J. Black Sea/Mediterranean Environment
Vol 12: 201-212 (2006)

Oil pollution in the surface water of the Aegean Sea

Ege Denizi yüzey suyunda petrol kirliliği

Bayram Öztürk[1*], Kasım C. Güven[2], Filiz Nesimigil[2], Selin Cumalı[2] and Ayhan Dede[1]

[1] İstanbul University, Faculty of Fisheries, Marine Biology Department, Laleli, İstanbul, Turkey.

[2] İstanbul University, Institute of Marine Sciences and Management, Vefa, İstanbul, Turkey.

Abstract

Oil pollution in the surface water of the Aegean Sea was investigated from the Çanakkale Strait (Dardanelles) to the Marmaris Harbour, during 17-25 April in 2005. The oil pollution of samples was determined by UVF, through various crude oils and also chrysene as references materials. The oil pollution in water was ranged from 6.17 µg/L at Datca to 59.58 µg/L at Kuşadası through Russian crude oil equivalent. The highest polluted areas were Babakale-Kuşadası Bay, West of Giadoros Island and Yalıkavak - Kardak Island. The comparison the results of present work with the earlier findings, showed that the pollution level is increased during the years in this area.

Keywords: Aegean Sea, oil pollution, surface water,

[*] Corresponding author

Introduction

The Aegean Sea, as a part of the Mediterranean Sea, is a semi-closed sea, thus isolated from other water bodies, though not completely. The most important peculiarity of this sea is exist numerous islands and islets (Öztürk and Öztürk, 2003). The area of the Aegean Sea is 241,000 km^2; the length from north to south is 660 km, and the width is 270 km in the north, 150 km in the middle and 400 km in the south. Its depth is exceeding 1000 m only in very limited areas (Zaitsev and Öztürk, 2001).

The Black Sea water enters to the Aegean Sea through the Turkish Straits Systems [TTS; İstanbul Strait (Bosphorus), Sea of Marmara and the Çanakkale Strait (Dardanelles)] as a less dense upper current, likewise the denser Aegean water enters through the Canakkale Strait in a deeper layer flow, and enters the Black Sea with the Istanbul Strait underflow during southerly winds.

The Aegean Sea is on the way of oil transportation between Mediterranean and the Black Sea and also opposite side. The number of vessels in the dense shipping traffic reaches approximately 55.000 in the İstanbul Strait and 35.000 in the Çanakkale Strait per year. This traffic will be increased due to the rich oil field found in the central Asia. Besides international traffic, there is a significant local maritime traffic in the Aegean Sea due to the cruising, yachting and other commuters.

It is clear that the Aegean Sea functions as a vital connection point for the isolated Black Sea countries, therefore keeping the sea clean, safe and open to maritime traffic has a crucial importance for the region. Environmental problems in the Aegean Sea were summarized by Öztürk and Öztürk, (2003).

Transportation of oil causes severe incidents therefore needs precautions before the accident happen. However, the level of oil contamination is not accurately known and should be monitored in the seawater, sediments and organisms for the entire sea.

Oil pollution of the sea has been aroused more and more attention and oil can enter to the seas in many different ways; by shipping operations, tanker accidents and especially from land based sources.

Oil enters to the Aegean Sea through the water exchange with the Mediterranean Sea, via Cretan Sea, in the south and with the Black Sea, via the İstanbul and Çanakkale Straits in the north. Besides, oil may enter to the Aegean Sea through the bilge water, leakage, spills and land based sources.

Oil pollution was monitored in the Black Sea and Turkish Straits since 1994 (Güven *et al*., 2005).

There are a few literatures concerning the pollution of petroleum hydrocarbon amount determined by in the Aegean Sea. Briefly the oil pollution in Aegean Sea can be summarized as fallows. Oil pollution of the Cretan Sea, Southern Aegean Sea was found at the range of 0.092-0.317 µg/L (Kornilios *et al*., 1998) in the region of Northern Aegean Sea (Thermaikos Gulf) , Greece , total PAH concentration was ranged from 9.7 to 36.2 ng/L (Hatzianestis e*t al.,*1998a*)*, in coastal and open area 4.4-16.8 ng/L in February (Hatzianestis and Sklivagou, 2004). In Turkish part of Aegean Sea, the oil concentrations were found 0.10-2 µg/L and in Aliağa and İzmir Bay 10-25 µg/L (Küçüksezgin *et al*.,1995), in coastal and open sea area 0.09-25.5 µg/L (Balcı, 1993), 0.14-1.39 µg/L (Sakarya*.,* 1985), in Northern Aegean Sea, 0.1-12.5 µg/L (Saydam *et al.,* 1988). Oil pollution at

surface water in exit of Çanakkale Strait (Dardanelles) 243.4 µg/L in 2005 (Güven *et al*. unpublished data) On the other hand hydrocarbons were determined in sediments of northern Aegean Sea (Saydam *et al*., 1988; Hatzianestis *et al*., 1998b; Sklivagou *et al*., 2004; Hatzianestis and Sklivagou, 2004; Darılmaz and Küçüksezgin, 2004) and in mussel (Balcı, 1993) and in fish (Arınç *et al*. 2001).

