

**Oil Pollution of Eastern Mediterranean Sea,
South of Turkey**

**Türkiye' nin Doğu Akdeniz kıyılarında
Petrol Kirliliği**

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Abstract

In our earlier work oil pollution of east Turkish Mediterranean area was determined before and after service of Iraq –Yumurtalık export pipeline in 1997. In this paper oil pollution amount is given in the same area in 1999. The highest pollution was found as 2690 µg/L at Botaş and 629.60 µg/L at Mersin. The determination was made by using Iraqi and Iranian crude oils as reference material. The oil amount was found lower when chrysene was used as a reference. The low amount of oil pollution measured by earlier workers in the same area can be attributed to this fact. The use of polluting crude oil as reference material gives reliable results to determine oil pollution.

Keywords: Oil pollution, eastern Mediterranean Sea, crude oil, chrysene

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Introduction

Oil pollution is an important problem of seawater. This subject is discussed for the vicinity of Ataş refinery in Mersin in 1995 and 1996 (Güven *et al.*, 1998).

The oil pollution had also been investigated earlier by various authors in Eastern Mediterranean area in 1982 and 1983 by Sakarya (1985), in 1983 by Saydam and Salihoğlu (1984), in 1987 by Ehrhardt and Petrick (1989), in 1989 by Yılmaz *et al.*, (1991), in 1990-1996 by Yılmaz *et al.*, (1998) and in 1985-1986 and 1995-1996 by Yılmaz *et al.*, (1998).

These authors (except Ehrhardt and Petrick, 1989) used chrysene and found lower values for oil pollution. Güven *et al.*, (1998) used crude oil as reference material. The results differed widely depending on the reference materials.

In this work the oil pollution was investigated in the east Mediterranean area in 1999 by using crude oils and chrysene as both references and the results were compared with those obtained by using chrysene.

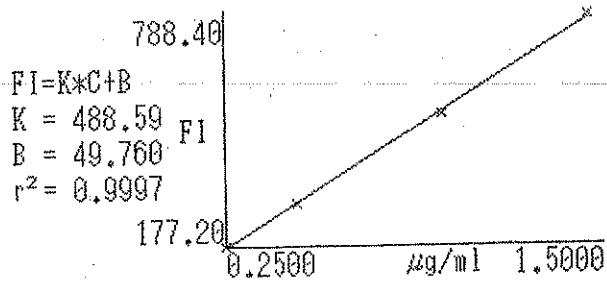
Materials and Methods

The samples were taken in 19.06.1999 at four stations in east Mediterranean Sea, south of Turkey. The sampling stations are shown in Fig.1.

2.8 L seawater samples were taken and extracted in portions of 700 ml with 50 ml dichloromethane (DCM). The extracts were combined and dried on anhydrous sodium sulphate then distilled. The residue was taken with hexane and the volume adjusted to 10 ml and analysed by UVF.

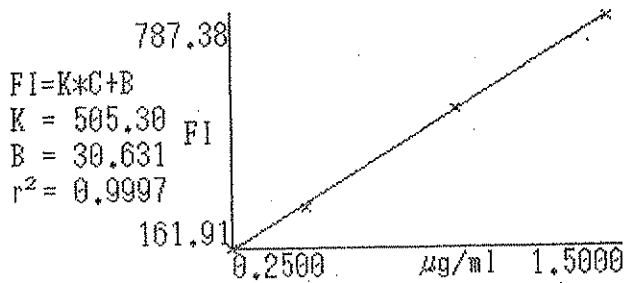


Figure 1. Sampling stations.



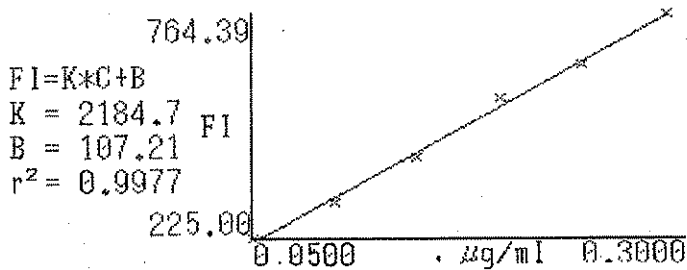
$FI: 488.59 \times C + 49.760$

Figure 2. Standard curve of Iraqi crude oil



$FI: 505.30 \times C + 30.631$

Figure 3. Standard curve of Iranian crude oil



$FI: 2184.7 \times C + 107.21$

Figure 4. Standard curve of chrysene

The calibration curves were plotted for concentrations of 0.25-1.5 µg/ml for Iraqi and Iranian crude oils and also 0.05-0.3 µg/ml for chrysene, the solvent being hexane (Ünlü and Güven, unpublished data). The fluorescence intensity was measured at 310/360 nm (ex/em) in spectrofluorophotometer (Shimadzu RF-1501). The calibration curves and their equations were taken from the apparatus.

Results and Discussion

The standard curves of crude oils and chrysene are shown in Figs. 2-4. The oil pollution levels found at four stations of east Mediterranean are given in Table 1.

The earlier workers (Sakarya, 1985, Saydam and Salihoğlu, 1984 Ehrhardt and Petrick, 1989, Yılmaz *et al.*, 1991, Yılmaz *et al.*, 1998 and Yılmaz *et al.*, 1998) gave generally low values for oil pollution in this area. According to their findings max. levels were 25.2 µg/L in 1982, 5.7 µg/L in 1983 and 2.2 µg/L in 1984 (Sakarya, 1985), 0.6-5.6 µg/L in 1983 (Saydam *et al.*, 1984), >0.4 µg/L in 1987 (Ehrhardt and Petrick in 1989), 0.84-1.25 µg/L in 1990-1996 (Yılmaz *et al.*, in 1989), 0.1-0.77 µg/L in 1985-1986 and 0.01-4.14 µg/L in 1995-1996 (Yılmaz *et al.*, 1998).

