA ship accident, seawater, alga, mussel.

Introduction

Bosphorus (Istanbul Strait) is a narrow stretch of water separating Europe from Asia. There is a heavy traffic of shipping approx. 60.000 vessels per year involving tankers 10%. The most extensive research on the oil pollution in this strait was undertaken by our institute since 1994 following Nassia tanker accident.

Many accidents of merchant ships and tankers occured in the strait. A comprehensive account on this subject was summarized by Akten (2003).The tanker accidents in Bosphorus are tabulated in Table 1.

Table 1. The tanker accidents occured in Bosphorus and Sea of Marmara (after Akten 2003)

15.09.1964	Norborn(Norwegian) v. Peter Zoranic 18 000 tons oil spilled and fire
01.03.1996	Lutsk (USSR) v. Kransky Oktiabr (USSR) 1850 tons oil spilled
15.11.1979	Independenta (Romania) v. Evriali (Greek) 70 000 tons oil spilled and 20 000 ton oil burnt.
09.11.1980	Nordic Faith (British)v. Stavanda (Greek) collision and fire
25.03.1990	Jambur (Iraqi) v. Da Tung Shan (Chinese) 2600 tons oil spilled
13.03.1994	Nassia (Philippines) v. Shipbroker (Philippines) 9 000 t oil was spilled and 20 000 t burnt
30.12.1999	Volgoneft(Russian) 1200 tons oil spilled (in Sea of Marmara)
13.02.1997	TPAO (in Sea of Marmara) burnt during repair 250 ton burnt and 214 ton spilled.
06.10.2002	Gotia(Malta) 2 tons oil spilled.

v: wreck

The major accidents happened by the large tankers Independenta in 1979 and Nasssia in 1994. M/V GOTIA sank into Bosphorus and 25 t fuel oil was spilt and pollution spread out into a large area by winds.

In this work, the oil pollution areas from GOTIA fuel spilt were determined in Bosphorus, in Golden Horn and at Yenikapı (Sea of Marmara).

Material

The sampling stations are shown in Fig. 1 and 2 and the dates were:

12 Oct 2002,	18 Oct 2002,	23 Oct 2002,
14 Oct 2002,	19 Oct 2002,	28 Oct 2002,
15 Oct 2002,	20 Oct 2002,	19 Dec 2002
16 Oct 2002,	21 Oct 2002,	
17 Oct 2002,	22 Oct 2002,	

