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Oil pollution in Tuzla Bay after TPAO Tanker accident

TPAO Tanker kazasından sonra Tuzla Körfezinde oluşan petrol kirliliği

Selma Ünlü, Kasım Cemal Güven, Ertuğrul Doğan and Erdoğan Okuş

University of Istanbul, Institute of Marine Sciences and Management,

Vefa, 34470, Istanbul

Abstract

The oil pollution was investigated in seawater, sediments and mussels in Tuzla Bay after the TPAO tanker accident. 214.3 ton oil was spilled and 250 ton oil burnt. The pollution level was determined in seawater, sediments and mussels after the accident. The highest pollution was found as 33.2 mg/L in seawater, 423.0µg/g in sediment on the first day after the accident and 2067µg/g in mussels 1 months after the accident. The pollution level decreased during the survey of 14 Feb 1997 to 13 Feb 1998.The origin of oil in seawater, sediments and mussels were identified by using fingerprinting analysis technique.

Keywords: Oil pollution TPAO tanker accident, crude oil, Tuzla Bay

Introduction

TPAO tanker was burnt during her repair on 13 Feb 1997 and thick oil layer covered the surface water of Tuzla Bay. The 214.3 ton oil was spilled in seawater and coast of Tuzla Bay. 173 ton oil was recovered from the seawater and 41.3 ton oil distributed to the Tuzla Bay.The areas of the rock platform of Tuzla Bay were covered by oil which also polluted later the Bay. The stronk winds spread the oil from along the coast of Bay to Sea of Marmara.

This paper reports the oil contamination of seawater, sediments and mussels in Tuzla Bay over a periods of one years after the spill.

Materials and Methods

From 1 to 360 days after the oil after the accident seawater, sediment and mussels samples were collected along the coast of Tuzla Bay. The sampling was carried out at 5 stations in Tuzla Bay by Research Vessel R/V ARAR (Figure. 1).

1-Sampling
1.1.Seawater

The samples were collected by a special bottle for surface water and Nansen bottle at various depths (5, 7, 10 and 20m) of water. Dichloromethane (DCM) was added to sample for preservation. They were stored at room temperature until extraction.

1.2.Sediment

The sediment samples were taken with van Ween bottom sampler of every month in the stations of Tuzla Bay (except H station) between 11 July 1997 to 13 Feb 1998. 1 cm of surface on sediment was removed with a spatula in glass jar tapped with aluminium foil and kept at -20 °C in deep freeze.

1.3.Mussels

The mussel (*Mytilus galloprovincialis)* samples were taken at station in Tuzla Bay between 4 and 27 March 1997 to 14 Jan 1998.
The samples were put in glass jars tapped with aluminium foil and kept at –30 °C in deep freeze.

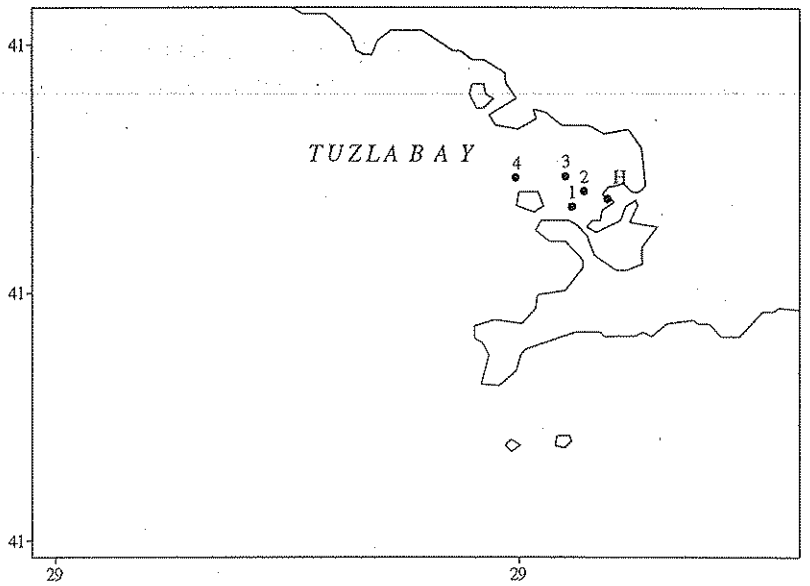


Figure.1. Location of stations in Tuzla Bay
H:Hidromak Shipyard (the place of TPAO tanker), 1: beside the ship, 2: opposite shore, 3: port mouth, 4: off port

