



Article

Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons in the Marine Surface Microlayer of an Industrialized Coastal Area in the Eastern Mediterranean

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Abstract: Concentrations of dissolved and particulate polycyclic aromatic hydrocarbons (PAHs) were determined seasonally in sea surface microlayer (SML) and sub-surface water (SSW) within the Saronikos Gulf, Greece, close to a highly industrialized coastal zone. For the 16 US EPA priority PAHs, the sum of dissolved PAHs (Σ_d PAHs) concentrations ranged from 40.4 to 237 ng L⁻¹ in SML, 22.8–180 ng L⁻¹ in SSW_{0.2}, whereas the corresponding concentrations in suspended particulate matter (Σ_p PAHs) were 30.8 to 177 ng L⁻¹ and 36.8–171 ng L⁻¹, respectively. The enrichment factor (EF) for dissolved Σ_d PAHs varied from 0.9 to 2.1 with a mean value of 1.5 ($n = 10$) being statistically significantly greater than unity, whereas for particulate Σ_p PAHs, no enrichment of the SML was reported. Enrichment factors of 5–6 ring PAHs were higher near the industrial zone. The possible sources, fate, and toxicity of PAHs are also discussed.

Keywords: polycyclic aromatic hydrocarbons; sea surface microlayer; subsurface water; enrichment; industrialized coastal area; Eastern Mediterranean Sea



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1. Introduction

The sea surface microlayer (SML) is a thin layer at the boundary between the ocean and the atmosphere, covering approximately 71% of the Earth's surface. This microlayer is defined as a unique physicochemical and biological environment, which ranges between 1 and 1000 μ m of the ocean surface [1–4]. The SML is generally considered as being enriched, relatively to underlying water (SSW), in a wide variety of chemicals accumulated to the air-sea interface due to their surfactant nature, hydrophobic properties, and possible association with floatable particles, vertical diffusion mechanisms or bubbles' scavenging [5,6]. Therefore, several pollutants are detected in the SML, including polycyclic aromatic hydrocarbons (PAHs), trace metals, microplastics, pathogenic microorganisms and nutrients, which serve as a source and sink for the atmosphere and the water column [7,8].

The SML maintains an important role in the fate and transport of pollutants especially in coastal areas, exerting potential effects on biological processes and cycling of contaminants [9], which may aggregate following formation of marine organic particles such as microgels, accelerating their vertical transport from the sea surface to the sea bottom [10]. Polycyclic aromatic hydrocarbons (PAHs) containing two or more fused aromatic rings form one of the most important classes of environmental pollutants. They are known to be ubiquitous in the environment, potentially causing a wide range of toxic effects based on their mutagenic and carcinogenic action on both the ecosystem and humans [11].

Being widespread in the marine environment, PAHs are associated with pyrolytic (incomplete combustion of fossil fuels), petrogenic (uncombusted petroleum) [12–14], diagenetic (short-term diagenetic degradation of biogenic precursors) [15], and natural sources (e.g., forest fires, volcano eruptions, biogenic formation) [16–18]. They are generally introduced to coastal SML waters mainly through anthropogenic coastal activities, as well as dry (aerosols, air-sea gas exchange) and wet (heavy rains) atmospheric depositions [19,20]. Nevertheless, in order to identify and assess the potential sources of PAHs, the diagnostic ratios of their isomers constitute useful indicators [21].

PAHs are hydrophobic compounds ($\log K_{ow} = 3\text{--}8$) with very low water solubility, characterized by the trend to rapidly adsorb onto suspended materials and sediments [22]. Their distribution between the dissolved and particulate phases of seawater is related to the octanol–water constant distribution. Since the solubility of aromatic compounds decreases accordingly to an increase of the octanol–water partition coefficient (K_{ow}) [23], PAHs solubility decreases with increasing molecular weight [24,25]. Lower molecular weight PAHs are hence preferentially dissolved, while heavier ones tend to be absorbed onto or associated with particles.

The Gulf of Elefsis, located near Athens, the capital of Greece, is characterized as the most industrialized area of the country. Along the northern coastline of the gulf, two of the largest oil refineries of the country are situated, together with metallurgical and cement industries, chemical plants, and shipyards. Although several data are available relatively with the distribution of PAHs in the water column and sediments within the Gulf of Elefsis and the wider area of Saronikos gulf [26–29], data referring to PAHs concentrations in the sea surface microlayer of coastal areas generally within the Eastern Mediterranean remain rather scarce [23].

In the present study, samples of sea surface microlayer (SML) and under layer water at 20 cm ($SSW_{0.2}$) and 2 m depth (SSW_2) were collected from two different coastal areas close to the industrialized area of the Gulf of Elefsis and the wider Saronikos Gulf, during five seasonal samplings. The objectives of the study were to provide recent data concerning PAHs behavior in the SML of the industrialized coastal area of the Gulf of Elefsis; to determine the seasonal distribution and differences in the composition of PAHs; to evaluate the enrichment of PAHs in SML in both dissolved and particulate phases; to identify the possible sources and fate of PAHs. The results presented in this work are the first reported so far concerning PAHs concentrations in the SML of Greek coastal areas, while pertinent literature for the eastern Mediterranean is rather limited.

2. Materials and Methods

2.1. Study Area

The areas studied are Loutropyrgos within the Gulf of Elefsis and Pahi of Megara located at the western entrance of the Gulf of Elefsis (Figure 1). The sites represent different microenvironments, with different topographical features (depth, presence of estuary systems) and degrees of pressure by anthropogenic activities (industries). The Gulf of Elefsis is a relatively shallow embayment (maximum depth 33 m) being in contact with the Saronikos Gulf through two narrow channels towards the east and west. The northeastern coastal area of the Gulf of Elefsis is influenced by significant industrial activity (oil refineries, shipyards, metallurgical and cement industries, etc.). The sampling station of Loutropyrgos (approximate depth of 15–20 m) is located at a relatively small distance from the industrial zone of the Gulf of Elefsis (the nearest installations are approx. 3 km away). Within the wider area of the Pahi of Megara sampling site (approximate depth 50 m), which is in direct contact with the open Saronikos gulf, the installation of the LNG (Liquefied Natural Gas) terminal is located, on the small island Revithoussa (approximately 500 m from the coast). The terminal is included in the 28 LNG terminals operating today within the wider Mediterranean region and Europe and the only one in Greece. Within the Gulf of Elefsis, a significant circulation mainly of small tankers is observed, while larger ones usually anchor at the entrances of the gulf. The latest significant oil spill at the area occurred in

September 2017 during the sinking of the oil/chemical tanker *AgiaZoni II*, close to the eastern entrance of the Gulf of Elefsis. Approximately 500 mt of heavy fuel oil (HFO; IFO 380) were released upon sinking and shortly thereafter [30].