Figure 1. Sampling stations in the Bosphorus and the Marmara Sea

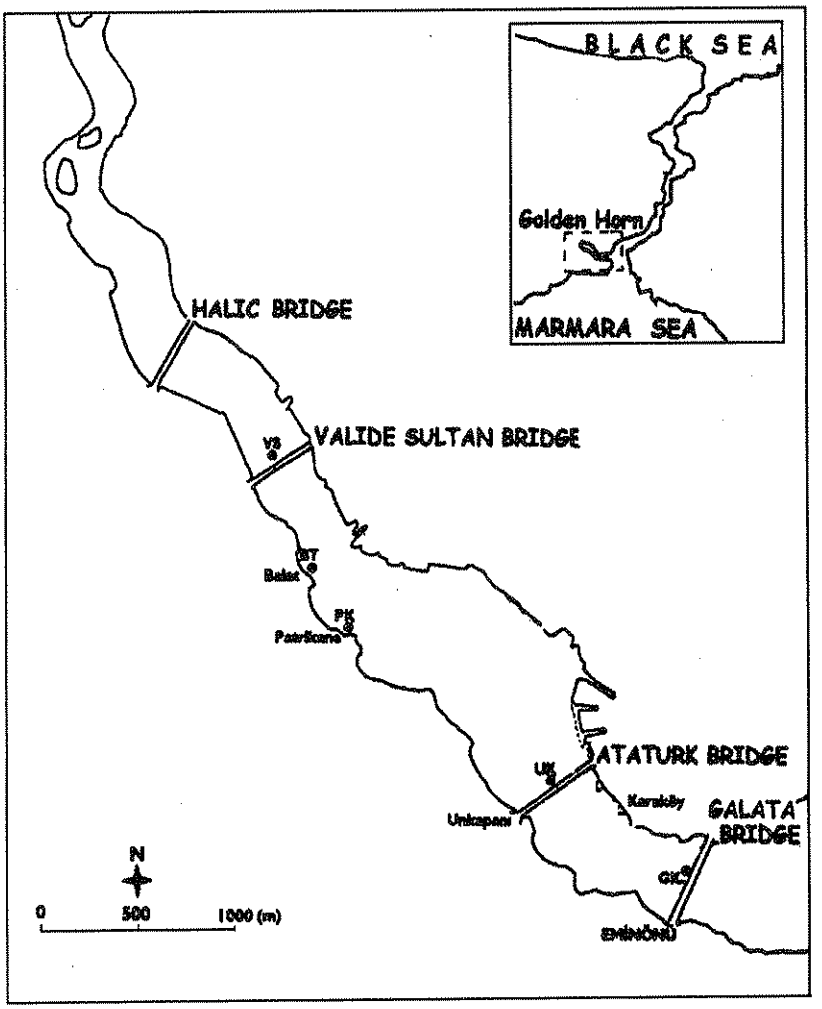

Figure 2. Sampling stations in the Golden Horn.
Sampling points: GK(Galata Bridge), UK (Unkapanı Bridge),
PK (Patrikane), BT(Balat), VS(Valide Sultan Bridge)

The samples are:
1- Sea water
Bosphorus: Istinye- Salıpazarı,
Golden Horn: Valide Sultan Bridge- Galata Bridge,
Sea of Marmara: Sarayburnu-Yenikapı.

2-Mussels (*Mytilus galloprovincialis (L.)*)
Bebek inlet, Galatasaray adası, Sabancı Tesisi
3-Marine algae
Bebek inlet in Bosphorus

Methods

1-Standard equation

Oil determination was made by UVF and oil components were analysed by GC/MS. Oil pollution was determined by using GOTIA fuel oil as standard in a conc. of 0.6-1.8 µg/µl in hexane. The standard curve was ploted at 310/360nm (ex/em) in UVF (Shimadzu RF- 1501).The equation of standard curve was taken from the apparatus.

2-GC/MS oil analysis

The oil components were analysed by GC/MS on the samples and also GOTIA fuel.
GC/MS (HP 6890) analysis :
The GC column was an HP 5-MS 30 mx0.25mm i.d.(film thickness 0.25µm) fused- methyl siloxane (Hewlett-Packard). Injections (2µl) were conducted in the splitless mode with the column held at 50°C for 1 min, from 50-320°C for 10°C/min, 320°C at 5 min; the carrier gas helium (0.8 ml/min). The injector temperature was held at 300°C. Mass spectral data were acquired in Selected Ion Monitoring (SIM) mode.

2.1-Oil determination in seawater

Sea samples were extracted 3 times with 50 ml DCM. The extracts were dried over, anhydrous sodium sulfate then distilled at 35°C. The residue was taken with hexane and the volume adjusted to 10 ml and its intensity was measured in UVF and oil pollution levels was determined by using standard equation of GOTİA fuel oil.

2.2 –Oil determination on mussel

The oil contamination was determined in shell and inner part of mussel.

2.2.1- Shell part
40 g Mussel shell parts were washed with DCM and oil amount was determined as indicated in sea water.

2.2.2- Inner part
25 g Inner part was mixed with 20 g anhydrous sodium sulfate and extracted with DCM in soxhlet apparatus for 8 h. The extract was dried with anhydrous sodium sulfate then distilled at 35°C. The residue was taken with hexane and oil amount was determined as indicated in sea water.

2.3- *Oil determination in alga*

Ulva rigida sample was extracted in soxhlet with 200 ml DCM for 8h.The extract was dried with anhydrous sodium sulfate then filtered and distilled. The residue was taken with hexane and oil amount was determined as indicated in sea water.

