

Polycyclic Aromatic Hydrocarbons in the Atmosphere of the Eastern Mediterranean

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Atmospheric processes governing the fate of the polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of the Eastern Mediterranean were studied for a two-year period (2000–2001). Atmospheric samples were collected off-shore over the Eastern Mediterranean Sea as well as at a background station in Northeastern Crete, Greece. PAH total concentration varied from 4.1 to 57.2 ng m⁻³, with >90% in the gas phase. Gas-to-particle distribution of PAHs was correlated (R^2 0.75–0.98, $p < 0.001$) with their subcooled vapor pressure. Seasonal changes in the total concentration of PAHs were not observed, while the origin of air mass was the dominant factor determining their atmospheric concentration levels. Air masses, originating from central and eastern Europe, were associated with the highest PAH concentrations. Gas-to-particle distribution of Σ PAHs correlated well (R^2 0.75–0.98, $p < 0.001$) with their subcooled vapor pressure. Tropospheric ozone concentration correlated with the vapor-phase PAH concentration ($p < 0.001$) but less ($p < 0.01$) with the particulate PAH concentration. Distribution of volatile PAHs over the Eastern Mediterranean basin was uniform. Conversely, particulate PAH concentrations were higher at sampling sites located close to urban centers. Calculated relative removal rates of PAHs associated with particles were significantly higher than those of volatile members.

Introduction

The ability of semi-volatile organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), to migrate from polluted areas through the movement of air masses to remote regions is now established (1). The ubiquitous PAHs, which are generally formed by incomplete combustion of carbon-containing fuels, can enter the marine environment and be deposited in the sediment through atmospheric deposition, municipal treatment discharges, and oil spills (2). Mass balance studies in the Western Mediterranean have shown that the atmosphere is an important path for PAHs import into the marine environment (3). The Eastern Mediterranean receives air masses emanating from eastern and central European regions for the longest time interval (70% of air masses (4)). As emissions of PAHs in Eastern and Central Europe are particularly high (5), pollutant transport from these areas to

the Eastern Mediterranean and, subsequently, their atmospheric deposition is always of special concern. Recently, atmospheric transport was identified as the major nonpoint source of PAHs in pristine marine sediments of the Eastern Mediterranean (6).

Since the atmosphere is supposed to be the major source and conveyor belt of semivolatile organic pollutants to this region, the investigation into the occurrence and behavior of these compounds in the atmosphere above the Mediterranean basin is a significant and challenging task due to the lack of regional data representative of the atmosphere above the Mediterranean Sea or South Europe.

The main objective of the work herein was to study the processes governing the occurrence and seasonal variation of PAHs in gas and particulate phase over the Eastern Mediterranean Sea. The specific tasks to achieve our goal were the following: (1) measurement of the gaseous and particulate PAH concentrations of atmospheric samples collected at a background station and off-shore over the Eastern Mediterranean Sea to study their spatial distribution and their removal rates; (2) study of the gas-to-particle distribution of PAHs; (3) investigation of the seasonal changes in the total concentration of PAHs; (4) evaluation of the influence of the origin of air mass on PAH atmospheric concentration levels; and (5) investigation of the potential correlation of PAHs atmospheric levels with the corresponding levels of other transported pollutants into the study area, such as ozone.

Experimental Section

Sampling. Twenty three air samples were collected monthly between February 2000 and February 2002 at a background coastal site (Finokalia, 35° 19' N, 25° 40' E, 130 m ASL), 70 km east of Heraklion (Island of Crete, Greece). The duration of sampling was 24 h and the sample volume was approximately 700 m³. Details about the area and its meteorological conditions are given by Mihalopoulos et al. (4) and Kouvarakis et al. (7). In addition, during a five-day cruise, between July 25 and 30, 2000, 13 air samples were collected aboard the research vessel "Aegeon", which cruised across the eastern Mediterranean basin area between the Greek mainland and the Island of Crete. The vessel cruised along selected tracks defined by forward and back trajectory modeling as calculated with the sampling site in Crete as the end point. Sampling was performed at 12-h intervals (from 08:00 to 20:00 and from 20:00 to 08:00 local time).

Samples were collected by using a modified high-volume (hi-vol) sampler. An oxidant denuder was used to minimize PAH degradation during high-volume air sampling. The efficiency of the sampler has been described in detail elsewhere (8). In brief, an oxidant denuder system was added in front of a conventional high-volume sampler (GMW-2000H). The denuder contained 841 tubes (with a section of 4 × 4 mm² and a height of 20 cm) coated with a water/glycerol KNO₂ solution in order to retain ozone and other oxidants. The air was drawn through a glass fiber filter (GFF) to collect particles and then through a polyurethane foam (PUF) plug (length 8.0 cm, diameter 7.5 cm) to collect compounds present in the vapor phase.

