

OIL POLLUTION IN MARMARA SEA AFTER NASSIA TANKER ACCIDENT

NASSIA TANKER KAZASI SONRASI MARMARA DENİZİNDE PETROL KİRLİLİĞİ

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Abstract

Oil pollution in Marmara Sea was investigated following the Nassia tanker accident. The results obtained by UVF and GC analyses were compared with those related to the Istanbul Strait due to the same accident. The pollution was much denser in the elongated but narrow Strait of Istanbul then in Marmara Sea that had a much larger surface area.

Introduction

The Marmara Sea is connected to the Black Sea and the Aegean Sea through of Istanbul and Çanakkale Straits. The surface area of the Marmara Sea is 11.500 km² and the volume is 3.378 km³. Its maximum length (Gelibolu- Izmit) is 276 km and the maximum width 76 km. The whole coastline extends 927 km of which 264 km lies in European and 663 km in Asian sides. The boundary of the continental shelf is 100 m deep. The deepest point is in the middle depression region reaching a depth of 1.335 m (Memorandum 1941, Ünlüata 1990, Kocataş *et al.*, 1993).

The Nassia accident occurred on 13 March 1994 near Rumeli Feneri Çakarı on the Istanbul Strait. It resulted in a spill of 2.000 tons of crude oil to the sea and more than 20.000 tons of oil was burnt. The oil contaminated seawater and the coasts of the Istanbul Strait, Black Sea and Marmara Sea. Two papers on pollution were published after this accident (Güven *et al.*, 1995, 1996). The 3,4 benzopyrene, 1,12 benzperylene and bituminous matters were determined in the Marmara Sea sediments by Shimkus *et al.*, (1993).

In this study, oil pollution measurements were made in the samples collected from six stations of Marmara Sea.

Materials

The samples were taken from the stations indicated on the map (Fig.1) from R /V Arar on the following dates: S₁: 21-27 April 1994, S₂: 5-11 July 1994, S₃: 23-28 September 1994.

Methods

1-Extraction technique

Seawater samples (surface, thermocline and deep) were collected in 3 L amber glass bottles which had previously been washed with dichlormethane (DCM), 50 ml of DCM was added for preservation and final extractions were made for analysis within 12 h.

Seawater sample was extracted three times with 50 ml DCM. The extracts were combined and then dried over anhydrous sodium sulphate, filtered and distilled in a rotary evaporator. The residue was redissolved with hexane and the volume adjusted to 10 ml and then subjected to UVF and GC analyses.

2-Analysis

2.1 UVF

Oil pollution of the samples was measured by UVF (Fluorospectrophotometer, Hitachi 650 10S). The calibration curve was plotted by using Nassia cargo sample in concentrations of 2.5, 5, 10 and 15 µg/ml in hexane. The absorption was measured at 310/360 nm (ex/em) (Ehrhardt and Burns, 1993).

2.2 Gas Liquid Chromatography

GC was carried out using a Perkin Elmer 8420 capillary GC with flame ionization detector (FID). Operating conditions were as follows: 25m x 0.33 mm (i.d.) Q C3/BP column; oven temperature programme: 40°C for 5 min, from 40°C to 200°C at 8°C / min, 200°C for 5 min and between 200 - 280°C at 8°C / min; detector temperature 340°C; splitless injector temperature 320°C; carrier gas N₂.

3-The estimation of petrogenic input

To estimate the petrogenic input in the samples the following methods were used:

C₁₈ /Ph (Phytane) and Pr/Ph (Pristane/Phytane) ratios (Clarck and Finley, 1974, Gearing *et al.*, 1976), Carbon Preference Index (CPI) calculated from $2(nC_{27} + nC_{29}) / nC_{26} + 2nC_{28} + nC_{30}$ (Clarck and Finley, 1974, Johansson *et al.*, 1980) and unresolved complex mixture (UCM) signal in the chromatogram (Farrington and Tripp, 1977, Johansson *et al.*, 1980, Barrick and Hedges, 1981).

Results and Discussion

The petroleum hydrocarbon pollution of seawater is shown in Table 1. Regarding the stations, the highest contamination in seawater samples was found in deep at M4 and at M6 in Marmara Sea.

