Assessment of Oil Pollution in the Eastern Mediterranean

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1. Introduction

The Mediterranean is one of the most oil polluted areas in the world. The reason for this is simple: the countries surrounding the Mediterranean, especially in the eastern and southern parts are oil producing countries. Oil pollution arises because of the normal operations of tankers flushing oil tanks into the sea, other ships clearing fuel tanks and bilges, the operation of refineries and petrochemical plants, the presence of loading and unloading oil terminals. In addition, activities related to pipe-lines, sewage outfalls which carry industrial wastes are considerable in this semi-enclosed sea. The Mediterranean coast line from Tasucu (Icel) to Iskenderun (Hatay) is a significant and heavily industrialized part of Turkey which has many types of industrial activity such as textile, food, metal, ferro-chrome, paper and pulp, iron and steel, paint, plastic, wood, soda, fertilizers and petroleum. Among the industries located in the Adana region, cotton processing and related textile production is the most important class. Turkey is also one of the largest cotton growing countries, ranking seventh in the world and exports textiles based upon an industry which is concentrated in the Adana region.

A high capacity petroleum refinery is located in Mersin. Furthermore, two petroleum pipe-line terminals are located on the Iskenderun Bay coastline which carry crude oil from Kirkuk in Iraq.

In this paper, the state of petroleum pollution will be discussed based on an evaluation of 16 years of data for the period 1982-1997 collected in the north-eastern Mediterranean. This data includes a study of trends against time, investigations on instantaneous events/accidents and their impacts on the marine environment.

2. Methodology

Water samples were collected from land-based source points before they have been introduced into the sea. Coastal stations were deliberately selected and fixed in front of these same source points, being located in the continental shelf area, but mostly in the Iskenderun and Mersin bays in the North East corner of the Mediterranean. A couple of offshore stations were also visited in order to obtain reference levels. Figure 1 shows the location of the major sampling sites around the Mediterranean coast.

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Petroleum pollution has been monitored for several years in the eastern Mediterranean Sea as part of the MED POL Programme (UNEP, 1986; UNEP, 1995). Dissolved/Dispersed Petroleum Hydrocarbon (DDPH) concentrations were determined in water samples seasonally. Marine biota was monitored less frequently (2 to 3 times a year) while the sediment samples were collected from shallow stations (total depth <200m) for the analysis of the poly-aromatic petroleum hydrocarbons (PAH) on a yearly basis. For seawater analyses, 2.5 L of seawater (or discharged waste) were extracted on board ship (or on the spot) with *n*-hexane. PAH concentrations were estimated by comparison of the fluorescence at 360 nm (excitation at 310 nm) with that of hexane solutions of chrysene (UNEP, 1986). Sediments were obtained by sampling using a van Veen grab and were frozen at -20 °C. Thawed samples were subsequently dried under vacuum at 40 °C, or were freeze-dried. Then 0.2 to 0.5 g of dried sediment was refluxed with 20 mL of ethanol and approximately 0.75 g of potassium hydroxide for 90 minutes. Products were then extracted three times with 20 mL of hexane. PAHs in hexane were estimated by comparison of the fluorescence at 360 nm (excitation at 310 nm) with that of hexane solutions of chrysene (UNEP, 1992). Over the period 1985 to 1986, the analysis of the sediments excluded the saponification step. Biota were treated similarly to sediments. PAH concentrations were calculated from the equivalent chrysene fluorescence.

