

## ***OIL POLLUTION OF IZMIT BAY***

### ***İZMİT KÖRFEZİNİN PETROL KİRLİLİĞİ***

KASIM C. GÜVEN, HÜLYA GÜNDAY, ERDOĞAN OKUŞ, SELMA ÜNLÜ,  
ERTUĞRUL DOĞAN, TUNCAY GEZGİN, SELMİN BURAK

Institute of Marine Sciences and Management, University of Istanbul, 34470  
Vefa, Istanbul, Turkey

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#### **Abstract**

The oil pollution was investigated at two stations in the Izmit Bay. The oil pollution varied between 12.74 - 383.44 µg/L at station 1 and 32.01-986.53 µg/L at station 2 . The findings are evaluated on the bases of crude oils of differing origins. Hence the results depended on the oil taken as the standard. The oil pollution in the Izmit Bay was found high.

#### **Introduction**

The Izmit Bay is located at the eastern edge of the Sea of Marmara, having a length of 26.8 miles. It is separated into three distinct regions as western, central and eastern and the depth at these regions are 200 m, 180 m and 35 m respectively. It has two layer, the upper layer is the Black Sea water and the lower layer is Mediterranean seawater.

The coastal areas of the Izmit Bay have high population density and various industrial plants such as cellulose and paper, chlore-alkali, sulfuric acid, antibiotics, metals, rubber, ammonia, pesticides, detergents, formaldehyde, dyes, solvents, polivinyl and dung.

The total oil imported to the Izmit refinery is 10 million t/a. A movement of 3600 tanker/a occur for oil transportation. Thus shipping activities related to tankers have also been a pollution source of petroleum hydrocarbons in the Izmit Bay seawater. So far, there has been no study carried out concerning oil pollution in the Izmit Bay.

In this study the oil pollution was measured in two stations of the Izmit Bay between 4.Nov.1994 - 2.Dec.1995.

### Material and Methods

The surface water sample was taken at 2 stations in the Izmit Bay (Figure 1). The sampling date in 1994 and 1995 are shown in Table 2.

Seawater samples were collected from surface in 2.8 L amber glass bottles which had previously been washed with dichloromethane (DCM) and 15 ml of DCM was added for preservation of the sample.

The samples were extracted three times with 50 ml DCM according to Ehrhardt *et al.*,(1993).The extracts were combined and then dried over anhydrous sodium sulphate, filtered and distilled in a rotary evaporator. The residue was redissolved in hexane and the volume adjusted to 10 ml and then subjected to UVF and GC/MS analyses.

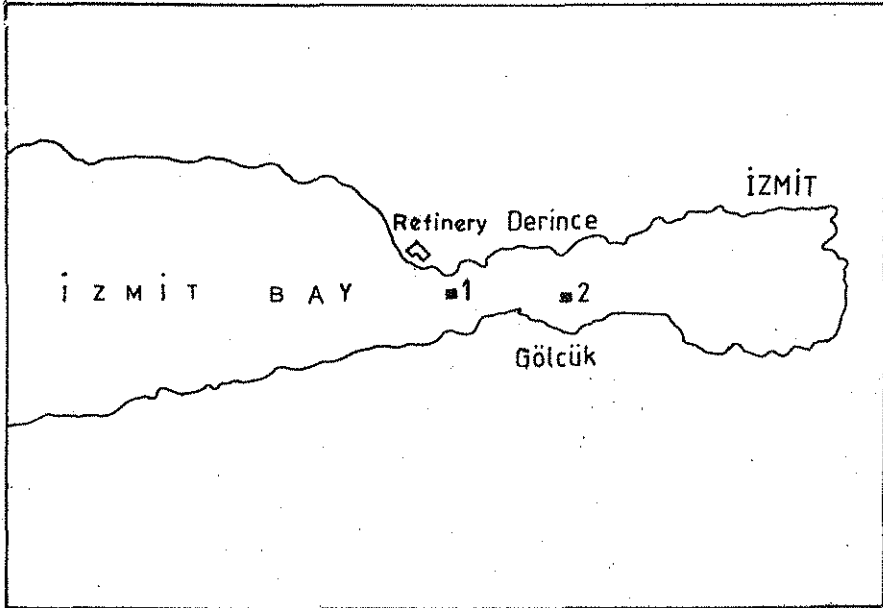


Figure 1. Sampling stations in Izmit Bay

Oil pollution in the samples was measured by UVF (Fluorospectrophotometer, Shimadzu RF-1501). The calibration curve was plotted by using crude oil of S. Arabia (Lihit) and also of Egypt, Libya, Syria, Russia and Persia. The concentrations of oil used were 0.25, 0.50, 1.00, 1.50 µg/ml in hexane. The absorption was measured at 310/360 nm (ex/em) (Ehrhardt and Burns, 1993). All the samples were taken from the Izmit refinery.