The highest values for oil pollution were found in the first survey : in thermocline water in M3 and in M1 and deep water in M4 and M6 stations.

C18/Ph, Ph/Pr ratios and CPI value of the samples are shown in Table 2. The ratios of C18/Pr and Pr/Ph are calculated only in M3 and M4 stations respectively. These values are low and indicated petroleum input to the seawater. CPI values are low in most calculated amounts in all chromatograms also indicating petroleum input to the seawater.

The selected GC chromatograms of the samples are shown in Fig 2-10. UCM in the chromatogram indicated petroleum hydrocarbons detected in some samples. The gas chromatograms of Marmara Sea samples clearly showed the presence of petrogenic hydrocarbons which are long term inputs.

As regards oil pollution of sediments, Shimkus *et al.*,(1993) found 3.4 benzpyrene (BP) 0.22-3.02 ng/g, 1.12 benzperylene (BPE) 0.92-5.6 ng/g and bituminous matter (BM) 0.01-0.15 g/kg in the Marmara Sea sediments. The maximum 3.4 BP in Büyükçekmece, 1.12 BPE in Marmara island and BM in Büyükada regions. Accumulation of oil in the Marmara Sea sediments was found as 4.1-166.8 mcg/g (Güven *et al.*, Unpublished data.). Apparent differences can be attributed to the varying locations, collection dates and the analysed compounds. In our work oil amount was determined on PAH.

The comparison of oil pollution between Istanbul Strait and Marmara Sea at surface, in thermocline and deep seawater are shown in Fig 11-13. As can be seen in these figures Istanbul Strait was more polluted than Marmara Sea. The pollution decreased rapidly during the surveys (Güven *et al.*, 1996). These findings are the first for the Marmara Sea.

Station	Surface			Thermocline			Deep		
	M1	M3	M4	M1	M3	M4	M1	M3	M4
BP	0.1	1.0	0.0	2.1	2.7	6.0	2.1	0.0	0.0
BPE	0.0	0.7	0.0	0.1	0.7	1.0	0.0	0.0	0.0
BM	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0
Ph	1.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0
Pr	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0
CPI	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

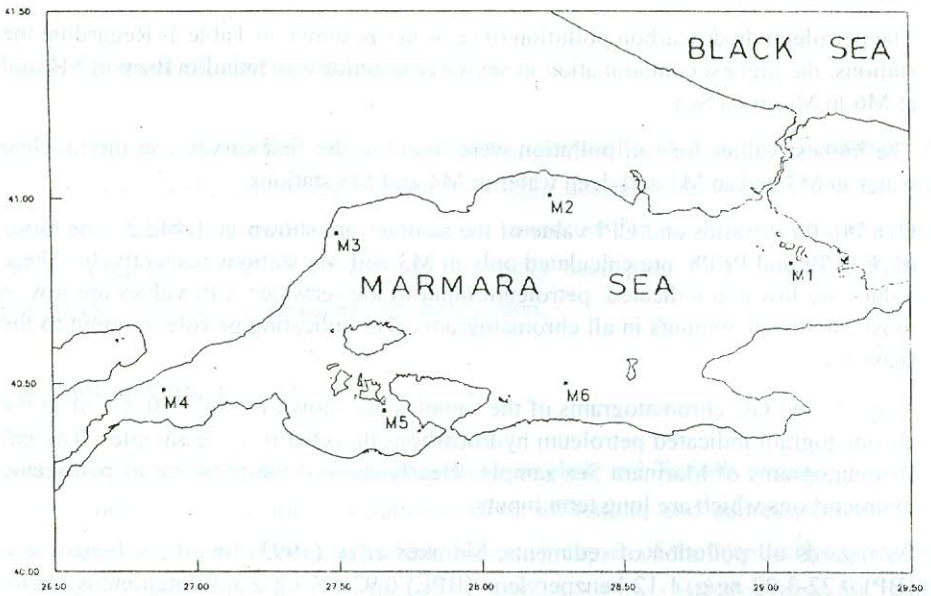


Fig. 1. The Sampling Stations in the Marmara Sea.

