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OIL POLLUTION ON SEA WATER AND SEDIMENTS OF ISTANBUL STRAIT, CAUSED BY NASSIA TANKER ACCIDENT

İSTANBUL BOĞAZI SUYU VE SEDİMENTİNDEKİ NASSIA TANKER KAZASININ SEBEP OLDUĞU PETROL KİRLİLİĞİ

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Key words : Istanbul Strait, Nassia tanker accident, oil pollution, sea water, sediment.

Abstract
Oil pollution was studied on sea water and sediments of Istanbul Strait following the Nassia tanker accident. The oil amount in the sea water and sediments was determined by UVF spectrophotometry. GC analysis was made on the sea water and on the aliphatic fractions of sediments. Oil amount found gradually decreased in sea water whereas increased in sediments after the accident.

Introduction

Istanbul Strait has a transit traffic, involving, an average of 35.000 ships annually, thus is prone to ship accidents. The most terrible accident involved the Nassia tanker on 13 March 1994. Following the collision (in Rumeli feneri çakarı) with M/V Shipbroker, No.1 port tank of Nassia exploded and both set on fire. In Nassia, crude oil cargo in No.1 port and centre tanks superstructure were completely burnt. The strait has been severely polluted and city of Istanbul had the risk of the flames / floating drifting with the help of the straight's natural current, and the fumes contaminated the atmosphere (Oğuzülgen, 1995).

Oil pollution of Istanbul Strait had not been determined until Nassia accident. The report was prepared on the accident by our institute (Doğan, 1995) and a related paper was published on oil contamination of mussels (Güven *et al.,* 1995)

Numerous publications appeared on oil contamination of sea water (Polikarpov *et al.*, 1991; Ahel, 1984; Miranov, 1991; Tretiyakova, 1992; Kamarov and Shimkus, 1992; Mikhailov, 1992) and sediments (Farrington and Tripp, 1977; Sellali *et al.*, 1992; Burns *et al.*, 1993; Dujmov and Sucevic, 1988). Various methods were given to determine oil pollution on them, such as UVF, HPLC, GC and GC/MS. Oil pollution is estimated by the ratios of C_{17}/pristane, C_{18}/phytane (Gearing *et al.*, 1976; Clark and Finley, 1974) and Pristane/Phytane (Tibbetts and Large, 1988; Barrick *et al.*, 1980) and Carbon Preference Index (CPI, Clark and Finley, 1974; Johansson *et al.*, 1980) and the unresolved complex mixture (UCM) signal in the GC chromatogram (Johansson *et al.*, 1980; Farrington and Tripp, 1977; Barrick *et al.*, 1980)

This paper reports the findings of oil pollution on the sea water and sediments of Istanbul Strait caused by Nassia tanker accident.

Material

Samples of sea water and sediments were collected from Istanbul Strait at the stations indicated on the map (Fig. 1) by R/V Arar on the following dates :

Survey N1 : 21-27 April 1994,
N2 : 5-11 July 1994,
N3 : 23-28 Sept. 1994.

Surface sea water was taken by usual way and deep sea water by Nansen flask. The samples were collected in 2.8 L amber glass bottles. Immediately after sampling 10 ml DCM was added and the extracted within 12 h. Sediment samples were taken with Van veen bottom sampler and top 1 cm was removed with a spatula and kept frozen in glass jars. The extraction solvents : Dichloromethane (DCM), hexane, pentane, isopropanol is HPLC grade (J.Baker). Sodium sulphate (J.Baker).

Method

1- Extraction and analysis

1.1- Sea water

Sea water sample was extracted two times with 50 ml dichloromethane (DCM) and the extracts were collected and dried with anhydrous sodium sulphate and distilled to a small volume in a rotary evaporator.

The residue was taken with hexane and the volume was adjusted to 10 ml, then applied to UVF and GC analysis. The ex/em at 310/360 nm. was read in UV Fluorospectrophotometer (Hitachi 650 10 S) and amount of oil was calculated on PAH_s by using the calibration curve plotted with Nassia crude oil (Fig.2)

1.2- Sediment

100 g sediment sample was extracted with 100 ml DCM in the first survey and 100 ml isopropanol : hexane mixture (80:20) in the second and third surveys. DCM or isopropanol : hexane extracts were distilled in a rotary evaporator and the residues were taken with hexane. The volume was adjusted to 10 ml and on part was applied on UV for

oil determination. The other part was hydrolysed by potassium hydroxide solution in alcohol for 12 h.. It was extracted with pentane and the extract was applied to silica gel column (dried silica gel 8 g. in 2x25 cm column). The elution was made with pentane for aliphatic fractions and with DCM for aromatic fractions. Both eluats were applied to GC. Only aliphatic fraction results are given in this work.

Gas liquid chromatography;
Instrument : Perkin Elmer 8420 Capillary GC
Data handling : Perkin Elmer GP-100 graphics printer
Column : 25 mx0.33 m i.d. QC_3/BP
Temperature programme : 40° C at 5 min, 40°-200°C at 8°C/min, 200°C at 5 min, 200°-280°C at 8°C / min.
Detector : FID at 340°C
Injector : Splitless at 320°C
Carrier gas : N_2

2- Estimation of oil pollution

Oil pollution was estimated by using C_{17}/pristane and C_{18} phytane ratio (Clark and Finley, 1974; Gearing *et.al.*, 1976), Carbon Preference Index (CPI) (Clark and Finley, 1974; Barrick *et al.*, 1980; Johansson *et al.*, 1980) calculated from 2(n C_{27}+nC_{29}) / n C_{26} + 2n C_{28} + nC_{30} and unresolved complex mixture as observed on the GC chromatogram. (UCM) (Farrington *et al.*, 1977).