2-Extraction

2.1.Seawater

2.8 L seawater sample was extracted three times with 50 ml DCM. Organic phases were combined, dried with anhydrous sodium sulphate and distilled. The residue was taken with hexane and the volume adjusted to 10 ml. The intensity was measured at 310/360 nm (ex/em) in a UV fluorospectrophotometer (UVF) (Shimadzu RF-1501).

2.2.Sediment

20 g sediment sample was mixed with 25 g of anhydrous Na_2SO_4 and extracted with DCM for 8 h in a Soxhlet apparatus. DCM phase was distilled at 40 °C, the residue was taken with hexane and the volume adjusted to 10 ml. The intensity was measured in UVF at 310/360 nm (ex/em) The remaining part was saponified with 5 % KOH in methanol for 4 h. After hydrolysis 50 ml distilled water was added then extracted with pentane. Organic phase was separated then distilled and the residue dissolved in hexane and analysed by GC/MS.

2.3.Mussel

10 g of mussel sample was extracted with DCM in a Soxhlet apparatus for 3 h. DCM phase was distilled at 40°C. The residue was saponified with 5 % KOH/methanol in a water bath for 4 h. After hydrolysis 50 ml distilled water was added and extracted with pentane and pentane phase dryed on anhydrous sodium sulphate then distilled. The residue was taken with hexane and the volume was adjusted to 10 ml with hexane. The analysis was made by UVF as indicated above for sediment. The remaining part was analysed by GC/MS .

3-Analysis
3.1. UVF Analysis, Standard curve

The oil concentration was calculated from the standard curve. The calibration curve was plotted by using TPAO tanker oil as reference. The oil concentrations were: 0.05, 0.1, 0.2 and 0.5µg/ml in hexane. The fluorescence intensity was measured at 310/360 nm (ex/em) in UVF and the calibration curve plotted. Its equation was taken from the apparatus.

3.2.GC/MS analysis

GC/MS analyses were run on a HP 6890 capillary GC connected to a Hewlett Packard Mass Selective Detector (MSD), controlled by a HP ChemStation. Operating conditions were: 50 mx0.20 mm fused HP PONA, methyl siloxane, glass capillary column; oven temperature programme: 40°C at 6 min, from 40-280°C at 10°C min, 280 °C at 10 min, from 280-290°C at 10°C/min, 290°C at 5 min; splitless injector temperature 300°C; carrier gas helium, 29.4 psi. press, flow rate; 1.2 ml/min..

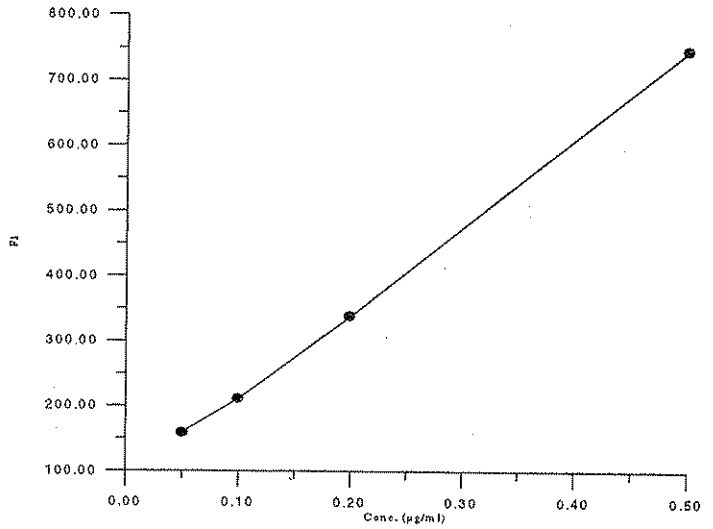
Source identification; Fingerprinting analysis

Fingerprinting analysis technique was used to identify the origin of oil in samples. The markers used were: Dibenzothiophene (DBT, m/z 184.03) and methylated C1-DBT (m/z 198.05) (Dreau *et al.*, 1997, Glegg *et al.*,1999, Nielsen *et al.*, 1990, Page 1998, Tibbetts *et al.*, 1988).The fingerprinting chromatograms of TPAO tanker oil and the samples were compared by using DBT and C1-DBT peaks.