Table 1 - Oil amount in Marmara Seawater samples ($\mu\text{g/L}$)

Station	Surface			Thermocline			Deep		
	N1	N2	N3	N1	N2	N3	N1	N2	N3
M1	6.6	1.5	0.4	13.8	1.5	0.6	0.1	1.0	0.4
M2	1.8	0.9	1.3	1.0	1.6	0.4	7.5	0.7	0.7
M3	0.1	0.3	0.1	45.7	1.8	0.1	4.0	0.8	0.1
M4	3.9	1.4	0.7	0.3	2.2	0.6	64.5	0.9	1.4
M5	4.5	1.4	0.8	11.5	2.3	0.4	11.3	1.7	0.7
M6	1.8	1.6	0.4	4.4	2.0	0.9	54.5	1.4	0.7

N. Survey Number.

Table 2- The ratios of Ph/Pr and CPI value from seawater ,

Sample	Pr/Ph			CPI		
	N1	N2	N3	N1	N2	N3
M2S	-	-	-	-	-	1.15
M3S	-	-	-	1.02	-	-
M4S	0.78	-	-	0.85	-	-
M6S	-	-	-	1.20	-	-
M2T	-	-	-	1.02	-	-
M3T	-	-	-	-	0.82	-
M4T	-	-	-	-	1.38	-
M6D	-	-	-	1.01	-	-

M: Marmara Sea , Pr: Pristane, Ph: Phytane, CPI: Carbon Preference Index, N: Survey number, S: Surface, T: Thermocline, D: Deep

- The peak of pristane/ phytane was not detected on chromatogram. In the first survey C_{26-30} were detected in sea water samples and not in the second and third surveys . In surface ,thermocline and deep waters C_{26-30} were not detected, and thus CPI value could not be calculated.

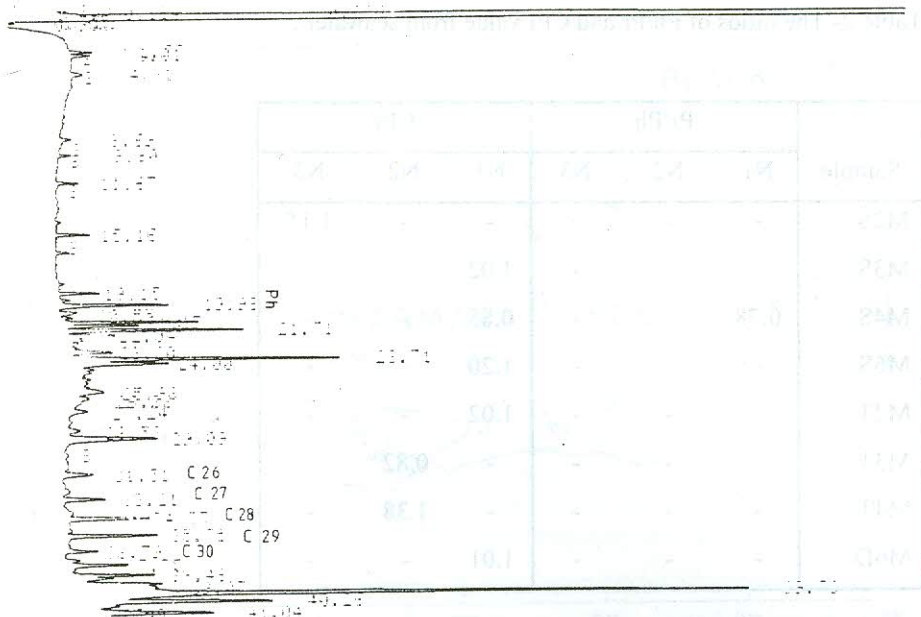


Fig.2. Gas chromatogram of surface seawater in station M1. Survey number 1.