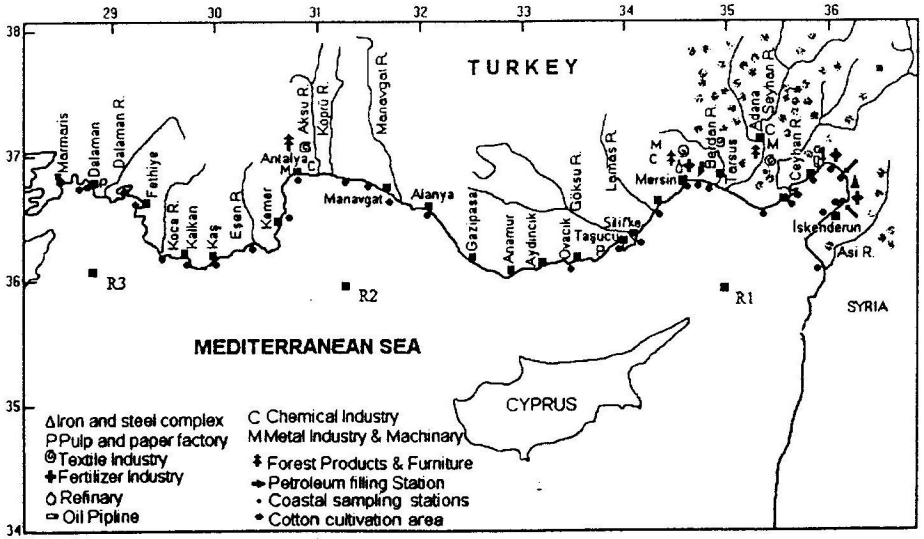

Figure 1. Source points and sampling stations in the northeastern Mediterranean

3. Results and Discussion:

Average DDPH concentration was measured in the range of 0.01 (=Detection limit of analytical method) and <5μgL^{-1} in the NE Mediterranean coastal and offshore surface waters for the 1982 to 1997 period. Relatively high concentration levels (up to 12 μgL^{-1}) were observed in Iskenderun Bay where the Iraq crude oil pipe-line is located. The average concentrations are presented for selected regions in the NE Mediterranean and for a certain period of time showing a decreasing trend if one goes from the east to west coast and from coastal areas to offshore (Table 1).

Table 1. The average DDPH concentrations in the coastal and offshore regions of the NE Mediterranean for 1990-1996 period. The recent data was compared with the previous data (1985-1986)

Region	DDPH (μgL^{-1})
Iskenderun Bay	1.25
Mersin Bay	0.84
Offshore of the above bays	0.50
Antalya Bay	0.77
Off Antalya Bay	0.35
West of Turkish Mediterranean Coast	0.70
Offshore (West Side of the study area)	0.20
Whole NE Mediterranean (1985-986)	0.28

Table 2 summarises the concentrations of PAHs in surface sediments of the NE Mediterranean shelf area. Average PAH concentration was observed to be 0.5 to 4.75 μg g^{-1} (dry weight) for the 1985-1996 period. At the beginning of this period, an oil terminal in the Yumurtalik region (Fig. 1) connected Iraq to the eastern Mediterranean. Throughout the ten-year period, the north eastern Mediterranean coast has attracted summer tourism and a population influx, this increasing to 5.2 million in 1990 (Mersin Chamber of Commerce,1995) and to approximately 10-12 million at present. Commercial shipping at Mersin, Iskenderun and Cyprus has also been significant and currently exceeds 11 million tonnes a year at Mersin (Yercan, 1996); this includes tankers supplying oil refineries at Mersin and Cyprus. Nevertheless, tables 1 and 2 provide a baseline against which to compare environmental quality in the future.

Table 2. PAH concentrations (μg g^{-1} dry weight) in surface sediments.

Date	Stations	Min.-Max.	Mean±SE
1985-1986	10	0.02-0.96	0.51±0.10
1995	19	0.69-4.8	2.6±0.3
1996	19	0.55-18.7	4.75±1.0

As demonstrated by table 1, the surface waters of the northeastern Mediterranean Sea do not suffer undue pollution by petroleum. The observed concentrations are not low but similar to those noted in surface waters off the coast of Antarctica which, in 1987, ranged between 0.15 and 4.65 $\mu g l^{-1}$ (Weber and Bicego, 1990). There has been a suggestion that higher evaporation leads to lower surface concentrations of the study area during summer periods (Sakarya, 1985). In contrast, the pollution of surface sediments by PAHs appears to have increased during the ten-year period considered here (table 2). Sediments containing approximately 0.5 $\mu g g^{-1}$ dry weight of PAHs have been deemed moderately contaminated and those possessing more than 10 $\mu g g^{-1}$ of PAHs highly contaminated (UNEP, 1994). Thus, for example, Lipiatov and Saliot (1991) observed PAH concentrations in western Mediterranean sediments which rose from 0.18 $\mu g g^{-1}$ dry weight in the open ocean to 2.4 $\mu g g^{-1}$ in the Rhone River delta. The contrast between the relatively clean northeastern Mediterranean water and the polluted surface sediment suggests that the water column is being scrubbed continuously by particulates which eventually sediment out. The findings of Bouloubassi and Saliot (1991) are relevant here, revealing the presence of high concentrations of PAH in the fine particles dispersed in the Mediterranean water column.