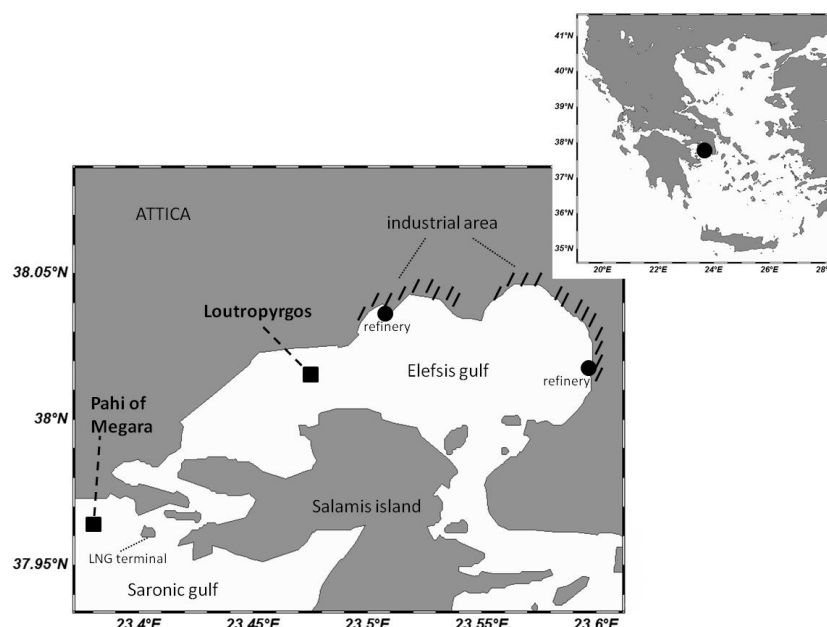


Figure 1. Sampling sites within the Gulf of Elefsis, Greece (Schlitzer, Reiner, Ocean Data View, odv.awi.de, 2021).

2.2. Sampling

A total of 30 single samples were collected in the present study from the sea surface microlayer (SML) and under layer water at 20 cm ($SSW_{0.2}$) and 2 m depth (SSW_2), from 2 sites namely Loutropyrgos and Pahi of Megara, during February, May, September 2018; July 2019; and January 2020. Sampling was performed under calm weather conditions (wind speed $<4 \text{ m s}^{-1}$) from a small rubber boat equipped with an electric engine, which was stationary during sampling. In brief, sampling was performed with a Garrett type screen [31] made of a stainless steel mesh, which provides a quite large sample volume within a relatively short time [32,33]. The thickness of the sampled microlayer was 100–150 μm . $SSW_{0.2}$ samples were collected manually by immersing an 1 L glass container at a depth of 20 cm below the sea surface, whereas SSW_2 samples were collected from 2 m depth with the use of a Nansen bottle. Samples were transported (refrigerated) immediately to the laboratory and separated into dissolved and particulate phases, following filtration under a low vacuum ($<50 \text{ mm Hg}$) using precombusted glass fiber filters (GF/F, approx. $0.7 \mu\text{m}$; 47 mm diameter, Whatman). Seawater temperature, pH, and salinity were measured in situ with a YSI 63 pH/conductivity meter (YSI, Brannan Lane, OH, USA), solar irradiation and air temperature with a DO9721 (probe LP9021) quantum photo-radiometer (Delta Ohm, Padova, Italia) and wind speed with a Testo 425 anemometer (Testo Inc., Sparta, NJ, USA) [34]. Measurements of seawater temperature, pH, and salinity were made in the upper 5 cm of the water column and at 20 cm and 2 m depths at each sampling site (Table 1).

Table 1. Sampling dates, and environmental and physicochemical conditions.

Sample	Date	Sampling Time, h	Weather Conditions	Solar Irradiation, W m ⁻²	T _{air} , °C	Wind Speed, m s ⁻¹	State of the Sea ^b	T _{sea} , °C	pH	Salinity, ppt
Loutropyrgos SML ^a	13.02.2018	7:45–9:15	Sunny with light fog	24,000	14.5	1.30	0	13.8	7.85	38.2
Loutropyrgos SSW _{0.2}								13.7	7.84	38.3
Pahi SML ^a Pahi SSW _{0.2}	13.02.2018	10:45–12:00	Sunny with light clouding	38,500	13.6	1.15	1	13.9 13.8	7.82 7.83	38.2 38.2
Loutropyrgos SML ^a								16.05.2018	7:30–8:50	Sunny with light clouding
Loutropyrgos SSW _{0.2}	16.7	7.99	38.1							
Loutropyrgos SSW _{2.0}	16.05.2018	10:00–12:30	Sunny with light clouding	45,000	22.0	0.50	0	16.1	7.97	38.1
Pahi SML ^a Pahi SSW _{0.2} Pahi SSW _{2.0}								17.0 16.8 16.6	7.96 8.00 7.99	38.6 38.5 38.4
Loutropyrgos SML ^a	05.09.2018	9:00–10:30	Sunny	41,500	29.3	5.2	1	23.6	8.08	38.5
Loutropyrgos SSW _{0.2}								23.6	8.09	38.5
Loutropyrgos SSW _{2.0}	05.09.2018	13:00–14:30	Sunny	75,000	33.6	3.5	2	23.2	8.06	38.3
Pahi SML ^a Pahi SSW _{0.2} Pahi SSW _{2.0}								23.4 23.5 23.2	8.10 8.14 8.15	38.4 38.4 38.2
Loutropyrgos SML ^a	06.07.2019	7:10–8:45	Sunny	32,000	29.0	1.80	1	23.6	8.08	38.5
Loutropyrgos SSW _{0.2}								23.6	8.09	38.5
Loutropyrgos SSW _{2.0}	06.07.2019	9:55–11:50	Sunny	85,000	30.0	0.70	0	23.2	8.06	38.3
Pahi SML ^a Pahi SSW _{0.2} Pahi SSW _{2.0}								23.0 22.9 22.7	8.02 8.04 8.05	38.7 38.6 38.5
Loutropyrgos SML ^a	11.01.2020	7:30–9:00	Sunny	19,000	16.0	0.60	1	22.8	8.05	38.1
Loutropyrgos SSW _{0.2}								22.8	8.07	38.0
Loutropyrgos SSW _{2.0}	11.01.2020	10:20–12:55	Sunny	44,000	19.2	0.50	0	22.6	8.03	38.0
Pahi SML ^a Pahi SSW _{0.2} Pahi SSW _{2.0}								23.0 22.9 22.7	8.02 8.04 8.05	38.7 38.6 38.5
Loutropyrgos SML ^a	11.01.2020	7:30–9:00	Sunny	19,000	16.0	0.60	1	23.0	8.02	38.7
Loutropyrgos SSW _{0.2}								22.9	8.04	38.6
Loutropyrgos SSW _{2.0}	11.01.2020	10:20–12:55	Sunny	44,000	19.2	0.50	0	22.7	8.05	38.5
Pahi SML ^a Pahi SSW _{0.2} Pahi SSW _{2.0}								14.0 13.8 13.7	7.76 7.81 7.83	38.0 38.0 37.9
Loutropyrgos SSW _{0.2}	11.01.2020	10:20–12:55	Sunny	44,000	19.2	0.50	0	15.2	7.71	38.3
Loutropyrgos SSW _{2.0}								15.2 15.0	7.74 7.72	38.3 38.2