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: 50m x 0.20 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.

The methods used for the estimation of petrogenic input in the samples were: Pr/Ph, C<sub>17</sub>/Pr and C<sub>18</sub>/Ph 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) observation on the GC chromatograms (Farrington and Tripp, 1977; Johansson *et al.*, 1980; Barrick and Hedges, 1981).

## Result and Discussion

The equations of calibration curves of tested crude oils are shown in Table 1. The mean average of oil pollution in Izmit Bay calculated from the tested oils and also from Arabia oil are shown in Table 2. The findings demonstrated that the polluting oil amount varied depending on the crude oils for plotting calibration curve.

The oil amount found in this bay varied between 12.74-383.44 µg/L in station 1 and 32.01-986.53 µg/L in station 2. The highest oil pollution was found in the station 2 for 30/4/1995. The concentration of petroleum hydrocarbon in the Izmit Bay surface water was generally high and it was not uniform. Figure 3 shows the graphical representation of oil pollution in stations 1 and 2. The selected GC/MS chromatograms and spectra are shown in Figure 2-3.

The predominant component in the aliphatic components varies from one sampling area to another. The major n- alkan C<sub>17</sub>-C<sub>27</sub> is detected in all chromatograms. Meanwhile nonane, decane, undecane, dodecane that have low boiling point and evaporate within a few hours especially in windy conditions were also detected. These findings show the fresh oil pollution in this area.

Table 1. The equations of standard curves of tested oils.

The oil tested	Equation curve: $F1=KxC+B$
Arabia	$F1=618.49xC+41.867$ $r^2=0.99$
Egypt	$F1=693.12xC+30.265$ $r^2=1$
Libya	$F1=611.11xC+33.669$ $r^2=0.99$
Syria	$F1=505.87xC+46.145$ $r^2=0.99$
Russia	$F1=662.49xC-0.2596$ $r^2=1$
Persia	$F1=505.30xC+30.631$ $r^2=0.99$

Pristane (Pr) and Phytane (Ph) are detected in the chromatogram of the station 2 on 7.3.1995 and station 1 on 28.5.1995 (Figures 2-3). The ratio of Pr/Ph, C17/Pr, C18/Ph and CPI values are shown in Table 3. Pristane is present in marine organisms but phytane is anthropogenic origin. It is found that the Pr/Ph ratio is lower than one. This ratio is an indicator showing that there is a fresh input of oil and it also indicates whether this pollution is generated by exogenic or anthropogenic sources.

The ratio of C27 and C29 n-alkanes to the 26, 28 and 30 carbon n-alkanes as calculated according to the formula given above shows a clear odd carbon predominance for all the stations. The mean CPI value is lower than one for all the sea water samples analysed. This indicates that the pollution is due to petroleum hydrocarbon.

n-C17/Pr and n-C18/Ph indicate the relative rate of biodegradation of n-alkane. The findings varied according to tested stations (Table 3).

Table 2. The results of oil pollution in Izmit Bay.

Sampling	Station 1		Station 2	
	Mean value of tested crude oils* ( $\mu\text{g/L}$ )	S.Arabia crude oil ( $\mu\text{g/L}$ )	Mean value of tested crude oils* ( $\mu\text{g/L}$ )	S.Arabia crude oil ( $\mu\text{g/L}$ )
4/11/1994	12.74 $\pm$ 1.49	11.33	856.70 $\pm$ 86.82	781.57
28/12/1994	237.24 $\pm$ 30.32	217.21	86.63 $\pm$ 11.81	80.52
29/01/1995	174.34 $\pm$ 21.39	157.67	427.20 $\pm$ 58.17	396.92
7/03/1995	238.74 $\pm$ 30.52	209.17	703.59 $\pm$ 86.40	636.71
2/04/1995	68.20 $\pm$ 8.87	57.25	246.02 $\pm$ 33.88	203.71
30/04/1995	364.60 $\pm$ 48.90	337.71	986.53 $\pm$ 126.64	904.28
28/05/1995	348.56 $\pm$ 46.60	322.53	262.68 $\pm$ 33.92	241.28
9/07/1995	343.53 $\pm$ 45.80	317.78	78.69 $\pm$ 9.89	64.78
2/08/1995	251.88 $\pm$ 32.40	231.03	32.01 $\pm$ 3.88	28.84
9/09/1995	228.76 $\pm$ 29.08	209.17	32.81 $\pm$ 3.98	29.59
30/09/1995	133.63 $\pm$ 15.90	119.17	33.15 $\pm$ 8.08	29.92
29/10/1995	337.97 $\pm$ 45.02	312.50	282.13 $\pm$ 36.83	259.67
2/12/1995	383.44 $\pm$ 51.71	355.53	137.52 $\pm$ 16.40	122.85