Results and Discussion

1. UVF Results

The calibration curve and its equation are shown in Figure 2.



F1:1318.C+83.062 r^2:0.9995, (F1: Abs, C: Cons.)

Figure. 2. Standard curve of TPAO crude oil

1.1.Seawater

Oil concentration(dispersed /dissolved) of the seawater samples of Tuzla Bay are given in Table 1. The highest oil pollution was found in surface water on the first day after the accident at station H; 33.2 mg/L (33235 µg/L), in 6rd day 376.4 mg/L (0.37µg/L), twenty one day later 86.8 mg/L (86857 µg/L) and 475.7 µg/L on 13 Feb 1998 one year later after the accident. At T1 in surface water in 3rd day 201.8 mg/L (201857µg/ml); at T2; at 7 m in 6rd 1.08 mg/L (1085 µg/L), at T3; in surface water on the first day after the accident 11.2 mg/L (11250µg/L). The oil concentration in Tuzla Bay stations (except H station) gradually increased till 19 Feb. 1997, then it fell irregularly.

These findings showed that the oil concentration in Tuzla Bay during 3 months were very high after the accident and the maximum dispersed oil level in surface water was 3764 mg/L.

Table1.Oil pollution (Dispersed/dissolved) on 14 Feb 1997-13 Feb 1998 in Tuzla Bay (µg/L)
H: Hidromak Shipyard, T1: Beside the ship, T2: Opposite shore, T3: Port mouth, T4: Off port, T5, T6, T7 : Off shore stations, - no sampling.

Stations	Date→	Tuzla Bay									
		Feb 97				March 97	May 97	July 97	Sep 97	Jan 98	Feb 98
	Day / Depth	14 th	16 th	19 th	27 th	4 th	14 th	11 th	12 th	14 th	13 th
H	Surface	33235	122000	3764285	17414	86857	500	942.5	152.8	23.17	475.7
T1	Surface	5542	201857	2371.4	178.5	55.35	17.3	12.8	3.36	7.20	5.21
	5 m	-	137.8	148.57	28.85	26.28	7.82	13.08	4.05	5.85	5.25
	7 m	-	-	-	48.82	26.33	7.84	11.16	6.20	4.14	4.01
T2	Surface	5.84	-	64.67	19.55	28.06	12.4	11.7	2.62	5.28	12.47
	5 m	-	-	11.78	22.83	38.78	9.45	16.18	5.31	3.42	15.2
	7 m	-	-	1085.71	28.22	126.42	9.69	8.65	10.2	3.88	4.42
T3	Surface	11250	-	4.60	11.07	48.23	6.91	9.01	3.07	2.35	15.8
	5 m	-	-	14.62	151.07	26.44	15.1	11.12	5.73	1.06	8.33
	10 m	-	-	34.36	48.60	40.41	13.7	34.42	5.76	5.70	2.89
T4	Surface	75.5	-	8.51	24.28	83.0	3.55	9.24	2.23	5.95	5.24
	5 m	-	-	6.01	31.78	49.85	23.6	8.18	9.67	3.15	11.7
	7 m	-	-	-	1.33	50.35	20.8	9.73	1.24	4.97	1.47
	20 m	-	-	26.0	58.83	20.71	22.5	11.6	11.6	1.26	1.06

1.2.Sediment

The oil pollution levels in the Tuzla Bay sediments are shown in Table 2. The highest pollution was found in station T1 at 11 m as 967.5 µg/g in July 1997. At all stations, the oil concentrations increased until the 5 th month after the accident then decreased rapidly and irregularly. As can be seen in this table, the oil concentration varied irregularly between 19 Feb 1997 to 13 Feb 1998. The oil concentration showed regularity in stations T2, T3, T4 after the accident until 11 July 1997.

