

RESEARCH ARTICLE

Spatial distribution of dissolved/dispersed petroleum hydrocarbons in seawater and sediments from the Mediterranean coastal area of Türkiye

Selma Ünlü^{1*}, Elif Özgür²

ORCID ID(s): S.Ü. 0000-0002-9156-4332; E.Ö. 0000-0001-5699-7565

¹ Institute of Marine Sciences and Management, Istanbul University, 34134 Istanbul, TÜRKİYE

² Turkish Marine Research Foundation, P.O. Box: 10, Beykoz, 34820, Istanbul, TÜRKİYE

*Corresponding author: su@istanbul.edu.tr

Abstract

In this study, the distribution of dissolved/dispersed petroleum hydrocarbons (DDPHs) in coastal water and sediments from the western coastline of Antalya Gulf (Mediterranean Sea, Türkiye) in December 2018 and in May 2019 was investigated by the UV-fluorescence spectroscopy method. The hydrocarbon concentrations ranged from 4.6 to 9.1 µg/L (Thetis-Oil equivalents) for coastal waters and from 6.5 to 11.2 µg/g, dry weight (Thetis-Oil equivalents) for sediments, respectively. No significant correlations were observed between petroleum hydrocarbons and physico-chemical parameters measured in seawater (except pH; $r = -0.62$, $p < 0.05$). When compared with various environmental hydrocarbon pollution criteria, the levels found in this study indicated that the coastal waters and sediments were considerably polluted. Intensive maritime activities, ship and boat traffic increased tourist influx, oil spills from ships, illegal discharge of oily wastewater, increase in population density, runoff, and atmospheric fallout during rainy periods were considered the main causes of local hydrocarbon pollution in the region. The findings suggest that regional monitoring programs need to be continued in all sensitive coastal areas to describe concentrations and distributions of hydrocarbons at the sea surface, in sediments, and in biota. The results of this study can contribute to the baseline data which can be used for future monitoring programs and regulatory actions to improve the environmental quality of the Mediterranean coastal zone of Türkiye.

Keywords: Petroleum hydrocarbons, coastal waters, surface sediment, UV-fluorescence spectroscopy, contamination, Mediterranean Sea

Received: 13.09.2022, **Accepted:** 15.11.2022

Introduction

Various resistant pollutants from land and ships, uncontrolled use of living resources, destruction of habitats, physical deformation of coastal areas, climate change, increasing population, industrialization, maritime transport and tourism are likely the most important threat factors for coastal areas (Cullinan 2006). Like many seas in the world, Mediterranean coastal areas are unfortunately affected by these pressure factors, especially oil and petroleum-derived pollution. Oil wastes appearing on our coasts are a threat to our country, which has a relative tourism advantage in the Mediterranean basin. The water-soluble fractions of crude oils and refined products include a variety of compounds that are toxic to the marine environment and human health. In aquatic systems, petroleum hydrocarbons undergo physical and chemical change between dissolved, colloidal phases (ITOPF 1993). Other significant factors affecting the distribution are water depth, sediment grain size, land-based pollutant sources, and biodegradation processes. Climate change may affect the hydrological cycle by altering the intensity of precipitation and runoff, thereby affecting the distribution of water-soluble fractions of petroleum hydrocarbons along coastal areas (Huntington 2006), especially considering the summer holiday season in the Mediterranean Region.

The distribution of petroleum hydrocarbon in water and sediments of the Mediterranean coastal areas of Türkiye has been the subject of several studies (Saydam *et al.* 1988; Balcı 1993; Yılmaz *et al.* 1991, 1998; Güven *et al.* 1998, 2004; Bildacı *et al.* 2000; Öztürk *et al.* 2007; Demir 2011; Telli Karakoç *et al.* 2016). Due to the lack of information regarding the average level of hydrocarbon contamination along the western coast of Antalya Gulf, this study was designed to investigate the spatial distribution of dissolved/dispersed hydrocarbon in the coastal waters and surface sediments. Furthermore, the acquired data were evaluated with several types of environmental hydrocarbon contamination criteria. The results of this study will contribute to the baseline data and provide valuable insights into future monitoring programs and regulatory actions to improve the environmental quality of the Mediterranean coastal zone of Türkiye.

Materials and Methods

Study area

The Mediterranean Sea has served as a critical transportation route since ancient times and has affected all the important civilizations that have occupied its shores (UNEP/MAP 2017). Shallow coastal areas host sensitive ecosystems. Marine recreational fisheries are an integral part of Mediterranean coastal life and are commonly practiced throughout the region (Grati *et al.* 2021). The areas surrounding the Mediterranean include some of the world's famous tourist destinations. Therefore, tourism is an important source of income for the countries that have a coast on the Mediterranean, especially Türkiye (Mejjad *et al.* 2022).

Antalya, the city on the Mediterranean coast of south-western Türkiye, is the Turkish capital of international tourism. In this study, five tourism districts (Kaş, Kekova, Finike, Adrasan, and Kemer -Ayıışığı) located along the western coastal area of Antalya were considered (Figure 1).

Kaş (S1) is an important tourism centre located in the westernmost part of Antalya (Figure 1A). In addition, it is a small but important port town in the Lycia region. Kaş and its harbor surrounding important ancient cities, such as Phellos, Antiphellos and Isinda, are the areas of intense tourism activities, especially diving tourism. In addition to diving, tour and fishing boats, it also shelters approximately 80 yachts.