\*:Crude oil from Egypt, Libya, Persia, Russia and Syria \*\*

\*\* : The highest value was obtained by Persian crude oil as 1138.71. $\mu\text{g/L}$ .

Table 3. Pr/Ph ratio, and CPI values and C17/Pr, C18/Ph of surface water samples in Izmit Bay.

Station	Pr/Ph	CPI	C17/Pr	C18/Ph
1*	0.73	0.62	1.32	1.31
2**	0.49	1.20	1.55	1.34

Pr:Pristane, Ph: Phytane

CPI: Carbon Preference Index

1\*: The surface water sample taken from Station 1, sampling data (28/05/1995)

2\*\*: The surface water sample taken from Station 2, sampling data (7/03/1995)

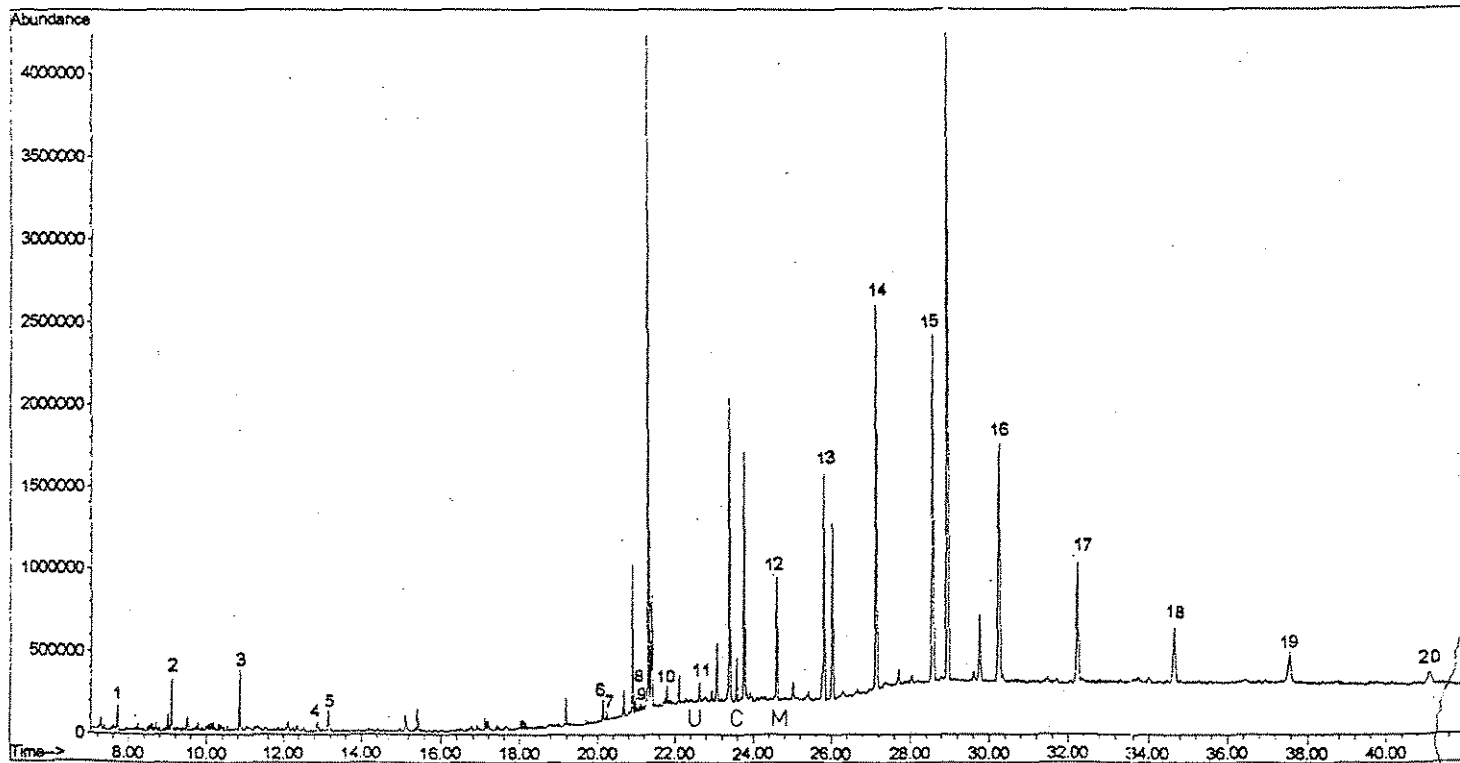


Figure 2. GC/MS chromatogram of surface water sample taken from station 1 (28/05/1995):  
 1. Nonane, 2. Decane, 3. Undecane, 4. Naphthalen, 5. Dodecane, 6. Heptadecane (C17),  
 7. Pristane, 8. Octadecane 9. Phytane, 10. Nonadecane, 11. Eicosane (C20), 12. Docasane (C22),  
 13. Tricosane (C23), 14. Tetracosane (C24), 15. Pentacosane (C25), 16. Hexacosane (C26),  
 17. Heptacosane (C27), 18. Octacosane (C28), 19. Nonacosane (C29), 20. Triacontane (C30).