^a Measurements of seawater temperature, pH, and salinity were made in the upper 5 cm of the water column; ^b Douglas sea scale.

2.3. Analytical Method and Quality Assurance

Sixteen US EPA priority controlled PAHs (naphthalene, NP; acenaphthylene, ACY; acenaphthene, ACE; fluorene, FL; phenanthrene, PHE; anthracene, ANT; fluoranthene, FLA; pyrene, PYR; chrysene, CHR; benzo[a]anthracene, BaA; benzo[b,k]fluoranthene, BbKF; benzo[a]pyrene, BaP; dibenzo[a,h]anthracene, DahA; indeno[1,2,3 cd]pyrene, IcdP; benzo[g,h,i]perylene, BghiP) were determined. Dissolved PAHs were extracted from seawater by liquid–liquid extraction with dichloromethane (3×30 mL per litre). Extracts were concentrated to nearly 2–3 mL by rotary evaporation at 30 °C. The samples were further evaporated under nitrogen steam up to 500 μ L. For particulate PAHs, the aforementioned procedure described for the dissolved fraction was modified with the addition of a purification step after rotary evaporation, as described in Karavoltsos et al. [34]. For both dissolved and particulate PAHs extracts, the determination of PAHs was carried out by using an Agilent (Santa Clara, CA, USA) 6890N Gas Chromatograph coupled to a 5975C Mass Spectrometer operating with EI (electron ionization), using the selected ion monitoring mode (SIM).

D10-phenanthrene and D12-perylene, used as both internal and surrogate standards, were added to all the samples prior to extraction. The relative response factors of standards to internal ones were employed for sample quantification.

Analytes' recoveries derived from spiked samples ranged from 73 (FL) to 112 (CHR) % in the dissolved phase and from 80 (NP) to 117 (BbkF) % in the particulate phase, while correction by surrogate recoveries was omitted in order to avoid overestimation.

The limits of detection (LODs) for PAHs determination, in ng L^{-1} , were calculated respectively equal to 0.109/0.051 (dissolved/particulate phase) for NP, 0.067/0.031 for ACY, 0.030/0.014 for ACE, 0.013/0.006 for FL, 0.039/0.018 for PHE, 0.016/0.008 for ANT, 0.054/0.025 for FLA, 0.022/0.010 for PYR, 0.015/0.007 for CHR, 0.024/0.011 for BaA, 0.021/0.010 for BbkF, 0.006/0.003 for BaP, 0.008/0.004 for IcdP, 0.004/0.002 for DahA and 0.005/0.002 for BghiP.

2.4. Statistical Analysis

For statistical analysis, the SPSS package, version 24 (SPSS Inc, Chicago, IL, USA) was used. The Kolmogorov–Smirnov and Shapiro–Wilk tests were used for assessing the normality of the data. Both tests provided p values lower than 0.05, and the null hypothesis (that the data are normally distributed) was rejected. Therefore, the Mann–Whitney U and Kruskal–Wallis non-parametric tests were used to statistically compare values between two groups and among more than two groups, respectively. The tests were two-sided, and p values less than 0.05 were considered as statistically significant.

3. Results and Discussion

3.1. Concentrations Patterns of PAHs

The sum of concentrations of the 16 US EPA priority total PAHs (including both dissolved and particulate PAHs ($\Sigma_T\text{PAHs}$)), ranged from 97.9 to 338 ng L^{-1} (median 237 ng L^{-1}) in the SML, from 85.6 to 289 ng L^{-1} (median 178 ng L^{-1}) in SSW_{0.2} and from 21.3 to 178 ng L^{-1} (median 70.5 ng L^{-1}) in the SSW₂. The sum of dissolved PAHs ($\Sigma_d\text{PAHs}$) concentrations ranged from 40.4 to 237 ng L^{-1} in SML, 22.8–180 ng L^{-1} in SSW_{0.2} and 15.5–145 ng L^{-1} in SSW₂, whereas the corresponding concentrations in suspended particulate matter ($\Sigma_p\text{PAHs}$) are 30.8 to 177 ng L^{-1} , 36.8–171 ng L^{-1} and 5.79–68.3 ng L^{-1} , respectively (Table 2; Figure 2A). In most of the samples analyzed, excluding January 2020 sampling, dissolved PAHs prevailed compared to particulate ones, with their percentages in terms of total PAHs ranging from 19.5 to 85.5% (median 60.8%) in SML, 16.0 to 72.6% (median 63.7%) in SSW_{0.2}, and 44.4 to 83.2% (median 76.2%) in SSW₂.

