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Oil pollution in sea water of Izmit Bay following the earthquake (17 Aug 1999)

İzmit körfezi deniz suyunda deprem sonrası petrol kirliliği

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Abstract

Oil pollution in Izmit Bay was investigated after the fire of Tüpraş refinery that followed the earthquake in 17 Aug. 1999. The highest oil pollution was found in Ereğli on surface water (covered wholly by oil) and in Ulaşlı as 179.2mg/L in 24-27 Aug 1999 and fell to 425 µg/L in 15-19Aug 2000. The maximum oil level in surface water in eastern part as 53.2-µg/ L, the central part as 1688 µg/L, in the western part as 463.6 µg/L and one year later it was changed as 10.40 µg/L, 13.68 µg/L and 12.98 µg/L respectively .

The determination of oil origin was made by the fingerprinting analysis method and found that its origin was Tüpraş refinery accident. The results of UVF and GC/MS and fingerprinting analyses are reported in this paper.

Keywords : Sea water, sediment, oil pollution, İzmit Bay

Introduction

The oil pollution of Izmit Bay was determined in 1994 and 1996. The oil pollution was measured in Izmit Bay after the earthquake on 17 Aug. 1999,then monthly in 1999 and quarterly in 2000.

Izmit Bay having a length of 49 km and width of 2-10 km and surface of 310 square kilometres, is separated into three distinct regions as western, central and eastern. The depth at these regions are 200 m,180 m and 35 m respectively. It has two distinct layers of water, the upper being the Black Sea water and the lower Mediterranean Sea water. There exist large

population and industries along the Izmit Bay. The Tüpraş refinery is located in the central region. The total crude oil imported into the refinery is 10 mio t/a.
The earthquake of 17Aug.1999 caused a fire in Tüpraş refinery and oil is spilt to Izmit Bay. The oil became diffused as a thick film for miles on surface of the seawater and suspended matter of oil particules plotted on sea surface, polluted on shore and deposited the sediments of the bay.

In this paper the oil pollution in Izmit Bay is reported following the accident in Tüpraş refinery in 1999 and 2000.

Material and methods

Seawater samples were collected from the 32 monitoring stations at surface, 10m and deep water from 24 Aug. 1999 to Dec.2000.The stations are shown in Fig 1.

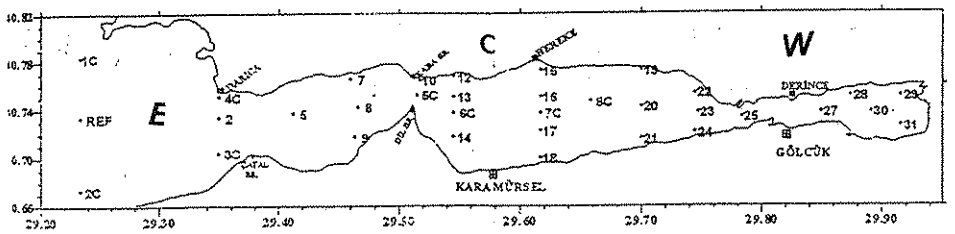


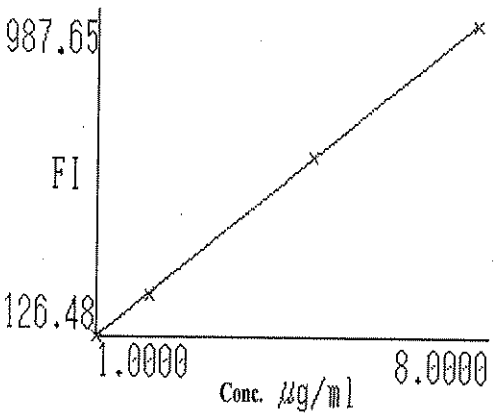
Figure 1. Sampling stations in Izmit Bay
(Regions: W: West, C: Central, E: East)

3 L samples were taken at surface, 10 m, and deep water. 15 ml Dichloromethane (DCM) was added to the sample for preservation.

The oil concentration was determined in 2.8 L seawater. The sample was extracted with 3x50 ml DCM. The extracts were combined, dried over anhydrous sodium sulphate and distilled at 40 °C. The residue was dissolved in hexane and the volume adjusted to 10 ml with hexane. The oil concentration was measured by using the equation of the calibration curve.