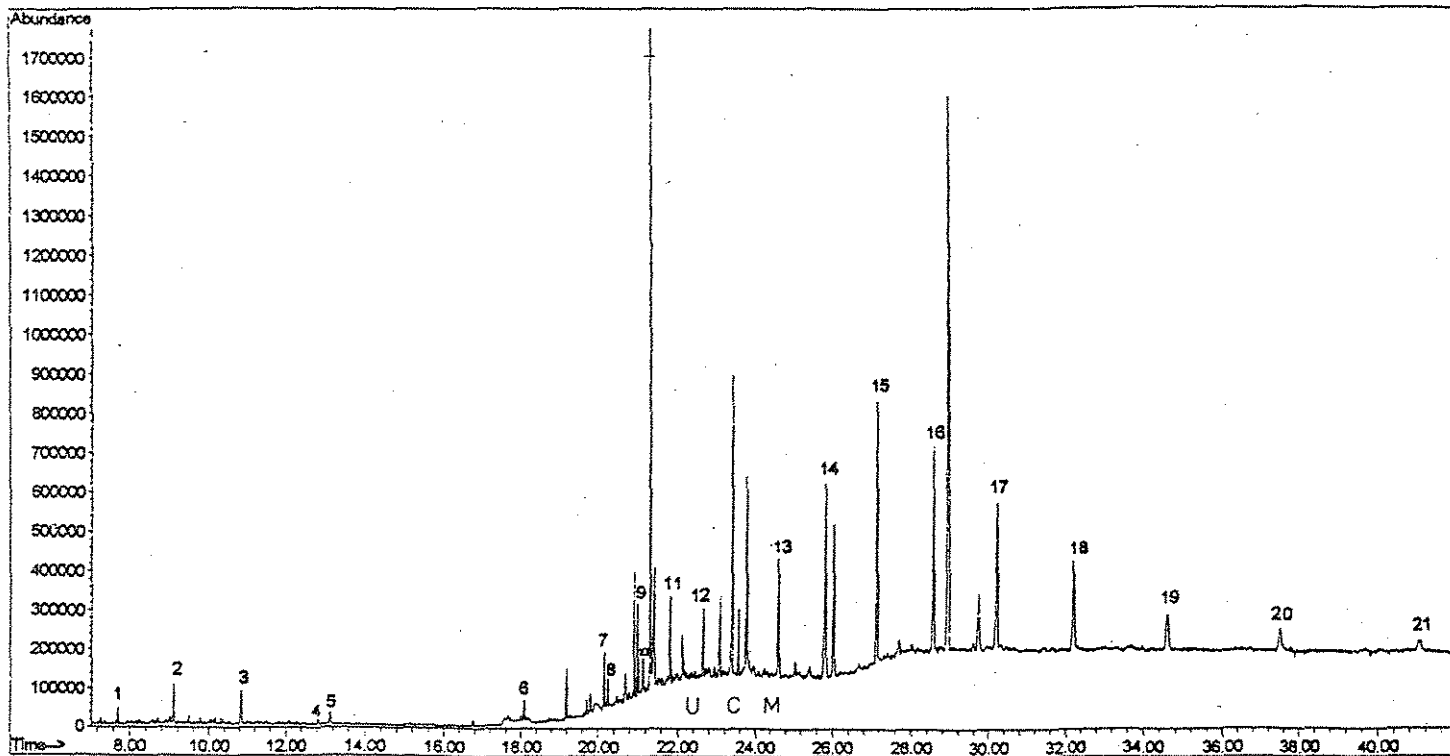


Figure 3. GC/MS chromatogram of surface water sample taken from station 2 (7/03/1995).  
 1. Nonane, 2. Decane, 3. Undecane, 4. Naphthalen, 5. Dodecane, 6. Phenol 2,4,6 tris (1,1 di metil)  
 7. Heptadecane (C17), 8. Pristane, 9. Octadecane, 10. Phytane, 11. Nonadecane, 12. Eicosane  
 (C20) 13. Docasane (C22), 14. Tricosane (C23), 15. Tetracosane (C24), 16. Pentacosane (C25)  
 17. Hexacosane (C26) 18. Heptacosane (C27), 19. Octacosane (C28), 20. Nonacosane (C29),  
 21. Triacontane (C30).

Figure 4 shows the comparison of oil pollution in surface waters at station 1 and station 2 .

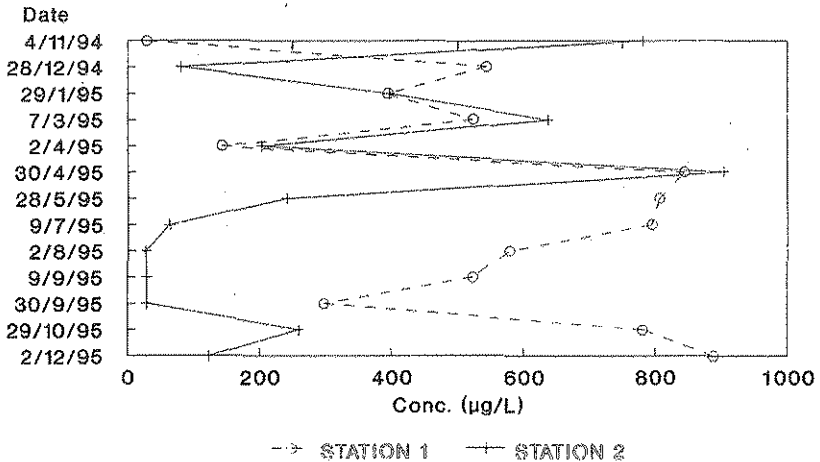


Figure 4. The comparison of oil pollution in surface waters at station 1 and station 2 .

Unresolved complex mixture (UCM) was observed in all chromatograms. The importance of the UCM signal clearly indicates the presence of oil pollution. Thus the Pr/Ph ratio and UCM findings are indicated a predominantly anthropogenic origin of oil.

On the otherhand the aromatic component such as naphthalene was found in all stations.

The comparison of oil concentration in seawaters of different bay as Varna Bay 0.26 mg/L (Bojkova, 1992) and sea water of the Black Sea coast Novorossiysk-Gelendzhik 0.13 mg/L (Komorov and Shimkus ,1992), Sevastapol 540 mcg/L, Yalta 180 mcg/L Alusta 50 mcg/L (Polikarpov *et al.*, 1991), showed that the oil pollution in the Izmit Bay is the highest.



