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Oil and detergent pollution in surface waters and sediments of the Istanbul Strait, Golden Horn, Izmit Bay (Sea of Marmara), Çanakkale Strait, Ali Ağa (Aegean Sea) in 2005-2007

Istanbul Boğazı, Haliç, Izmit Körfezi (Marmara Denizi), Çanakkale Boğazı ve Ali Ağa (Ege Denizi) deniz suyu ve sedimentlerinde petrol ve deterjan kirliliği, 2005-2007

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Abstract

In this work the oil and detergent pollutions were investigated in sea water, near the refinery of TUPRAŞ and Ali Ağa, Istanbul Strait, Golden Horn and Çanakkale Strait. The pollutions were higher in refinery areas. The results inadequate that there is apparently no regular seasonal variation in oil and detergent amount. The maximum oil concentration in sea water was found 29.55 µg/L for Istanbul Strait 4214.29 µg/L for Golden Horn and 42.96 µg/L for Çanakkale Strait in 19.02.2005 and 90.02 µg/L for TUPRAŞ 3, 71.77 µg/L for Ali Ağa 2, in 07.Agust. 2006, in sediment 9573.38 µg/g for Istanbul Strait, 1126.45 µg/g for Golden Horn, 31.52 µg/g for Çanakkale Strait in 21.02.2005, 1500.6 µg/g for TUPRAŞ in 13.11.2006, 58.64 µg/g for Ali Ağa in 7.12.2006. These oil levels found are higher than the limit values for sea water and sediment. The LAS levels found are similar in earlier findings of this area.

Keywords: Oil, detergent, Turkish Strait, TUPRAŞ (Izmit Bay), Ali Ağa (Aegean Sea)

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Introduction

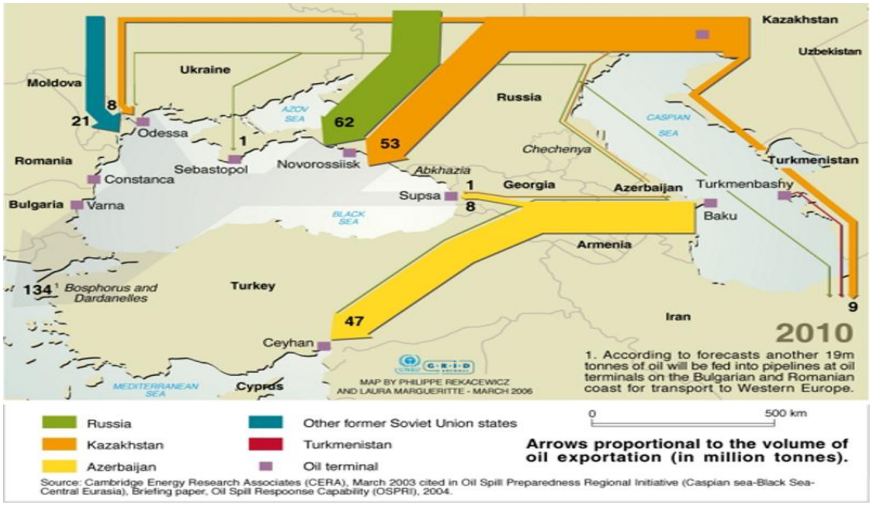
Oil and detergent pollutions are a problem appreciable in the last decade. The pollutants in the sea water come from chemical industries and refinery, transportation of oil, tanker clean up, ship and tanker accidents, sewage and industrial discharge. Origin of oils are biogenic (biogenous, autochthonous) from marine animals and algae and exogenic (anthropogenetic, allochtothonous) from petroleum hydrocarbons.

The composition of exogenic oils varies, depending on the origin of crude oil. It contains approximately thousand components which are aliphatic and aromatic. Especially aromatic compounds are very toxic for biota and habitat. Bioaccumulations of contaminants (oil, detergent) in marine organisms (mussels, fishes, shellfishes) are responsible for food contamination. Its consumption by humans causes toxic effects.

Turkish Straits Systems are composed of the Istanbul Strait Sea of Marmara and Çanakkale Strait, Golden Horn inclusive. Turkish Strait connects the Black Sea to the Mediterranean Sea by way of the Aegean Sea.

Turkish straits are an important route for oil exports from Eurasia via Black Sea, Bosphorus to Mediterranean Sea (Fig. 1) (Annon, 2007).