Table 2. Oil pollution of Tuzla Bay in sediment samples (µg/g)

Sampling Stations / Date	T1 (11m)	T2 (8m)	T3 (11m)	T4 (26m)
19 Feb. 1997	407.8	401.7	86.1	423.0
27 Feb. 1997	636.2	491.3	181.7	377.8
4 March 1997	517.3	467.9	191.4	386.1
14 May 1997	279.0	497.5	189.9	
11 July 1997	967.5	752.0	204.5	
12 Sept. 1997	267.6		143.3	352.0
14 Jan. 1998	778.8	269.2		145.3
13 Feb. 1998		295.5		78.8

1.3.Mussel

The oil pollution of mussel samples are given in Table 3. The highest oil pollution was found in station T4(b) as 2066 µg/g in 27 March 1997.The oil pollution levels in samples collected in H station was found high one year later after the accident. The oil levels of mussels in Tuzla Bay after tanker accident were high compared with the values given in the literature for mussels.

Table 3. Oil pollution in mussel samples (wet weight, µg /g).

Mussel	Date	H	T4(a)	T4(b)
Mytilus galloprovancialis	04 March 1997	1799	1265	-
	27 March 1997	-	-	2066
	14 Jan 1998	1965	-	-

- : no sampling H: Hidromak Shipyard, T4a and T4b: off port

2.GC/MS and Fingerprinting results

GC/MS chromatograms of TPAO tanker oil (Figure 3) and a selective example of the seawater, sediment and mussel samples of Tuzla Bay are shown in Figures 4,5,6. Identified compounds in TPAO Tanker oil and seawater are shown in Table 4 and 5 respectively, and in sediment sample in Table 6. In the chromatograms was identified the petroleum hydrocarbons as 14 aliphatic and 3 aromatic groups in seawater.

The unresolved complex mixture (UCM) humps were observed on the chromatograms providing that the oil pollution was recent.
Fingerprinting chromatograms of TPAO tanker oil are shown in Figure 7 and a selective example of seawater, sediment and mussel samples in Figures 8, 9, 10. DBT and methylated C1-DBT peaks are similar in both chromatograms. These findings prove that the origin of Tuzla Bay relates to TPAO tanker oil.

2.1. Seawater

GC/MS chromatograms of the surface water sample taken one day after the accident from the Tuzla shipyard are given in Figure 4. The identified compounds in seawater sample are listed in Table 5.

Fingerprinting markers, DBT and methylated C1-DBT peaks were observed on the chromatograms in the sample taken from H, T1-T6 stations (Figure 8). These results showed that the origin of oil pollution in seawater is due to TPAO oil.

2.2. Sediment

A selective fingerprinting chromatogram of sediment sample is shown in Figure 9. Fingerprinting markers were also observed on the chromatogram. The similarity of the chromatograms of TPAO oil and sediment sample show that the pollution originates from TPAO tanker.

2.3. Mussel

The chromatograms of mussel sample collected from Tuzla Bay on 14/02/1997, 13/1/1998 and 4/03/1998 are similar to that of TPAO tanker crude oil. A selective fingerprinting chromatogram of mussels is shown in Figure 10. The comparison of the distribution and concentration of DBT and

homologues of C1-DBT peaks on chromatograms of mussel are similar to that of TPAO tanker oil.

Table 4. Identified compounds in TPAO tanker oil by GC/MS chromatogram

	Compounds
1.	Tridecane
2.	Tetradecane
3.	Pentadecane
4.	Hexadecane
5.	Heptadecane
6.	Pristane
7.	Octadecane
8.	Phytane
9.	Nonadecane
10.	Eicosane
11.	Heneicosane
12.	Docasane
13.	Tricosane
14.	Tetracosane
15.	Benzo(ghi)perylene

Table 5. Identified compounds in seawater sample by GC/MS chromatogram

	Compounds
1.	Tridecane
2.	Tetradecane
3.	Pentadecane
4.	Hexadecane
5.	Heptadecane
6.	Pristane
7.	Octadecane