This curve was plotted with the spillt oil collected from the sea, near Tüpraş refinery. The oil concentrations were 1, 2, 5 and 8 µg/ml in

hexane. The fluorescense intensity was measured at 310/360 nm (ex/em) in UVF (Shimadzu RF-1501).



F1=123.47 C+1.6431 r^2:=1.0000

Figure 2. Calibration curve of crude oil the spillt from Tüpraş refinery

GC/MS analysis

GC/MS analysis was run by a HP 6890 capillary GC connected to a Hewlett Packard Mass Selective Detector (MSD) controlled by HP ChemStation. Operating conditions were: 50 mx0.20mm fused HP PONA, methyl siloxane, glass capillary column, oven temperature programme: 110-290°C at 10°C/min, at 10°C/min, 290°C at 10 min, split injector temperature 250°C, the carrier gas was helium, flow rate 1.2 ml/min.

GC/MS analysis was made on crude oil and extracts of sea water.

Identification of origin of oil :(Fingerprinting analysis)

To identify the origin of oil in the samples GC/MS was used (Tibbetts and Large, 1987; Nielsen and Lygre, 1990; Page *et al.*, 1998). The markers were: Dibenzothiophene (DBT, m/z 184.03), methylated C1-DBT (m/z 198.05), and C2-DBT (m/z 212.70). The chromatograms were taken from the crude oil spilt by Tüpraş refinery and extracts of sea water.

Results and Discussion

The calibration curve and its equation of the crude oil spillt from Tüpraş refinery are shown in Figure 2. The oil concentrations measured in bay are listed in Table 1. The oil pollution measurements showed that the oil spread over a wide area in first few days.

The highest pollution was found at Ereğli station and the oil determination was not made because this region was covered wholly by oil. The highest pollution was in surface water of Ulaşlı as 179.2 mg/L in Aug. 1999 . Ulaşlı station showed a high trend in concentration along time. The oil level decreased to 10.5 mg/L in Sept. 1999 and then to 3.3 mg/L in Oct. 1999. The highest pollution recorded at station 19 as 1159µg/L in Aug 1999 and 24.15 µg/L in Aug 2000, at station 23 as 1688.5 µg/L in Aug. 1999 and 13.69 µg/L in Aug 2000, at station 25 as 463.36µg/L in Aug 1999 and 1.98 µg/L in Aug 2000, at station 28 as 320.99 µg/L in Aug 1999 and 15.25 µg/L in Aug 2000.The depth water at station 17 was an exception of which oil level was very high, but generally the oil levels were low in the other stations. The oil concentration in surface water decreased after the accident in the following months but increased in 10 m depth caused by the descending water mass.The northeasterly dominant winds in this area brought about a rapid dispersion. The winds (NE) spread the oil through the bay and finally the eastern part was polluted dramatically. The influence of meteorological conditions during sampling played an important role.

The central part of the bay was most influenced by pollution. The pollution level in the regions ranked as central > eastern > west. It should be mentioned that petroleum hydrocarbon load of the Izmit Bay was not uniform in time and space. The rocky coastal lines were still covered by the oil.

As can be seen in the Table 1 oil levels decreased during the monitoring programme.

In earlier investigations in the area the highest oil pollution in Sea of Marmara in 1994 at surface water as 0.1-6.6 µg/L at thermocline as 0.1-45.7 µg/L at deep water as 0.1-64.5 µg/L (Okuş *et al.*, 1996), in 1995 at surface water 3.65-36.9 µg/L and at 10 m as 3-4.4 µg/L and in 1996 at surface water as 2.06- 103.7 µg/L and 10 m as 1.09-164.9 µg/L (Güven *et*

al., 1998), in western part of Izmit Bay in 1997 at station 1 383.44µg/L and at station 2 as 986.53 µg/L (Güven *et al.*, 1997 and following TPAO tanker accident in 19 Feb 1997 as 3.7g/L in Tuzla Bay (This area is very small, covered a thin oil film) at surface water and in 13 Feb 1998 as 475.7 µg/L (Unlu *et al.*, 2000).