Kekova (S2) is located around Üçağız and Kaleköy, near the Demre district of Antalya (Figure 1B). The Kekova coastline has been under water since ancient times due to the continuous rise of the waters. The area covering Kekova Island and its surroundings has been taken under protection as Kekova Special Environmental Protection Area. Üçağız (Teimoussa) port, which is one of the sampling points, is known as the winter port. There is Üçağız Village as a settlement in the north, which carries the remains of the ancient city of Lycia and was established in its place. It has 7-8 meters of muddy ground all over the port. However, there is an anchorage area for yachts on the west of the harbour and a dockyard on the east. The pier in the harbour is the station for daily and weekly boats that sail to the bays for tourism purposes.

Finike (S3), located at the eastern Mediterranean Sea (Figure 1C), has special importance for the protection of biological diversity with its Submarine Mountains (Anaximander). The region is the first protected area declared in our country's territorial waters and open seas (Öztürk 2021).

Adrasan (S4) coastline has the longest beaches to the west of Antalya (Figure 1D). There are hotels and restaurants, markets and water sports centres located along both sides of Adrasan Stream and Adrasan Bay.

Kemer (S5), located in the west of Antalya Gulf (Figure 1E), has very indented shores and a fully equipped marina with a capacity of 250 yachts. The depth of the marina area is approximately 2.5-5 m. Since Kemer town has no other port to be allocated to commercial boats, these boats are moored in a separate part of the marina. Due to its location and technical competence, it is frequently used by yacht owners. There are many health, transportation, accommodation and shopping opportunities and beautiful beaches and ancient city ruins around the marina.

Sampling collection

Two marine surveys were realized within the scope of the project TR2013/0327.05.01-02/072, "Climate Change Adaptation for the Sea and Coasts

of Antalya,” carried out jointly by the Antalya Metropolitan Municipality and the Turkish Marine Research Foundation (TÜDAV). The first survey was administered in 4-12 December 2018, and the second in 25-27 May 2019.

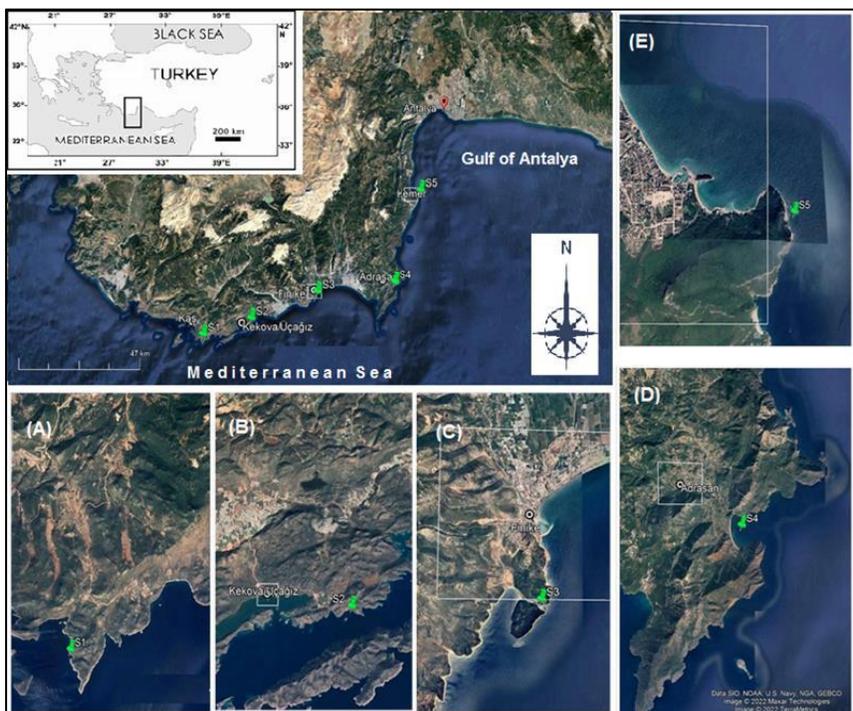


Figure 1. Location of the study area and sampling sites (Google map Imagery@2022TerraMetrics) **(A):** Kaş (S1), **(B):** Kekova (S2), **(C):** Finike (S3), **(D):** Adrasan (S4), **(E):** Kemer (S5).

Coordinates (latitude; longitude): S1–36°8'30.43"N; 29°40'42.42"E, S2–36°11'32.15"N; 29°52'33.71"E, S3–36°16'28.17"N; 30°8'56.51"E, S4–36°18'21.68"N; 30°28'17.46"E, S5–36°35'41.83"N; 30°35'32.43"E.

The sampling sites are shown in Figure 1. At five stations, the basic physical (temperature and Secchi depth) and chemical (salinity, dissolved oxygen, and pH) properties of sea-surface water were measured using MRC sonde and Secchi disk (30 cm) simultaneously with samplings. Duplicate surface seawater samples were collected from five stations by surface sampler apparatus. The surface seawater samples were taken in 2.8 L amber glass bottles, and 15 ml dichloromethane (DCM) was added immediately for preservation. Sediment samples were collected by SCUBA diving from the upper infralittoral region in the coastal region of the station using a spatula, scraping surface sediment to a maximum depth of approximately 2 cm. The samples were boxed on dry ice and transported to the laboratory as soon as possible for analysis.