Figure 1. Route of oil from Russia and Caspian Sea.



The route of oil for Europe from Middle East is shown in Fig. 2.

Figure 2. Route of oil for Europe from Middle East.

Around 90 % of the oil for Turkey in 2008 was supplied by the Middle East (Saudi Arabia, Iran, Iraq and Syria) and Russia. Port of Ceyhan in East part of Mediterranean of Turkey is major outlet with pipeline from Iraq and the Caspian Sea oil exports. These alternative means of transport could reduce the risk of shipping accidents in Turkish straits. The transportation of Russian-Kazaks oils will continue through the Turkish Straits in tankers. Greece imports oil from Iran, Saudi Arabia, Russia, Libya and Egypt. The major source of oil is located in the Middle East, Russia, and Kazakhstan and Caspian region.

Oil transportation via Turkish Straits, ship traffic, atmospheric deposition and industrial discharge are the major causes of the pollution of Turkish sea environment.

Oil contains many toxic compounds. Unicellular algae and fauna are more susceptible than other organisms. Zooplankton and crustacean larvae are also susceptible to small oil concentrations. Non petroleum pollutant is city sewages which also effect on algae and marine animals.

Oil pollutions also came in these areas from the oil transported to refineries (TUPRAŞ, Ali Ağa). The transported oil in these refineries as mentioned above came from the Russian, Caspian Sea and various Arabian countries.

Detergent pollution came from city sewage.Detergents contain many components as surfactant, wetting and antifoaming agents, phosphates and solubilizers. Surfactant is a surface active agent. Among the surfactants, anionic compounds, namely linear alkylaryl sulfonate (LASs) were usually used. LAS is not a unique compound. It is a mixture of C_8-C_{16} alkylaryl groups linked to a benzene sulfonate group. It contains many homologous and isomers of hydrocarbons.

The type of detergents (anionic, cationic, non ionic) varies depending on utilization. Detergents are toxic for sea life as it decreases the surface tension of water and has effect on sensitive marine organisms. Especially phosphates in detergent increase the toxicity. It causes eutrophication, which is called secondary pollution. Detergents are distributed at the air- sea interface and affect the exchange of oxygen from the air to the sea and reduce the dissolved oxygen concentration in sea water. The oils have also the same effect.

In this area, previous pollution studies were performed:
at Istanbul Strait: Guven et al. 2005;
at Izmit Bay: Güven et al. (1996, 1997, 1999), Darılmaz 2004, Gunday et al. (2006),
at Çanakkale Strait: Güven et al. (2002) and Güven and Ilgar (2002), Güven et al. (2003, 2005);
at Aegean Sea: Sklivagou et al. 2004, Shimkus et al. 1993, Balcı 1993, Küçük Sezgin et al. (1995, 1999), Hatzineastis et al. 1998 a,b, 2004, Kornialis et al. 1998, Öztürk et al. (2006, 2007).

Materials and Methods

The sampling stations and coordinates are shown in Fig 1 and Table 1 respectively, for sampling periods between 2005-2007.

Table 1. The coordinates of sampling station of TUPRAŞ and Ali Ağa.

Station	Number	Coordinates					
TUPRAŞ	1	40	44	56.907	29	45	26.439
	2	40	44	57.765	29	45	8.978
	3	40	44	49.527	29	44	53.185
Ali Ağa	1	38	48	337.015	26	57	377.403
	2	38	48	457.014	26	57	157.409
	3	38	49	0.7012	26	56	547.416

Sampling stations of Istanbul Strait, Golden Horn and Çanakkale Strait are shown in Fig. 5-6.

Figure 3. Sampling station of TUPRAŞ refinery.

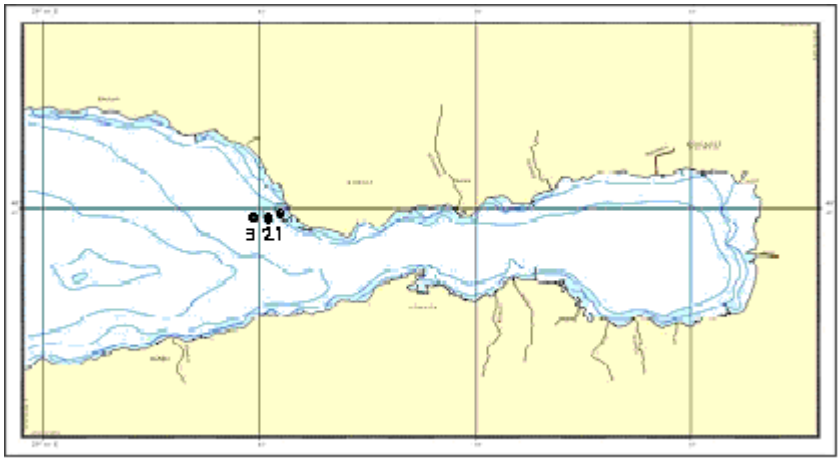


Figure 4. Sampling statiomn of Ali Ağa refinery.

