Research Article

Investigation of petroleum hydrocarbon pollution along the coastline of South Attica, Greece, after the sinking of the Agia Zoni II oil tanker

Konstantinos Kapsalis[1] · Maria Kavvalou[1] · Ioanna Damikouka[1] · Olga Cavoura[1]

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Abstract

Oil spills at sea pose risks to the marine environment and to the economy of many nations. Marine ecosystems are very vulnerable and precious as producers of oxygen and as regulators of climate. Therefore, their protection and preservation are necessary. In the event of an oil spill, anthropogenic clean-up activities and natural weathering processes can minimize the negative effects on marine organisms, and the marine environment in general. The target of this study was to investigate the status of the sea along the coastline of the Saronic Gulf, Greece, a year after the sinking of the Agia Zoni II oil tanker. Seawater samples from 15 sampling locations from Phlisvos coast to Anavissos, an area easily approached by bathers with recreational interest, were collected and analysed for total petroleum hydrocarbons. Concentrations up to a maximum of 56.6 μg/L were detected. Despite the large extent of the initial hydrocarbon pollution, the immediate clean-up operations and natural weathering and/or sorption processes have reduced the impact of the spill on surface waters.

Keywords Agia Zoni II · Marine pollution · Oil spill · Petroleum hydrocarbons · Saronic Gulf · Tanker

1 Introduction

Maintaining good ecological and environmental status of the marine environment is considered a prime concern for the welfare of future generations. A precondition for achieving this objective is to protect and conserve biodiversity, preserve ecosystems and prevent pollution from anthropogenic activities.

Oil is a necessity for industrialized societies and an important element of modern life. While its extraction and transportation are essential, accidents that result in large oil spills occur and attract the interest of the public and the media. In recent decades, much of this interest has focused on the dangers posed by oil spills and their consequences on the environment. Experts estimate that about 30–50% of oil spills are directly or indirectly caused by human error, while 20–40% are caused by equipment failure or malfunction. The average cost of cleaning oil spills worldwide ranges from $40–400/L depending on the type of oil and where the leak occurred. Cleaning coastlines is usually the most expensive clean-up process [1].

Oil spills at sea pose risks to the economy, social life and the environment of the polluted regions. The severity and extent of the adverse effects from oil spills occurring in the marine environment vary with the amount of oil spilled, its composition, the presence of different microorganisms able to metabolize hydrocarbons [1], location and weather conditions prevailing at the time of the accident. Evaluating management options of pollution incidents [2] like oil spills is crucial in order to mitigate negative effects on marine organisms and on the environment, in general. In addition to the anthropogenic interventions of oil spill response operations [3], natural weathering processes play a significant role in the fate, compositional changes and toxicity of fresh crude oil spills. Primary weathering processes include evaporation of the lower molecular weight

✉ Ioanna Damikouka, idamikouka@uniwa.gr | [1]Department of Public Health Policy, School of Public Health, University of West Attica, 196 Alexandras Avenue, 115 21 Athens, Greece.

volatile fraction of hydrocarbon compounds in the first days of the incident, dissolution, biodegradation, emulsification, dispersion, sedimentation and photooxidation or photodegradation, emulsified oil also posing significant environmental risk and toxicity through ingestion [4].

The main causes of accidents associated with shipping are: (a) sinking of a ship or damage to the ship's structure due to adverse climatic conditions, possible displacement of cargo, poor maintenance, etc., (b) grounding of the ship, that usually occur in coastal areas due to mechanical damage, loss of control, bad weather, etc., (c) ship collision caused by human error, (d) fire or explosion on ships, (e) various accidents such as fire and sinking, impact and sinking, deliberate sinking of the ship, (f) casualties due to hostilities [3, 5].

In 2017, two major leaks (> 700 tons) and four medium leaks (7–700 tons) of oil in the marine environment were recorded worldwide. The first major leak occurred in June, when a tanker sank in the Indian Ocean with a cargo of more than 5000 tons of oil. The second incident involved a tanker that sank in the Saronic Gulf, Greece, in September with a leak of about 500 mt of heavy fuel oil (group IFO 380) [6]. Of the four medium-sized leaks, two were recorded in January 2017, one in South Asia and the other in Southeast Asia, both of which resulted from the collision of the ship and the release of fuel. A third leak was reported in East Asia in August and emerged after a boat landed due to bad weather. The fourth medium-sized leak occurred in October in the USA [7].