This study is a part of the monitoring study on the oil pollution in the Aegean Sea from Çanakkale Strait to Marmaris to understand some busy Turkish harbors oil level of the surface water, some island and high sea of the Aegean Sea.

Material and Methods

Sampling stations are shown in Fig. 1 and their coordinates in Table 1.

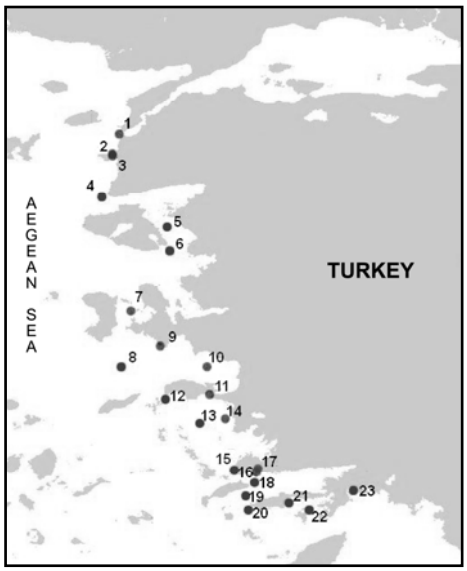

Fig 1. Sampling stations.

Sampling period was from 17 to 25 April in 2005. 3L sea water samples were taken from the surface and 10 ml dichloromethane (DCM) added for preservation. The sample was divided to four as 700 ml and each portion was extracted three times with 50 ml (DCM). The extracts were combined, dried over anhydrous sodium sulfate, filtered and then distilled at 36 °C. The residue is taken with hexane and the volume was adjusted to 10 ml. Its intensity was measured at 310/360 nm (ex/em) by the Ultraviolet fluorospectrophotometer (UVF) (Shimadzu RF 1501). The standard curve was plotted in a concentration of 0.25-1.5 µg/L in hexane for references oils used as Russian, Iranian, and Iraq crude oil. In addition to this measurement the calibration curve was also plotted through chrysene (Aldrich) as reference compound in a concentration of 0.05-0.3 µg/L in hexane. After plotting of calibration curve the equations were taken from apparatus. The reference materials used in the determination of oil contamination in sea water was discussed by Erhardt and Burns (1998) and they suggested that the use of crude oil as reference must be transported area under investigation. This problem, due to the complexity of determination of the oil in this area was solved, by using the standard equation of various crude oil which was transported in this area and also compared with chrysene equivalent.

GC/MS analysis was used for identification of oil component in sea water samples. After determination oil amount in the sample by UVF the remaining part was applied to GC/MS analysis.

GC/MS analysis: GC/MS (HP 6890) HP-5 29.5m x 0.250µm x 0.25µm film thickness mode. The injection port was operated at 250 °C, in the splitter mode, the initial temperature was 40 °C and it was programmed to increase

at 5°C min^{-1} to a final temperature of 280 °C. Gas: helium, flow rate: 1 ml min^{-1}.

Results and Discussion

The standard equations of the reference materials are:

For Russian crude oil $F_1 = 552{,}67xc + 51{,}554$ $r^2 = 0.98$

For Iranian crude oil $F_1 = 505.30 \times c + 30.631$, $r^2 = 0.99$

For Iraqian crude oil $F_1 = 488.59 \times c + 49.758$, $r^2 = 0.99$

For Chrysene $F_1 = 1353.18\ c + 18.124$, $r = 0.999$

The amount of oil pollution in sea water samples were calculated from this equation.

The oil pollution levels in the examined area are shown in Table 1.

The maximum oil pollution through Russian crude oil equivalent was found as 59.98 µg/L in Kuşadası Bay, followed 51.65 µg/L in South Çeşme and 50.33 µg/L at station Babakale (Çanakkale). The later area is a beginning part of Russian oil transportation to Aegean Sea and also imported oil by İzmit Refinary. The lowest level of oil was found 6.17 µg/L in Datça, South Aegean Sea. The oil pollution levels determined in Aegean Sea were ranged as 6.17-59.96 µg/L through Russian crude oil and 1.59-15.49 µg/L through chrysene equivalent. The oil pollutions over 10 µg/L (international limit value for oil) amount were found at the stations of 1-18 and 23. The high values found by Russian crude oil equivalent could be attributed to high content of fluorescent compounds (PAHs).