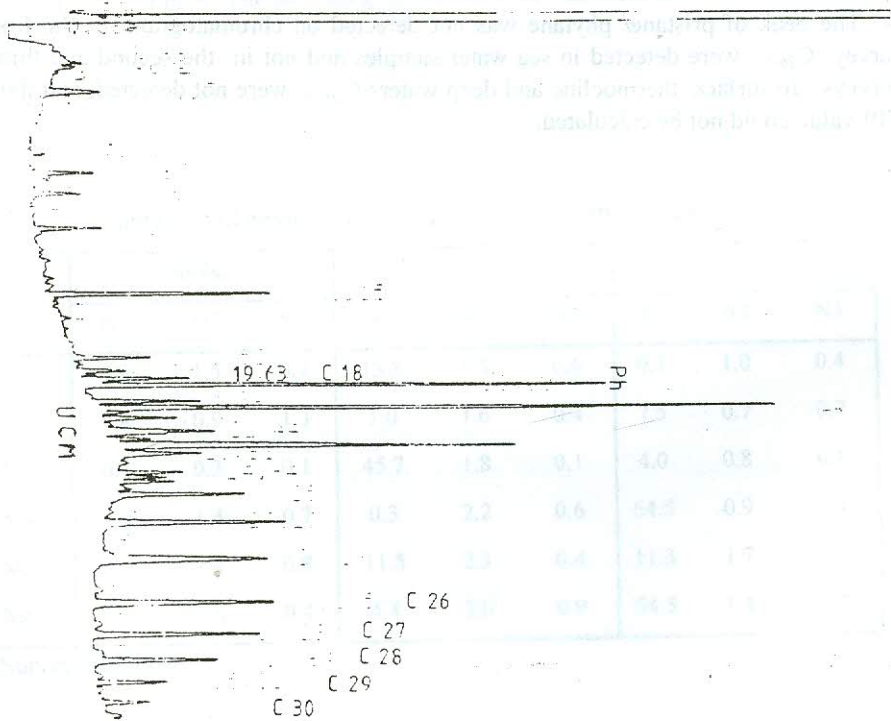


Fig. 3. Gas chromatogram of surface seawater in station M1. Survey number 2.

Fig. 4. Gas chromatogram of surface seawater in station M3. Survey number 1.

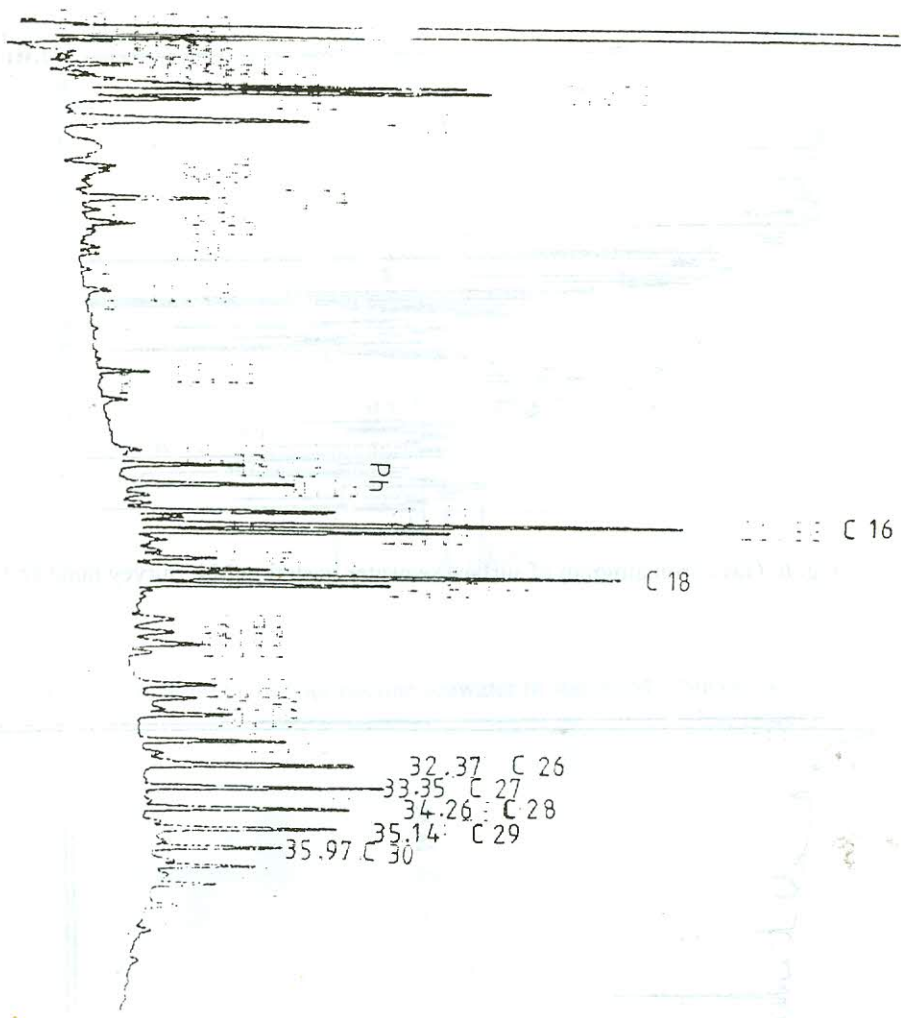
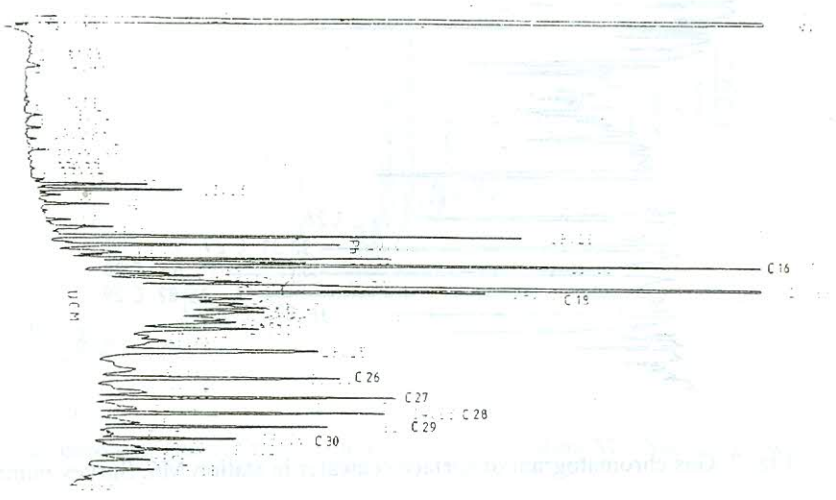