3-Fingerprinting analysis

After determination of oil amount of the sample by UVF analysis the remaining part was hydrolysed with 2% NaOH/ ethanol under reflux in water bath. 50ml water was added on hydrolysate and re-extracted with pentane. Organic phase was distilled and residue was taken with hexane and analysed by GC/MS. Fingerprinting method was used for the identification of source of oil. The chromatograms were compared with GOTIA fuel oil chromatogram. Dibenzthiophene (DBT m/z 184.03 and it homologes C_1 (m/z 198.05) and C_2 (m/z 212.06)) were used to identify the origin of oil.

Results

1-*UVF*

1.1. The standard equation of GOTIA fuel oil is:

$F_1 : 693.3 \times C - 331.29 \qquad r^2: 0.999$

1.2. Sea water

The oil contamination in examined areas are shown in Tables 1, 2 and 3.The max. oil contamination was found on 19 Oct 2002 in Arnavutköy as 154.6 mg/L, in Bebek as 813.5 mg /L. The oil level was appreciably high at the various stations depending on wind direction. The highest contamination determined at the stations are:

in Bosphorus

Sabancı Tesisi 508.4 mg/L on 15 Oct 2002
Hisar 26.2 mg/L on 15 Oct 2002
Emirgan 30.9 mg/L on 19 Oct 2002
Baltalimanı 3.3-4.4 mg/L on 17-19 Oct 2002
Galatasaray adası 70.9 mg/L on 12 Oct 2002
Arnavutköy 154.6 mg/L on 10 Oct 2002
Bebek inlet 813.5 mg/L on 14 Oct 2002 (in beginning)
Istinye 58.3 mg/L on 19 Oct 2002
Ziya Kalkavan School of Marine 68.4 mg/L on 10 Oct 2002
DGM (Goverment Security Court) front 22.7 mg/L on 18 Oct 2002
Beşiktaş 0.3 mg/L on 14 Oct 2002
Dolmabahçe 1.3 mg/L on 20 Oct 2002
Sarayburnu 175 mg/L on 23 Oct 2002

in Golden Horn

Unkapanı Bridge 7.3 mg/L on 10 Oct 2002
In front of Patrikhane 0.6 mg/L on 21 Oct 2002
Balat 0-4 mg/L on 12 Oct 2002
Valide Sultan Bridge 0.4 mg/L on 16 Oct 2002

in Marmara Sea

Kumkapı 27.4 mg/L on 17 Oct 2002
Sarayburnu 175.0 mg/L on 23 Oct 2002

Table 1. The oil pollution levels (mg/L) in the sea water of the middle areas of Bosphorus after the GOTIA ship accident

Sampling Date	Stations										
	BEBEK COVE				ARNAVUTKÖY		GALATASARAY ADASI				
	entrance	Inlet inside	exit	Canal	Harbour	Quay front	Out of oil boom	East	North	South	Canal
10 Oct 02	-	188.2	-	0.30	154.6	*	7.40	-	*	-	-
12 Oct 02	-	9.9	0.30	-	499.3	*	-	-	70.9	-	4.80
14 Oct 02	6.20	813.5	9.50	9.10	120.3	124.8	11.50	-	-	-	-
15 Oct 02	-	0.07	-	-	*	0.40	-	-	37.0	0.03	5.30
16 Oct 02	0.70	-	41.20	-	*	27.5	50.50	1.60	1.10	2.90	-
17 Oct 02	-	40.10	122.4	0.70	-	0.06	-	0.60	30.6	1.80	-
18 Oct 02	312.7	6.40	0.10	0.05	-	4.90	-	0.20	13.6	7.30	-
19 Oct 02	-	1.60	-	0.03		58.7	-	0.30	0.60	0.02	0.30
20 Oct 02	-	2.00	-	-		0.04	-	54.3	0.20	5.80	-
21 Oct 02	-	28.9	-	0.005		1.80	-	0.10	1.50	0.30	-
22 Oct 02	-	0.02	-	-		0.09	-	0.03	0.01		-
23 Oct 02	-	-	0.03	-		0.80	-	0.04	0.04		-
28 Oct 02	-	0.06	1.60	-	-	3.30	-		1.40	0.20	0.03
19 Dec 02	-	0.02	0.02	0.008	-	0.01	-	0.05	0.005	0.005	0.006