Extraction procedures and analysis

Extraction of the petroleum hydrocarbons from the water and sediment samples collected was achieved using liquid-liquid and Soxhlet extraction techniques, respectively, followed by column clean up. Details of sample preparation and quantitative analysis can be found in the MARPOLMON protocol -IOC (1984) and Ünlü *et al.* (2009). The water sample (1.0 L) was extracted with dichloromethane (3x 50mL) using separatory funnel. The organic extracts were combined, dried with anhydrous sodium sulphate and concentrated using a rotary evaporator reduced about 2 mL. Sediment samples were air-dried for about 3 days before extraction. Sufficient quantity of anhydrous sodium sulphate (Na₂SO₄) was mixed with 10 g of the dried sample for further removal of moisture, and extracted with 100 mL dichloromethane in a Soxhlet extractor for 8h with activated copper. The extract was run through a glass funnel containing anhydrous sodium sulphate, concentrated in a rotary evaporator and solvent exchanged to n-hexane, ready for cleanup (IOC 1984; Ünlü *et al.* 2009), and then analyzed by spectrofluorometer.

The UV fluorescence method is used to monitor spatial and temporal concentration gradients of petroleum hydrocarbons due to its simplicity, sensitivity, and easy application (Erhardht and Petrick 1989; Zanardi *et al.* 1999; Rodriquez and Sanz 2000). The petroleum hydrocarbons were analyzed by UV fluorescence spectroscopy (UVF, Shimadzu RF-5301). The intensity of the samples was measured at 310 nm excitation (ex.) and 360 nm emission (em.) wavelengths. Standard response curves of fluorescence intensity versus concentration are generated for a) chrysene (Merck), the standard aromatic hydrocarbon which is used conventionally in many studies and b) Thetis-Oil as defined by Ünlü *et al.* (2009). The excitation and emission wavelengths were fixed at 310 and 360 nm, respectively. One cm length quartz cuvettes were used for the measurements.

Data Analysis

Pearson's correlation coefficients (r) were calculated as statistical measures of the strength of linear relationships among the petroleum hydrocarbon concentrations, physico-chemical parameters. The statistical significance was defined as $p < 0.05$. Data analysis was performed using STATISTICA 6.0 software package (StatSoft, USA).

Results and Discussion

The water qualities in sampling sites were evaluated according to the Turkish Water Quality Regulations and EU directive [79/923/EEC] and physicochemical parameter values of the surface water are given in Table 1. The correlation analysis revealed the relationships between the physicochemical parameters and dissolved/dispersed petroleum hydrocarbon levels (Table 2). Measurements of Secchi disc depth (SDD) exhibited remarkable spatial and seasonal variability in

the coastal waters affected directly by land-based inputs of nutrients. Also, SDD variations can reflect changes in particulate matter from runoff or wind-induced turbidity, changes in phytoplankton biomass, or mostly humic and fulvic acids in the water (Falkowski and Cara 1992). In this study, SDD values ranged from 3.5 to 30m (mean = 15.0 ± 9.6 m) in winter period and from 12.5 to 22 m (mean = 18.3 ± 3.8) in the summer period (Table 1), indicating a significant increase with temperature ($r = 0.64$; $p < 0.05$) (Table 2). Our measurements showed a much more rapid change in Secchi depths than in these previous studies (Figure 2). Temperature is an important quality parameter that is considerably affected by many factors (such as depth, geographic location, and air circulation). Also the increase in temperature accelerates biochemical processes in the water column (Literathy and Al-Bloushi 1988). In this study, temperature varied from 18.9 to 21.2°C (mean 20.4 ± 0.9 °C) in the winter period and from 20.9 to 23.9°C (mean = 22.4 ± 1.2 °C) in the summer period (Table 1). Similar to previous studies (Figure 2), sea surface water temperatures increased by 2.5 degrees in the summer of 2019, especially at sampling stations S3 (Finike), S4 (Adrasan), and S5 (Kemer).

In this study, the pH obtained ranged from 8.0 to 8.2 (mean 8.1 ± 0.07) (Table 1), similar to previous studies (Figure 2). All the values are within the Turkish Water Quality Regulations permissible range (Table 1) across the sampling stations. Petroleum hydrocarbon biodegradation occurs over a range of pH values. However, it is generally optimum at near-neutral to slightly alkaline conditions (pH 6.5-8) (USEPA-CADDIS 2022), explaining the negative correlation with petroleum hydrocarbon levels ($r = -0.62$, $p < 0.05$, Table 2). Salinity is an important water quality monitoring parameter that helps determine many aspects of the chemistry of natural waters and the biological processes within them. EU directive [79/923/EEC] has specified "a range of 12–38 PSU as the tolerable limit for salinity in coastal water". The recorded salinity levels were in the range of 37–37.2 PSU (mean 37.1 ± 0.1 PSU) (Table 1), and all the measurements in the sampling stations were within the EU permissible range. The results compared favourably with earlier findings documented (Figure 2), and the variability of the figures was very limited. No significant spatial differences were observed between the sampling locations, but a negative correlation was established between Secchi disc depth and salinity in the seawater ($r = -0.62$, $p < 0.05$)(Table 2). The dissolved oxygen (DO) ranged from 4.1-7.7 mg/L (mean 6.3 ± 1.3 mg/L) in the winter period to 6.4-8.5 mg/L (mean 7.3 ± 0.8 mg/L) in the summer period (Table 1), similar to previous studies (Figure 2). Surface DO levels measured in this study were above the accepted limit level (5 mg/L) for aquatic organisms to survive. In addition, according to the classification of "Regulations on the Quality of coastal Waters", all of the sampling sites (except station S1-Kaş) were evaluated as good quality (Class II) in winter season and as very good (Class I) quality in the summer season (see Table 1).