The marine environment in Greece is characterized by rich marine diversity. Of the 579 Mediterranean fish species, 447 are found in Greek seas [8]. However, it is subject to chronic severe anthropogenic pressures, especially in the Saronic Gulf, mainly, due to the proximity of the port of Piraeus and the industrial zone of Elefsis Bay [9]. The environmental status of Elefsis Bay is exacerbated by its closed, longitudinal morphology and cyclonic winds, and in 2005, the bay was designated a "major environmental concern" by the European Environment Agency (EEA) and the United Nations (UN) Environment Program/Mediterranean Action Plan (UNEP/MAP) [10].

In Greece, most marine tanker accidents occur in the Saronic Gulf as it is the Piraeus port, the largest port in the country, and the largest shipbuilding repairs are active in the region. Oil spills in the area have occurred over the years and include 400 tons of oil from the La Guardia tanker ship leaked after impact with the jetty in October 1994, at Aspropyrgos refineries, 300–500 tons of oil leaked into the sea in August 1996, during the loading of the Kriti Sea oil tanker at the Motor Oil refineries in Agioi Theodoroi, that reached the coasts of Aegina and Agistri and 600 tons of oil in May 2000, in Kinesoura when a floating slops separator caught fire [11]. In March 2012, the sinking of Greek tanker ALFA I, which carried 2100 tons of oil, in Elefsis Bay, Greece, led to the release of oil at the sea (estimation of 100 tons of oil), resulted in extensive pollution, affecting 20 km of coastline, local beaches and the Salamina Island [12].

The establishment of coordinated monitoring programmes especially for post-incident monitoring and impact assessment is important [13]. For the systematic monitoring of the Saronic Gulf following oil spills, a system of sampling water, sediment, phytoplankton macrophytes, benthic fauna, etc., has been established by the Hellenic Centre of Marine Research (HCMR), since 1998. Additionally, National Emergency Plans for the treatment of oil pollution and other harmful substances have been established [14]. Presidential Decree No. 11 [14] established the National Emergency Plan to deal with oil and other harmful pollution incidents. Depending on the severity of the pollution incident (related to the amount of oil leaked), three levels of mobilization are enforced, based on the national system being followed.

The most recent incident, which negatively affected marine environmental quality in Greece and reached the shore of Athens, was the oil spill from the sinking of the tanker Agia Zoni II on September 10, 2017. Following a possible influx of water, the Agia Zoni II vessel, which was anchored in the maritime area southwest of Atalanti, west of the port of Piraeus, Greece, and had sailed the day before from the Aspropyrgos refineries with 2200 tons of fuel oil and 370 tons of marine gas oil, sank releasing a large amount of this oil into the sea [15]. The oil spill that was formed was not limited to the area of the accident, but spread as far as the area of Lagonissi.

Clean-up and remediation actions to contain the spread of the oil spill included the oil recovery from the Agia Zoni II tanker by another tanker [16] or the European Maritime Safety Agency (EMSA) contracted vessel [17] and the lifting of the tanker according to environmental legislation. In the anti-pollution work carried out no chemicals were used; only mechanical processes were implemented. This included the deployment of anti-pollution vessels that carried out development, dredging and harvesting operations, the implementation of floating dams and the mechanical and physical cleaning of the coast using high-pressure pumps and washing machines. Booms were also used to protect the coastline from oil pollution [18].

The concentrations of petroleum hydrocarbons monitored by HCMR, until approximately 6 months after the incident, indicated that the main effects of the accident were confined to the coastal zone, particularly in the areas of Salamis, Glyfada and Elliniko for the first three months after the accident [6]. The target of the present study was to monitor the dissolved total petroleum hydrocarbons (TPH) levels in the seawater in locations frequented by bathers along the coastline of the Inner Saronic Gulf affected by the spill a few days to 1 year after the incident.

2 Materials and methods

2.1 Study area description

In order to evaluate the presence of dissolved petroleum hydrocarbons due to the fuel oil spill from the tanker Agia Zoni II, seawater samples were collected from 15 sampling locations where water visibility to bathers was high, and the assurance of public health protection necessary.

The locations were along the main coastal metropolis of Athens. Sampling in Lagonissi, Saronida, Palaia Fokaia and Anavissos was conducted a few days after the incident, on September 20, 22 and 27, on October 11 and 25, 2017, and again in the period 7–13 months after the incident on April 25, June 13 and September 12, 2018. On 23–24 of October in 2018, samples were collected from the 15 sampling positions. The 15 sampling locations were recorded by a global positioning system (GPS) and are depicted in Fig. 1. A total of 47 samples were collected.