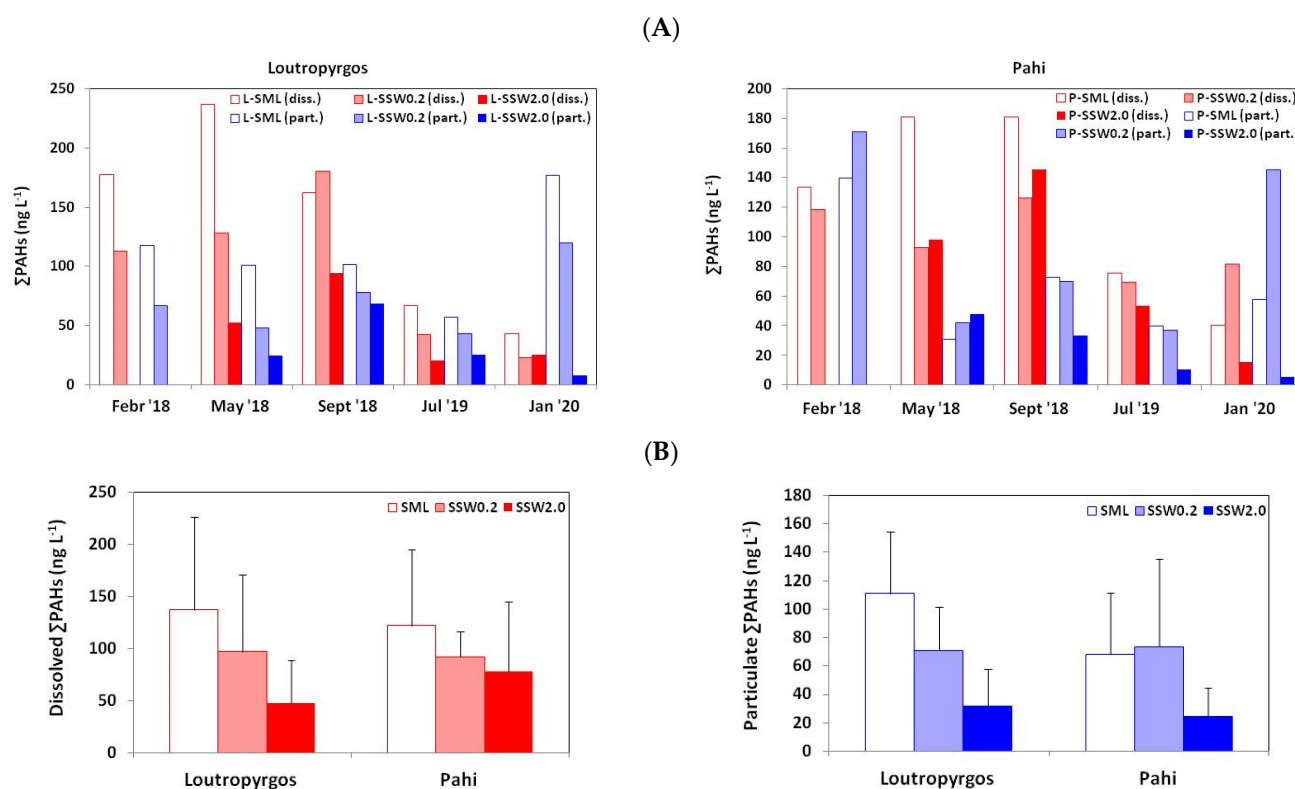
The preferential accumulation of PAHs towards the dissolved phase in respect to the particulate one, also reported by Ya et al. [35] for Xiamen Island, China; Tedetti et al. [36] and Guige et al. [7] for coastal waters of Marseilles; and Manodori et al. [37] for the Venice Lagoon, is contrary to the observation of Hardy et al. [38], according to which most PAHs tend to associate with the particulate matter, especially in polluted environments. Bouloubassi and Saliot [39] supported that dissolved PAHs might be even more significant than the corresponding particulate pool, particularly in systems characterized by relatively low loads of suspended matter. Such observations may be attributed to the presence of slicks, which by the dissolution of PAHs lead to their increased levels in the dissolved phase [5], while temperature, salinity, and the amount of suspended particulate matter constitute additional regulating factors [40,41]. However, the ultimate fate of PAHs in the environment is determined by a series of processes including deposition, volatilization, sinking, resuspension, and degradation [42].

No statistically significant differences characterized the concentrations of ΣPAHs in both dissolved and particulate phases among the different sample depths (SML, SSW_{0.2}, SSW_{2.0}) between Loutropyrgos and Pahi of Megara sites ($p > 0.05$ Mann Whitney test, in all correlations) (Figure 2B). This lack of variance could be attributed to similar PAHs sources affecting both stations, to the fact that PAHs in the atmosphere are generally well distributed at relatively small regions due to atmospheric advection, as well as to atmospheric deposition and rainwater, which represent the predominant inputs determining the levels and distribution of contaminants in aquatic systems [43,44]. Nevertheless, the study of PAHs composition is necessary for drawing safe conclusions.

Table 2. Concentrations (ng L⁻¹) of Σ PAHs in the dissolved and particulate phases of seawater.

	February 2018	May 2018	September 2018	July 2019	January 2020
Dissolved phase					
Loutropyrgos SML	177	237	162	67.1	42.9
Loutropyrgos SSW _{0.2}	113	128	180	42.6	22.8
Loutropyrgos SSW _{2.0}	- *	52.3	93.8	20.2	24.9
Pahi of Megara SML	133	181	181	75.2	40.4
Pahi of Megara SSW _{0.2}	118	92.6	126	69.0	81.3
Pahi of Megara SSW _{2.0}	-	98.3	145	53.4	15.5
Particulate phase					
Loutropyrgos SML	118	101	102	57.0	177
Loutropyrgos SSW _{0.2}	66.7	48.3	78.1	43.0	119
Loutropyrgos SSW _{2.0}	-	24.5	68.3	25.2	7.78
Pahi of Megara SML	140	30.8	72.6	39.7	57.3
Pahi of Megara SSW _{0.2}	171	42.0	69.6	36.8	145
Pahi of Megara SSW _{2.0}	-	47.9	33.7	10.8	5.79

* Sample loss.

**Figure 2.** Concentrations of dissolved and particulate Σ PAHs (A) during the samplings performed, (B) mean values for the different sampling sites.