Table 1. Physico-chemical parameters measured in seawater during the sampling period and the comparison with some regulations - (W.D: Water Depth (m), T: Temperature (°C), SDD: Secchi disk depth (m), S:Salinity (PSU), D.O: Dissolved Oxygen (mg/L))

Sites	WINTER SEASON						SUMMER SEASON					
	(2018)						(2019)					
	WD	SD	T	pH (a)	S (b)	DO (c)	WD	SD	T	pH (a)	S (b)	DO (c)
S1-	35	30	21.2	8.2	37	4.1	32	22	21.8	8.2	37.2	7.4
S2-	65	15.5	21	8.2	37	6.6	56	17	20.9	8.1	37.1	6.4
S3-	20	12	20.4	8.2	37.2	6.6	20	12.5	22	8.1	37.2	7.3
S4-	19	14	20.5	8.1	37.1	7.7	20	19	23.3	8.1	37	8.5
S5-	20	3.5	18.9	8	37.2	6.6	25	21	23.9	8.1	37	6.9
<i>Min.</i>	19	3.5	18.9	8	37	4.1	20	12.5	20.9	8.1	37	6.4
<i>Max.</i>	65	30	21.2	8.2	37.2	7.7	56	22	23.9	8.2	37.2	8.5
<i>Mean</i>	31.8	15	20.4	8.1	37.1	6.3	30.6	18.3	22.4	8.1	37.1	7.3
<i>±SD</i>	±19.7	±9.6	±0.9	±0.1	±0.1	±1.3	±15.0	±3.8	±1.2	±0.1	±0.1	±0.8
^(a) pH	Between 6 and 9											
^(b) S	12–38 PSU (as the tolerable limit for salinity in coastal water)											
^(c) DO	Class I			Class II			Class III			Class IV		
	≥ 7 Very good			6 Good			5 Middle			< 5 Poor		

(a): Turkish Water Quality Regulations-(2016) (Table 6- Standard values to be provided by coastal and transitional waters used for recreation- [OG-10/8/2016-29797]

(b): EU directive [79/923/EEC]

(c): Turkish Water Quality Regulations-(2016) (Environment quality criteria for coastal waters in terms of general chemical and physicochemical parameters (-for Black Sea and Mediterranean Sea [Revised: OG-16/6/2021-31513] and the classification of quality criteria.

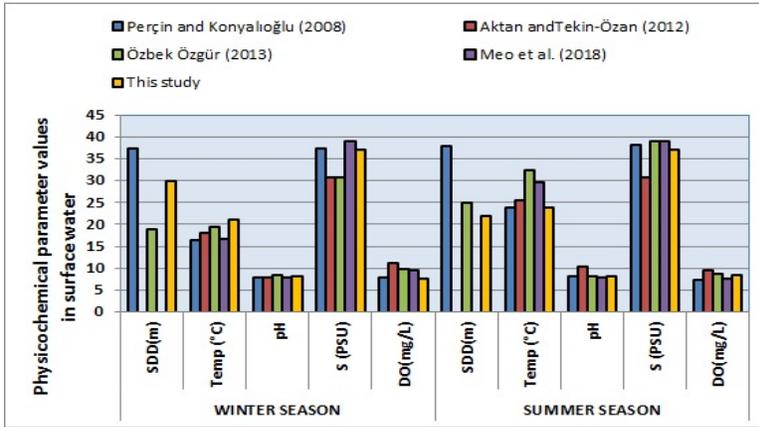


Figure 2. Comparison of previous and present data for physicochemical parameter values measured in surface water

Table 2. Pearson coefficient correlation matrix (r) between environmental parameters and dissolved/dispersed petroleum hydrocarbons content in seawater (n=10).

Variables	Temp	S	DO	pH	DDPH (seawater)
SDD	<u>0.64</u>	<u>-0.62</u>	-0.02	0.36	-0.32
p -value	0.043	0.048	0.95	0.29	0.35
Temp		-0.02	0.37	0.01	-0.41
p -value		0.95	0.28	0.95	0.23
S			0.24	-0.47	0.31
p -value			0.49	0.16	0.37
DO				-0.33	-0.28
p -value				0.35	0.43
pH					<u>-0.62</u>
p -value					0.048

Statistically significant at $p < 0.05$ level, shown in red.