*: surface completely covered with petroleum

-:No sampling

Table 2. The oil pollution levels (mg/L) in the sea water northern part of Bosphorus after the GOTIA ship accident

Sampling Date	Stations														
	İSTİNYE	EMİRGAN	BALTALİMANI	HİSAR	SABANCI TESISI	ORTAKÖY	ZKDMYO	DGM	BEŞİKTAŞ	DOLMABAHE	SALI PAZARI	KIZKULESİ	SARAY BURNU	KUMKAPI	YENİKAPI
10.Oct 02	-	0.01	0.07	2.50	-	0.05	68.4	*	0.001	-	0.60	-	-	-	-
12.Oct 02	-	0.40	0.04	-	-	0.02	0.30	-	0.01	0.05	0.04	-	-	-	-
14.Oct 02	-	0.07	0.01	-	-	0.10	0.03	0.05	0.30	0.04	0.005	-	-	-	-
15.Oct 02	-	0.02	0.05	26.2	508.4	0.03	0.02	0.03	0.03	0.02	0.05	0.02	0.03	-	0.05
16.Oct 02	-	0.05	0.03	0.03	27.50	0.03	0.02	0.02	-	-	0.02	0.05	4.40	-	0.006
17.Oct 02	-	0.05	3.30	2.30	*	2.60	0.70	0.02	-	0.04	0.09	0.03	0.06	27.4	0.07
18.Oct 02	-	0.20	3.30	7.90	2.50	0.10	0.05	22.7	-	0.08	0.06	0.06	0.20	-	0.10
19.Oct 02	58.3	30.9	4.40	26.7	0.09	0.03	0.04	0.004	-	-	0.03	0.02	0.02	-	0.005
20.Oct 02	-	0.02	0.03	0.10	0.03	0.05	0.05	0.050	-	1.30	0.02	0.01	29.2	-	0.007
21.Oct 02	-	0.004	0.006	0.03	0.03	0.60	0.03	0.03	-	0.05	0.02	0.05	0.004	-	0.01
22.Oct 02	-	0.01	0.019	0.02	0.02	0.50	-	-	-	0.03	0.004	-	0.003	-	0.006
23.Oct 02	-	0.05	0.027	0.03	0.03	0.03	0.03	-	-	0.02	0.002	0.03	175.0	-	0.10
28.Oct 02	-	0.03	0.20	-	0.03	0.60	0.03	0.05	-	0.03	0.10	0.003	0.02	-	-
19.Dec.02	-	0.006	0.03	-	0.01	0.02	0.006	0.006	-	0.02	0.01	0.03	0.005	-	0.06

*: surface completely covered with petroleum

-:No sampling

. ZKDMYO: Ziya Kalkavan School of Marine, DGM:Goverment Security Court.

Table 3. Oil pollution levels (mg/L) in Golden Horn after the accident

Sampling Date	Stations				
	Galata Bridge (GK)	Unkapanı Bridge (UK)	Front of Patrikhane (PK)	Balat (BT)	Valide Sultan Bridge (VS)
10 Oct 02	-	7.30	0.04	-	-
12 Oct 02	-	0.40	0.02	0.40	-
14 Oct 02	-	-	-	-	-
15 Oct 02	-	-	0.04	0.03	0.004
16 Oct 02	0.005	-	0.05	0.04	0.50
17 Oct 02	0.09	0.70	0.20	0.06	0.04
18 Oct 02	-	0.10	0.10	0.01	0.02
19 Oct 02	-	0.05	0.03	0.02	0.02
20 Oct 02	-	0.03	0.03	0.08	0.04
21 Oct 02	-	0.02	0.60	0.06	0.005
22 Oct 02	-	0.05	0.01	0.02	0.02
23 Oct 02	-	0.02	0.03	0.02	0.03
28 Oct 02	-	0.005	0.01	0.04	-
19 Dec 02	0.01	0.07	0.01	0.003	0.03

-:No sampling

Before the GOTIA accident, oil pollution level in the Bosphorus are 0.05 mg/L (Güven *et al.*, unpublished data). According to these data the oil contamination due to GOTIA ship accident is 16260 times as high for 2002 oil pollution results in this area.