Table 1.Oil pollution in eastern part of Izmit Bay (µg/L)

Station	Depth (m)	8/1999	9/1999	10/1999	12/1999	2/2000	5/2000	8/2000
1c	Surface	-	10.2	12.70	9.11	159.7	76.7	17.05
	10	-	23.13	11.29	12.1	16.7	108.5	20.95
	95	-	5.66	7.18	8.61	16.9	12.7	24.18
R	Surface	38.25	14.44	11.68	17.06	108.2	45.18	21.48
	10	11.89	13.29	9.81	20.9	109.2	27.95	22.53
	200	19.70	9.21	57.34	9.18	21.3	44.65	10.68
2c	Surface	-	16.46	12.39	50.3	408.1	57.36	14.44
	10	-	25.64	9.55	43.85	46.5	49.89	15.78
	55	-	14.34	13.91	12.8	23.7	25.38	14.54
4c	Surface	-	25.13	16.81	22.8	154.9	3090	17.65
	10	-	41.79	11.13	15.1	23.4	106.7	9.18
	52	-	21.17	10.98	8.15	773.6	42.44	8.48
2	Surface	22.08	9.37	14.23	11.20	63.2	76.84	14.41
	10	76.48	13.65	10.46	18.6	86.1	43.10	10.55
	200	18.03	11.56	9.04	4.97	39.8	54.86	7.34
3c	Surface		17.48	18.21	17.59	1309	76.71	16.67
	10	-	18.52	7.71	12.6	157.0	22.28	25.30
	47	-	424.7	4.24	6.90	483.2	20.98	11.62
5	Surface	45.02	27.99	14.20	9.84	118.0	221.2	22.64
	10	42.35	12.05	4.47	11.7	48.8	18.89	10.67
	78	19.16	10.52	5.88	7.63	50.3	23.58	9.81
7	Surface	53.01	7.68	11.87	18.8	118.9	23.76	10.40
	10	56.40	14.63	4.45	23.27	36.7	33.79	40.2
	63	20.09	8.03	12.50	10.12	25.2	28.05	12.93
8	Surface	40.26	11.93	10.56	11.2	51.5	8.51	13.06
	10	34.48	7.33	16.27	15.6	74.5	149.4	13.64
	51	22.38	6.81	6.00	5.21	18.7	50.5	14.82

-:No sampling.

Table 2. Oil pollution in central part of Izmit Bay (µg/L).

Station	Depth (m)	8/1999	9/1999	10/1999	12/1999	2/2000	5/2000	8/2000
8c	Surface	-	69.13	15.11	19.27	129	27.91	14.74
	10	-	22.78	16.95	17.4	40.3	25.80	18.62
	114	-	9.86	11.04	35.71	26.6	20.82	12.13
9	Surface	270.29	8.95	14.99	13.9	107.6	69.07	14.59
	10	55.18	5.83	10.96	16.3	109.5	126.9	22.87
	35	40.80	10.99	6.34	9.29	27.7	57.60	14.41
10	Surface	40.75	14.40	13.00	17.30	311.9	46.95	18.19
	10	137.40	13.47	15.51	17.9	52.1	23.06	15.15
	26	23.5	5.62	6.24	9.80	23.8	24.21	24.55
12	Surface	34.21	106.5	49.19	10.7	93.6	17.30	43.98
	10	14.91	88.40	15.79	23.1	26.6	30.58	14.37
	20	132.41	112.83	11.45	27.53	22.4	41.50	22.38
13	Surface	64.76	88.12	15.17	170.2	84.6	42.58	21.53
	10	27.71	18.60	14.23	1190	36.5	24.05	15.91
	51	23.60	65.22	13.87	288.18	24.7	55.28	13.41
14	Surface	65.36	13.83	15.64	681.7	114.0	30.82	17.81
	10	34.56	22.17	6.08	570.3	116.0	23.56	13.01
	43	20.96	5.16	21.72	563.75	15.2	28.13	15.09
15	Surface	50.89	1096.7	18.44	109.7	71.4	177.8	19.94
	10	23.58	28.02	14.56	6.86	39.6	26.66	17.91
	49	9.19	26.25	6.83	24.52	28.4	23.75	17.63
16	Surface	-	19.00	113.53	20.2	87.9	45.17	17.89
	10	-	21.58	26.04	19.14	41.4	18.93	16.00
	77	-	14.96	9.34	10.99	18.6	49.26	28.23
17	Surface	258.15	13.76	632.85	110.7	131.6	36.58	23.06
	10	17.63	50.85	14.35	24.2	168.8	24.27	39.88
	157	22.31	21.20	8.52	21.09	97.8	47.28	935.12
19	Surface	1159.4	117.39	18.64	412.1	66.5	38.10	24.15
	10	1910.7	23.38	16.77	1474.9	33.5	74.62	19.54
	25	101.85	14.69	23.88	85.2	67.6	28.19	14.03
20	Surface	281.33	25.85	17.14	19.6	123.6	20.58	18.23
	10	50.40	165.46	13.31	100.3	202.0	21.96	13.06
	102	14.30	96.31	21.40	7.08	487.5	16.03	20.88
21	Surface	-	15.15	3385.6	14.8	63.1	16.00	15.26
	10	-	880.83	14.18	22.3	24.6	17.57	14.22
	61	-	26.47	14.67	10.59	2.05	14.11	12.25
22	Surface	26.86	16.00	51.02	68.1	54.3	22.9	14.17
	10	28.06	19.80	52.30	23.3	33.3	22.9	14.49
	20	18.06	28.73	10.36	13.93	27.5	20.82	17.26
23	Surface	1688.5	59.76	39.70	21.4	78.6	21.09	13.68
	10	152.36	19.09	15.26	14.15	14.7	18.91	11.77
	40	22.67	50.89	10.58	19.85	21.9	16.01	14.07
24	Surface	244.21	159.04	108.96	26.9	69.8	18.61	23.02
	10	57.19	19.79	15.33	44.6	128.8	15.28	13.03
	53	15.37	17.05	10.74	10.4	95.8	17.58	101.02
Tupraş	Surface	140.64	67.86	105.00	3974.2	716.0	159.9	425.2
Ulaşlı	Surface	179294	10579.2	-	259.5	173.5	-	152.3