3.2. Composition and Partitioning of PAHs

Regarding PAHs distribution patterns, the 2 ring NP, which is the simplest among oil PAHs compounds, the most easily degradable and highly volatile [45], was not detected in most of the samples examined, neither in dissolved nor in particulate phases. In all seawater depths studied 3 and 4 ring PAHs dominated, accounting for $81 \pm 15\%$ of total in the dissolved phase and $72 \pm 20\%$ in the suspended particulate matter. The most abundant 3 and 4 ring PAHs in the filtrates were PHE (21%), FLA (15%), and FL (13%), while PHE (17%), FLA (11%), and PYR (11%) prevailed in the particulate matter, with PHE being detected in all samples. These results are in accordance with those of Huang et al., (2020) [46], who demonstrated the prevalence of PYR, PHE, and FLA in the dissolved phase

of SML and that of PHE, PYR, B α A, and FLA in the particulate one. As expected, PAHs with 5 and 6 rings were detected at higher percentages in the suspended particulate matter ($26 \pm 19\%$) compared to the dissolved phase ($15 \pm 15\%$).

Regarding the vertical distribution of PAHs in the water column (Figure 3), in the SML, the percentages of 2 ring, 3 and 4 ring and 5 and 6 ring PAHs were calculated respectively equal to $3.5 \pm 3.5\%$, $74 \pm 15\%$, and $22 \pm 14\%$ for the dissolved phase and $2.1 \pm 3.5\%$, $62 \pm 15\%$, and $36 \pm 14\%$ for the particulate one. In the SSW_{0.2} the corresponding percentages were $5.4 \pm 3.2\%$, $83 \pm 13\%$, and $11 \pm 11\%$ for the dissolved phase and $2.1 \pm 2.3\%$, $69 \pm 21\%$, and $29 \pm 20\%$ for the particulate one, while for SSW_{2.0}, the values calculated were $3.1 \pm 3.8\%$, $86 \pm 18\%$, and $11 \pm 17\%$ for the dissolved phase and $2.9 \pm 2.4\%$, $87 \pm 16\%$, and $10 \pm 15\%$ for the particulate one, demonstrating similar composition patterns of dissolved and particulate matter in deeper seawater layers. Overall, 3 and 4 ring PAHs seem to prevail in both the dissolved and particulate phases for the three layers examined. Similarly, Ya et al. (2017) showed that in the upper waters of the northwestern coast of South China Sea, the 3 and 4 ring PAHs are prevailing in both the dissolved and the particulate phase [35]. It has been shown that after entering coastal surface waters, particle–water partition of PAHs is controlled by their interaction with dissolved and particulate organic matter [47], which could be expressed by the partition coefficient (K_p) [40]. However, no correlation was found herewith between partition coefficients ($\text{Log}K_p$) and octanol–water partition coefficients ($\text{Log}K_{ow}$) for all groups of PAHs analyzed ($p < 0.05$).

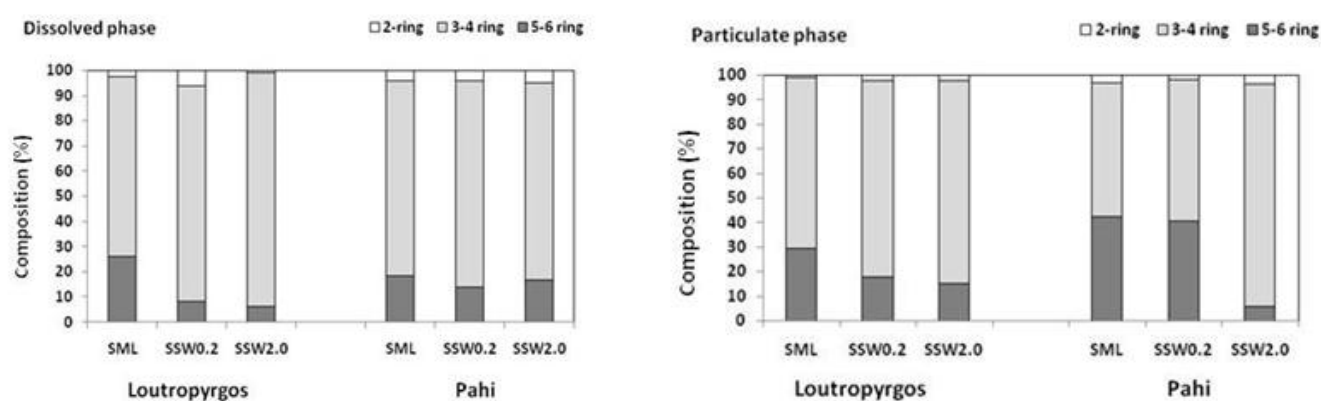


Figure 3. Composition patterns (% percentage) of mean PAHs concentrations measured in the dissolved and particulate phases at the sampling sites studied.

3.3. Possible Sources of PAHs

It is supported that petrogenic PAHs, originating from organic matter low temperature alterations, correspond to low molecular weight (LMW) 2–3 ring PAHs, having a large proportion of alkylated homologues. Pyrogenic PAHs, deriving from high temperature combustion processes, correspond to high molecular weight (HMW) 4–6 ring PAHs, characterized by a low abundance of alkylated products [13]. The detection of parent compounds with 4 or more aromatic rings typifies the presence of pyrogenic sources within the study area [15].

The potential sources of PAHs, either from petrogenic or pyrolytic origin, can be evaluated by the ratios of specific PAHs compounds [13,23,48,49]. Nevertheless, the unquestionable application of PAHs diagnostic ratios has been criticized, due to the fact that they may be subject to significant alterations attributed to degradation processes during the transport of PAHs isomers from sources to receptors, occurring within a complex multimedia environment [50] and to a possible underestimation of total petrogenic PAHs concentrations [51]. Despite the fact that PAHs isomers degradation in seawater column occurs in depths exceeding 1 m [52], it should hence be considered in the attempt of identifying their potential sources.