1.3. Mussel Samples

The oil amount found in mussel (shell and inner part) are shown in Table 4.

Table 4. The oil pollution level in the mussel samples

Sampling date	Station	Examined part	mg/g (wet weight)
16 Oct 02	Galatasaray adası	inner	0.30
	Bebek	inner	0.03
	Sabancı Tesisi	shell	0.01
		inner	0.02
23 Oct 02	Bebek	shell	0.02
		inner	0.20

The highest oil contamination was found in Galatasaray adası as 0.30mg/g in flesh. The oil contamination of the mussel collected

after Nassia Tanker accident in 1994-1995 was 5-250 µg/g (Güven *et al.,* 1995).This result showed that the oil contamination is 60-125 times higher than the of Nassia Tanker accident.

1.4. Alga

The oil contamination in *Ulva rigida* was 179 mg/g on 23Oct 2002 (Table 5).

Table 5. The oilpollution level in alga(*Ulva rigida)*

Sampling Date	Station	mg/g (Wet weight)
23 Oct 02	Bebek	0.20

When the results of oil pollution on the algae following the GOTIA tanker accident on 06 Dec 2002 are compared with those obtained earlier (in 1995) from Bosphorus it is apparent that the pollution on the algae due to the accident increased 100 times.

2-*GC/MS Results*

The total GC chromatogram of GOTIA fuel oil and the samples are shown in Figure 3,4,5. A n-alkane sequence were detected in samples collected from sea water at all stations in the Bosphorus. Pristane and phytane (Pr/Ph) ratio calculated is 0.62. Meanwhile the unresolved complex mixture (UCM) is observed in all chromatograms. The findings of n-alkane sequence, Pr/Ph ratio and UCM hump (indicate fresh pollution) shown that the pollution is GOTIA fuel oil. The same oil components were in all the samples examined by GC/MS analysis