Results and Discussion

The oil amounts found in the sea water samples are shown in Table 1. The highest value in surface water was found at the station B_1 followed by B_2 in the first survey; in thermocline water K_1 station followed by B_1, in bottom water B_3 station gave the highest contamination.

Concentration of petroleum hydrocarbons varied widely in the investigations carried out, e.g. 0.1-38.6 µg/L in Rijeka Bay (Yugoslavia) (Ahel, 1984), 130 µg/L in Novorossiysk-Galendzhik area (Eastern Black Sea) (Komarov and Shimkus, 1992) and 0.4-5.6 µg/L in North Eastern Mediterrenaen Sea (Saydam *et al.*, 1984), 400 ng/L (Erhardt and Patrick, 1988) in sediments 3.57-14.35 µg/g Eastern Adriatic (Dujmov and Sucevic, 1988), 1.8-28.8 µg/g in Algeria (Sellali *et al.*, 1992), 13-540 µg/g in Gulf in Saudi Arabia (Burns *et al.*, 1993), 22-50 µg/g in Kerchensky Strait (Tretiyakova, 1992).

Our findings when compared with these values, indicated that Istanbul Strait was polluted with petroleum more than the other areas as a result of Nassia accident.

The contamination decreased as the time elapsed because of the highly dynamic nature of water movement and mixing in the strait.

Table 1. UVF Results of sea water samples (μg/L)

Station	Surface			Thermocline			Bottom		
	N 1	N 2	N 3	N 1	N 2	N 3	N 1	N 2	N 3
K1	12.1	2.1	0.7	56.5	1.1	0.7	2.3	1.3	1.6
B1	24.9	9.8	1.3	-	-	-	1.3	2.3	1.5
B2	18.6	2.2	0.4	28.6	2.0	0.5	22.0	4.3	0.4
B3	12.3	3.2	0.6	-	-	-	34.0	1.5	0.7

Pr/Ph ratio and CPI values are shown in Table 2. The selected gas chromatograms of sea water samples are shown in Fig. 3-17. Pr/Ph ratios and CPI values obtained from the sea water samples proved oil contamination.

Table 2 : Pr/Ph ratio and CPI value of sea water samples.

Sample	Pr/Ph	CPI
K1N1S	0.47	1.09
K1N2S	*	**
K1N3S	*	**
B2N1S	*	**
B2N3S	*	**
K1N1T	*	0.89
K1N3T	0.59	1.45
B2N1T	*	0.74
B2N2T	*	**
B2N3T	*	0.77
K1N1B	0.65	0.81
K1N2B	0.35	0.88
K1N3B	*	**
B2N2B	0.66	**
B2N3B	*	**

N : Survey number, S: Surface, T: Thermocline, B:Bottom

* : The peak of pristane / phytane was not detected on chromatogram and thus the ratio is omitted

** : In the first survey $c_{26\text{-}30}$ were detected in sea water samples. In the second and third surveys not. In surface, thermocline and bottom waters $C_{26\text{-}30}$ were not detected hence CPI value could not be calculated.

2- Sediment

The UVF results on sediment samples are shown in Table 3. The level of the oil pollution is lower in the first survey than in the second and third surveys at both stations; the difference being due to the use of different extraction solvent.

In sediment the highest value was found at the station; B_3 in first survey and B_2 and B_3 in third survey.

The selected gas chromatograms of aliphatic fractions of sediments taken from station K_1 and B_2 are shown in Fig.18-23 and for Nassia cargo reference (Aliphatic fraction) in Fig. 24.

The doubled peak shape of the maturity markers, pristane and phytane are clearly discernible in all sediment chromatograms except B2N3. Detection of the maturity markers demostrated the presence of petrogenic oil contamination in these extracts (Gassmann, 1982). The chromatogram of Nassia Cargo oil supports this conclution.

Pr/Ph ratio and CPI value obtained in gas chromatogram are shown in Table 2.

The values of C17/pristane, C18/phytane ratios and CPI (Carbon Preference Index) are low in most chromatograms, an indication of petroleum input to these sediments (Gearing *et al.*, 1976; Farrington *et al.*, 1077; Johansson *et al.*, 1980). In addition, the unresolved complex mixture (UCM) signal in the chromatogram indicating petroleum hydrocarbons was detected in all sediment samples as indicated by Farrington et.al., 1977. The chromatograms of K1N1, B2N1 and B2N2 also show fresh petrogenic input, which is interpreted as coming from Nassia crude oil.

Table 3. UVF results of sediment samples (µg/g - dry weight)

Station	N1	N2	N3
K1	28	48	110
B1	-	100	125
B2	100	250	270
B3	130	170	260

Table 4 : Aliphatic hydrocarbons from sediments

Sample	C17/Pr	C18/Ph	Pr/Ph	CPI
K1N1	1.17	0.86	0.48	0.80
K1N2	-	0.82	0.93	-
K1N3	-	1.28	-	0.34
B2N1	1.14	1.01	0.81	0.50
B2N2	1.04	0.93	0.73	0.49
B2N3	-	-	-	0.89

Pr : Pristane, Ph : Phytane
CPI : Carbon Preference Index
2 (nC27+nC29)/nC26+2nC28+nC30
CPI and ratios of C17/Pr, C18/Ph and Pr/Ph determined from corrected peak areas of gas chromatograms.
K_1 : Karaburun, B_2 : Altınkum, N : Survey number

On the contrary the finding of sea water, the contamination on sediments increased with time due to the sedimention of oil particules.

