The Agia Zoni II oil spill: Short-term fate and imprint on the marine ecosystem of the Saronikos Gulf, Greece

Parinos C.*, Hatzianestis I., Chourdaki S., Plakidi E., Gogou A.

Institute of Oceanography, Hellenic Centre for Marine Research (H.C.M.R.), Mavro Lithari, 19013 Anavyssos, Attiki, Greece

*corresponding author: C. Parinos: e-mail: ksparinos@hcmr.gr

Abstract
Herein we examine the spatial and temporal imprint of the September 2017 Agia Zoni II tanker heavy fuel oil spill on the marine ecosystem of the Saronikos Gulf, Greece. Based on the chemical fingerprinting approach we characterize changes in the composition of the spilled oil across sampling sites and evaluate major mechanisms affecting its fate during the first six months from the spill. Overall, the main effects of the incident were confined to the coastal zone during the first three months after the spill where an extended petroleum imprint was recorded in many cases. In the first three months from the spill the oil was affected by combination of rapid biodegradation, volatilization processes and photodegradation, the later playing a role in its early days weathering. Regarding sediments, an imprint related to the incident was recorded in some cases but mild in respect to the chronic petroleum associated anthropogenic background of the affected area.
Keywords: Agia Zoni II, oil spill, Saronikos Gulf

1. Introduction

On September 10th 2017 the oil tanker Agia Zoni II sank at the Piraeus anchorage area in the Saronikos Gulf (Fig. 1). Around 500 mt of HFO (IFO 380) were released upon sinking, quickly stranding along ~30 Km of shoreline on Salamis Island and the Piraeus/Athens Riviera. From the first days of the incident H.C.M.R. studied the short- and medium- term environmental consequences of the incident in affected areas (H.C.M.R., 2018). Herein, we examine the spatial and temporal imprint of the spilled oil and characterize changes in its composition by evaluating the mechanisms affecting its fate (dissolution/dispersion, evaporation, biodegradation, photo-oxidation, sediment accumulation) during the first six months from the spill. Care has been taken in differentiating the incident imprint in respect to the chronic petroleum-associated anthropogenic background of the study area.

2. Sampling Strategy and Chemical Analysis

In order to evaluate the spatial/temporal distribution of dissolved/dispersed petroleum hydrocarbons in the water column of the study area, seawater samplings have been conducted in coastal and open sea areas of the Saronikos Gulf. Coastal sea-surface water samples were collected with a manual sampling device, while open sea water samples with *R/V* Aegaeo by Niskin bottles. Sediment samples (top 1-cm) were collected with a stainless steel box corer to investigate any possible accumulation of petroleum hydrocarbons on the seabed. Major weathering mechanisms affecting the composition of the spilled oil were examined in oil patches collected along shore. The survey effort included 69 seawater sampling sites with 247 samples considered and 22 sediment sampling sites with 57 samples considered. A total of 16 oil patches collected along shore Glyfada were considered spanning in detail the first three months from the spill (Fig. 1). Seawater samples were analyzed for total petroleum hydrocarbons (TPH) by GC/FID and 32 PAH compounds ($\sum PAH_{32}$) by GC/MS, while the collected oil patches and sediments were analyzed for aliphatic hydrocarbons, the isoprenoids pristane (Pri) and phytane (Phy) and $\sum PAH_{32}$ by GC/MS. A source oil was considered as a reference. H.C.M.R's chemistry lab is accredited by ISO/IEC 17025 for the analysis of PAHs in seawaters and sediments.

3. Results and Discussion

The Agia Zoni II source oil displayed an *n*-alkane range from *n*-C_{10} to *n*-C_{36} and by a bimodal distribution with the first mode centered at *n*-C_{11} and the second at *n*-C_{22}, consistent to the dilution of the HFO with a lighter distillate. Regarding PAHs, the source oil is characterized by a high relative abundance of naphthalene and its alkylated homologues (~40% of $\sum PAH_{32}$) followed by phenanthrene, dibenzothiophene, pyrene and chrysene series, originating from the lighter blending oil, and also contained traces of 5-and 6-ring PAHs each being < 0.3 % of $\sum PAH_{32}$. Terpanes (*m/z* 191) concentrations were very low while steranes (*m/z* 217) were absent.

Regarding the spatial/temporal distribution of dissolved/ dispersed petroleum hydrocarbons in the study area, TPH and $\sum PAH_{32}$ concentrations at 37 out of 55 coastal sites were recorded within background levels (< 20 μg L^{-1}; < 640 ng L^{-1} respectively) at the time of their sampling in all cases. Regarding open sea areas, the determined TPH and PAH levels were low (< 6.8 μg L^{-1}; < 125 ng L^{-1} respectively) indicative of the rapid transport of the spilled oil to the coast in the first days from the incident. Indeed, an extended petroleum imprint, in many cases > 1500 μg L^{-1}; up to 3800 μg L^{-1}, for TPH and 62.6 μg L^{-1} for $\sum PAH_{32}$ was recorded as early as 8 days and on from the incident in coastal areas of Elliniko, Glyfada and Selinia and Kinousoura at Salamina Island (Fig. 1) were the main

mass of the spill beached. TPH and $\sum PAH_{32}$ concentrations progressively declined at background levels till December 4th, 2017 following the conclusion of clean-up operations. In the following months severe weather events (W/SW winds and rough sea) did not alter the December 2017 status, except of two cases i.e. Batis and Aigyptiotes Naval Club in Elliniko on January 19th 2018, where a slight imprint of petroleum hydrocarbons related to the incident was recorded (Fig. 1).