Measurements. Continuous measurements of ozone concentration were recorded by using an ozone analyzer (Dasibi 1008 O₃). Temperature (T), relative humidity (RH), wind speed (WS), and wind direction were measured by the meteorological facility of "Nikos Kazantzakis" airport of Heraklion. Backward trajectories of air masses were calculated using the atmospheric circulation model, HYSPLIT 4 (9, 10),

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TABLE 1. Average (Min–Max) Concentrations (ng m⁻³) of Studied Gaseous and Particulate PAH in the Atmosphere of Eastern Mediterranean

PAH member (abbreviation)	gas phase	particulate phase	total
Fluorene (Fl) ^a	1.8 (0.2–5.7)	0.02 (<0.001–0.1)	1.8 (0.2–5.8)
Phenanthrene (Phe)	7.3 (1.5–27.7)	0.05 (0.004–0.2)	7.3 (1.5–27.8)
Anthracene (An)	0.9 (0.1–4.5)	0.004 (<0.001–0.02)	0.9 (0.1–4.5)
Σ Methyl-Phenanthrenes (Me-Phe)	4.4 (0.6–15.2)	0.005 (0.001–0.3)	4.5 (0.6–15.3)
Fluoranthene (Fluo)	1.8 (0.07–6.0)	0.1 (0.04–0.2)	1.9 (0.1–6.6)
Σ Dimethyl-Phenanthrenes (DMPs)	0.9 (0.08–3.3)	0.04 (0.01–0.1)	1.0 (0.1–3.4)
Pyrene (Py)	0.9 (0.1–2.8)	0.04 (0.01–0.01)	1.0 (0.1–2.8)
Σ Methyl-Fluoranthene/Pyrene (Me-202)	0.27 (<0.001–1.7)	0.02 (<0.001–0.1)	0.3 (0.01–1.1)
Retene (Ret)	0.03 (<0.001–0.3)	0.002 (<0.001–0.01)	0.03 (<0.001–0.3)
4(H)-cyclo[cd]pyrene (4H-CY)	0.08 (<0.001–0.3)	0.02 (<0.001–0.1)	0.1 (<0.001–0.4)
Benzo[a]anthracene (BaA)	0.04 (<0.001–0.2)	0.03 (0.003–0.1)	0.1 (0.01–0.2)
Chrysene/Triphenylene (Chr/T)	0.2 (<0.001–0.6)	0.1 (0.02–0.3)	0.3 (0.1–0.6)
Σ Methyl-Chrysenes (Me-Chr)	0.02 (<0.001–0.1)	0.004 (<0.001–0.02)	0.02 (0.001–0.1)
Benzo[b]fluoranthene (BbF)	0.02 (<0.001–0.1)	0.04 (<0.001–0.2)	0.1 (<0.001–0.2)
Benzo[k]fluoranthene (BkF)	0.02 (<0.001–0.2)	0.04 (<0.001–0.2)	0.1 (<0.001–0.3)
Benzo[b/j/k]fluoranthene (BbjkF)	0.01 (<0.001–0.05)	0.04 (0.004–0.2)	0.1 (0.004–0.2)
Benzo[e]pyrene (BeP)	0.02 (<0.001–0.2)	0.04 (0.01–0.1)	0.1 (0.02–0.3)
Benzo[a]pyrene (BaP)	0.01 (<0.001–0.1)	0.02 (0.01–0.05)	0.04 (0.007–0.2)
Perylene (Per)	0.002 (<0.001–0.03)	0.004 (<0.001–0.01)	0.01 (<0.001–0.1)
Anthranthrene (Anthr)	0.002 (<0.001–0.02)	0.01 (0.003–0.1)	0.02 (0.003–0.1)
Indeno[1,2,3-cd]pyrene (IP)	0.004 (<0.001–0.1)	0.03 (0.009–0.2)	0.03 (0.01–0.2)
Dibenzo[a,h]anthracene (DBA)	<0.001	0.002 (<0.001–0.02)	0.002 (<0.001–0.02)
Benzo[ghi]perylene (BghiP)	0.01 (<0.001–0.2)	0.03 (0.010–0.09)	0.03 (0.01–0.2)
Coronene (Cor)	<0.001	0.002 (<0.001–0.02)	0.002 (<0.001–0.02)
ΣPAH	18.8 (3.6–56.3)	0.7 (0.3–1.6)	19.5 (4.1–57.2)

developed by the U.S. National Oceanic and Atmospheric Administration (NOAA) (<http://www.arl.noaa.gov/ready.html>). These trajectories (72 h back) were defined in constant air pressure (850 hPa, 1200–1400 m, height varying according to season and atmospheric temperature).