The diagnostic PAH ratios ANT/(PHE + ANT) and FLA/(FLA + PYR), of 3–4 ring parent compounds [53–55] were applied in the present study (Figure 4). PAHs in the SML of Loutropyrgos site, both in the dissolved as well as in the particulate phase, seem to relate mainly with pyrolytic-related inputs (Figure 4A,B respectively). This finding is consistent with the presence of numerous heavy industrial factories, including two of the largest scale oil refineries, at a relatively small distance from the site of Loutropyrgos.

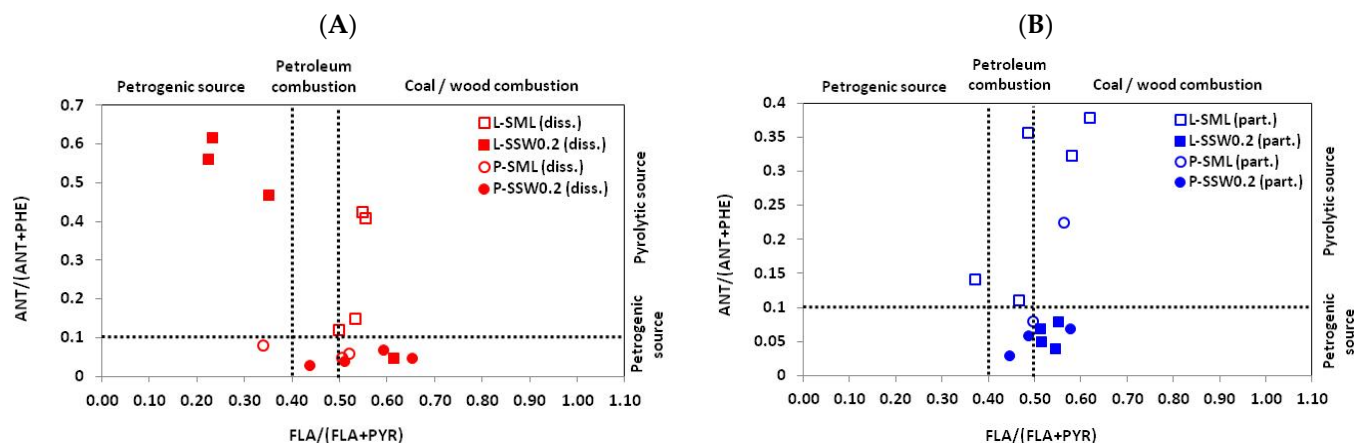


Figure 4. ANT/(PHE + ANT) and FLA/(FLA + PYR) ratios of PAHs in the dissolved (A) and particulate (B) phases of Loutropyrgos (L) and Pahi of Megara (p) sampling sites.

3.4. Assessment of Potential Enrichment of SML

The SML is generally considered to be enriched, relatively to underlying water, in various organic materials [1] as well as compounds of anthropogenic origin [7]. Several mechanisms have been suggested for explaining SML enrichment in PAHs, such as accumulation via enhanced absorption to organic films and oil slicks formed in the SML regarding the dissolved phase [56,57] or atmospheric fallout for the particulate one [38].

Enrichment features of SML might be evaluated through the calculation of enrichment factors (EFs) Equation (1), defined as the ratios of SML to corresponding SSW concentrations:

$$EF = C_M / C_S \quad (1)$$

where C_M is the concentration of any substance in the microlayer and C_S its corresponding concentration in the subsurface water [37]. EF values > 1.0 denote enrichment, while EF values < 1.0 are designated as depletions [58]. However, considering the measurement uncertainty in the analytical techniques applied (multiplied by 2 due to the measurements in SML and SSW), the existence of significant enrichment in the SML imposes $EF > 2$. In the present work, apart from the usual enrichment factors of the ratio of SML concentration to the corresponding SSW in 20 cm depth (EF_1), PAHs enrichment factors of the ratio of SML concentration to the corresponding SSW in 2 m depth (EF_2) were additionally calculated.

In Table 3, EF_1 and EF_2 values of Σ PAHs in the dissolved and particulate phases for the sites studied are presented. Regarding EF_1 , an enrichment of the SML in Σ PAHs was denoted for most of the paired samples in both dissolved and particulate phases (in 15 out of 20 pairs in total). The calculated EF_1 for dissolved Σ_d PAHs varied between 0.9 and 2.1 with a mean value of 1.5 ($n = 10$) being significantly greater than unity ($p = 0.0009$), whereas for particulate Σ_p PAHs, the mean value of EF_1 was equal to 1.1 ($n = 10$), not being significantly greater than unity ($p = 0.3212$). EF_1 values were slightly higher in the dissolved in comparison with the particulate phase (mean \pm stdev; 1.6 ± 0.4 and 1.4 ± 0.6 , respectively, at Loutropyrgos; 1.4 ± 0.6 and 0.8 ± 0.3 at Pahi of Megara), with the difference being statistically significant at Pahi of Megara ($p = 0.048$, Mann Whitney, NY, USA), however not at Loutropyrgos ($p > 0.05$). Several researchers have calculated higher EF values for the particulate phase of SML relatively to the dissolved one [5,23,59], whereas

others have demonstrated the absence of statistically significant differences between the two phases [7,60]. However, additional external factors such as the size and absorbance ability of suspended particulate matter or the strength of exchange between SML and SSW might alter the enrichment features of the two phases at different sampling sites [35].

Table 3. Enrichment factors (EF_1 , EF_2) of Σ PAHs in the dissolved and particulate phases.

	Loutropyrgos				Pahi of Megara			
	Dissolved		Particulate		Dissolved		Particulate	
	EF_1^a	EF_2^b	EF_1	EF_2	EF_1	EF_2	EF_1	EF_2
13 February 2018	1.6		1.8		1.1		0.8	
16 May 2018	1.8	4.5	2.0	1.8	2.1	4.1	0.7	0.6
5 September 2018	0.9	1.7	1.4	1.2	1.3	1.5	1.0	2.2
6 July 2019	1.6	3.3	1.1	1.4	1.3	2.3	1.1	3.7
11 January 2020	1.9	1.7	0.5	2.6	1.5	22.7	0.4	9.9
Mean \pm st dev	1.6 ± 0.4	2.8 ± 1.4	1.4 ± 0.6	1.8 ± 0.6	1.5 ± 0.4	7.6 ± 10	0.8 ± 0.3	4.1 ± 4.1

^a $C(\Sigma\text{PAHs})_{\text{SML}}/C(\Sigma\text{PAHs})_{\text{SSW}0.2}$ (SSW_{0.2}: subsurface water at 20 cm depth); ^b $C(\Sigma\text{PAHs})_{\text{SML}}/C(\Sigma\text{PAHs})_{\text{SSW}2.0}$ (SSW_{2.0}: subsurface water at 2 m depth).