Fig. 5. Gas chromatogram of surface seawater in station M2. Survey number 3.



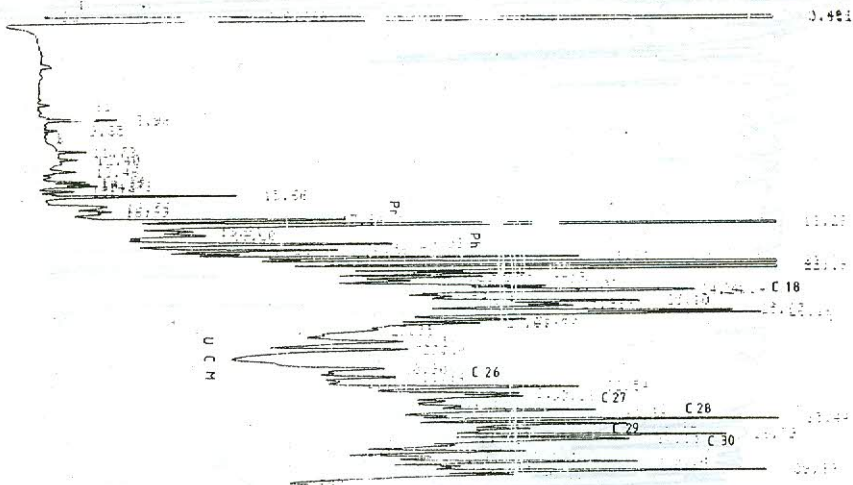


Fig. 6. Gas chromatogram of surface seawater in station M4. Survey number 1.