Oil spills in seawater by tanker accident (cruch, fire, ballasting, flushing of bilges), fracture pipeline, industries, seapage from refinery plant, polluted rivers. Source of pollution was identified for 65% of incidents and only 23 spills were attributed to tankers. The tanker accidents in Turkish Strait occured and spilled oil are in 14.12.1960 (18.000 t), 15.09.1964 (unknown), 01.03.1966 (1850 t), 15.11.1979 (94600 t), 09.11.1980 (unknown), 29.10.1998 (1000 t),25.03.1990 (2600 t), 13.03.1990 (9000 t).The spilled oil amount of TPAO tanker accident is a few as 214.3 t and recovered oil was 173 t. The oil was spilled over 6 km^2 area of the semi-enclosed Tuzla Bay. In

some sea conditions, a water in oil emulsion is produced, this way contain high amount oil and forms a viscid mass, its appearence is like a chocolate mousse. The heavy residues of crude oil form tar balls flows on surface water than deposite on sediment. These conditions were observed in Tuzla Bay after the accident.

Table 6.Identified aromatic compounds in sediment samples by GC/MS chromatogram.

	Compounds
1.	Naphthalene
2.	Naphthalene,2-methyl
3.	Naphthalene,1-methyl
4.	1,1'Biphenyl
5.	2-Ethylnaphthalene
6.	1,7-Dimethylnaphthalene
7.	2,3-Dimethylnaphthalene
8.	2,6-Dimethylnaphthalene
9.	1,3-Dimethylnaphthalene
10.	1,4-Dimethylnaphthalene
11.	1,1'Binephyl,4-methyl
12.	Acenaphthane
13.	1,1'Binephyl,2-methyl
14.	Naphthalene,2-(1-methylethyl)
15.	1,1'Biphenyl,2,2'dimethl
16.	9H-Fluorene
17.	9H-Fluorene, 1-methyl
18.	Phenanthrene
19.	Anthracene
20.	1H-Indene, 1-(phenylmethylene)
21.	Dibenzthiophene,4-methyl
22.	Phenanthrene,3-methyl
23.	Anthracene,1-methyl
24.	Anthracene,2-methyl
25.	Phenanthrene,2-methyl
26.	Phenanthrene,1-methyl
27.	2-Phenylnaphthalene
28.	Phenanthrene, 1,5-dimethyl
29.	Fluoranthene
30.	Pyrene
31.	Benz(a)anthracene
32.	Chrysene
33.	Benz(a)anthracene, 7-methyl

The oil measurement was made 1 day after the accident. The pollution level in seawater was found as high as 3.7g/L in 5rd day The pollution was continued in high concentration until 7th month. The presence of hydrocarbons in the sediments of Tuzla Bay was evident in 19 Feb1997, just 6 days after the accident.

The measured oil after the accident in sea water and sediment and mussel were found very high from the oil pollution results given in the literature.

The oil pollution of sediments was also found high during the monitoring time between 19 Feb 1997 to 14 Jan 1998. The reason of this high concentration of oil spill in the bay, is that the sediments accumulated largely significant amounts of oils.

Oil, especially PAHs accumulate in aquatic organism, particularly in invertebrate species that cannot metabolize them. Mussel is a filter-fee er organism that accumulates in tissues in excess of 1000 times the exposure levels and exhibits a rather rapid loss of hydrocarbons for the first 15 to 20 days (Fassoto and Canzonier, 1976). The amount of accumulated oil is found to be high in mussel samples of Tuzla Bay after the accident. The maximum oil level found in mussel samples after the Nassia tanker accident was 250 µg/g (Güven *et al.*, 1995). Hydrocarbon levels in mussel found were in Heraklion Bay 140.48 µg/g (Lamond *et al.*, 1990) and in Rijeka Bay 2-112µg/g (Ahel, 1984). The comparison these results with our findings showed that the oil pollution are high in mussel in Tuzla Bay. This fact is due to the geographic future of Tuzla Bay which is a small and closed by were no major circulation occur.

The origin of oil in all samples was identified by using Finger printing analysis. All the chromatograms showed similarity with that of TPAO tanker oil. Thus the origin of pollutant oil is TPAO tanker oil in seawater, sediments and mussels.

In this work the effect of a tanker accident was investigated in the bay on the pollution of seawater , sediment and mussels.