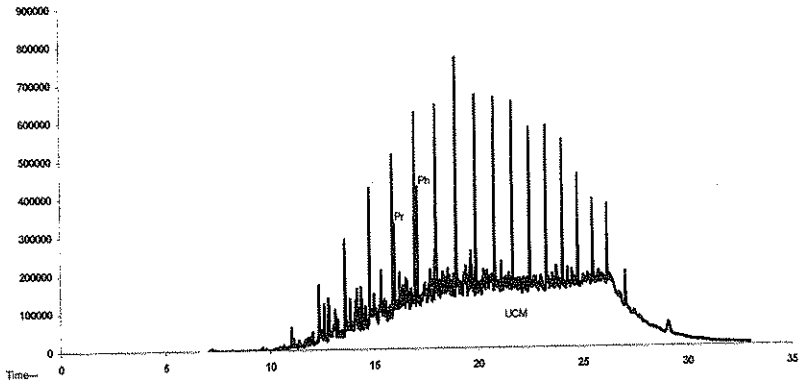

Figure 3. GC/MS chromatogram of GOTIA fuel oil

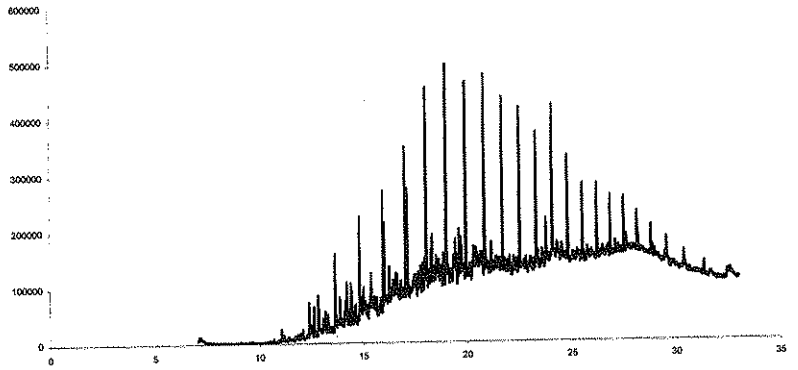

Figure 4. GC/MS chromatogram of sea water from Arnavutköy

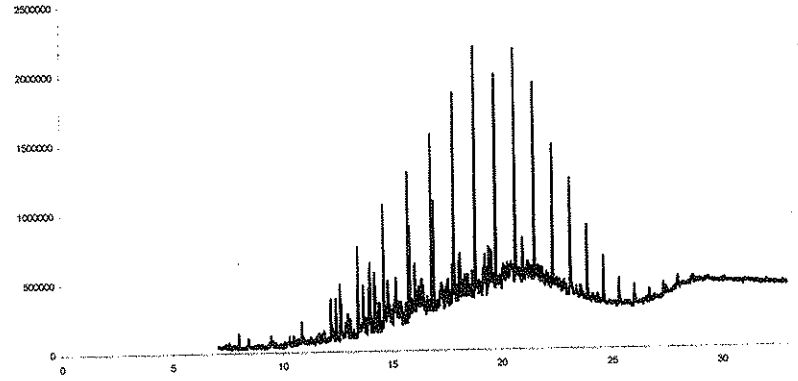

Figure 5. GC/MS chromatogram of sea water from Kumkapı

The fingerprinting of GOTIA fuel oil and the samples collected Bosphorus Golden Horn and Marmara Sea are shown in Figure.6-12. All the chromatogram of fingerprinting are the same with GOTIA fuel oil.