The influence of meteorological conditions and sampling time also played an important role on oil pollution. It should be mentioned that petroleum hydrocarbon load in the Izmit Bay is not uniform in time and space. The prevailing wind in this area (NE) brought a rapid dispersion of pollutants through the Izmit Bay towards the Marmara sea .

It is clear that the sources of petroleum hydrocarbon pollution in Izmit Bay are the refinery, industrial discharges and ship traffic.

On the other hand, the largest peaks concerning the dibutyl phtalate, dioctyl phtalate and diethylhexyl phtalate are observed in all the chromatograms.

When these findings are compared to those of the Bosphorus, the Sea of Marmara and Dardanelles (Güven *et al.*,1996; Okuş, *et al.*,1996) it is clear that the oil pollution is higher in the Izmit Bay.

#### Özet:

Bu çalışmada İzmit Körfezinde alınan yüzey suyunda petrol kirliliği iki istasyonda araştırılmıştır. Bu kirliliğin miktarı 1.istasyon da 12.74-383.44µg/L, 2.istasyonda 32.01-986.53 µg/L arasında bulunmuştur. Ayrıca Petrol kirliliğinin tayininde standart eğri çizimi için kullanılan ham petrole göre denizde ölçülen petrol kirliliğinin farklılık gösterdiği tespit edilmiştir. Bu çalışma sonunda İzmit Körfezinde ölçülen petrol kirliliğinin diğer ülkelerin körfezleri ve deniz sularındaki petrol kirliliğinden fazla olduğu saptanmıştır.

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