GC analysis based on proved contamination by fresh crude oil spealed by Nassia Tanker.

Hydrocarbon in sea water originated exogeneously due to tanker accidents, ballasting, flushing of from refinery plants, polluted rivers or biogeneously as marine organisms such as plankton, algae and fish. Various methods were used to seek the origins of hydrocarbon such as the ratios Pr/Ph, C_{17}/Pr and C_{18}/Ph, C_{13}/C_{12}, ALK/ISO, 17α(H)-hopane / 17 β (H)-moretane, 17 α(H) hopane / 17 β (H)-trisnor hopane, P/B, and CPI value, and UCM humps. In this work C_{17}/Pr and C_{18}/Ph, Pr/Ph ratios and CPI value and UCM signal were used to distinguish the origins of hydrocarbon. It was proved that the contamination originated from Nassia accident.

Fig. 1. The sampling stations in the Istanbul Strait K1 : Karaburun, B1 : Poyraz, B2 : Altınkum, B3:Beykoz.

x : Rumeli feneri çakarı.

K1 : To where Nassia tanker has been pulled after the accident.

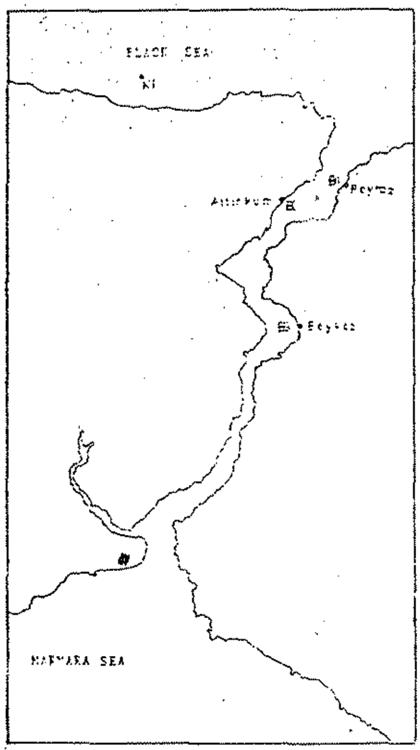


Fig. 2. The UVF standard calibration curve of Nassia crude oil.