-: No sampling.

Table 3. Oil pollution in western part of Izmit Bay (μg/L).

Station	Depth (m)	8/1999	9/1999	10/1999	12/1999	2/2000	5/2000	8/2000
25	Surface	463.36	18.74	95.79	12.88	47.5	36.55	12.98
	10	46.64	10.72	17.25	27.0	18.9	26.03	12.76
	38	51.88	12.15	11.80	11.14	14.2	51.89	13.09
27	Surface	177.96	19.20	38.58	159.0	79.1	19.62	15.69
	10	24.60	16.17	15.17	26.31	27.3	7.63	15.47
	29	45.48	24.31	11.44	15.73	15.3	24.00	14.34
28	Surface	320.99	90.90	104.29	234.0	321.2	22.06	15.25
	10	27.29	11.38	17.88	20.5	22.8	18.17	16.48
	17	-	12.26	26.94	15.1	24.1	23.59	23.22
29	Surface	19.95	29.14	16.14	66.1	72.5	277.29	17.97
	10	10.57	14.79	22.85	18.57	37.4	5.92	15.49
	17	19.63	17.91	15.66	78.6	19.5	27.55	14.67
30	Surface	36.17	15.19	11.56	25.5	95.9	130.10	22.25
	10	508.14	13.14	20.93	4.35	25.2	19.72	27.03
	27	245.24	8.04	21.00	6.58	20.6	17.31	433.9
31	Surface	109.61	16.51	13.42	57.1	105.1	22.46	18.05
	10	46.45	15.76	25.03	22.79	28.3	137.68	147.5
	43	24.19	34.45	14.83	12.43	43.7	17.23	25.39

Oil concentrations in the present findings were compared with those of Izmit Bay and Sea of Marmara and those following the TPAO tanker accident in Tuzla Bay. It was found that the pollution values were much higher after the accidents than those of the earlier times.
Unresolved Complex Mixture (UCM) hump was observed in all chromatograms. It proved that the pollution was fresh .

GC/MS results showed :
1-that the aliphatic fraction contains the majority of the compounds in petroleum alkanes,
2-that unresolved complex mixture signal should be detected in medium resolution GC analysis.

The GC/MS chromatograms of oil of Tüpraş refinery and of sea water extract are shown in Figures 3,4 and 5.

The samples were analysed for aliphatic and aromatic hydrocarbons together with the uncharacterised complex material (UCM) using GC/MS..