SDD: Secchi disk depth (m), Temp: Temperature (C), S:Salinity (PSU), DO: Dissolved Oxygen (mg/L), DDPH: dissolved/dispersed petroleum hydrocarbon

Distribution of petroleum hydrocarbon levels in seawater samples

The results of the UV-fluorescence analyses of the seawater samples are given in Figure 3. The distribution along the western coastline of Antalya Gulf during the first cruise (December 2018) ranged from 5.3 to 9.1 $\mu\text{g/L}$ equivalents of Thetis-oil (0.6-0.9 $\mu\text{g/L}$ chrysene eq.), and the second cruise (May 2019) ranged from 4.6 to 6.7 $\mu\text{g/L}$ equivalents of Thetis-oil (0.3-1.0 $\mu\text{g/L}$ chrysene eq.). As shown in Figure 3, the higher concentrations were detected at station S5 (Kemer; 9.1 $\mu\text{g/L}$ and 6.7 $\mu\text{g/L}$) and the lowest at S1 (Kaş; 4.6 $\mu\text{g/L}$). The order of increase in the hydrocarbon values could be given as S5 (Kemer) > S4 (Adrasan), S2 (Kekova) > S3 (Finike) and S1 (Kaş). The comparison of the petroleum hydrocarbon

concentrations found in the present study with those of the other surface seawater samples previously published showed that the levels obtained in this study were lower than those detected in the Eastern part of the Mediterranean Sea (30.4 $\mu\text{g/L}$, Güven *et al.* 1998), in Fethiye (326.7 $\mu\text{g/L}$, Güven *et al.* 2004), in Göçek (14.00 $\mu\text{g/L}$, Güven *et al.* 2004), in Antalya Gulf-inner part (19.3 $\mu\text{g/L}$, Öztürk *et al.* 2007), in Finike Harbour (44.1 $\mu\text{g/L}$, Öztürk *et al.* 2007), and Kalkan Harbour (55.9 $\mu\text{g/L}$, Öztürk *et al.* 2007). The comparison of the hydrocarbon concentrations found in the present study with those of the other surface seawater samples published in the literature showed that the levels obtained in this study were lower than those detected in the Eastern part of the Mediterranean Sea (30.4 $\mu\text{g/L}$, Güven *et al.* 1998), in Fethiye (326.7 $\mu\text{g/L}$, Güven *et al.* 2004), in Göçek (14.00 $\mu\text{g/L}$, Güven *et al.* 2004), in Antalya Gulf-inner part (19.3 $\mu\text{g/L}$, Öztürk *et al.* 2007), in Finike Harbour (44.1 $\mu\text{g/L}$, Öztürk *et al.* 2007), and Kalkan Harbour (55.9 $\mu\text{g/L}$, Öztürk *et al.* 2007).

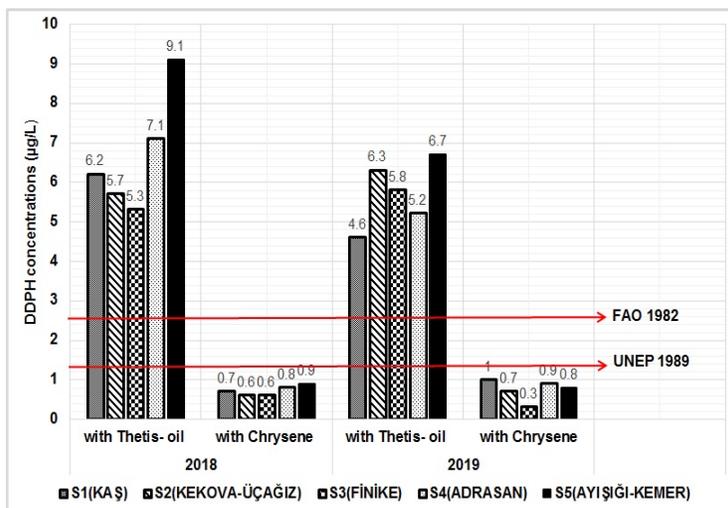


Figure 3. The concentrations of dissolved/dispersed petroleum hydrocarbon in seawater samples from the sampling sites and the limit values accepted by FAO (1982) and UNEP (1989) for oil and petroleum-derived pollution

On the other hand, a similar hydrocarbon concentration level) (9.5 $\mu\text{g/L}$ and 9.2 $\mu\text{g/L}$) was found in Kemer and Demre by Öztürk *et al.* (2007). Direct comparison of previous data is challenging due to differences in the compounds considered in each study, phase analyzed (dissolved, particulate, or both), and analytical methods. Unfortunately, to our knowledge, there is no Turkish legislation regulating the petroleum hydrocarbon contamination of the coastal waters. Hence, the ones based on the FAO and UNEP are used in Turkey. The concentrations in this study recorded higher than the average limits of 2.5 $\mu\text{g/L}$ (FAO 1982) and 1.2 $\mu\text{g/L}$ (UNEP 1989) for oil and petroleum-derived pollution in coastal areas and indicating that the coastal waters were polluted. The higher

levels could have emanated from the intensive tourism and shipping activities in the sampling sites. In addition, oceanographic characteristics a (such as the winds, tidal regime, wave pattern, currents, shoreline morphology, and light transmission), some physico-chemical conditions, and biological activities could be the main cause of the variations of petroleum hydrocarbon levels in surface water.