Özet

Bu çalışmada, Tuzla Körfezindeki TPAO tanker kazasından sonra deniz suyu, sediment ve midyeler üzerindeki petrol kirliliği araştırılmıştır. TPAO tanker kazası ile 214.3 ton petrol dökülmüş, 250 ton yanmıştır. Kazadan sonra kirlilik miktarları deniz suyu, sediment ve midye örneklerinde tayin edilmiştir. Kazadan sonra en yüksek kirlilik deniz suyunda 33.2 µg/L, sedimentte; 423.0 µg/g ve kazadan 1 ay sonrada midyede 2067 µg/g bulunmuştur. Kirlilik miktarında izleme dönemi boyunca 14 Şubat 1997 den 13 Şubat 1998 e doğru azalma göstermiştir. Bu çalışmada deniz suyu, sediment ve midyedeki petrol kirliliğinin orjini parmak analizi tekniği kullanılarak teşhis edilmiştir.Bu çalışmada parmak izi tekniği kullanılarak örnekleme yapılan midyelerde bir sene sonra TPAO tanker petrolünün izlerine rastlanmıştır.

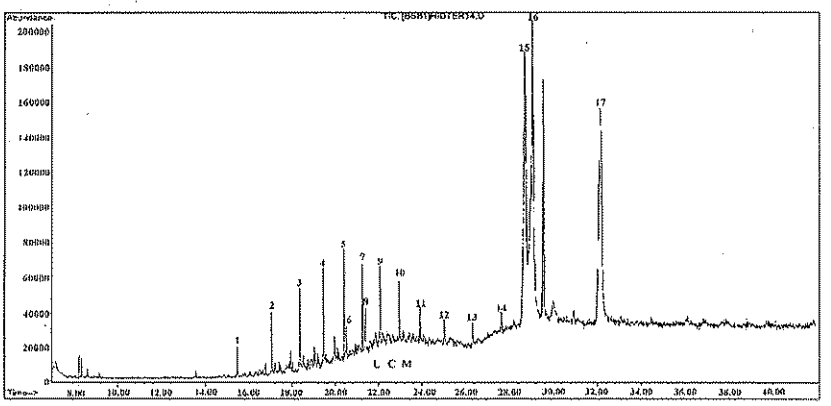


Figure 3.GC/MS chromatogram of TPAO tanker oil

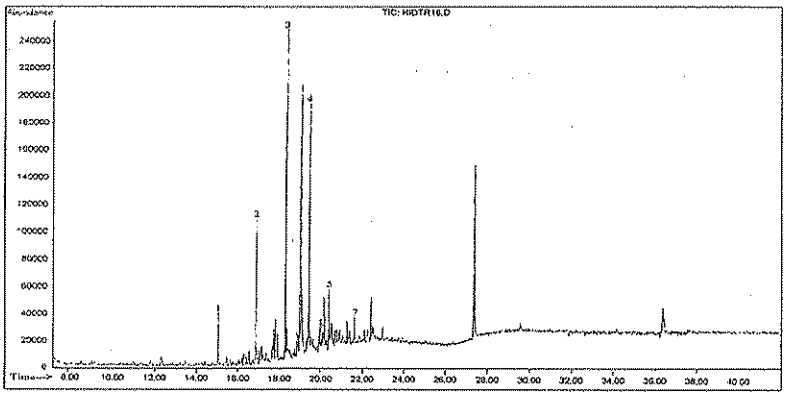


Figure 4.GC/MS chromatogram of surface water (H station)