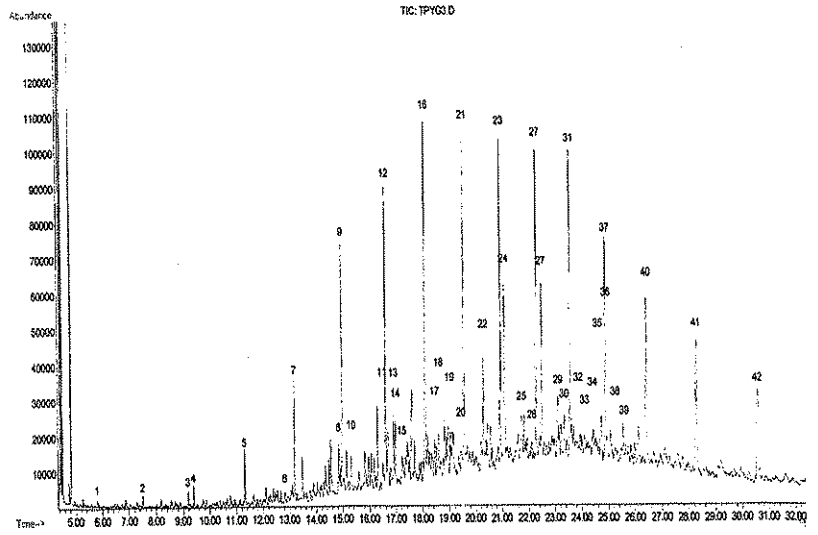


Figure 3. GC/MS chromatogram of DCM extract collected in front of Tüpraş refinery

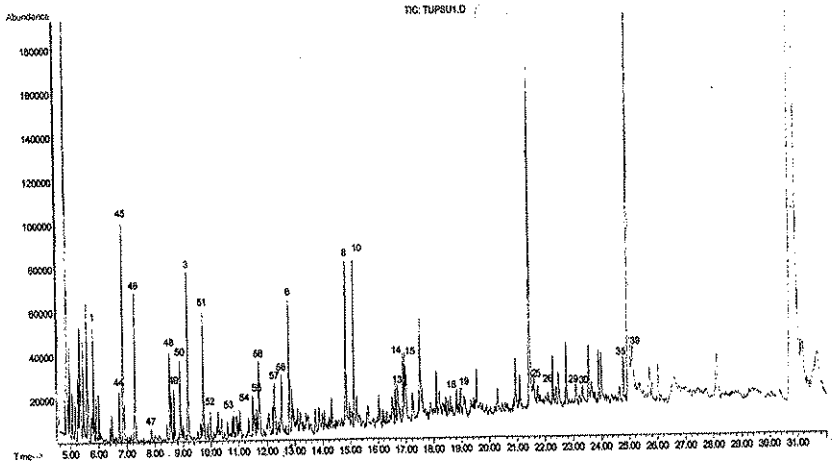


Figure 4. GC/MS chromatogram of DCM extract obtained from the seawater collected at Ulaşlı station in Aug 1999.

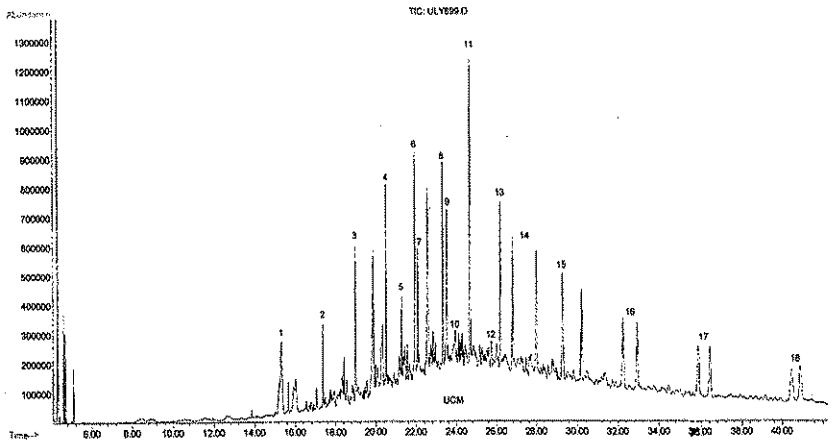


Figure 5. GC/MS chromatogram of DCM extract obtained from the seawater collected at Ulaşlı station in Aug 1999.