The earlier studies the oil pollution in this area were determined through chrysene equivalent (Sakarya 1985, Saydam 1988, Balcı 1993, Küçüksezgin *et al*., 1995, Kornilios *et al*., 1998; Hatzianestis *et al*., 1998 ;). Hatzianestis and Sklivagou (2004) used GC/MS analysis. We determined the oil pollution by using various crude oils which is transported in this area. The difference between our results with other authors due to reference material of chrysene. The oil determination based on chrysene equivalent gives low level value while the content of this compound in crude oil by various origin were not the same. The high pollution found in Babakale which is near of Dardanelles from 50.33 µg/L. Oil pollution in exit of Dardanelles was found as 243.4 µg/L(Güven *et al*. unpublished data). The pollution levels were high at in Northern of Aegean Sea, in exit of Dardanelles and Babakale, while vessels traffic was high from Aegean Sea to Marmara Sea and other wise? Oil level was found high in Turgut Reis Marina (Kuşadası) while there are also vessels traffic. The Harbour Bodrum, Marmaris, Bozcaada were also high polluted from oil. The highest polluted area were ranked as Babakale-Kuşadası Bay > off Bodrum- Kos Island > West of Giadoros Island and Yalıkavak - Kardak Island.

The detected compounds in sea water by GC/MS of the examined stations were mostly aliphatic and a few aromatic hydrocarbons. The compounds identified were:

In aliphatic groups; nonadecane, hexadecane, undecane, eicosane, squalene, 10-dimethyl squalene , tricosane, pentacosane, heptacosane, triacontane, hexatriacontane dotriacontane,

In ketone groups; 3-hexanone; 2-hexanone,
In alcohol group; 3-hexanol
In cyclic aliphatic group; cyclotetradecane
In aromatic group; toluene, xylene, ethylbenzene.

The oil pollutions were also found high in bay and marinas as Kuşadası, Marmaris and Turgutreis. The pollution was also high at stations 8, 13 and 15 were international water or high seas in the Aegean Sea which is route of the oil transportation. The other stations were more coastal in the Aegean Sea between Turkey and Greece was also polluted.

This level is oil contamination may be harmful if the trend will continue and to the regional tourism activities. Oil spill response plan also should be prepared by the riparian countries.

In conclusion, the oil pollution was found high in examined area and in the Aegean Sea more comprehensive studies is needed. Both Turkey and Greece is a part of the Convention of the Barcelona which is one of the important tools to protect and monitor surrounded seas. Besides, oil spill preparedness convention is also important. To mitigate petrol hydrocarbons in the Aegean Sea, number of port receiving facilities should be increased and the implementation of the MARPOL 73-78 Convention and Annex should be strengthen. More stringent measure should be taken by the coast guard against bilge water, illegal discharge and leakage at the Aegean Sea.

Acknowledgement

The authors thank Adnan Hepgül for his kind help during the sampling.

Table 1. Oil pollution calculated by different references crude oils in the stations of Aegean Sea (µg/L).

Stations	Locations	Coordinates	Iranian	Iraq	Russian	Chrysene
1	Off Mehmetçik Lighthouse	N 40°01'08", E 26°10'41"	24,49	18,88	29,32	7,69
2	Off Tavşan Islands	N 39°51'40", E 26°06'51"	39,76	30,88	36,90	11,06
3	Bozcaada Harbour	N 39°51'01", E 26°06'28"	26,16	23,90	28,13	16,11
4	Babakale	N 39°28'84", E 26°03'34"	43,81	31,79	50,33	13,43
5	Dikili	N 39°10'72", E 26°36'52"	43,09	29,94	47,45	12,70
6	Midilli – Cape of Agrelios	N 39°01'69", E 26°37'72"	44,19	27,64	43,74	11,65
7	Off Çeşme	N 38°26'41", E 26°17'14"	29,72	28,69	44,83	11,47
8	South of Çeşme	N 37°55'02", E 26°10'93"	46,22	32,72	51,65	13,66
9	Sığacık Bay – İnce Burun	N 38°08'04", E 26°33'25"	38,88	32,38	50,25	12,57
10	Kuşadası Bay	N 37°55'85", E 26°59'40"	54,74	38,28	59,98	15,49
11	Dilek Strait - Bayrak Island	N 37°41'08", E 27°01'05"	20,24	12,67	20,16	5,46