Poly-aromatic petroleum hydrocarbon (PAH) concentrations in biota samples [mostly commercial fish (such as *Mullus barbatus, Mugil cephalus, Upeneus moluccensis, Solea solea*) caught in the region] were measured in the range of 1.1-14.5 $\mu g g^{-1}$ (dry weight). In general, the fish caught in Iskenderun and Mersin bays exhibited higher concentrations in their tissues (table 3). Fish ingest, assimilate and excrete PAHs (Malins and Hodgkins, 1981). Species such as the mullet (*Mugil* sp.) which ingest sediments and fish in such polluted waters as the busy harbours maintain significant concentrations of PAHs in their tissues. Similar concentrations have been noted in Aegean fish (Saydam *et al.*, 1988). The observations in 1996 show the variance within a species to be rather large. Nevertheless, species in two localities, 55 km apart, possessed very similar concentrations of PAH. It is to be hoped that future observations will show whether this phenomenon is of general occurrence.

The level of DDPH in Iskenderun Bay was monitored in some detail and the results for a 10-year time series is presented in figure 2. The Bay is oil polluted because of high quantity of input from land based sources and high tanker traffic. There are many loading-unloading stations, a high capacity (70.9×10^9 t/y) pipe-line carrying Iraq crude oil through Yumurtalik, and many types of industries (such as iron and steel, fertilisers, textiles) in the Bay (figure 1). As is clearly seen from figure 2, the embargo applied after the Gulf War in 1990 caused a significant decrease in DDPH concentrations in the Bay.

Table 3. PAH concentrations ($\mu g g^{-1}$, dry weight) in the flesh of fish from the eastern Mediterranean Sea.

Year	N	Station	Fish Species	PAH
1987	10	Mersin Harbour	*Mugil* sp.	10.0-14.5
1991	6	Turkish coast	*Mullus* sp.	1.1±0.4
1991	2	Turkish coast	*Mugil* sp.	1.6±1.2
1995	15	Mersin Area	*Mixed* sp.	2.8±0.5
1996	6	Iskenderun Bay	*Mugil* sp.	8.7±1.1
1996	7	Iskenderun Bay	*Shrimp*	6.4±1.0
1996	10	Iskenderun Bay	*Upeneus moluccensis*	7.5±1.1
1996	6	Karatas	*Mugil* sp.	10.7±2.1
1996	6	Karatas	*Shrimp*	6.2±0.9
1996	7	Karatas	*Upeneus moluccensis*	8.8±1.5
1996	4	Karatas	*Solea solea*	4.6±1.3

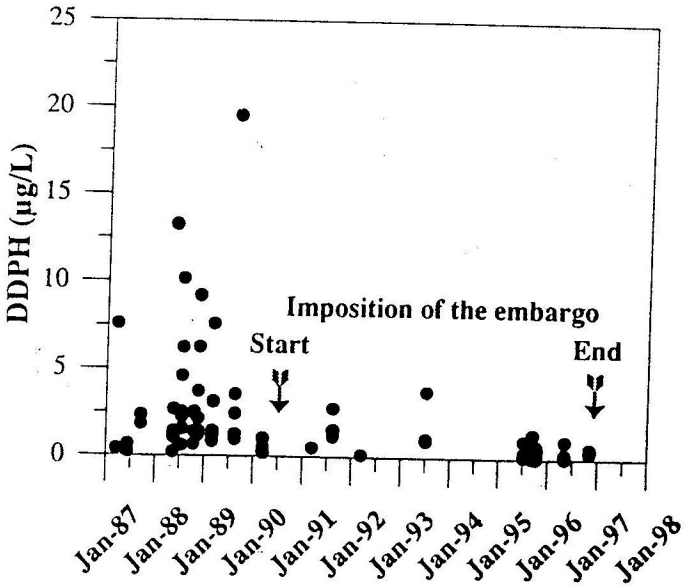

Figure 1. Time serie for the Dissolved/Dispersed Petroleum Hydrocarbons (DDPH) in Iskenderun Bay surface waters. Gulf War (Jan 1990) and the embargo period (1990-1996) befit with this time period