Within the aliphatic fraction of the considered oil patches a decrease of the $<n\text{-}C_{20}$ alkanes (from day 8 of the spill) was indicative of the rapid loss of light hydrocarbons by evaporation. The $n\text{-}C_{17}$/pristane and $n\text{-}C_{18}$/phytane ratios also decreased from day 8 of the incident indicating the early onset of biodegradation and overall denoted biological activity over the first 85 days of the spill. Within the aromatic fraction, the rapid decrease of the relative abundance of napthalene and its alkylated derivatives indicated evaporation/ dissolution. However, in the corresponding PAH profiles of seawater samples collected during the same period a low relative abundance of napthalene and its alkyl homologs was also noted, likely indicating evaporation as the dominant weathering process for these compounds. The ratios of Phe/BaP, Phe/(C_1-Phe+C_2-Phe) and diagnostic ratios related to C_1- and C_2- derivatives of phenanthrene were indicative of biodegradation, although dissolution processes acting on phenanthrene cannot be ruled out. Finally, the probable effect of photodegradation on aromatic compounds weathering was examined using ratios of parent and alkyl-substituted PAHs which photodegrade at different rates while weather similarly by other processes. A decrease of the 2MA/1-C_1Phe and BaP/BeP ratio values was evident in the early days of the spill with both ratio values remaining constant in the following months. This indicates that although photodegradation might have played a role in the early days weathering of the oil it was not dominant the coming months (Wang et al., 2007).

Regarding sediments, concentrations of total aliphatic hydrocarbons (AHCs) and $\sum PAH_{32}$ ranged from 23.4 to 1220 μg g^{-1} and 53.1 to 4570 ng g^{-1}, comparable to those previously reported for surface sediments in the Saronikos Gulf. AHCs and $\sum PAH_{32}$ burden was clearly attributed to the chronic petroleum-associated anthropogenic background of the area in most of the cases, with a mild recent oil imprint evident in September 2017 at the Agia Zoni II shipwreck, offshore from Palaio Faliro (OS3), Elliniko (OS4) and Glyfada (OS6) (Fig.1).

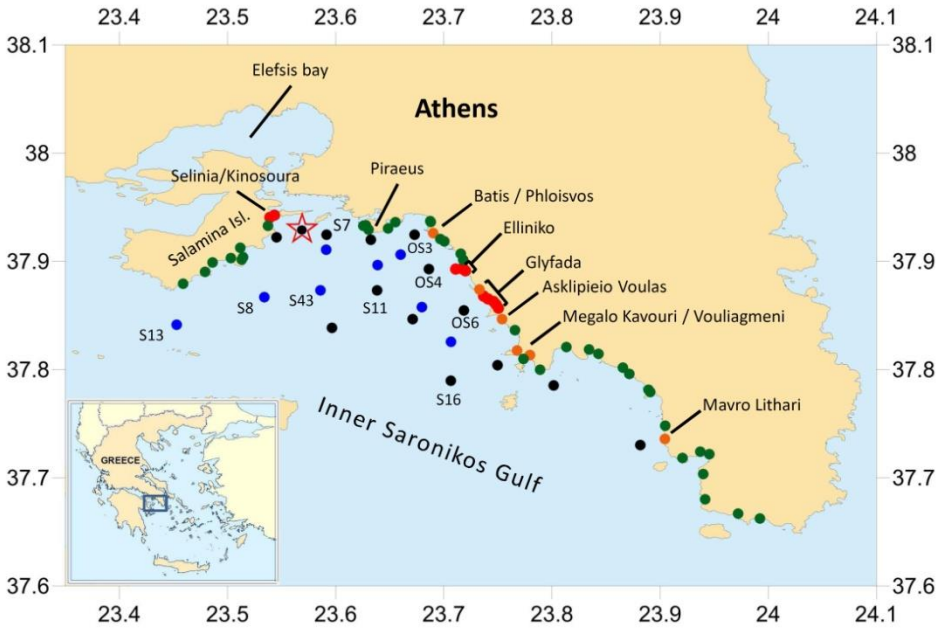

Figure 1. Map of the Inner Saronikos Gulf annotated with features discussed in the text. The red star marks the Agia Zoni II sinking position, coastal stations marked green are the ones where TPH concentrations were recorded within background levels in all cases while coastal stations marked red and orange respectively are the areas where an extended or smaller burden of petroleum hydrocarbons was initially recorded. Seawater sampling positions in open sea areas are marked as black, while sediment sampling positions in open sea areas refer to both black and blue spots.

References

H.C.M.R., (2018). Study of the Short and Medium Term Environmental Consequences of the Sinking of the Agia Zonia II Tanker on the Marine Ecosystem of the Saronikos Gulf. Final Scientific Report, 182 p. Information document of the 13th Meeting of the Focal Points of REMPEC, Malta, June 2019. Available at: http://www.rempec.org/rempec.asp?pgeVisit=New&theID=2013.

Wang, Z., Yang, C., Fingas, M., Hollebone, B., Hyuk Jae Yim, U., Ryoung Oh, J., (2007). Petroleum Biomarker Fingerprinting for Oil Spill Characterization and Source Identification, Oil Spill Environmental Forensics, pp. 73-146.