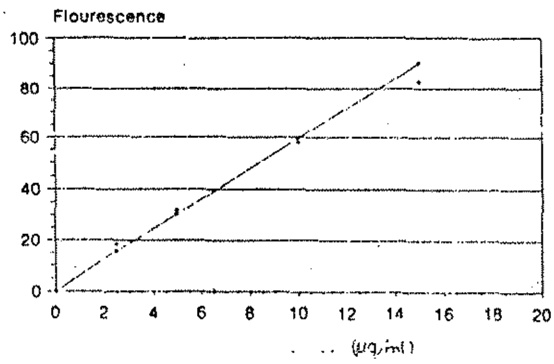


Fig. 3-17. Gas chromatogram of sea water samples taken from station K_1 and B_2

K_1 : Karaburun, B_2 : Altınkum, N : Survey number

Fig. 3. K1N1S

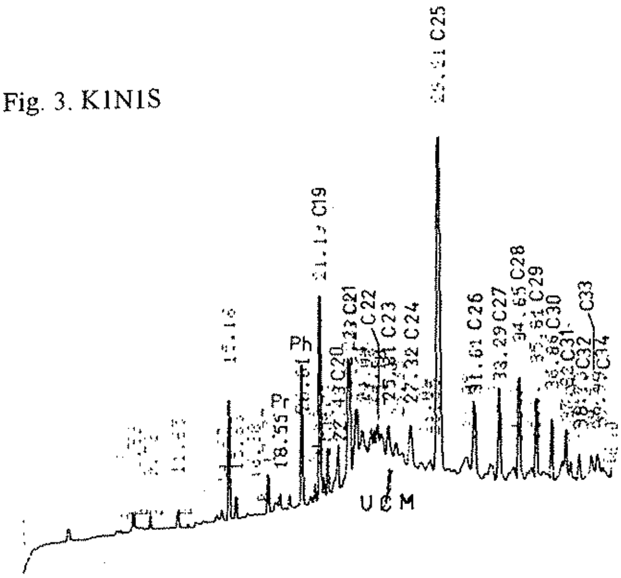


Fig. 4. K1N2S

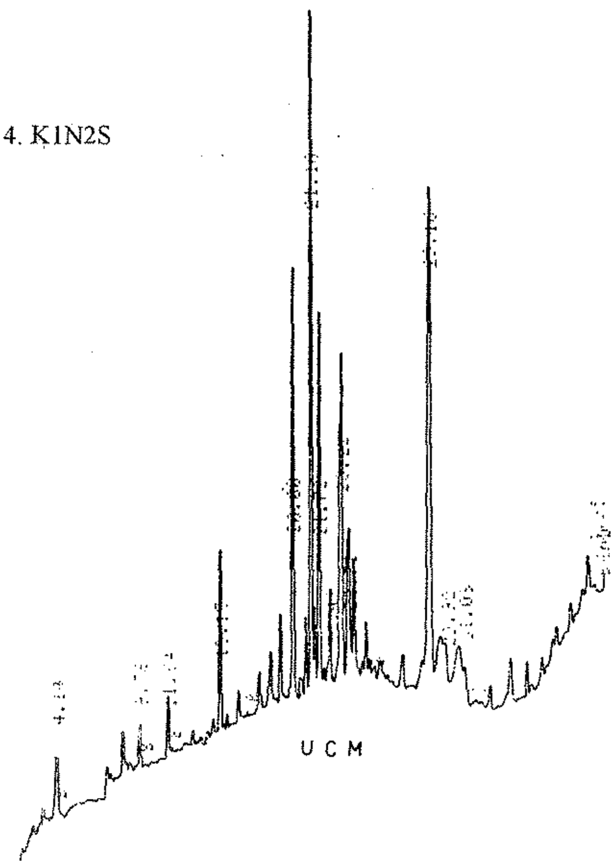


Fig. 5. K1N3S

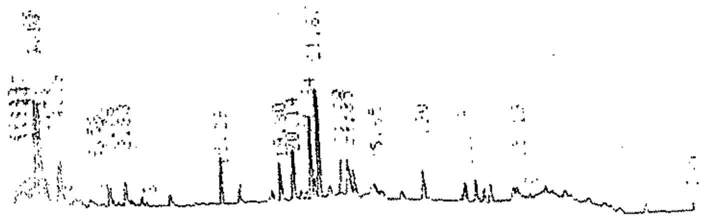


Fig. 6. B2N1S