The EF_2 enrichment factors values (ratio of Σ PAHs concentrations between SML and SSW at the depth of 2 m) are significantly higher compared to those of EF_1 values for both the dissolved and the particulate phases (Table 3). A gradual decrease of Σ PAHs concentrations is observed, appearing quite intense by the depth of 2 m examined. The transformation and degradation mechanisms of PAHs occurring by a 2 m depth might differ to some extent to the corresponding characterizing the SML, being however equally important. It has been reported that in the Mediterranean, low molecular-weight PAHs are efficiently metabolized by zooplankton due to highly oligotrophic conditions occurring [61,62].

In Figure 5, the enrichment factors (EF_1) calculated for PAHs with 3, 4 and 5–6 rings are presented. A gradual enrichment of the SML in PAHs in relation to the number of aromatic rings, mainly in the dissolved phase and to a lesser extent in the particulate one, is recorded at Loutropyrgos sampling site, however not at the area of Pahi of Megara. Similarly, Huang et al. [46] have reported an increase in the average EFs of individual PAHs with the PAH molecular weight, which they assign to PAHs hydrophobic characteristics. The fact that no corresponding increase was reported in the EFs of high molecular weight PAHs at both study areas enhances the consideration that except for their hydrophobic characteristics, PAHs sources may also exert a considerable impact. Specifically, the quite significant enrichment calculated for the SML of the coastal area of Loutropyrgos in high molecular weight PAHs constitutes an indication that PAHs of pyrogenic origin represent a particularly important source at the specific area. This consideration is in accordance with the specific features of the area, since a great number of industries (including combustion procedures at high temperatures) are situated at a small distance.

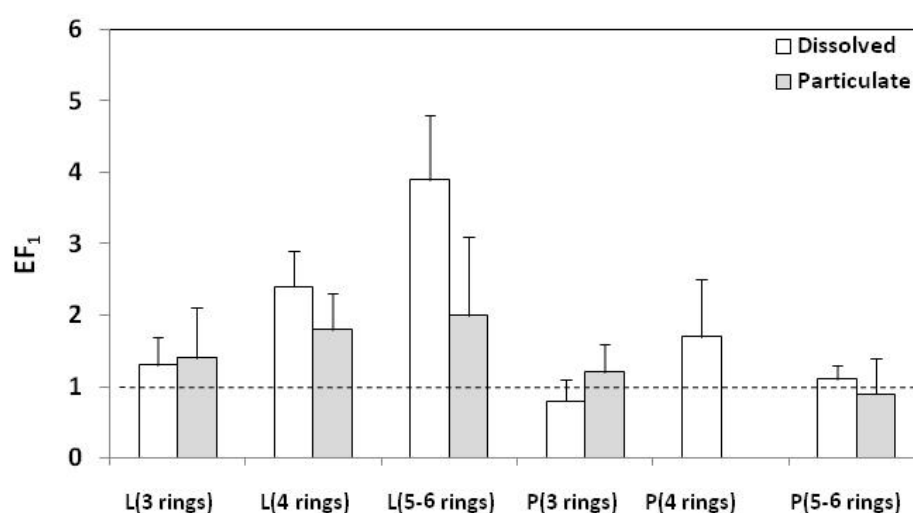


Figure 5. Average enrichment factors (EF_1) of 3, 4, and 5–6 rings PAHs, for dissolved and particulate phases, at the sampling sites of Loutropyrgos (L) and Pahi of Megara (P).

3.5. Toxicity Assessment

The potential ecological toxicity of PAHs levels determined in the present work was estimated (Table 4), through the comparison of both individual and total PAHs concentrations in the particulate phase of seawater, with sediment quality guidelines corresponding to range-low (ERL) and range-median (ERM) adverse biological effects related to chemical concentrations in marine sediments [63,64]. Concentrations not exceeding ERL indicate that an adverse effect would rarely be observed, whereas concentrations exceeding ERM indicate potential occurrence of adverse effects. In 6 out of the 16 PAHs, analyzed ERL values were exceeded, with the particulate phase of SML posing a higher potential risk to the marine ecosystem than SSW. The compounds more frequently exceeding ERL were FL with 25% (SML), 32% ($SSW_{0.2}$), and 14% ($SSW_{2.0}$) of the samples analyzed containing FL at levels higher than ERL, ACE (21%, 18% and 11%, respectively) and PHE (14%, 7% and 4%, respectively). ACY concentrations detected exceeded the corresponding ERL value in 11% ($SSW_{0.2}$) and 14% ($SSW_{2.0}$) of the samples, while for the case of ANT in 18% (SML) of the samples. The ERM values were not exceeded, whereas total PAHs levels were lower than both ERL and ERM values reported.

Table 4. Toxicity assessment comparing the individual and total PAHs levels in the particulate phase ($ng\ g^{-1}$) of the sea-surface microlayer (SML) and sub-surface water ($SSW_{0.2}$; $SSW_{2.0}$) with standard pollution criteria guidelines.

	Concentration ($ng\ g^{-1}$)		SML		$SSW_{0.2}$		$SSW_{2.0}$	
	ERL ^a	ERM ^b	n ^c > ERL	n > ERM	n > ERL	n > ERM	n > ERL	n > ERM
ACY	44	640	0	0	3	0	4	0
ACE	16	500	6	0	5	0	3	0
FL	19	540	7	0	9	0	4	0
PHE	240	1500	4	0	2	0	1	0
ANT	85.3	1100	5	0	0	0	0	0
FLA	600	5100	0	0	0	0	0	0
PYR	665	2600	0	0	0	0	0	0
BaA	261	1600	0	0	1	0	0	0
DahA	63.4	260	2	0	1	1	0	0
Total PAHs	4022	44,792	0	0	0	0	0	0

^a Effect range-low; ^b Effect range-median [63,64]; ^c Number of samples exceeding standard pollution criteria guidelines.