2.2 Sampling and sample preparation

Amber-glass bottles were used to collect 1 L of seawater from each point to prevent photodegradation. Samples were collected 2 m from the coastline at a depth of 40–50 cm from the surface where total depth was at least 1 m. Containers were rinsed three times with the seawater in question before being filled to the mouth and hermetically sealed. All samples were taken at a point from the centre of the coast approximately [19].

The water samples were transported to the laboratory within few hours in cool bags to prevent changes due to physical, chemical or biological reactions [20] and stored at ≤ 6 °C until their analysis [21].

2.3 Method

All seawater samples were analysed for TPH, taken to be the sum of *n*-alkanes ranging from *n*-C_{10} to *n*-C_{40}. Other *n*-alkanes, alkenes and aromatic hydrocarbons were not included in the determination. The method applied was appropriate for the determination of hydrocarbons in drinking water and seawater, by gas chromatography–flame ionization detector (GC/FID) [22]. A SHIMADZU GC-2010 PLUS with importers PTV, automatic sampler AOC 20i model was used for GC analysis.

Hydrocarbons were separated from the aqueous phase using liquid–liquid extraction with *n*-hexane (ULTRA Residue by JT Baker) extraction solvent. The organic layer was removed using a microseparator and passed through a florisil column as an additional purification step to remove polar compounds before GC separation using a DB-1 MS, 15 m, id 0.53 mm, df 0.15 μm column (U.S. Silica Company). Quantification was performed by constructing a

Fig. 1 Map of the seawater sampling locations from Palaio Faliro to Anavissos, of the inner Saronic Gulf, Greece

calibration curve of four standard solutions containing a specific mineral composition [22].

2.4 Quality assurance

Samples and blank samples were processed using the same method. Calibration standards in the range 20–600 mg/L were prepared daily from serial dilutions of stock solutions in *n*-hexane covering initial sample concentrations of 20–600 μg/L prior to extraction and preconcentration. Retention times and peak integration were checked daily using a 200 mg/L solution of *n*-decane and *n*-tetracontane in *n*-hexane. Blank samples were run between samples to ensure no instrumental contamination [22]. The limit of detection for TPH was 8 μg/L.

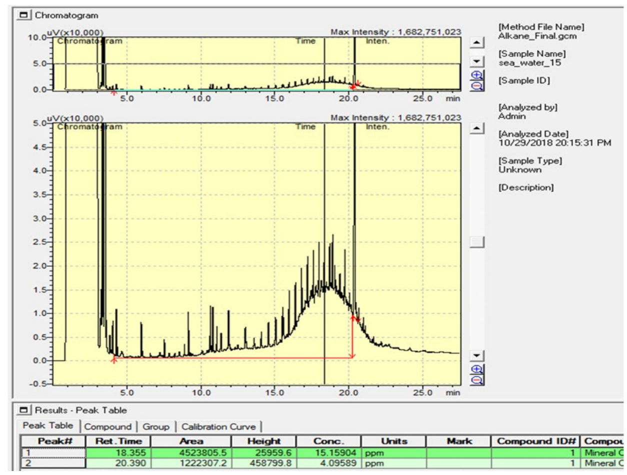

Fig. 2 GC chromatograph profile of total petroleum hydrocarbons (TPH) in a water sample from the Anavissos area, Greece

3 Results and discussion

Sampling positions, sampling dates and TPH concentration for the period between 20/09/2017 and 23–24/10/2018 are depicted in Table 1. An example of chromatographic profile from the sample taken from the 15th sampling location in the area of Anavissos is given in Fig. 2.

Results of TPH concentrations obtained up to 367 days and 398–399 days after the incident are given in Figs. 3 and 4, respectively.

As seen from results (Fig. 3) from sampling periods on September 20, 22 and 27, October 11 and 25, 2017, April 25, June 13 and September 12, 2018 (respectively, in 10, 12, 17, 30, 45, 227, 276 and 367 days after spill), concentrations were generally not detectable, except for those sampling sites depicted in Fig. 3.