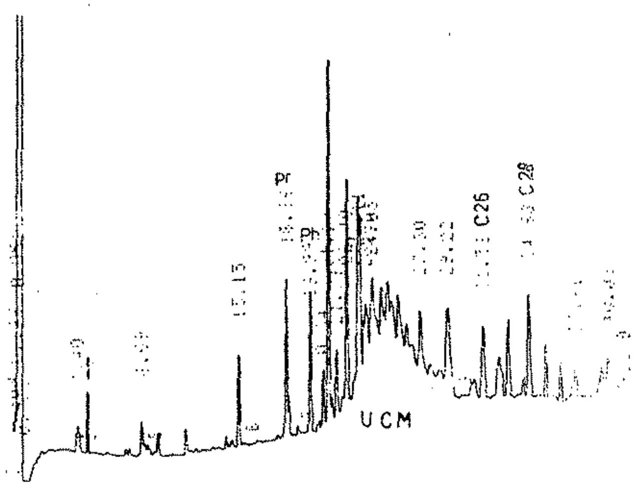


Fig. 7. B2N3S

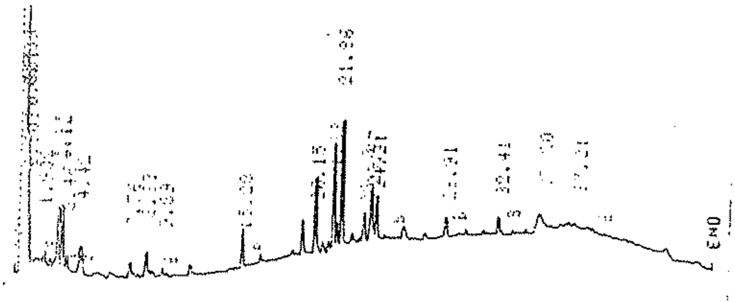


Fig. 8. K1N1T

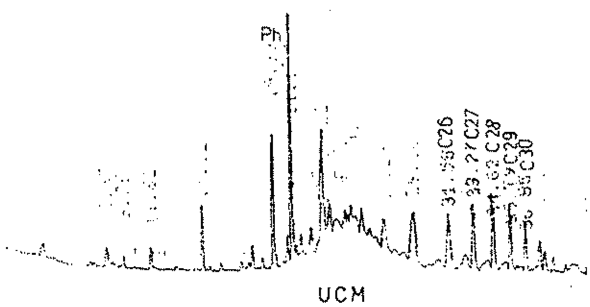


Fig. 9. K1N3T

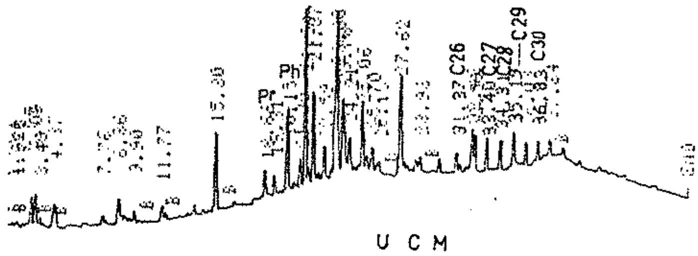


Fig. 10. B2N1T

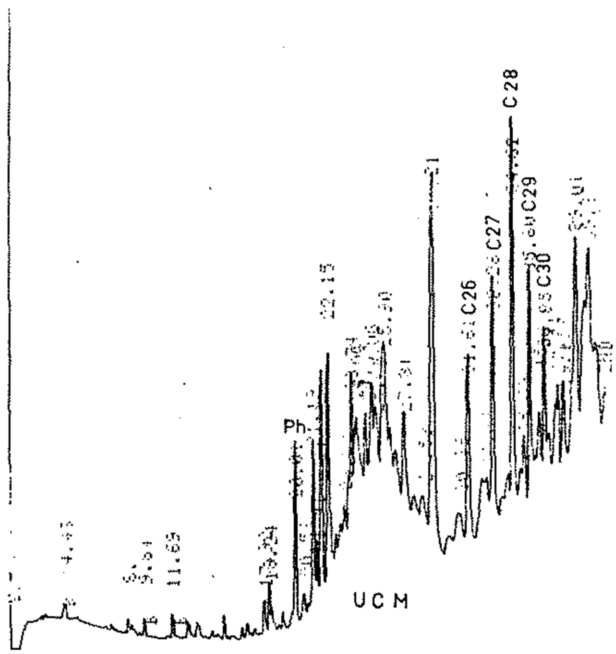


Fig. 11. B2N2T

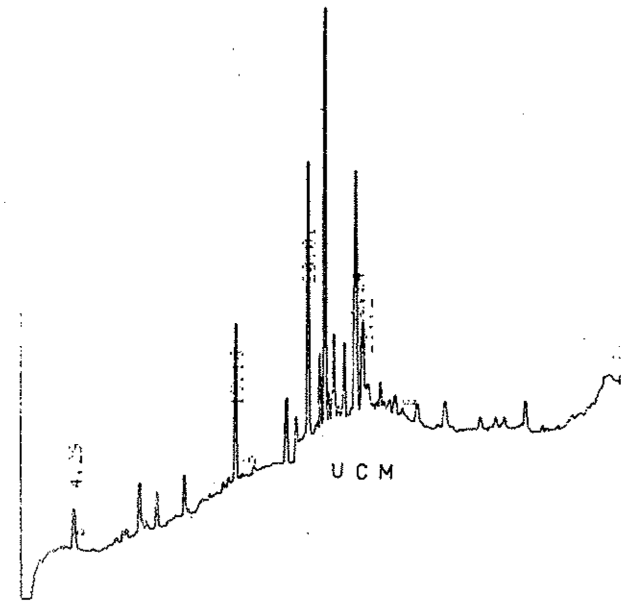


Fig. 12. B2N3T

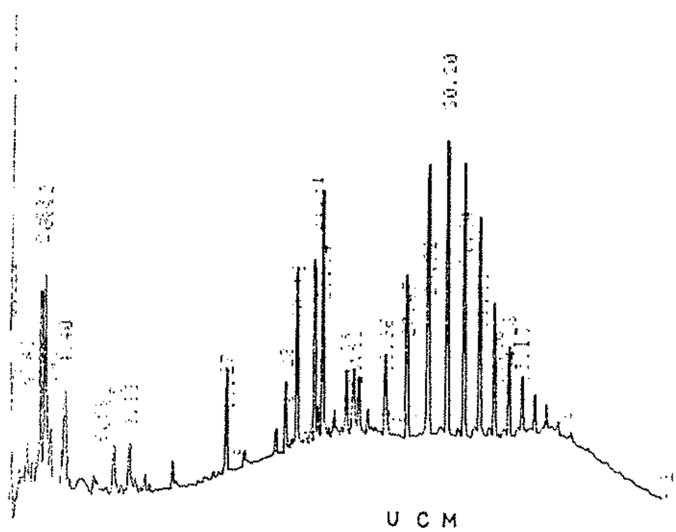