Distribution of petroleum hydrocarbon levels in the sediment samples

Data in Figure 4 show the distribution of DDPH concentrations in the surficial bottom sediments collected along the western coastal areas of the Antalya Gulf in the summer of 2019. The values expressed on a dry weight (DW) basis ranged from 1.6 to 10.5 µg/g equivalents of Thetis-oil (0.2-2.6 µg/g, DW., eq. chrysene). The highest concentrations were observed at stations S5 (Kemer) and S4 (Adrasan) (10.5 µg/g and 9.2 µg/g, DW, Thetis-oil equivalents) and the lowest at station S2 (Kekova-Üçağız) (1.6 µg/g, DW). The order of increase in the PH levels is given as follows: S5(Kemer), S4(Adrasan) > S3(Finike) > S1(Kaş) > S2 (Kekova). The distribution of petroleum hydrocarbon in marine environments can be affected by factors such as depth, sources of pollutants, grain size, physical, chemical and biological degradation processes (Literathy and Al-Bloushi 1988). The low values observed at stations S1-S3 could be attributed to physicochemical sea conditions and some of the removal processes (e.g., weathering, photolysis, photo-oxidation, biodegradation, metabolization, sedimentation, sediment burial, and transfer into the atmosphere), which selectively reduce the level of contamination. To our knowledge, there are no historical data regarding petroleum hydrocarbons in sediments from this study area. Thus, the data presented here established a baseline for future monitoring and managing these pollutants in this area.

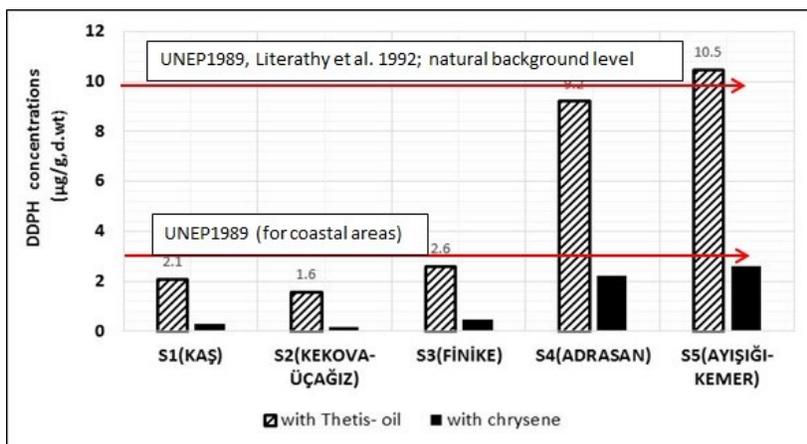


Figure 4. Dissolved/dispersed petroleum hydrocarbon (DDPH) concentrations (µg/g, d.w) in sediment samples from the sampling sites

The accepted petroleum hydrocarbon background limit level for marine sediments is $\leq 10 \mu\text{g/g}$ for uncontaminated areas other than oil refineries and waterways where transportation is made, while this value is $>50 \mu\text{g/g}$ for contaminated areas directly exposed to oil pollution (UNEP 1989; Literathy *et al.* 1992). The levels of DDPH at stations S5 (Kemer) and S4 (Adrasan) ($10.5 \mu\text{g/g}$ and $9.2 \mu\text{g/g}$, DW) were not significant and both levels were close to $10 \mu\text{g/g}$, DW, which corresponds to similar marine areas generally considered unpolluted (UNEP 1989; Literathy *et al.* 1992). However, according to UNEP (1989), the average concentration levels for general coastal areas are established at $2.8 \mu\text{g/g}$ for sediment and $0.1 \mu\text{g/g}$ for reference areas. Based on this classification, it can be stated that the levels of petroleum hydrocarbon obtained from the present investigation in both the Kemer and Adrasan coastal areas are above the alarming pollution level. Intensive maritime activities, ship and boat traffic increased tourist influx, oil spill from ships, illegal discharge of oily wastewater, increase in population density, runoff and atmospheric fallout during rainy periods are considered the main causes of hydrocarbon pollution in these regions.

Conclusions

The present investigation evaluated the level of petroleum hydrocarbon contamination in the western coastline of Antalya Gulf water and sediment samples. The concentration in seawater provides the recent source of petroleum hydrocarbons. However, the distribution of sediment patterns reflects the petroleum hydrocarbon accumulation/persistence over the year (*i.e.*, temporal concentration). Therefore, based on coastal pollution criteria, it can be stated that the levels of petroleum hydrocarbon obtained from the present investigation in both the Kemer and Adrasan coastal areas are above the alarming pollution level. It seems to pose a severe threat in the future with the rapid development of ecotourism, surface runoff, direct discharge into rivers, drainage from port areas, domestic effluent discharge, and various contaminants from ships. Oil wastes appearing on our coasts at the beginning of the tourism season are a threat to our country, which has a relative tourism advantage in the Mediterranean basin. Strict measures and rules should be implemented to prevent oil pollution, which takes months and years to clean up. Inspections should be tightened. Such places or hot spots on the Mediterranean coastline need urgent and particular action, therefore should be included in regular monitoring programs that fully conform to international standards. Monitoring the contaminant concentrations is crucial for understanding the biogeochemical processes of hydrocarbons in sediments. It is imperative that planned and continuous monitoring of pollutants be carried out in the polluted areas specified in this study and other vulnerable coastal areas. Such information is essential for ecological risk assessment and managing coastal regions with pollutant input.

Acknowledgments

This study was performed in the context of the project TR2013/0327.05.01-02/072 "Climate Change Adaptation for the Sea and Coasts of Antalya" within the framework of "Capacity Building in the Field of Climate Change in Turkey Grant Scheme." We thank both project partners, the Metropolitan Municipality of Antalya and Turkish Marine Research Foundation for their support during the study. We would like to express our gratitude to Prof. Dr. Bayram Öztürk and Assoc. Prof. Dr. Bülent Topaloğlu, the project staff Şeyma Merve Kaymaz Mühling and Merve Tan for their valuable efforts in the samplings and all necessary permissions were taken for the sampling procedures from the Republic of Türkiye, Ministry of Agriculture and Forestry.