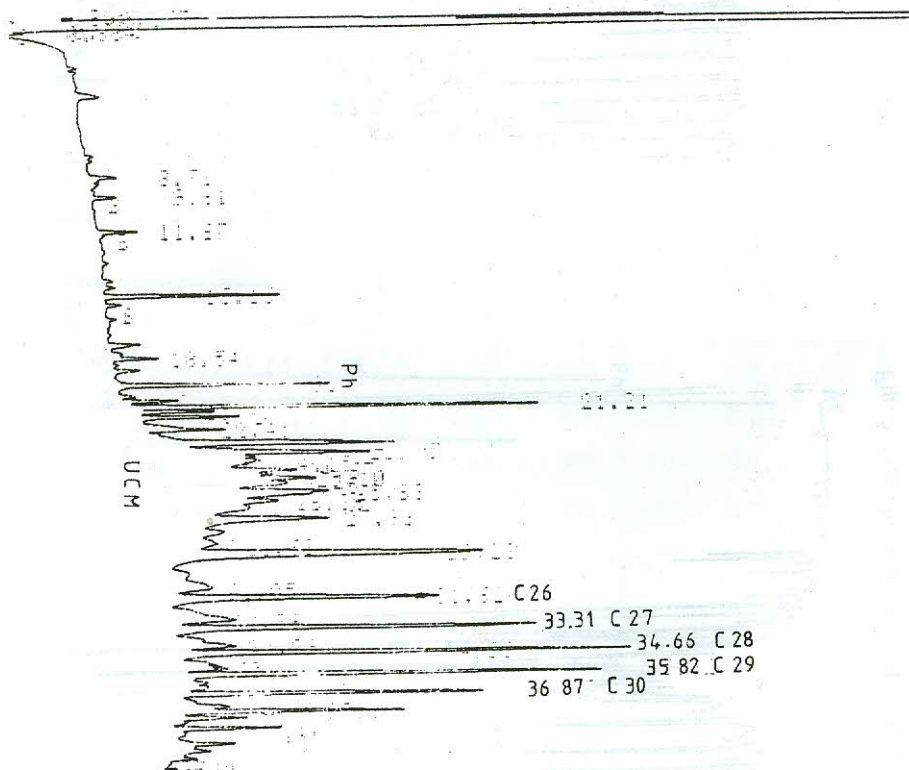


Fig. 7. Gas chromatogram of surface seawater in station M6. Survey number 1.

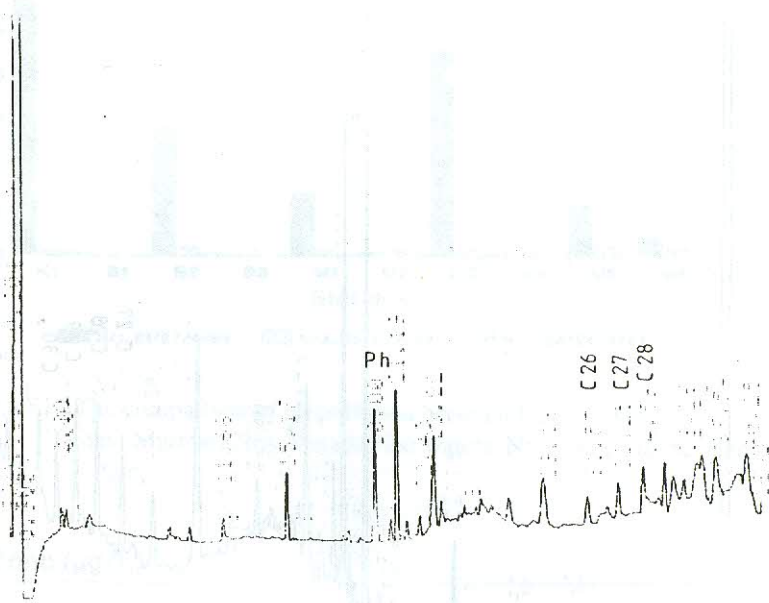


Fig. 8. Gas chromatogram of thermocline seawater in station M1. Survey number 1.