Fig. 13. K1N1B

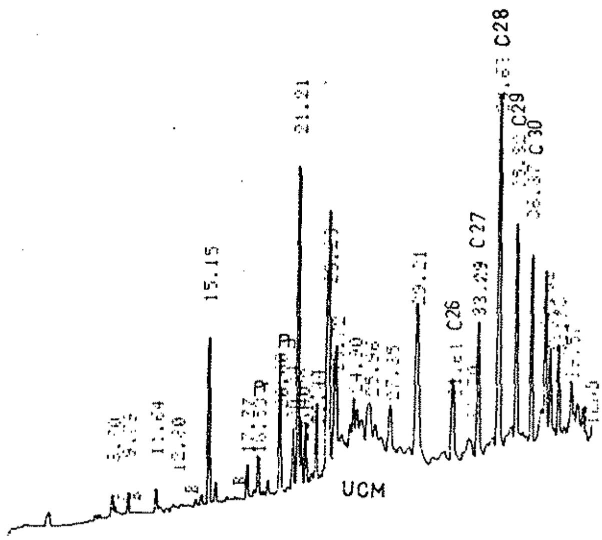


Fig. 14. K1N2B

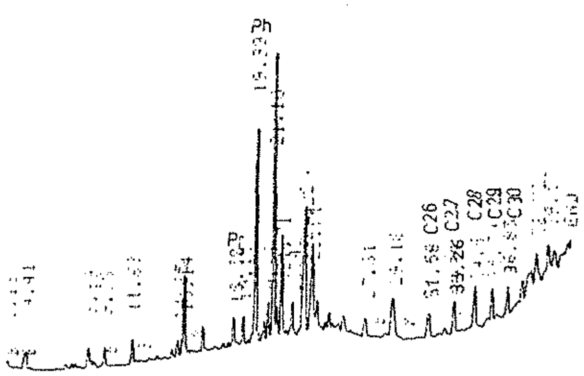


Fig. 15. K1N3B

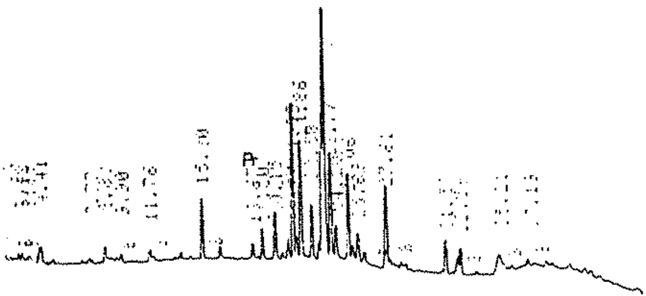


Fig. 16. B2N2B

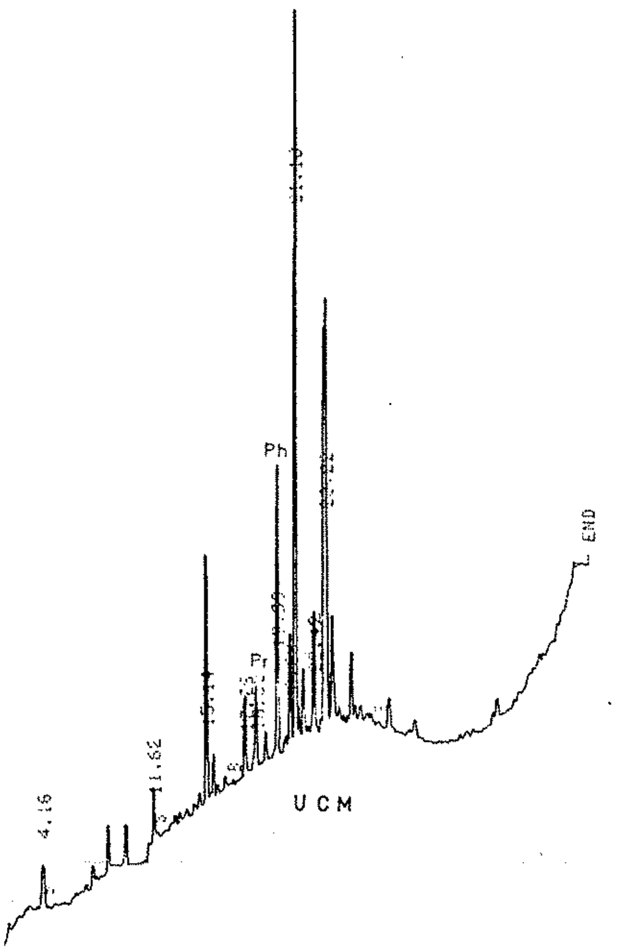


Fig. 17. B2N3B

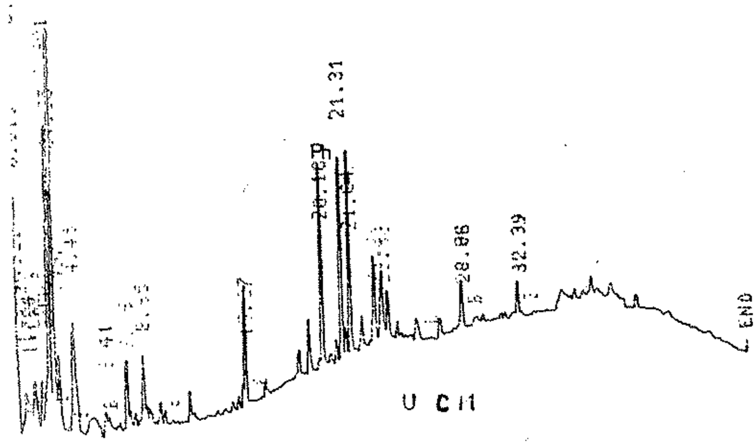


Fig. 18-23. Gas chromatogram of sediments taken from, K_1 and B_2 stations.