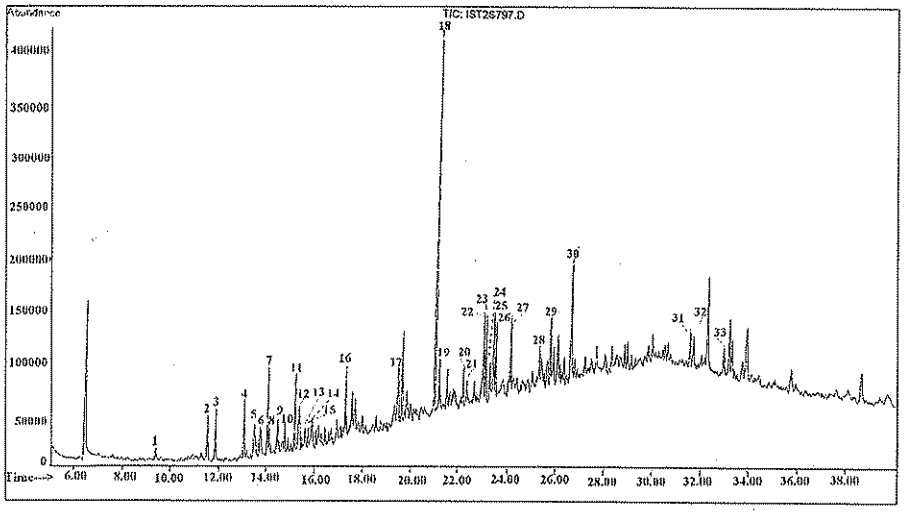


Figure 5.GC/MS chromatogram of T2 station sediment

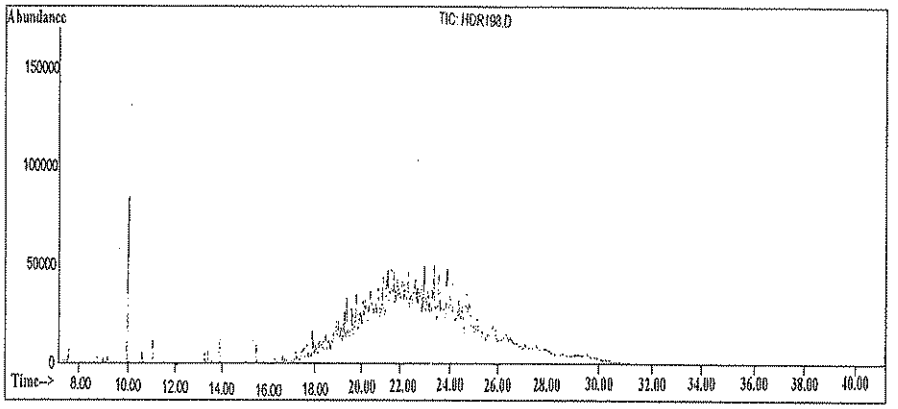


Figure 6. GC/MS chromatogram of mussel sample

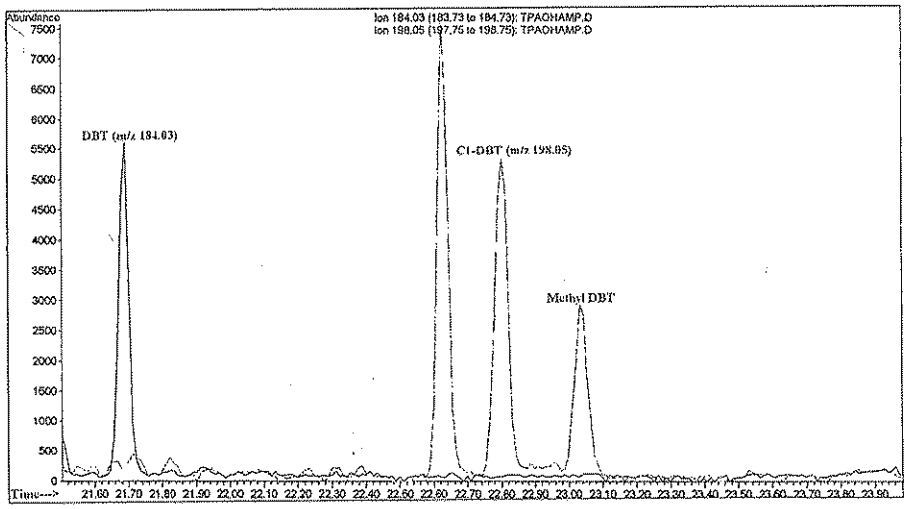


Figure 7. Fingerprinting chromatogram of TPAO tanker oil

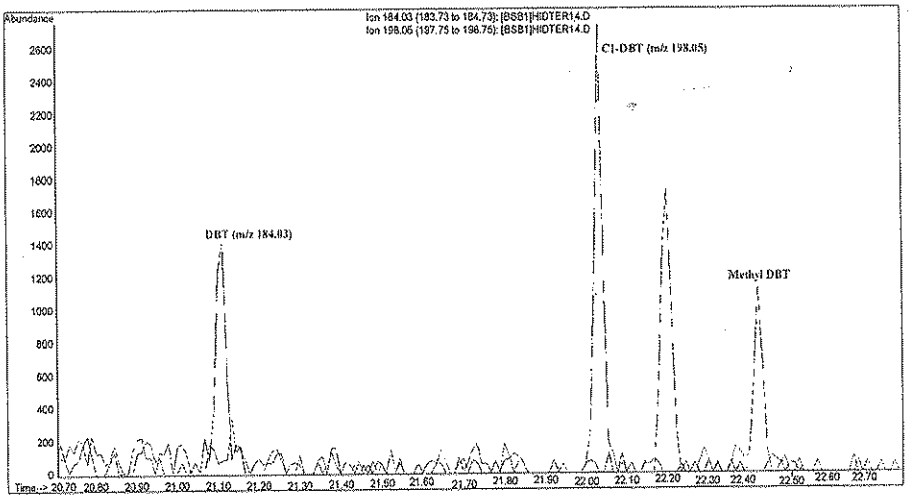