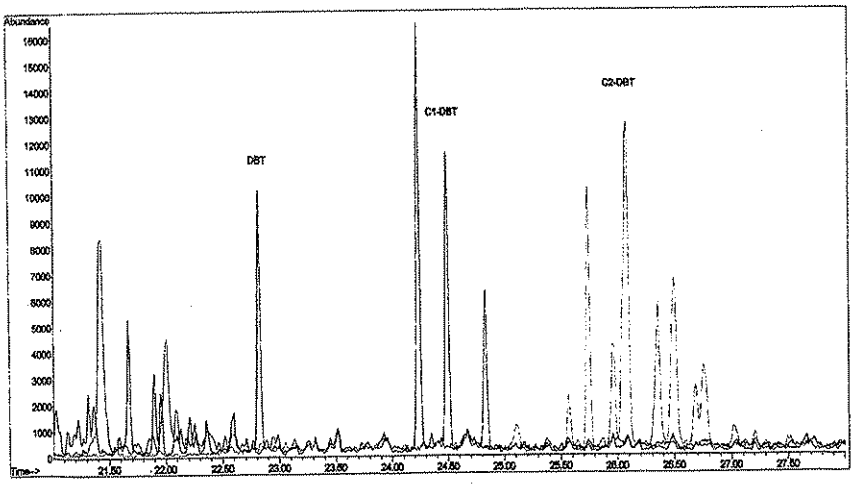


Figure 6. Fingerprinting chromatogram of DCM extract collected in front of Tüpraş refinery

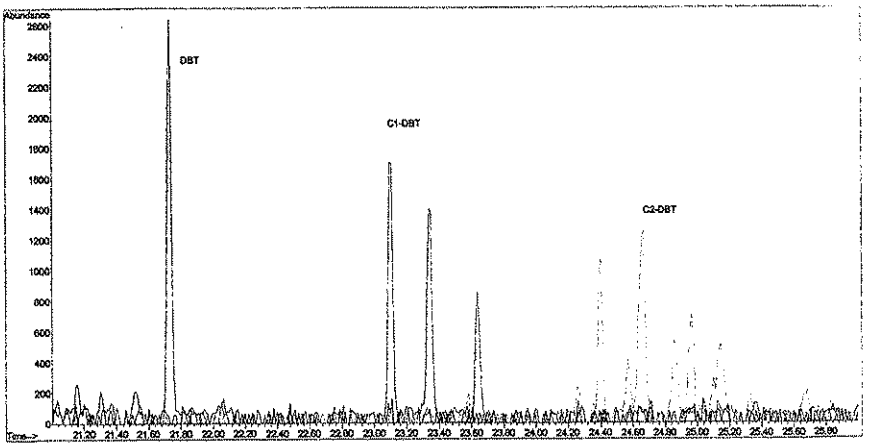


Figure 7. Fingerprinting chromatogram of DCM extract obtained from the seawater collected in front of Tüpraş refinery

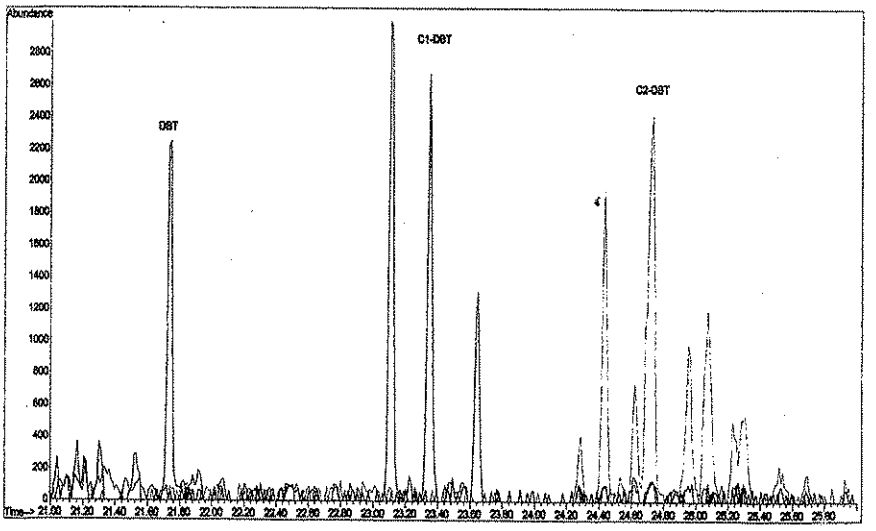


Figure 8. Fingerprinting chromatogram of DCM extract obtained from the seawater collected at Ulaşlı station in Aug 1999.