K_1 : Karaburun, B_2 : Altınkum, S : Survey number

Fig. 18. K1N1

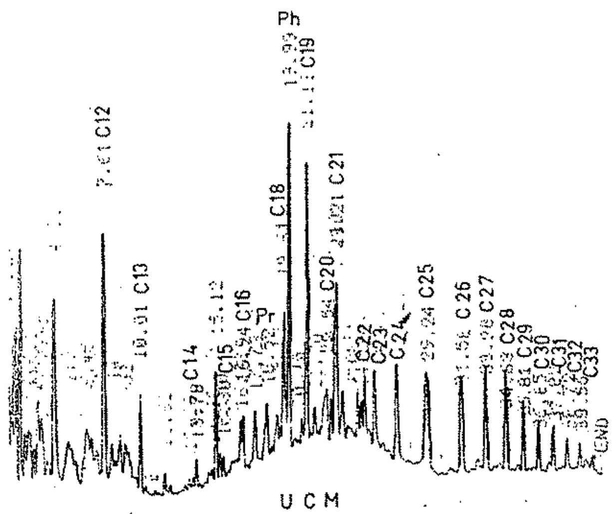


Fig. 19. K1N2

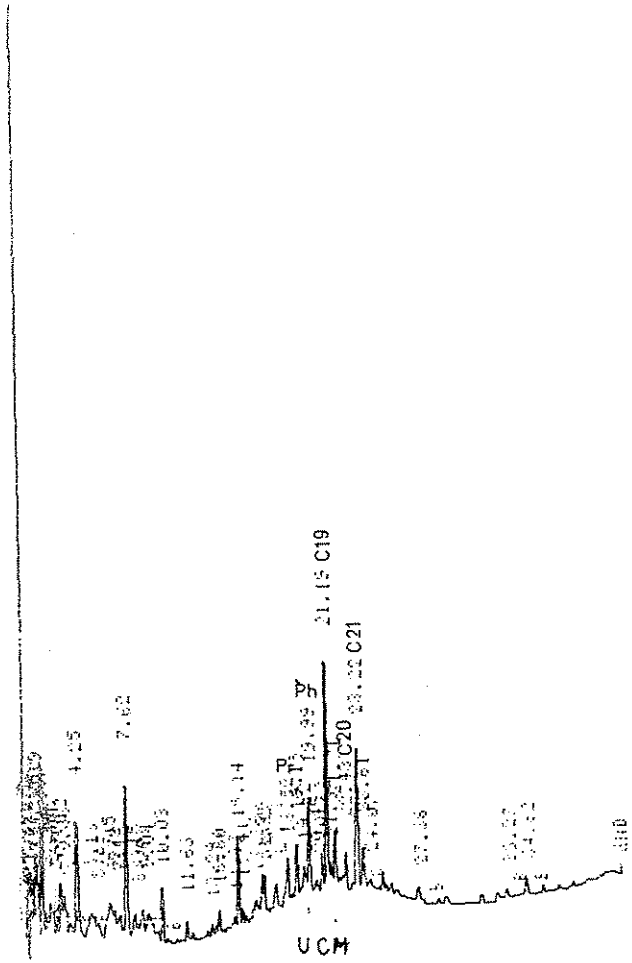


Fig. 20. K1N3

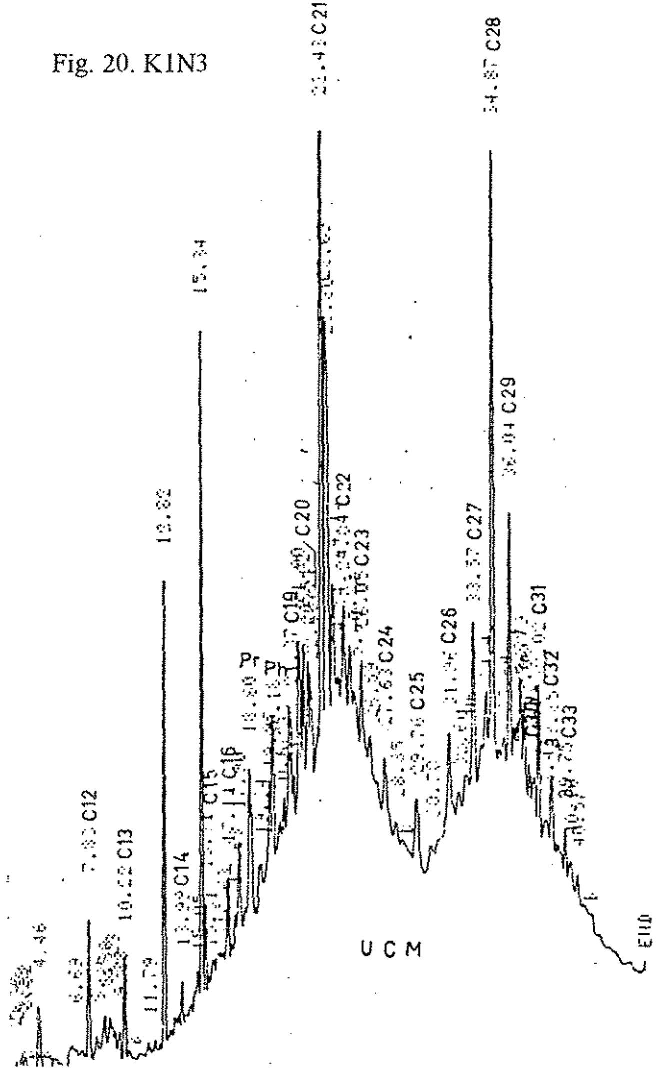


Fig. 21. B2N1

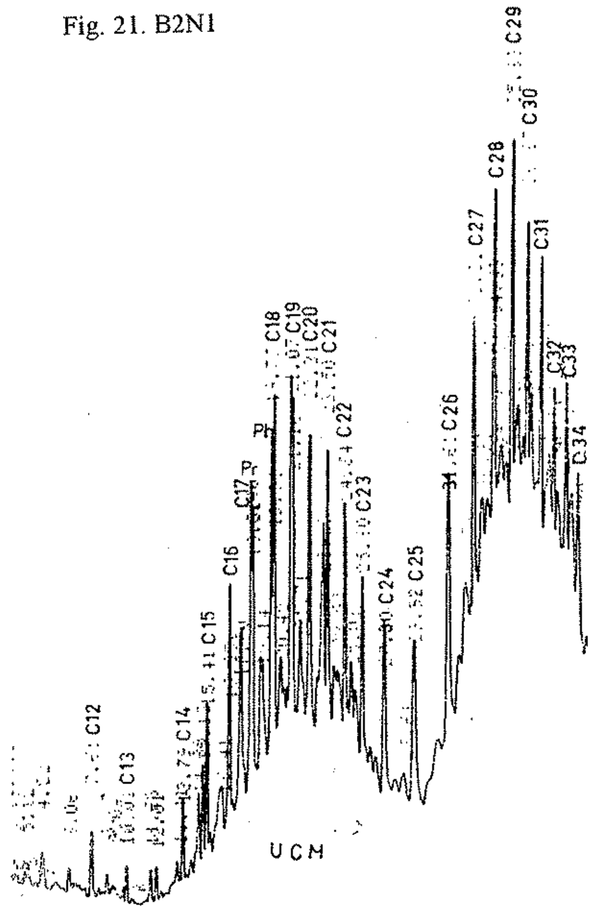


Fig. 22. B2N2

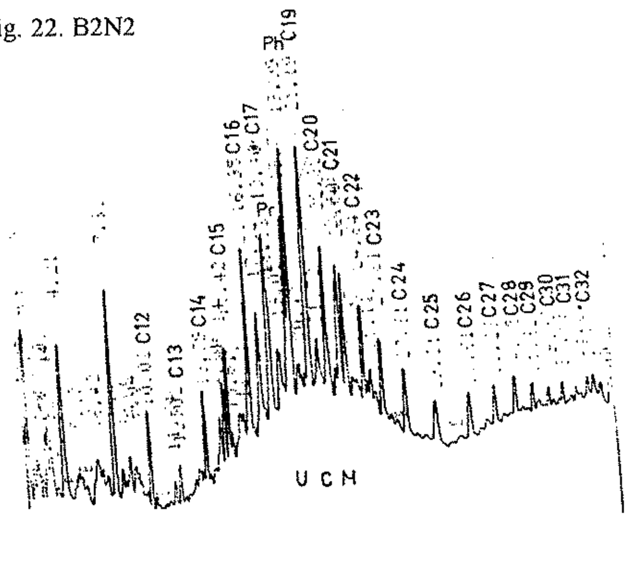


Fig. 23. B2N3

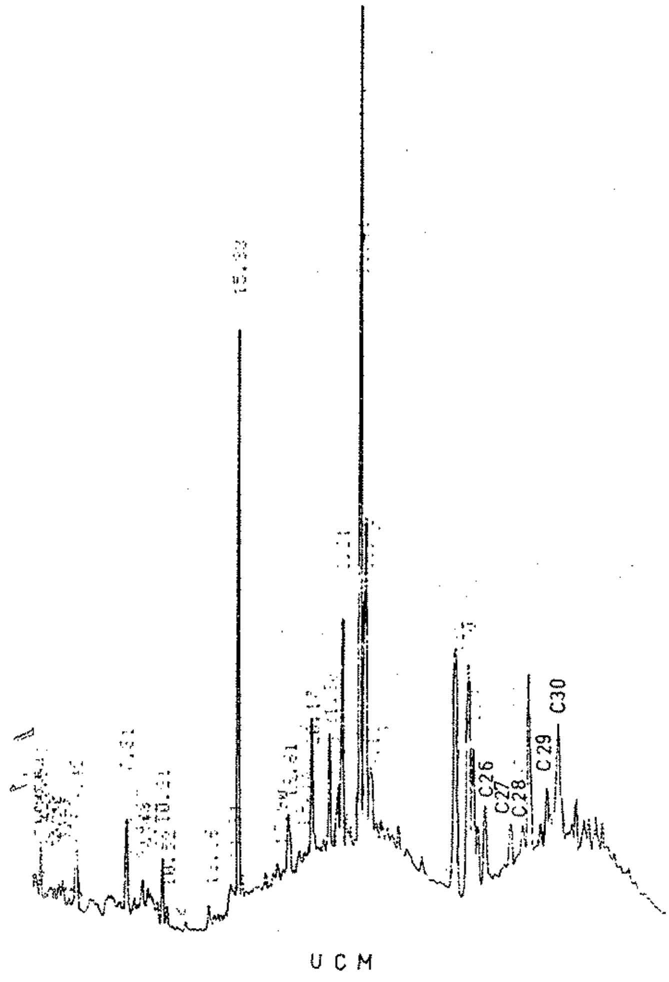
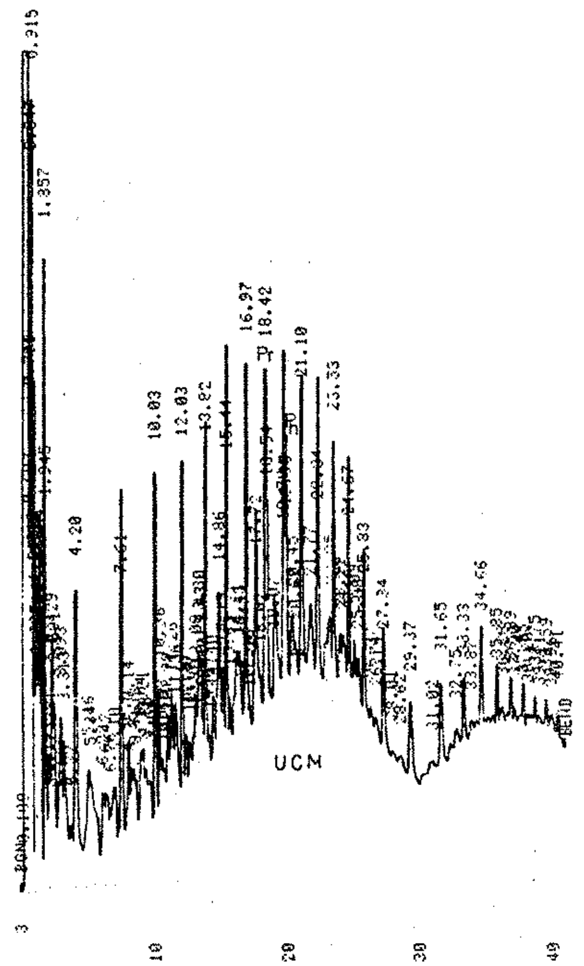


Fig. 24. NASSIA cargo reference (Aliphatic Fraction)



Özet

İstanbul Boğazında 13 Mart 1994 tarihinde meydana gelen Nassia tanker kazası ile İstanbul Boğazı ve dolayısı ile Marmara Denizi petrol ile kirlenmiştir. Bu petrol kirliliğinin araştırılması bütünü ile enstitümüzde yapılmıştır. Buna ait ilk yayınımızda İstanbul Boğazı'ndaki midyeler ele alınmış ve bunların petrol ile kontaminasyonu bildirilmiştir. Bu yayında UVF ve GC analizi ile İstanbul Boğazı deniz suyu ve sedimentinde petrol kirliliği sonuçları verilmiştir. Bu kirliliğin Nassia tanker kazasına bağlı olduğunu ispatlamak için C_{17}/Pr ve C_{18}/Ph, Pr/Ph oranları ile CPI değerleri ve ayrıca UCM sinyalleri esas alınmıştır. Bu bulgular sonunda İstanbul Boğazı'ndaki kirliliğin Nassia tanker kazasına bağlı olduğu saptanmıştır.

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