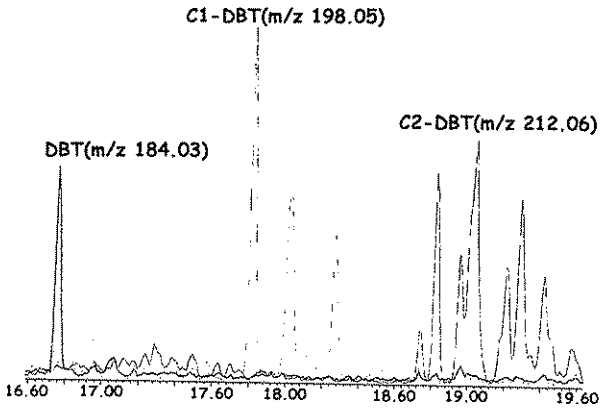

Figure 6. The fingerprints of GOTIA fuel oil

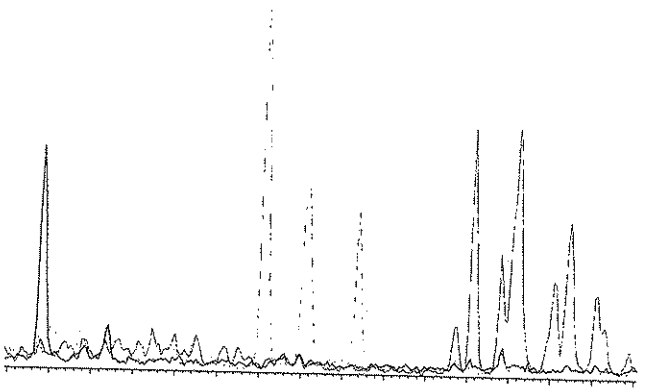

Figure 7. The fingerprints of sea water sample from Bebek Cove

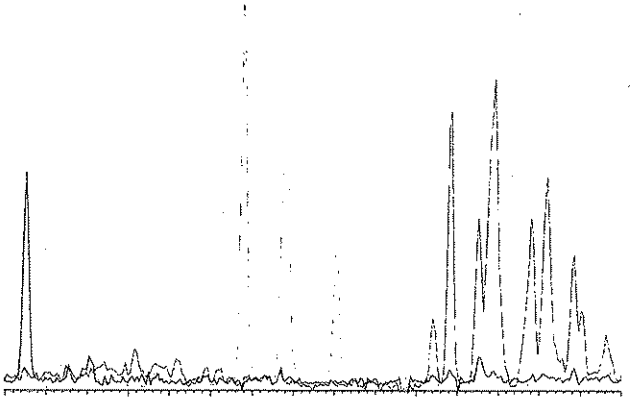

Figure 8. The fingerprints of sea watersample from Istinye

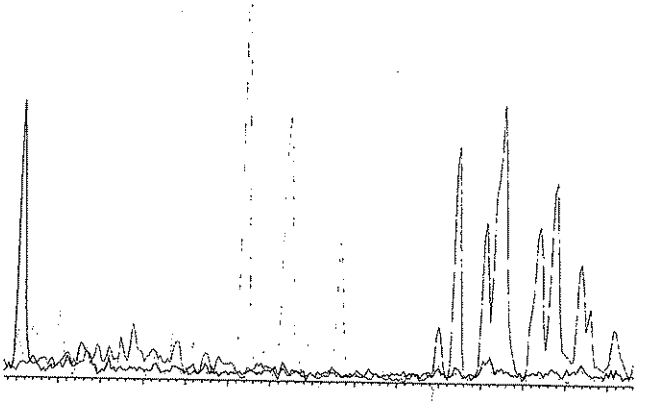

Figure 9. The fingerprints of sea watersample from Sarayburnu

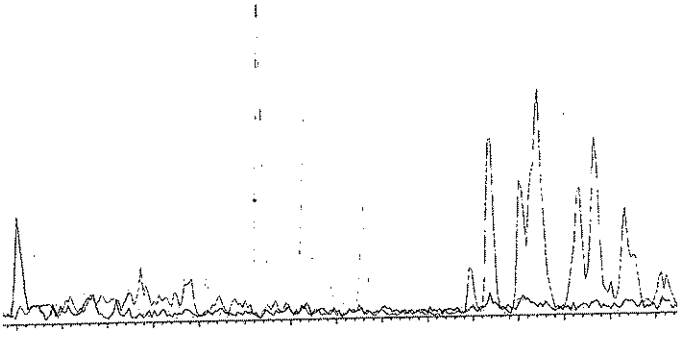

Figure 10. The fingerprints of sea watersample from Kumkapı

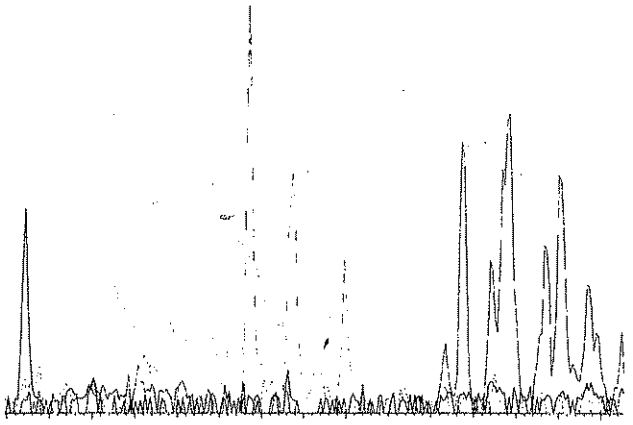

Figure 11. The fingerprints of sea water sample from Golden Horn (Valide Sultan Bridge)