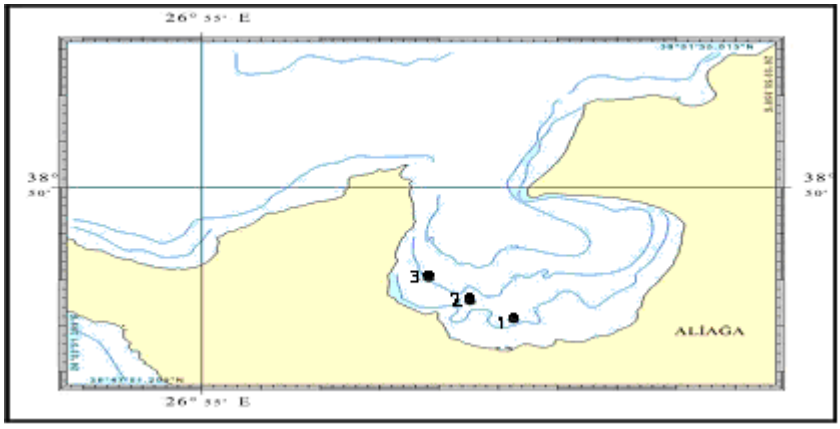


Figure 5. Sampling stations of Istanbul Strait.

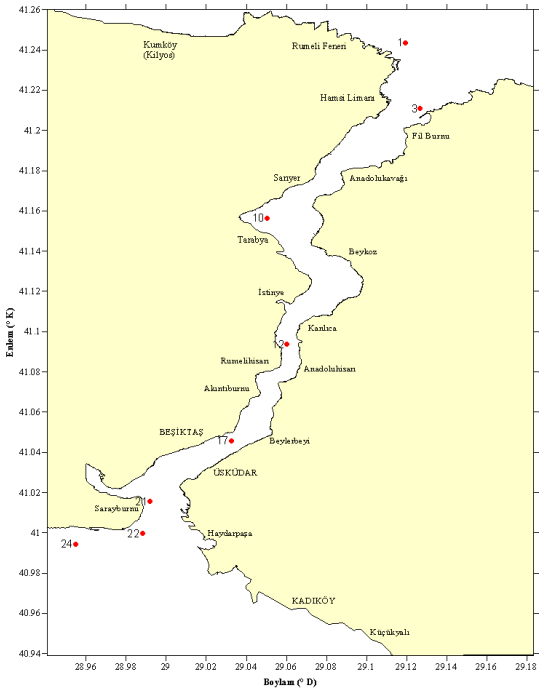


Figure 6. Sampling stations of Golden Horn.