The hydrocarbon compounds identified by GC/MS in crude oil and seawater extract were similar as listed below:

Aliphatic group: Octane *(1)*, Nonane *(2)*, Decane (3), Undecane (4), Dodecane (6), Tridecane (8), Tetradecane (11), Pentadecane (15), Hexadecane (20), Nor-pristane (Pentadecane, 2,6,10 trimethyl) (21), Heptadecane (22), Pristane (23), Octadecane (26), Phytane (27), nonadecane (30), Eicosane (36), Heneicosane (39), Docosane (40), Tricosane (41), Tetracosane (42)

Aromatic group: Naphthalene (5), Naphthalene 1-methyl (7), Naphthalene 2-methyl (9), Naphthalene 1,2-dimethyl (10), Naphthalene 1,4-dimethyl (12), Naphthalene 1,5-dimethyl (13), Naphthalene 2,7-dimethyl (14), Naphthalene 1,6,7-trimethyl (16), Naphthalene 2,3,5-trimethyl (17), Naphthalene 2,3,6-trimethyl (18), 9H fluorene (19), Dibenzthiophene (24), Anthracene(25), Dibenzthiophene, 3-methyl (28), Dibenzthiophene, 9-methyl (29), Anthracene,1-methyl (31), Anthracene,2-methyl (32), Phenanthrene,4-methyl (33), 2,8 Dibenzthiophene (34), Naphto (2,3-b) thiophene,4,9-dimethyl (35), 3,6 dimethylbenzthiophene (37), Anthracene, 2,5-dimethyl (38), Ethyl benzene (44), m-Xylene (45), p-Xylene (46), isopropil benzene (47),benzene 1-ethyl-2-methyl (48), benzene 1-ethyl-2-methyl (49), 1,3,5-trimethyl benzen (50), 1,2,5-trimethyl benzen (51), 1H Indene,2,3 dihydro (52), Benzene,4-ethyl1,2 dimethyl(53), 2,6-dimethyl phenol (54), p-methyl benzyl alchol (55), phenol, 2,4 dimethyl (56), benzene, 2 ethenyl,1,4dimethyl (57), phenol,3,4 dimethyl (58).

The origin of oil was identified by using fingerprinting analysis. The chromatograms of seawater extract showed similarity with that of Tüpraş crude oil sample (Figures 6,7 and 8-).

Conclusions

After the accident in Tüpraş refinery following the earthquake, the oil pollution level increased in Tuzla Bay. The measured oil concentrations in this area are 56 times higher than those of earlier findings.

GC/MS chromatograms were similar to those of the Tüpraş crude oil. Fingerprinting analysis proved that the origin of oil pollution in sea water was depended the crude oil spills from Tüpraş accident.

Özet

17 Ağustos 1999 tarihinde meydana gelen deprem sonrası Tüpraş rafinerinde meydana gelen yangın sonucu İzmit Körfezinde petrol kirliliği incelenmiş ve en yüksek kirliliğin kazayı takip eden günde Ulaşlı da 179.2 mg/L ve Tüpraş rafinerisi önünde Ekim 1999 da 3.97 mg/L bulunmuştur. Kazayı takiben 24-27 Ağustos 1999 da İstasyon 19 da yüzey suyunda 1.15mg /L 10 m de 1.9 mg/L ve istasyon 23 de yüzey suyunda 1.6 mg/L bulunmuştur. 1 sene sonra yapılan ölçümlerde ise petrol kirliliği azalmış, ancak istasyon 17 de dip suyunda 935 µg/L, istasyon 24 de dip suyunda 101µg/L, Tüpraş önü yüzey suyunda 425.2 µg/L , Ulaşlı yüzey suyunda ise 152.3 µg/L bulunmuştur. Bu sonuçlara göre petrol kirliliği 1 sene içersinde azalmış bu azalma Ulaşlı istasyonunda kirlilik miktarı bin misli azalmıştır. İzmit Körfezinde meydana gelen bu kirliliğin evvelce yaptığımız çalışmalar ile mukayesesinde seviyesinin çok yüksek olduğu saptanmıştır. Bu çalışmada ayrıca GC/MS analizinde parmak izi metodu kullanılarak petrol kirliliğinin Tüpraş yangınından kaynaklandığı saptanmıştır.

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