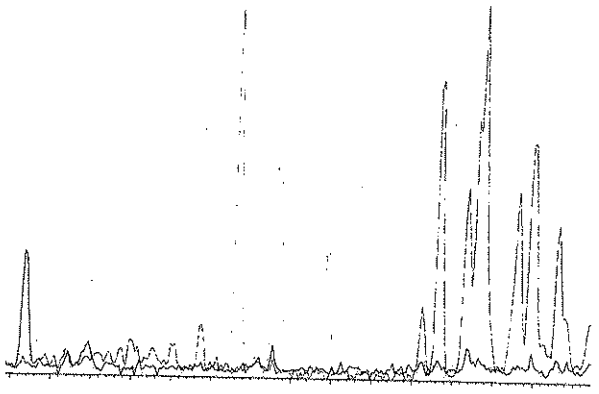

Figure 12. The fingerprints of sea water sample from Yenikapı

Discussion

The comparision of oil pollution due to spill after major tanker accidents World wide is:
Tsesis: Stockholm, Sweeden 1977 17 575 t fuel oil spilled and levels of 50 ppb were measured in the spill path (Johansson *et al.*, 1980).

Exxon Valdez: Alaska, U.S.A.1989, 9330000t oil spilled, pollution level on sea;6.24 µg/L (Boehm *et al.*, 1997; Rice *et al.*, 1996).
Amoco Cadiz: in Brittany, France 1978, 221 000t oil spilled, pollution level on sea;100µg/L (Marchand, 1980; Dauvin, 1998).
North Cape: in Rhode Island U.S.A. 1996, 2700 t fuel oil , pollution level on sea; 50 ppb (Reddy and Quinn, 1998) .
The *Braer* accident in Shetland, 85 000 tonnes of oil spilled levels reaching as much as 5000 ppb in the immediate vicinity of the wreck and over 1000 ppb in other inshore areas (Newey and Seed, 1995).
After the 1991 Gulf War 6800 t oil spill and remained on the sea surface, 161.6 mg/m^2 (Sen Gupta *et al.*, 1993), 10 816 700 barrels oil relased Tawfiq and Olsen (1993) (oil from fires unknown) and it was over 40 times larger than the Exxon Valdez Spill (Michel *et al.*,1993 ; Shriadah, 1998; Mostafawi, 2001).
Independenta accident (1979) in Haydarpaşa (Sea of Marmara) when 94 600 tons oil spilled and fire, pollution undetected.
Nassia tanker accident in Sarıyer (1994) when 9000 tons oil of spilled and 20 000 tons oil fired. The highest pollution level was found as 24.9 µg/L in surface water (Güven *et al.*, 1996).
TPAO tanker accident (1997) in Tuzla (Marmara Sea) 214.3 ton oil was spilled and 250 ton oil burnt. The highest pollution level was found as 33.2mg/L in sea water (Ünlü *et al.*, 2000).
The pollution level of sea which we found after the GOTIA accident in Bosphorus in 2002 seems to be the highest when compared with the figures indicated above for the major tanker accidents in the World and also specifically with those in the main straits.It is the highest ever contamination recorded according to the data given in the literature.

Özet

6 Ekim 2002 tarihinde İstanbul Boğazı Emirgan iskelesine çarpan GOTIA isimli gemiden kaza sonrası 25 ton fuel oil denize dökülmüştür. Bu çalışmada denize dökülen fuel oil İstanbul Boğazı, Haliç ve Marmara Denizine yayılımı takip edilmiş ve oluşan petrol kirliliği miktarı tayin edilmiştir. Bunun için 279 deniz suyu örneği, 6 midye örneği ve 1 alg örneği ve GOTIA fuel oil olmak üzere toplam 287 örneğin UVF analizleri yapılmıştır. Ayrıca kirliliğin orijinini tayin etmek için 200 örnekte GC/MS ile parmak izi analizi yapılmıştır. Fuel oil kontaminasyonu İstinye koyu, Haliç ve Yenikapı ya kadar yayılmıştır.

En yüksek kirlilik miktarları Boğaziçinde Arnavutköy de 813.5 mg/L, Haliçte 7.3 mg/L ve Marmara Denizi Yenikapıda 27.4 mg/L olarak bulunmuştur. Bu kaza sonrası deniz kirliliği 1 sene takip edilmiş kirliliğin normal boyutlara indiği saptanmıştır.

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