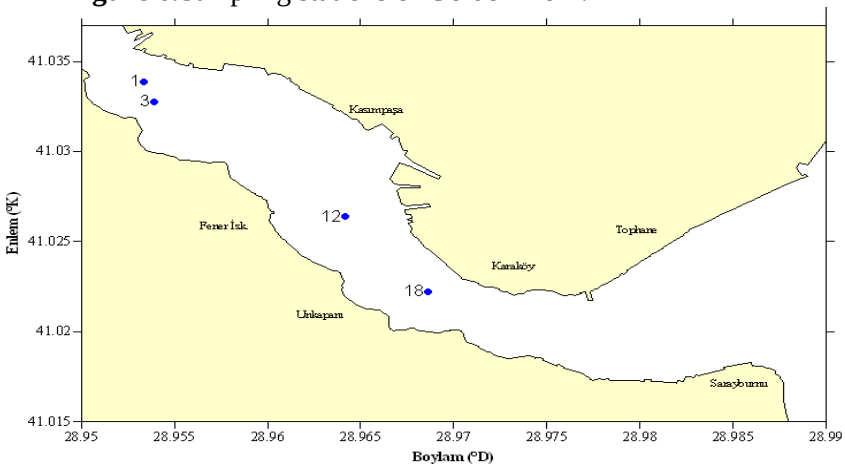
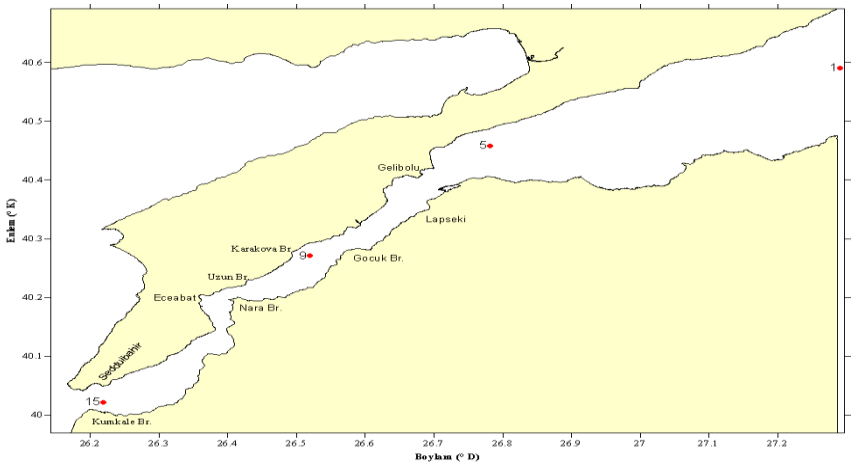


Fig.7. Sampling Stations of Çanakkale Strait.



Determination of oil concentration
In sea water

3L sea water samples were taken from the surface and 10 ml dichloromethane (DCM) added for preservation. 700 ml sea sample were extracted three times with 50 ml DCM. The extracts were combined, dried over anhydrous sodium sulfate, filtered and then distilled at 40 ^{o}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). Oil pollution in sea water and sediments were determined by using the standard curve equation of crude oil which was transported through the Istanbul Strait.

The Standard curve of Russian crude oil was used as reference in the concentration of 0.25-1.5 µg/L in hexane. The oil pollution in examined sample were calculated from the equation of calibration curve
(y= 301.82x c-1.54).

These samples were obtained from TUPRAŞ refinery, İzmit, Turkey in 2005, 2006 and 2007.

In sediment

20 g of sample were mixed with sodium sulphate anhydrous and extracted with dicholomethane (DCM) 100 mL and then with DCM in Soxhlet

apparatus during 8 h. The extracts were collected and dried over sodium sulphate anhydrous, filtered and distilled at 40 ^{o}C. The residue was dissolved in 10 mg hexane and it intensity was measured at indicated in part of sea water.

Determination of detergent concentration (Standard Methods 1995)

700 ml sample were added to a separatory funnel. The solution alkalinized by addition drop wise of 1 N NaOH using phenolphthalein indicator, then discharge the pink color by dropwise addition of 1 N H_2SO_4.10 ml chloroform and 25 ml methylene blue reagent were added to solution then vigorously shaken for 30 sec and let the phases separate. The chloroform layer was transferred into a second separatory funnel. The extraction was made three times. The chloroform extracts were combined in the second separatory funnel. 50 ml wash solution was added and shaken vigorously for 30 sec. The chloroform layer was filtered through glass wool into a 100 ml volumetric flask.

Its absorbance was measured in UV spectrophotometer (Shimadzu 1601) at 652 nm against a blank of pure chloroform. The calibration curve of LAS was plotted in a concentration of 10, 50, 100, 150 µg/L. Using standard curve equation of LAS level in sea water was calculated (y=0.0159xc-0.047).

Reference substances of LAS (97.7%) were obtained from Lever (Gebze, Turkey).

Chloroform (Pro analysis) and all chemicals used were Merck products (Darmstad). Sodium sulfate was obtained from BASF (Germany)

Stock LAS solution was prepared with 100 mg LAS in 100 ml distilled water.

Standard LAS solution: 1 ml LAS solution was diluted to 100 ml in distilled water.

Base and acid solution: 1 N NaOH, 1 N H_2SO_4.

Methylene Blue (MB) solution: 100 mg MB was dissolved in 100 ml distilled water; 30 mg was taken and adjusted to 1000 ml in distilled water.

Washing solution: 50 g $Na_2HPO_4H_2O$ were dissolved in 500 ml distilled water, 41 ml of 6 N H_2SO_4 were added and the volume adjusted to 1000 ml.