Türkiye'nin Akdeniz kıyı alanından gelen deniz suyu ve sedimentlerindeki çözünmüş/dağılmış petrol hidrokarbonların mekansal dağılımı

Öz

Bu çalışmada, Antalya Körfezi'nin batı kıyı şeridinde (Akdeniz, Türkiye) Aralık 2018 ve Mayıs 2019'da kıyı sularında ve sedimanlarda çözünmüş/dağılmış petrol hidrokarbonlarının (DDPH) mekansal dağılımı UV-floresan spektroskopi yöntemi ile incelenmiştir. Petrol hidrokarbon konsantrasyonları sırasıyla deniz suyu için 4.6 ile 9.1 µg/L (Thetis-oil eşdeğerleri) ve sediment için 6.5 ile 11.2 µg/g, (Thetis-oil eşdeğerleri) arasında değişmektedir. Çözünmüş/dağılmış petrol hidrokarbonları ile deniz suyunda ölçülen fiziko kimyasal parametreler arasında önemli bir korelasyon gözlenmedi (pH hariç; $r = -0.62$, $p < 0.05$). Çeşitli çevresel hidrokarbon kirlilik kriterleri ile karşılaştırıldığında, bu çalışmada bulunan seviyeler, kıyı sularının ve sedimentlerin önemli ölçüde kirlendiğini açıkça göstermektedir. Yoğun denizcilik faaliyetleri, gemi ve tekne trafiği, artan turist akışı, gemilerden kaynaklanan petrol sızıntıları, yağlı atık suların yasadışı deşarj, nüfus yoğunluğunun artması, yüzey akışı ve yağışlı dönemlerde atmosferik serpinti bölgedeki yerel hidrokarbon kirliliğinin başlıca nedenleri olarak kabul edilmektedir. Deniz yüzeyinde, sedimentlerde ve biyotadaki hidrokarbon konsantrasyonlarını ve dağılımlarını tanımlamak için tüm hassas kıyı alanlarında bölgesel izleme programlarının sürdürülmesi gerekmektedir. Bu çalışmanın sonuçları literatüre yeni veriler ekleyecek ve Türkiye'nin Akdeniz kıyı çevresinin çevresel kalitesini iyileştirmek için gelecekteki izleme programları ve düzenleyici eylemler için değerli bilgiler sağlayacaktır.

Anahtar kelimeler: petrol hidrokarbonlar, kıyı suları, sediment, UV-floresan spektroskopisi, kirlilik, Akdeniz

References

Aktan, N., Tekin-Özan, S. (2012) Levels of some heavy metals in water and tissues of chub mackerel (*Scomber japonicus*) compared with physico-chemical parameters, seasons and size of the fish. *Journal of Animal and Plant Sciences* 22 (3): 605-613.

Balçı, A. (1993) Dissolved and dispersed petroleum hydrocarbons in the Eastern Aegean Sea. *Marine Pollution Bulletin* 26: 222-223.

Bıldacı, I., Ünlü, S., Güven, K.C. (2000) Oil pollution of eastern Mediterranean Sea, south of Turkey. *Turkish Journal of Marine Sciences* 6(1): 1-7.

Cullinan, C. (2006) Integrated Coastal Management Law: Establishing and Strengthening National Legal Frameworks for Integrated Coastal Management. FAO, Rome, Italy.

Demir, V. (2011) Biodiversity Research in Kaş-Antalya Marine Protected Area Planning via Decision Support Systems. PhD Thesis, Institute of Marine Sciences and Management, Department of Marine Environment, Istanbul University, İstanbul, Turkey (in Turkish).

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

Falkowski, P. G., Cara, W. (1992) Phytoplankton productivity in the North Pacific Ocean since 1900 and implications for absorption of anthropogenic CO₂. *Nature* 358 (6389): 741-743.

FAO (1982) The Review of the Health of the Oceans. FAO/IMCO/UNESCO/WMO/WHO/IAEA/UNEP Joint Group of Experts on Scientific Aspects of Marine Pollution (GESAMP). Rep Stud Gesamp 15: 108.

Grati, F., Carlson, A., Carpentieri, P., Cerri, J. (2021) Handbook for Data Collection on Recreational Fisheries in the Mediterranean and the Black Sea. FAO Fisheries and Aquaculture Technical Paper No: 669. FAO, Rome.

Güven, K.C., Öztürk, B., Ünlü, S., Balkıs, N., Aksoy, A., Cumalı, S. (2004) The oil, detergent and heavy metals pollution of Ölüdeniz, Fethiye and Göçek, south west of Turkey. *Journal of the Black Sea/Mediterranean Environment* 10(3): 233-244.

Güven, K.C., Ünlü, S., Bıldacı, I. Doğan, E. (1998) An investigation on the oil pollution of the eastern Mediterranean coast of Turkey. *Turkish Journal of Marine Sciences* 4: 51-60.

Huntington, T.G. (2006) Evidence for intensification of the global water cycle: review and synthesis. *Journal of Hydrology* 319: 83-95.