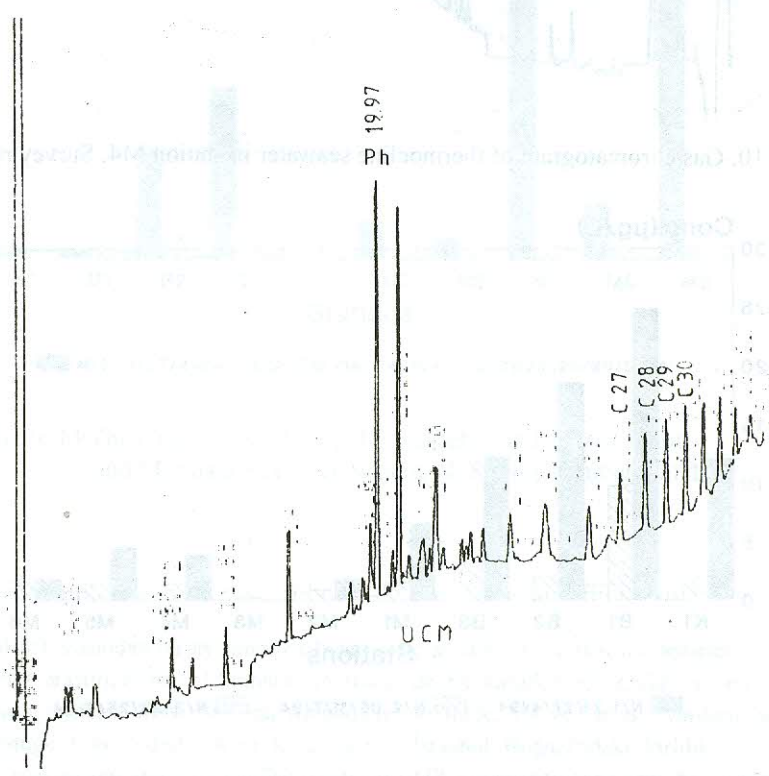


Fig. 9. Gas chromatogram of thermocline seawater in station M3. Survey number 2.

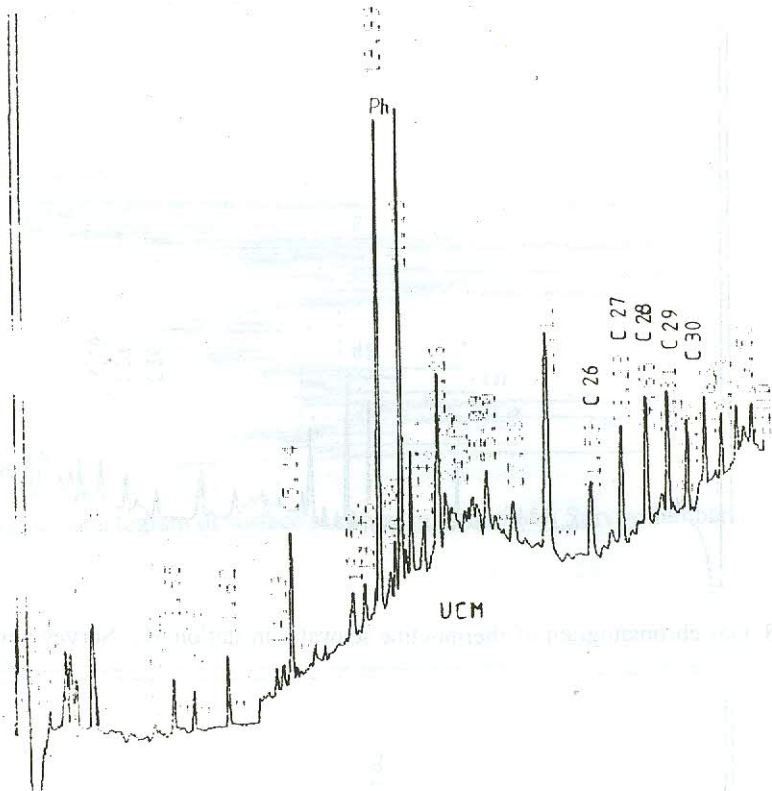


Fig. 10. Gas chromatogram of thermocline seawater in station M4. Survey number 2.