Results and discussion

1.Oil pollution

1.1. Oil pollution in sea water

*1.1.1.*Oil amounts in sea water of found in İstanbul Strait, Golden Horn and Çanakkale Strait are shown in Table 2.

Table 2. Oil pollution in İstanbul Strait, Golden Horn and Çanakkale Strait. (18-19. Feb.2005) (μg/L)

Station	Number	Depth (m)	Found
Istanbul Strait	1	28	6.82
	3	20	7.86
	10	33	17.51
	12	67	25.74
	17	46	28.15
	21	30	29.55
	22	18	29.42
	24	30	10.90
Golden Horn	3	S	273.95
	12	36	70.10
	13	52	532.47
	14	S	4214.29
	21	32	52.04
Çanakkale Strait	1	S	32.99
	5	S	41.55
	9	S	42.96
	15	S	34.22

S: Surface

1.1.2. Oil concentrations in sea water from Ali Ağa and TUPRAŞ are shown in Table 3.

Table 3. Oil concentrations in TUPRAŞ and Ali Ağa refineries. (µg/L)

Station	07.Agust.06	13.Nov.06	07.Dec.06	27.July.06	24.July.2007	22.August.2007
Aliağa 1	64.68	-	33.03	37.41	147.5	-
Aliağa 2	71.77	-	21.99	31.44	125.0	-
Aliağa 3	62.19	-	50.74	57.67	230.0	-
Tüpraş 1	87.34	36.93	-	-	-	42.91
Tüpraş 2	77.92	34.25	-	-	-	46.61
Tüpraş 3	90.02	49.37	-	-	-	78.84

-Not examined

1.2. Oil pollution in sediments

Oil concentrations in sediments are shown in Table 5.

*1.2.1.*Oil concentrations in sediment of Istanbul Strait, Golden Horn and Çanakkale Strait are shown in Table 4.

Table 4. Oil concentrations in sediments in İstanbul Strait, Golden Horn and Çanakkale Strait. (18-20.02.2005) (µg/g).

Station	Number	Depth (m)	21.02.2005
Istanbul Strait	10		554.71
	12		8.19
	13		3.49
	17		9573.38
	21		970.37
	25		957.61
Golden Horn	1	7	1086.88
	3	10	1126.45
	12	36	895.44
	18	52	679.03
Çanakkale Strait	1	80	7.01
	5	42	17.67
	9	65	31.52
	13		14.32
	15		13.10

1.2.2. Oil concentrations in TUPRAŞ and Ali ağa refinery area.

Table 5. Oil concentrations in sediment area11.13.2006, 7.12.2006.(µg/g)

TÜPRAŞ-20 m	1500.6
Ali Ağa	58.64

2.Detergent pollution

Detergent concentrations in Istanbul Strait, Golden Horn and Çanakkale Strait are shown in Table 6 a and b.

Table 6 a.Detergent concentrations in Istanbul Strait, Golden Horn and Çanakkale Strait. (14-20.02.2005) (ug/L).

Station	No	Depth (m)	Found
Istanbul Strait	1	28	40.41
	3	30	39.47
	10	33	41.05
	12	67	31.23
	17	46	20.48
	21	30	18.58
	22	8	27.03
Golden Horn	3	S	-
	12	S	-
	14	S	-
	18	S	-
	22	S	-
Çanakkale Strait	1	S	30.90
	5	S	30.26
	9	S	34.55
	13	S	14.32
	15	S	24.98

S: Surface, - not determined.

Table 6 b. Detergent pollution in Çanakkale Strait (04.06.2005) (ug/L).

Station	Depth	Found
Gelibolu	S	15.17
Gelibolu	10 m	18.3
Gelibolu	Middle S	14.13
Gelibolu	Middle 10 m	18.66
Lapseki	S	24.92
Lapseki	10m	19.25
Çanakkale	S	21.83
Çanakkale	10m	25.02
Çanakkale	Middle S	16.93
Çanakkale	Middle 10m	19.8
Kilitbahir	S	13.9
Kilitbahir	10m	11.51

S. Surface

Detergent concentrations in TUPRAŞ and Ali Ağa refineries are shown in Table 7 (ug/L).

Table 7. Detergent concentrations in refineries area (ug/L).