A maximum concentration of 161 μg/L TPH was determined in samples from the coastal area of Saronida in April 2018 (227 days after the incident) (Fig. 3). A concentration of 39 μg/L of TPH, the second highest concentration

Table 1 Sampling sites, dates and total petroleum hydrocarbons (TPH) concentration in μg/L of seawater samples along the coast of the inner Saronic Gulf

A/A	Sampling area	Coordinates		Sampling dates						
		Longitude	latitude	20/09/17, 22/09/17, 27/09/07	11/10/17	25/10/17	25/04/18	13/06/18	12/09/18	23–24/10/18
1	Flisvos-Palaio Faliro	37.933	23.685	–	–	–	–	–	–	21.8
2	Mpatis-Palaio Faliro	37.921	23.696	–	–	–	–	–	–	11.1
3	Edem-Palaio Faliro	37.919	23.699	–	–	–	–	–	–	12.4
4	Kalamaki	37.909	23.713	–	–	–	–	–	–	25.2
5	Glyfada-beach a′	37.868	23.737	–	–	–	–	–	–	18.4
6	Glyfada -beach b′	37.874	23.733	–	–	–	–	–	–	23.0
7	Kavouri	37.818	23.768	–	–	–	–	–	–	14.4
8	Vouliagmeni	37.810	23.774	–	–	–	–	–	–	N.D
9	Varkiza	37.818	23.803	–	–	–	–	–	–	N.D
10	Agia Marina-Kropias	37.814	23.844	–	–	–	–	–	–	10.9
11	Agios Dimitrios-Kropias	37.802	23.864	–	–	–	–	–	–	13.6
12	Lagonissi	37.778	23.894	N.D.*	61	35	68.5	N.D	N.D	28.9
13	Saronida	37.747	23.905	N.D	N.D	29.4	161	N.D	38.9	N.D
14	Palaia Fokaia	37.723	23.945	N.D	N.D	14.4	35.3	N.D	N.D	N.D
15	Anavissos	37.722	23.938	N.D	N.D	N.D	N.D	39.8	28.7	56.6

*N.D.: not detected

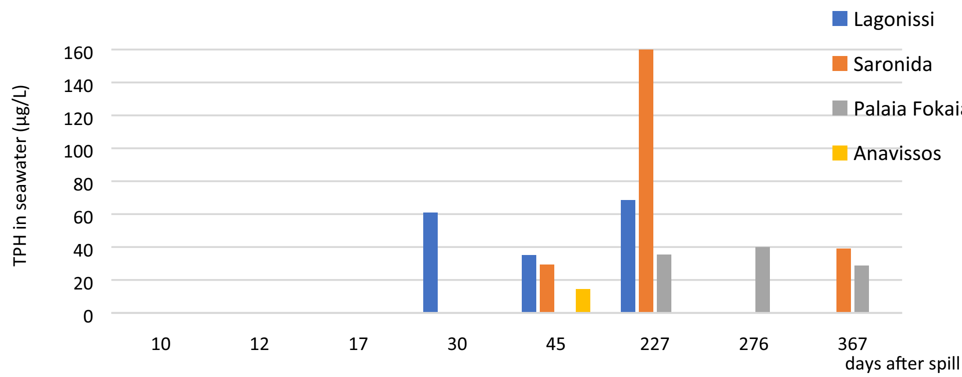

Fig. 3 Concentration of total petroleum hydrocarbons (TPH) along the coastline of South Attica, Greece, from samples taken 10, 12, 17, 30, 45, 227, 276 and 367 days after the Agia Zoni tanker spill in the areas of Lagonissi (blue bars), Saronida (orange bars), Palaia Fokaia (grey bars), Anavissos (yellow bars). When there is no bar, TPH were not detected

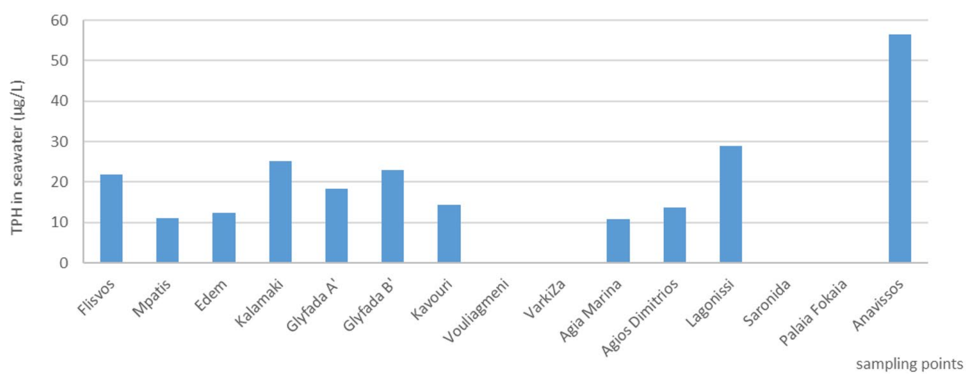

Fig. 4 Concentration of total petroleum hydrocarbons (TPH) along the coastline of South Attica, Greece between October 23 and 24, 2018. When there is no bar, TPH were not detected