PAH Analysis. Preceding sampling, GFFs were heated at 450 °C for 5 h. PUF plugs were boiled in water, rinsed with acetone, and then Soxhlet extracted twice for 24 h with *n*-hexane (Merck, Suprasolve). PUF plugs were dried in a vacuum desiccator, placed in glass cylinders, and sealed in glass jars. Before and after sampling filters were weighted to obtain total suspended particle (TSP) concentrations.

GFFs and PUFs were spiked with a mixture of three perdeuterated PAHs (D₁₀-phenanthrene, D₁₀-pyrene, and D₁₂-perylene) and then extracted in a Soxhlet apparatus for 24 h with *n*-hexane (Merck, Suprasolve). Sample extracts were concentrated to 1 mL by using a rotary evaporator. The extracts were loaded onto a 1.5-g activated silica gel (100–200 mesh) and eluted with 11 mL of *n*-hexane and 15 mL of *n*-hexane/toluene (9.5/5.5) under nitrogen pressure (1.4 mL min⁻¹). PAHs were collected in the second fraction. Each fraction was concentrated under a gentle stream of nitrogen. Prior to injection, a solution of D₁₀-anthracene was added as a recovery standard.

GC–MS analysis of PAHs was carried out on a Hewlett-Packard mass-selective detector (5891A) operating in selected ion monitoring (SIM) mode. The mass spectrometer was directly coupled with the GC equipped with a 30 m × 0.25 mm, 0.25-μm film thickness, HP-5MS fused silica column.

Quality Assurance. The identification of each compound was based on the use of the mass spectra of reference standards (Dr. Ehrenstorfer GmbH, Germany). Relative response factors (RRFs) for PAHs were determined each time prior to sample analysis by using a standard mixture containing the reported analytes and three internal standards. RRFs were then used to calculate the amount of PAHs in the samples. A chromatographic peak was quantified as PAH when the following criteria were met: (1) the signal-to-noise ratio (S/N) should be higher than 5, (2) the isotopic ratio of the monitoring and confirmation ion should be within ±20% of those observed for reference standards, and (3) the retention time should be within ±10 s of those observed for reference standards.

Field and laboratory blank samples were routinely analyzed to evaluate analytical bias and precision. The detection limits were set at three times the mean blank concentration for each PAH member. PAHs with 5 and 6 rings were not detected in the GFF and PUF blanks. PAHs with molecular weight ≤206 were above the detection limits for all samples (gas and particles). PAH concentration varied from 1.5 to 23 and from 0.6 to 11.7 ng for PUF and GFF blank samples, respectively. Thus, the estimated detection limits ranged from 2.5 to 38.3 pg/m³ in the vapor phase and from 1 to 19.5 pg/m³ in the particulate phase.

Results and Discussion

PAH Occurrence and Origin. The total (gas plus particle) concentration of PAHs (Σ₃₇ PAH; for abbreviations see Table 1) at Finokalia varied from 4.1 to 57.2 ng m⁻³ and their average concentration was 19.5 ng m⁻³ (Table 1). The PAH total concentration in the gas phase varied from 3.6 to 56.3 ng m⁻³, with an average of 18.8 ng m⁻³. Considerably lower concentrations were observed for particulate PAHs, ranging from 0.3 up to 1.7 ng m⁻³ (Table 1). PAHs in the gas phase were the major fraction of the total amount measured over the Eastern Mediterranean. The contribution of gaseous PAH members varied from 78.9% up to 98.7%, with an average of 93.9%. Similar observations have been reported in other urban and rural regions worldwide (11–14).

PAHs with three and four aromatic rings (e.g., Phe, Me-Phe, Py, etc.) were the most abundant members in the gas phase, while the concentration of members with higher molecular weight (MW > 242) was low (Table 1). The average (min–max) concentrations of Phe, Py, and Fluo in the gas phase were 7.3 (1.5–27.7), 0.9 (0.1–2.8), and 1.8 (0.1–6.0) ng m⁻³, respectively (Table 1). These levels were lower (3.3 times on average) than those observed in the urban area of Heraklion (15). The most abundant members in the particulate phase were Chr and Phe with average (min–max) concentrations of 0.1 (0.02–0.3) and 0.1 (0.004–0.2) ng m⁻³, respectively (Table 1). Concentrations of particulate PAHs in the study area were considerably lower (24 times) than those found in the Heraklion urban area (15).

Mean concentrations of selected PAH members at Finokalia and other background areas worldwide are presented

TABLE 2. Total (Gas and Particulate) Concentration (ng m⁻³) of Selected PAHs^a in Rural and Background Sites Worldwide.

area	Fl	Phe	Fluo	Py	Chr/T	BaP	IP	reference
Finokalia (2000–2002)	1.8	7.3	1.0	1.0	0.3	0.04	0.03	this study
Green Bay, WI (1988)	4.1	9.6	1.7	0.8	0.4	0.12	0.13	Cotham, Bidleman; 1995 (11)
Sandy Hook, NJ (1997–98)	<2.0	4.9	<0.6	0.5	<0.001	0.006	<0.001	Gigliotti et al.; 2000 (13)
Lake Superior, (1986)	0.5	2.7	0.18	0.3	0.07	0.01	0.02	Baker, Eisenreich; 1990 (16)

^a For abbreviations see Table 1.