Figure 8. Fingerprinting chromatogram of seawater sample

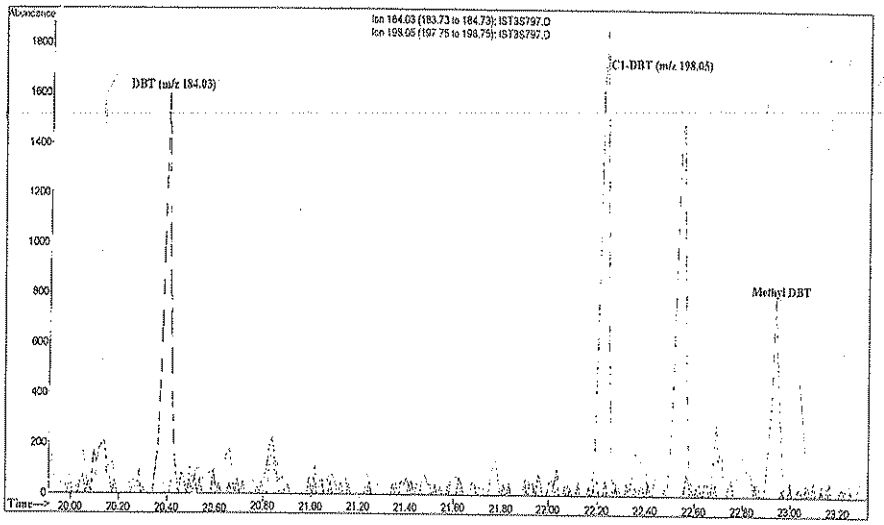


Figure 9. Fingerprinting chromatogram of sediment

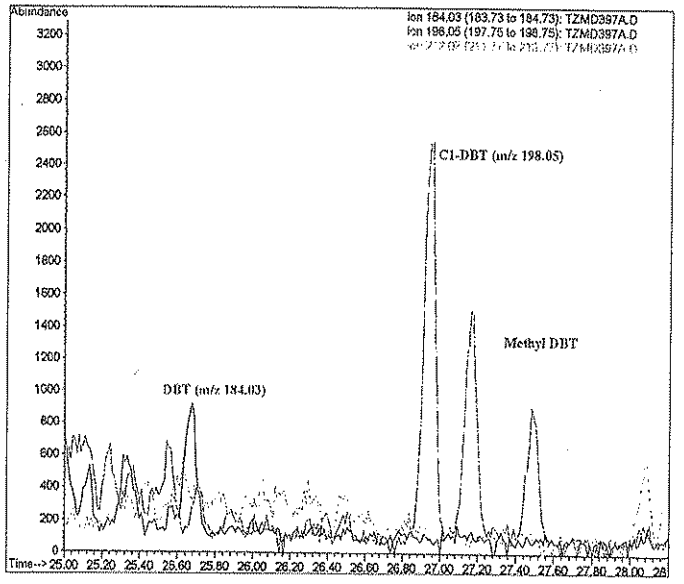


Figure 10. Fingerprinting chromatogram of mussel sample

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