detected, was found in the same area 367 days after the spill. In all other samples from Saronida, no TPH were detected. In samples from Lagonissi in October 2017 (30 and 45 days after the incident) and in April 2018 (227 days after the spill), concentrations were 61, 35 and 69 µg/L TPH, respectively. In the remaining samples from Lagonissi, TPH were not detected. In samples from Palaia Fokaia in April, June and September 2018 (227, 276 and 367 days after the spill, respectively), concentrations ranged from 29 to 40 µg/L TPH. In the remaining samples from Palaia Fokaia, no TPH were detected.

Considerable variation in hydrocarbon concentrations was found approximately one year after the spill (October 23 and 24, 2018) (Fig. 4). This can be attributed to the fact that Saronikos Gulf is subjected to several pollution sources such as the industrial zone of Elefsis Bay, the port of Piraeus and intense marine traffic which affect the marine environment [2, 6, 9, 23]. Concentrations ranged from non-detectable in the coastal area of Vouliagmeni to 56.6 µg/L in the coastal area of Anavissos. The presence of hydrocarbons in the Flisvos, Kalamaki, Glyfada B′, Lagonissi, Saronida, Palaia Fokaia and Anavissos samples after the first coastal clean-up and clean-up operations was carried out and a year after the sinking. However, in the samples from the coastal area of Anavissos on October 2018 (398 days after the incident) 56.6 µg/L of TPH was determined. Since this significant concentration was detected only once, and not in previously collected samples from this sampling site, it may be related to recreational activities or some other coastal activity in the area, rather than the oil spill.

The chromatographic profile of TPH in the Anavissos area (Fig. 2) indicates a sample with a molecular profile of *n*-alkanes ranging from *n*-C_{25} to *n*-C_{35} with the presence of unresolved complex mixture (UCM), likely due to the presence of lubricants in the sample [24, 25]. At 10 out of 15 coastal sites in the study area (Fig. 4), the concentration of TPH was lower than 20 µg/L, which is considered background level [6] for the waters in the inner Saronic Gulf.

High concentrations of TPH up to 3080 µg/L were detected at Salamina Island (Selinia and Kynosoura) [6] and at the coasts of Glyfada region (> 1500 µg/L) 8 days after the spill.

In agreement with the results from this study, the results from the determination of TPH of HCMR [6, 26] from relevant sampling locations used in this study also indicate the variation between the points. Further reduction of TPH concentration in coastal waters was observed since HCMR monitoring in 2017 [6]. For example, concentrations at the beaches of Glyfada Coast A and Coast B, a few days after the accident and one year following, were, for coast A, 97.8 µg/L (8 days after the incident) [6] and 18.4 µg/L (398 days after the spill), respectively, and for coast B > 1500 μg/L (8 days after the incident) [6] and 23.0 μg/L (398 days after the spill), respectively.

One of the highest levels of TPH was detected in the Deepwater Horizon, Gulf of Mexico (260,000 μg/L) [27]. In a case of low-level oil contamination in coastal seawater in Malaysia, levels of TPH ranged from 1.40 to 21.8 μg/L [28]. From an oil spill in west coast of Korea [29], the levels of TPH in seawater immediately after the incident ranged 1.5–7310 μg/L. After one month, there was a decrease in the concentration (2–224 μg/L) due to shoreline clean-up activities, waves and tidal cycling. After an oil spill in the North Cape [30], concentration of TPHs in seawater samples from 2 to 132 days did not exceed 3940 μg/L.

4 Conclusion

When oil spills occur in a region, the environmental and economic effects may be long lasting and irreversible. However, immediate clean-up operations and natural processes can mitigate negative impact. While considerable variation in hydrocarbon concentrations one year after the sinking of the Agia Zoni II oil tanker may be attributed to other pollution sources, marine traffic and high anthropogenic background of the study area, the mechanical cleaning of the coast and physical lifting of the tanker done relatively quickly and according to environmental legislation, combined with the type of the fuel spilled, the Mediterranean climate, natural attenuation and natural weathering processes, can reduce the impact of the oil spill on the surrounding aquatic environment.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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