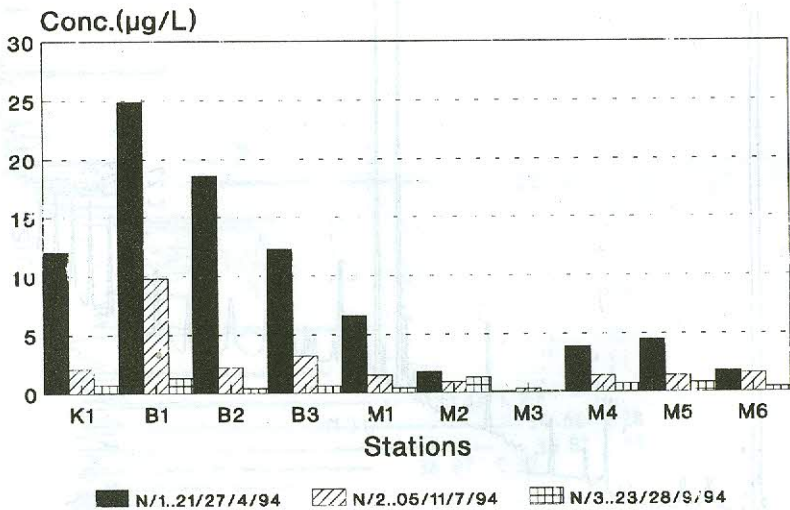


Figure 11. The comparison of oil pollution between Istanbul Strait and Marmara Sea surface waters. N: Survey number and date.

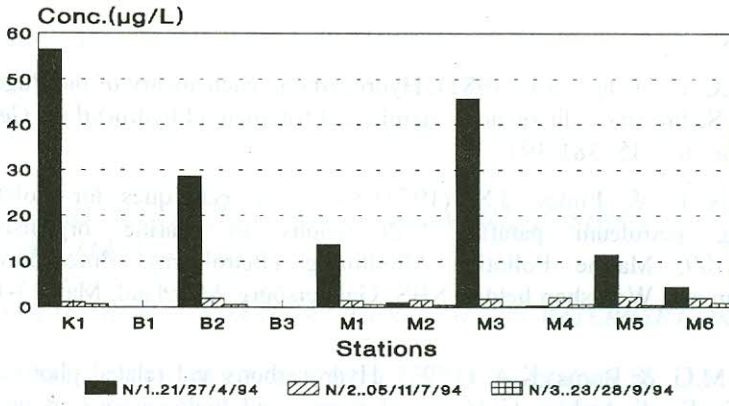


Figure 12. The comparison of oil pollution between Istanbul Strait and Marmara Sea thermocline waters. N: Survey number and date.

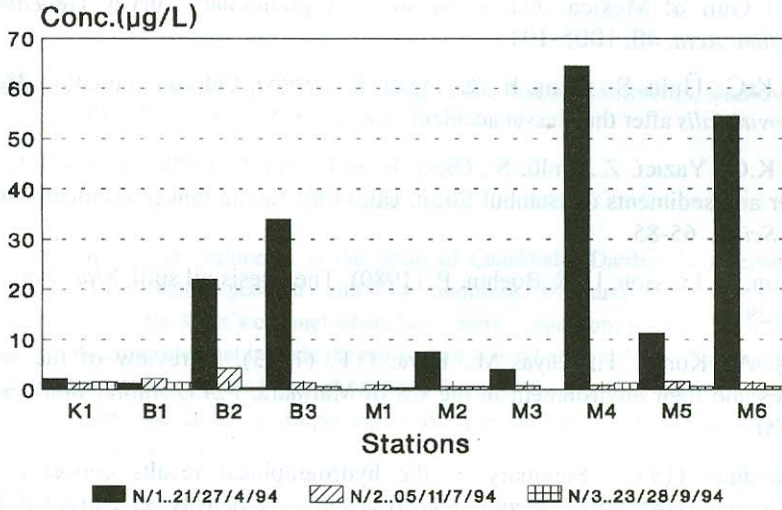


Figure 13. The comparison of oil pollution between Istanbul Strait and Marmara Sea deep waters. N: Survey number and date.

Özet

Nassia Tanker kazasından bir ay sonra başlayan ve üç ay süre ile yapılan incelemeler sonucu deniz kirliliği araştırmasında; Marmara Denizinin de bu kazadan etkilendiği ve en fazla kirliliğin birinci seferde M1 ve M3 istasyonunda termokline, M4 ve M6 istasyonlarında dip suyunda olduğu tespit edildi. Aynı kaza sonucu İstanbul Boğazı'ndaki kirlilik ile ilgili çalışmanın mukayesesinde Marmara Denizindeki kirlilik boyutunun daha az olduğu görüldü. Yalnız bu husus Marmara Denizinin boyutunun büyüklüğü dolayısı ile kirliliğin dilusyonuna bağlanabilir.

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