According to the recent study of Huang et al. [46] referring to PAHs in the SML of harbor water in Taiwan, overall, the particulate phase of SML poses a higher risk to the marine ecosystem than that contained in the SSW. However, it is noteworthy that the

SML constitutes a special habitat, comprising organisms which have developed specific adaptation mechanisms. The SML might be a stressful environment, receiving intense solar irradiation, especially in the low wavelength range of ultraviolet-B (300–320 nm), which is detrimental to organisms [65].

3.6. PAHs Levels Reported in the SML of Other Marine Areas

Due to the heterogenous nature of SML, the comparison of pollutants' concentrations both on spatial and temporal scales is rather challenging. Towards this direction, the adoption of a standard procedure for SML sampling would be crucial, ensuring not only consistency in the operation of sampling devices but also collection of SML samples exclusively under suitable environmental conditions also referred by Wurl and Obbard [14]. The fact that the total concentrations of PAHs mixtures reported in literature do not always relate to the same sum of individual compounds, hindering hence inter-site comparisons, imposes that they should be considered with caution.

Data reported in literature demonstrate that contamination of the marine environment with PAHs increases in areas where anthropogenic coastal activities occur, such as harbors, shipping traffic, and operation of local industries [14]. Accordingly, the total (dissolved and particulate) PAHs concentrations in the SML reached up to $6 \mu\text{g L}^{-1}$ in Chesapeake Bay [66], $56 \mu\text{g L}^{-1}$ in Los Angeles harbor [67], and $170 \mu\text{g L}^{-1}$ in Leghorn in Tyrrhenian Sea [5]. Comparing PAHs concentrations in the SML reported in literature for different geographical areas, a wide range of values was observed (Table 5). The ΣPAHs levels determined herewith in the SML demonstrate a moderate contamination of the area studied, with maximum concentrations being comparable to those previously reported for coastal areas such as the Alexandria coast, Egypt, by El Nemr and adb-Allah [23]; the Venice Lagoon, Italy, by Manodori et al. [37]; Xiamen Island, China, by Ya et al. [35]; and Kaohsiung Harbor and adjacent area, Taiwan, by Huang et al. [46]. Interestingly, the minimum concentrations of ΣPAHs in SML measured in this study appear elevated compared to those of other areas, being characteristic of enclosed coastal areas affected by intense anthropogenic activities. The SSW demonstrates a similar trend, indicating a continuous enrichment of surface seawater layers in PAHs.

Table 5. Concentrations of ΣPAHs in the sea surface microlayer (SML) and sub-surface water (SSW) of different coastal regions.

Area	n ^a	SML (ng L ⁻¹)		SSW (ng L ⁻¹)		Sampling Year	Ref
		Dissolved PAHs	Particulate PAHs	Dissolved PAHs	Particulate PAHs		
San Diego Bay, USA	26		20.4–79.2		551–7540	1994	[68]
Leghorn, Tyrrhenian Sea, Italy	15	214–15,200	826–154,000		63–3050 ^b	1999	[5]
Baltic Sea			4.5–53 ^b			1992–1998	[69]
Alexandria coast	7		103–523 ^b		13–120 ^b	2002	[23]
Barcelona, Spain	14	11.9–93.4		4.9–19.9		2001	[70]
Venice Lagoon, Italy	20	8.32–138	30.3–163	6.31–259	5.68–45.2	2001–2003	[37]
Terra Nova Bay, Antarctica	13	4.67–7.79	5.68–14.1	2.24–4.01	1.65–3.65	1998–1999	[71]
Singapore	16	2.7–46.2	3.8–31.4	3.4–36.5	6.7–30.3	2005	[44]
Barcelona, Spain	16	4.6–41.7	2.3–31.2	3.6–30.7	0.5–5.7	2001–2002	[9]
Banyuls-sur-Mer, France		2.5–25.9	0.6–14.5	4.6–12.9	0.4–8.6		
Terra Nova, Antarctica	13	4.25–8.11	3.07–15.8	2.14–2.85	2.81–4.66	2000–2001	[60]
Barcelona, Spain	16	16.7–35.7	2.3–16.7	4.4–17.7	0.5–0.8	2002–2003	[42]
Banyuls-sur-Mer, France		2.4–22.3	0.6–6.7	4.6–7.6	0.4–2.4		
Port-de Bouc, Marseilles, France		1842	148	6.4	553	2008–2009	[36]
Marseilles, France	17	50–217	6.0–1597	1.9–98	1.9–21	2009–2010	[7]
Xiamen Island, China	16		93.4–424 ^b		42.3–279 ^b	2005	[35]
Lagos Lagoon, Nigeria	17		9100–16,200 ^b		8900–13,300 ^b	2014	[72]
Kaohsiung Harbor and adjacent area, Taiwan	15	2.90–192	14.4–268	1.25–9.39	12.9–26.4	2014	[46]
Saronikos gulf, Greece	16	40.4–237	30.8–177	22.8–180	36.8–171	2018–2020	This study

^a Number of PAH compounds; ^b Total PAHs (dissolved + particulate).

4. Conclusions

Five sampling campaigns were carried out in order to evaluate PAHs levels in sea surface microlayer and sub surface water samples at two coastal sites of the Eastern Mediterranean, within the Gulf of Elefsis, a marine area highly affected by long-term industrialization and several anthropogenic pressures. PAHs were overall found to preferentially accumulated in the dissolved rather than the particulate phase of seawater. For the majority of the paired samples (SML and SSW) examined, the denoted enrichment of the SML in Σ PAHs was statistically significant only for the dissolved phase. Although the application of diagnostic PAHs ratios in both the dissolved and particulate SML and SSW water samples implies a mixed origin of PAHs deriving from both petrogenic and pyrolytic sources, the enrichment factors calculated for PAHs between the SML and SSW layers highlight pyrolytic procedures as principal PAHs sources for the coastal area studied. In particular, a significant enrichment of the SML in high molecular weight PAHs was observed near the industrial zone, indicating that PAHs of pyrogenic origin represent a particularly important source at the specific area. Although the ecological impact of PAHs in the SML was found to be rather limited, it poses a relatively higher risk to the marine ecosystem, compared to that attributed to PAHs in the subsurface water. However, further research is required for the elucidation of processes involving PAHs transport and transformation among atmosphere, SML, and SSW.

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