A pipeline accident was experienced in Iskenderun region in April 1982. 8000 tons of Kirkuk (Iraqi) crude oil were introduced into the Bay through Ceyhan River. The immediate (six days continuous sampling) and after effects (monthly sampling) of this episode have been monitored in sea water, marine biota and sediment samples. By the end of third day, the spread of the spill was observed in the whole Bay by the influence of the surface current system. Besides the Bay, Akyatagan Lagoon which has a considerable fish production was also affected by the crude oil. About half of the stocks died together with some birds. Before the accident, the DDPH concentration was in the range of BDL-12 µg L^{-1} and this increased two-fold to reach the 25 µgL^{-1} level in the Bay just after the pipe-line breakage (Table 4). It was at its saturation level (about 200 µg L^{-1}) in the Ceyhan River where the crude oil was introduced by the accident. After a couple of months, the concentrations in sea water were observed to be normal (Salihoglu et al.,1987). The immediate effects were observed in biota samples showing the accumulation of petroleum in their tissues (table 5) . The same trend was observed in the sediment in the vicinity of the Ceyhan River (Table 6).

Table 4. DDPH concentration (µgL^{-1}) in Ýskenderun Bay surface waters before, during and after pipeline accident in 1982.

Date	Range	Mean	No of samples
Nov 1981	0.7-3.7	1.44	7
Feb 1982	1.1-11.8	3.79	22
Apr 1982	0.8-11.2	3.14	14
May 1982	0.8-25.2	3.88	22
Jul l982	0.5-3.9	1.47	19
Aug 1982	0.2-2.0	0.64	10
Nov 1982	0.2-1.8	0.68	9
Apr 1983	0.04-5.7	2.07	12
Aug 1983	0.4-5.2	1.0	18
Oct 1983	0.1-1.0	0.42	27

Table 5. Average PAH Concentrations in Fish Samples (µg g^{-1}, dry weight) caught in Iskenderun Bay during the Iraqi Pipeline Accident (*)(Salihoðlu et al.,1987)

	Mullus barbatus		*Solea solea*	
Date (1982)	Liver	Flesh	Liver	Flesh
January	0.5	0.1	0.4	0.1
March	3.6	1.3	-	0.2
April*	5.3	0.8	2.8	0.6
May	6.5	0.3	2.0	0.2
June	10.2	0.4	2.2	0.3
July	14.9	1.4	11.7	0.5
Aug	2.9	0.5	9.4	0.5
Oct	5.3	1.7	3.0	1.2
Nov	1.9	0.2	1.4	0.1

L=Liver F=Flesh Number of samples analyzed: Min=3 Max=30 individuals for each month

Table 6. Average PAH Concentrations in Sediment Samples (µg/g) in Ýskenderun Bay during Iraqi Pipeline Accident (*) (Salihoglu et al.,1987)

Sampling Date	Concentration (Dry weight, (µg g^{-1})	# of Samples Analyzed
Nov 1981	0.5	6
Dec 1981	0.4	6
Feb 1982	0.5	16
Apr 1982*	0.6	8
Jun 1982	1.3	3
Jul 1982	0.6	5
Sep 1982	0.2	5

Conclusion

All these results clearly show that the study area is oil polluted and will be subject to even more polluted due to the accelerated industrialisation of the region, especially if the ongoing proposals to build new pipe lines, carrying crude oil from Central Asia to the Mediterranean, come to fruition.

Thus, although the concentrations of PAHs in the Turkish Mediterranean coastal waters are relatively low, discharges provide point sources of pollution. The waters and (especially) the sediments in the harbours and their neighbourhood are sufficiently polluted to present a hazard to the physiology of any fish which may assimilate the PAHs. Such regions may pose a carcinogenic hazard to humans through the consumption of contaminated fish.

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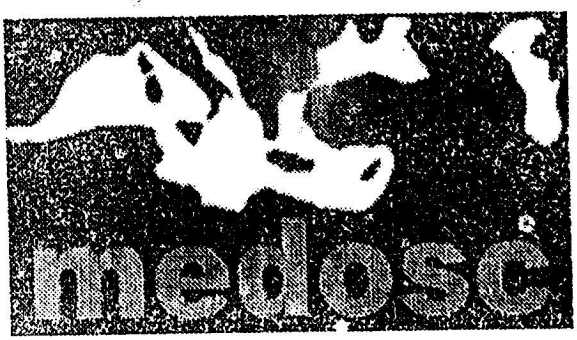

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