Table 1. Continued

12	West of Samos Island	N 37°40’83”, E 26°33’30”	23,98	18,34	28,90	7,60
13	West of Gaidaros Island	N 37°26’16”, E 26°55’55”	23,18	29,83	47,08	12,44
14	N. Giadoros – Düz Burun	N 37°29’05”, E 27°07’37”	44,43	29,56	46,76	12,45
15	Yalıkavak - Kardak Island	N 37°00’345”, E 27°15’308”	36,28	32,03	49,77	12,52
16	Turgutreis Marina	N 36°59’99”, E 27°24’05”	24,64	21,86	34,40	9,01
17	Bodrum Harbour	N 37°02’05”, E 27°25’42”	17,83	13,76	21,39	5,39
18	Off Bodrum–Kos Island	N 36°52’33”, E 27°23’45”	32,07	31,86	49,67	12,62
19	Off Datça –Kos Island	N 36°47’32”, E 27°20’81”	3,95	6,28	9,74	2,44
20	Off Knidos	N 36°39’50”, E 27°22’01”	2,93	4,22	6,60	1,69
21	Datça Harbour	N 36°43’220”, E 27°41’638”	2,79	3,93	6,17	1,59
22	Off Simi Island	N 36°40’89”, E 27°50’72”	3,10	4,57	7,14	1,82
23	Marmaris Harbour	N 36°50’334”, E 28°16’336”	19,37	22,13	35,33	9,66

References

Arınç, E., Kocabıyık, S., Şen, A and Su, E. (2001). Biomonitoring of toxic, carcinogenic pollutants by molecular and biochemical responses of fish Cytochrome P450 1A1 (CYP1A1) along the İzmir Bay on the Mediterranean Sea. Rapp. Comm. int. Mer. Médit., 36: 179-180

Balcı, A. (1993). Dissolved and dispersed petroleum hydrocarbons in the Eastern Aegean Sea . . *Mar. Pollut. Bull.* 26: 222-223 .

Darılmaz, E. and Küçüksezgin, F. (2004) Distribution and origin hydrocarbons in surficial sediments from İzmir Bay Turkey.Rapp Comm. int. Mer.Médit., 37:186

Ehrhardt, M., Petrick, G (1989). Relative concentrations of dissolved/dispersed fossil fuel residues in Mediterranean surface waters as measured by UV Fluorescense. *Mar. Pollut. Bull.* 20: 560-565.

Hatzianestis, I., Sklivagou, E. (2004). PAH distribution in water column and surface sediments of Thermaikos golf, Greece. Rapp. Comm. int. Mer. Médit,. 37: 206

Hatzianestis, I., Sklivagou, E and Firiligos, N. (1998a).Hydrocarbons in surface sediments from the Northern Aegean Sea,.Rapp Comm. int. Mér. Medit., 35: 264-265

Hatzianestis, I., Sklivagou, E, Zervakis, V.,Georgopoulos, D. (1998b). Polycyclic aromatic hydrocarbons (PAH) in sea water from the Northern Aegean Sea, Greece. International Symposium on Marine Pollution, Monaco 5-9 October, Extended Synopses. pp. 511-512

Kornilios, S., Drakopoulos, G.P., Dounas, C. (1998). Pelagic tar, dissolved / dispersed petroleum hydrocarbons and plastic distribution in the Createn Sea ,Greece .*Marine Mar. Pollut. Bull* 36:989-993.

Küçüksezgin, F., Altay, O., Kontaş, A. (1995). Dissolved and dispersed petroleum hydrocarbons in the Aegean Sea. *Toxicological and Environmental Chemistry* 52:85-95.

Sakarya, M (1985). Petroleum hydrocarbons in the marine environment. Ms.thesis METU (Middle East Technical University), Institute of Marine Sciences, İçel, Turkey.

Saydam, C., Yılmaz, A., Başturk, Ö., Salihoglu, I. (1988). Petroleum hydrocarbons in sea waters, marine organisms and sediments from the Northeastern Mediterranean and Aegean Sea, Rapp.Comm. int.Mer.Médit., (31), 2.

Sklivagou, E., Hatzianestis, I., Rori, N., and Rigas, F. (2004) Distribution and origin of hydrocarbons in sediments from Elefsis Bay, Greece (Eastern Mediterranean) . Rapp Comm. int. Mer.Médit., 37:244

Öztürk, B. and Öztürk, A.A. (2003). Environmental problems in the Aegean Sea .The Stockholm Declaration and Law of the Marine Environment. pp. 359-366. M.H. Nordquist, J.N. Moore, Mahmudi, S. (Eds) .Kluwer Law International .

Zaitsev, Y., Öztürk, B. (eds.), (2001). Exotic species in the Aegean, Marmara, Black Sea, Azov and Caspian Seas. Published by Turkish Marine Research Foundation (TUDAV), İstanbul, Turkey

Received:25.08.2005

Accepted: 07.12.2005