Station	07.Agust.06	13.Nov.06	07.Dec.06	27.July.07	22.Agust.07
TÜPRAŞ 1	13.73	56.33	-	-	18.74
2	12.59	46.41	-	-	27.3
3	7.80	35.15	-	-	14.39
Aliağa 1	21.88	-	38.67	38.38	-
2	40.73	-	60.39	25.54	-
3	23.74	-	52.52	32.39	-

Comparison of the maximum concentration of oil with earlier findings in 1997-2003 (Güven et al. 2005) and 2003-2005 (Güven et al. unpublished) as:

In Istanbul Strait: the oil pollution level was generally found lower than 1997-2005 results (Güven et al. 2003, 2005).

In Golden Horn: the oil level was found very higher (42114.29 µg/L) than the findings of Güven et al. (unpublished data)

In Ali Ağa (Aegean Sea): The oil level is lower than the results of Öztürk et al. 2006.

In TUPRAŞ refinery: The oil level was found very higher than in Ali ağa refinery.

In Çanakkale Strait: oil level found is generally lower than in 1996-1997 (Güven and Ilgar 2002) and 2001-2002 (Güven et al. 2002).

The limit of oil concentration in sea water was 2.5µg/L through FAO (1982) and 10 µg/ L through UNESCO (1982 a,b) and when sea water contains hydrocarbon levels lower than 2.5 µg/ L or 10 µg/ L it can be classified as unpolluted. In this survey the concentrations of oil (dispersed/ dissolved hydrocarbons) in sea water found were about 20 and 40 times higher than the international limits. Law (1981) considered that the concentration of about 5 $\mu g l^{-1}$ is low for inshore waters.

The limit of oil in sediment was 10 µg/ g. When comparing the oil concentrations measured in this work with limit for sediments they are about 150 times higher for TUPRAŞ and 5.8 times for Ali Ağa. 957 times for Istanbul Strait, 112 times for Golden Horn and 3 times for Çanakkale Strait.

In the literatures are not found a limit value for detergent pollution in sea water. Because detergent LAS_s are not stable. The loss time of LAS in sea water was differed through the environmental condition as salinity, aeration phenyl attachment to carbon chain, carbon number, time, type of number of microorganisms in sea water.

When comparing the concentration of detergent in both refinery TUPRAŞ refinery seems to be more polluted than Ali Ağa refinery (Güven et al. 1997).

Conclusions

The oil concentrations measured in this area did not refer significantly to pollution. The results varied according to sampling time, and environmental condition. On the other hand the pollution changes time to time, depending on the process of refineries. The oil levels found in these investigations are higher than the limit published by WHO.

The maximum concentration of oil in sediment was 9573 µg/g for Istanbul Strait, 1126.45 µg/g for Golden Horn and 1500.6 µg/g near TUPRAŞ

refinery. When we compare the oil pollution in sediments between TUPRAŞ and Ali Ağa refineries, TUPRAŞ refinery is more polluted.

Özet

Bu çalışmada, Türk Boğazları, TÜPRAŞ ve Ali Ağa rafinerileri sahasında petrol ve deterjan kirliliği araştırılmıştır. Bu kirlilik unsurlarının değişik bir seyir takip ettiği ve mevsime bağlı olarak değiştiği tespit edilmiştir. En yüksek petrol kirliliği deniz suyunda Istanbul Boğazı'nda 29.55 µg/l, Haliç'te 4214.29 µg/L ve Çanakkale Boğazında 42.96 µg/L olarak bulunmuştur. Sediment üzerinde yapılan çalışmada en yüksek petrol kirliliği Istanbul Boğazı'nda 9573.38 µg/g, Haliç'te 1126.45 µg/g ve Çanakkale Boğazı'nda 31.52 µg/g saptanmıştır.

Rafineri civarındaki sedimentlerde yapılan çalışmada ise TUPRAŞ civarında 1500.6 µg/g, Ali Ağa'da ise 58.64 µg/g petrol kirliliği bulunmuştur. TUPRAŞ rafinerisi sedimentinde saptanan kirlilik en yüksek kirliliktir.

Gerek deniz suyunda ve gerekse sedimentlerde tespit edilen kirlilik miktarı uluslararası kabul edilen sınırlardan çok yüksektir.

Deterjan kirliliği için her hangi bir sınır değer yoktur. Bu incelenen bölgelerde bulunan deterjan kirliliği daha evvelki çalışmaların sonuçlarına benzerdir.

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