IOC (1984) Manual for Monitoring Oil and Dissolved/Dispersed Petroleum Hydrocarbons in Marine Waters and on Beaches. Intergovernmental

Oceanographic Commission, UNESCO, Paris. 35pp. DOI: <https://doi.org/10.25607/OBP-1417>

ITOPF (1993) Response to Marine Oil Spills. The International Tanker Owners Pollution Federation Ltd., London.

Literathy, P., Al-Bloushi, A. (1988) Behaviour and Fate of Oil in the Marine Environment: Physical, Biological and Chemical Processes. EES-122 Report KISR 3040, Kuwait Institute for Scientific Research, Kuwait.

Literathy, P., Morel, G., Zorba, M., Samhan, O., Al-Bloushi, A., Al-Hashash, N., Al-Matrouk, K., Jacob, P.G. (1992) Petroleum Compounds in the Marine Environment of Kuwait. EES-100Final Report, Kuwait Institute for Scientific Research, Kuwait.

Mejjad, N., Rossi, A., Pavel, A.B. (2022) The coastal tourism industry in the Mediterranean: A critical review of the socio-economic and environmental pressures and impacts. *Tourism Management Perspectives* 44: 101007 doi: <https://doi.org/10.1016/j.tmp.2022.101007>.

Meo, I., Miglietta, C., Mutlu, E., Deval, M.C., Balaban, C., Olguner, M.T. (2018) Ecological distribution of demersal fish species in space and time on the shelf of Antalya Gulf, Turkey. *Marine Biodiversity* 48: 2105-2118.

Özbek Özgür, E. (2013) Macrobenthic Echinoderm fauna of the littoral zone of the gulf of Antalya and some ecological factors affecting their seasonal distribution, PhD thesis, Institute of Natural and Applied Sciences, Department of Fisheries, Akdeniz University, Antalya. 431pp. (in Turkish).

Öztürk, B. (2021) Non-indigenous Species in the Mediterranean and the Black Sea. Studies and Reviews No. 87 (General Fisheries Commission for the Mediterranean). FAO, Rome.

Öztürk, B., Altuğ, G., Çardak, M., Çiftçi, P.S. (2007) Oil pollution in surface water of the Turkish side of the Aegean and Eastern Mediterranean Seas *Journal of the Black Sea/Mediterranean Environment* 13(3): 207-214.

Percin, F., Konyalıoğlu, S. (2008) Serum biochemical profiles of captive and wild northern bluefin tuna (*Thunnus thynnus* L. 1758) in the Eastern Mediterranean. *Aquaculture Research* 39(9): 945-953.

Rodriquez, J.J.S., Sanz, C.P. (2000) Fluorescence techniques for the determination of polycyclic aromatic hydrocarbons in marine environment; an overview. *Analisis* 28(8): 710-717.

Saydam, A.C., Yılmaz, A., Baştürk, O., Salihoğlu, İ. (1988) Petrol hydrocarbon in sea water, marine organism and sediments from Northeastern Mediterranean and Aegean Sea. *Rapports et Procès-Verbaux des Réunions de la Commission Internationale pour l'Exploration Scientifique de la Mer Méditerranée* 31(2): 163.

Telli Karakoç, F., Ediger, D., Günay, A.S. (2016) Oil Pollution in Turkish waters of the Mediterranean Sea. In: *Oil Pollution in the Mediterranean Sea: Part II.*, (eds., Carpenter, A., Kostianoy, A.), *The Handbook of Environmental Chemistry*, Vol: 84, Springer, Cham.

UNEP (1989) Evaluation of MED POL- Phase II Monitoring Data-Part IV- Petroleum and Chlorinated Hydrocarbons in Coastal and Reference Areas (UNEP (OCA)/MED WG.5/Inf.6) UNEP, Athens.

UNEP/MAP (2017) Mediterranean Quality Status Report. United Nations Environment Programme, Mediterranean Action Plan. Available at: https://www.medqsr.org/sites/default/files/inline_files/2017MedQSR_Online_0 (accessed 6 July 2022).

USEPA-CADDIS (2022) pH -Sources, Stressors, Responses. Volume 2. Available at: <https://www.epa.gov/caddis-vol2> (accessed 6 July 2022).

Ünlü, S., Alpar, B., Aydın, Ş. (2009) Spectrofluorometric characterization of aromatic hydrocarbon contamination in the sediment from the Zonguldak Industrial Region, Black Sea, Turkey. *Fresenius Environmental Bulletin* 18: 474-480.

Yılmaz, A., Saydam, A.C., Baştürk, Ö., Salihoğlu, İ. (1991) Transport of dissolved/dispersed petroleum hydrocarbons in the Northeastern Mediterranean. *Toxicological and Environmental Chemistry* 31(32): 187-197.

Yılmaz, K., Yılmaz, A., Yemenicioğlu, S., Sur, M., Salihoğlu, İ., Karabulut, Z., Telli Karakoç, F., Hatipoğlu, E., Gaines, A.F., Phillips, D., Hewer, A. (1998) Polynuclear aromatic hydrocarbons (PAHs) in the eastern Mediterranean Sea. *Marine Pollution Bulletin* 36: 922-925.

Zanardi, E., Bicego, M.C., Weber, R.R. (1999) Dissolved /dispersed petroleum aromatic hydrocarbons in the Sao Sebastiao, Sao Paulo, Brazil. *Marine Pollution Bulletin* 38: 410-413.