Table 1. Oil amounts measured by different references in eastern Mediterranean Sea (µg/L).

Sampling stations	Reference compounds		
	Iranian crude oil	Iraqian crude oil	Chrysene
BOTAŞ	2690	2596	455.42
DÖRTYOL	1088	1088	218.38
YUMURTALIK	26.60	24.60	3.53
MERSİN	629.60	623.20	120.64
İSKENDERUN	9.84	9.33	3.46

The pollution in this study varied 9.84-2690 µg/L calculated from Iranian crude oil and 9.33-2596 µg/L Iraqi crude oil. The results are similar for both crude oil references. The highest pollution was found as 2690 µg/L at Botaş. This is the highest amount for Turkish sea environment. It is followed by Mersin as 623.20 µg/L. In our earlier study Botaş showed the highest pollution as 514.28 µg/L.

When calculated from chrysene the oil amount was found 455.42 µg/L at Botaş, 218.38 µg/L at Dört y l, 3.53 µg/L at Yumurtalık, 120.64 µg/L at Mersin, 3.46 µg/L at İskenderun.

The main problem is the choice of the reference material used for plotting the calibration curve. The compounds used are chrysene or crude oils. Only Erhardt and Petrick (1989) used crude oil (Agha Jari, Iranian crude oil) but the others used chrysene as reference. When chrysene is used the crude oil results must also be mentioned, as did by many workers (Abdullah *et al.*, 1996, Badawy *et al.*, 1991).

As seen Table 1 the values of pollution are higher when crude oil is used as reference. The similar findings were reported in earlier work. The method based on crude oil reference technique gave as much as 10-12 times higher values than when chrysene technique was used. According to Ehrhardt and Petrick (1987) chrysene, if present at all is certainly not the only PAH extractable from oil contaminated seawater. If it is used as quantitative reference substance, the fluorescence intensity of a seawater extract is obtained in mass of chrysene equivalents per unit volume of water.

The use of crude oil as the reference material is more reliable since a particular kind of oil is responsible for polluting a specific area. The usual reference substance is a crude oil likely to be used or transported in the area under investigation (Ehrhardt and Patrick, 1989) Likewise we used Iranian and Iraq crude oils which were imported by Mersin refinery (Ataş) or transported by pipeline to Botaş and exported therefrom.

Furthermore the extraction solvent also affected the oil level in seawater. DCM is considered the best solvent for the extraction of oil. Hexane was used by earlier workers. Thus appreciable discrepancies occurred. UNESCO adopted dichloromethane (DCM) instead of hexane as an extraction solvent (Domenico *et al.*, 1994).

In conclusion: The oil pollution is determined in this investigation as to have increased in the east Mediterranean area from 1996 to 1999.

 zet

Bu alıřmada 1999 yılına ait T rkiye sahilleri doęu Akdeniz b lgesinde Botaş ve İskenderun arasındaki denizde petrol kirlilięi arařtırılması sonuları verilmiřtir. Bu b lgede petrol kirlilięi deęiřik referanslara g re hesaplama da İnan petrol ne g re 9.84-2690 µg/L, Irak petrol ne g re 9.33-2596 µg/L arasında bulunmuřtur.

En yüksek kirlilik 2690 µg/L olarak saptanmıştır. Bu iki referans madde kullanılması arasında fark bulunmadı. Bundan önceki çalışmamızda ise bu bölgede kirlilik en yüksek petrol kirliliği miktarı 514.28 µg/L bulunmuştu. Bu bölgede yapılan bir çalışmada ise bulunan kirlilik miktarının 0.0-25.2 µg/L arasında bulunmuş, genelde ise bu miktarın 5.7 µg/L olduğu bildirilmiştir. Bizim bulgularımız ile bu bulgular arasındaki büyük farklılığın sebebi kullanılan yöntemeye aittir. Ehrhardt ve Petrick (1987) hariç diğerleri referans olarak chrysene 'i esas almışlardır. Chrysene floresans gösteren poliaromatik maddelerden yalnız bir tanesidir. Bu madde ham petrolerde eşit miktarlarda bulunmadığından buna dayanarak yapılan tayinler düşük sonuç vermektedir. Bu husus bu çalışma ile ispatlanmıştır. Her ne kadar chrysene 'i referans olarak kullanan literatürde varsa da, genelde o bölgeyi kirleten ham petrol referans bileşiği olarak kullanılması doğru sonuç verir. Chrysene kullanılması halinde ham petrole ait sonuçlarda beraberinde verilmiştir.

Bu çalışmada ayrıca ekstraksiyon solvanı olarak DCM kullanılmıştır. DCM hekzan a göre daha iyi bir çözücüdür. UNESCO da ekstraksiyon solvanı olarak DCM yi kabul etmiştir. Bu bölgedeki diğer çalışmalarda hekzan kullanılmıştır. Bu da sonuçların düşük bulunmasında etkindir. Bu bölgedeki önceki çalışmamız ile mukayesede petrol kirliliğinin 1996 yılından 1999 yılına doğru arttığı tespit edilmiştir.

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