TABLE 3. Average, Minimum, and Maximum Values of Distribution Factor logK_p of PAHs^a in Finokalia Atmosphere

PAH member	average	min	max
Fl	-3.49	-4.46	-2.27
Phe	-3.7	-4.82	-2.57
An	-3.83	-5.22	-2.37
Me-Phe	-3.54	4.43	-3
Fluo	-2.73	-3.49	-1.31
DMPs	-3.10	4.54	-0.87
Py	-2.76	-3.47	-1.88
Me-202	-2.67	3.76	-0.79
4H-CY	-2.33	-4.02	-1.24
BaA	-1.56	-2.77	-0.36
Chr/T	-1.7	-2.91	-0.26
Me-Chr	-1.94	-3.62	-0.66
BbF	-0.82	-2.14	0.15
BkF	-0.68	-1.73	0.44
BbjkF	-0.85	-1.79	0.21
BeP	-0.74	-1.83	1.23
BaP	-0.66	-1.88	1.22
ΣPAH	-2.59	-3.69	-1.13

^a For abbreviations see Table 1.

in Table 2. The concentration of PAHs in the Eastern Mediterranean was comparable to that measured in Green Bay, WI (11), but higher than those reported for Sandy Hook, NJ and Lake Superior (13, 16).

Recently, radiocarbon analysis of atmospheric PAHs from Finokalia was performed to apportion their origin between fossil and biomass combustion (17). The radiocarbon content (Δ¹⁴C) of PAHs in Finokalia air samples (gas and particles) was -914‰. All chemical species originating from fossil carbon sources have a Δ¹⁴C of -1000‰, thus the value measured at Finokalia indicates that the combustion of fossil fuels is the main source of PAHs in this area. Indeed, on the basis of Δ¹⁴C and by using an isotopic mass balance approach it was calculated that fossil fuel combustion contributes nearly 90% of the total PAH burden in the study area (17).

Gas-to-Particle Distribution. The distribution of PAHs between gas and particles is an important factor controlling their fate in the atmosphere (18). The numerical expression of this distribution can be calculated using the distribution factor, K_p eq 1 (19)

$$K_p = (F/TSP)/A \quad (1)$$

where K_p (m³ μg⁻¹) is the distribution coefficient, TSP is the concentration of total suspended particulate matter (μg m⁻³), and F and A are the analyte concentrations in the particulate and gas phase, respectively. By definition, larger K_p values show the tendency of the compound to adhere preferentially to atmospheric particles.

The mean (min–max) values of logK_p measured in the Finokalia atmosphere are presented in Table 3. The mean value of logK_p for total PAHs was -2.59, implying their weak tendency to adhere to particles. The significant difference observed for logK_p values among PAH members (Table 3) is characteristic of their different distribution between gas and particulate phase. Phe which was almost exclusively found

TABLE 4. Slope (m_r), Intercept (b_r), and Correlation Factor (R²) of the Linear Regression of logK_p Relative to logp for Finokalia Samples

date	m _r	b _r	R ²	level of significance	temperature (°C)
2/25/2000	-0.94	-6.18	0.75	p < 0.01	8.5 ± 4.5
2/26/2000	-0.56	-5.39	0.79	p < 0.01	12.1 ± 5.3
3/23/2000	-0.70	-5.42	0.90	p < 0.001	10.8 ± 3.3
4/18/2000	-0.96	-7.64	0.93	p < 0.001	16.6 ± 5.4
4/19/2000	-0.57	-6.10	0.90	p < 0.001	16.0 ± 4.5
5/14/2000	-0.83	-6.69	0.88	p < 0.001	20.4 ± 5.1
7/11/2000	-0.78	-6.81	0.85	p < 0.001	25.3 ± 5.4
7/12/2000	-0.66	-6.50	0.84	p < 0.005	29.9 ± 6.4
7/25/2000	-0.98	-7.52	0.94	p < 0.001	24.8 ± 6.4
7/27/2000	-0.67	-6.31	0.83	p < 0.005	29.5 ± 7.1
7/28/2000	-0.59	-5.54	0.79	p < 0.005	29.0 ± 6.2
10/13/2000	-0.76	-6.03	0.84	p < 0.005	21.4 ± 5.2
12/15/2000	-0.82	-5.81	0.89	p < 0.001	16.1 ± 4.1
1/10/2001	-1.00	-6.23	0.91	p < 0.001	13.9 ± 3.1
1/27/2001	-0.87	-5.67	0.96	p < 0.001	15.1 ± 4.1
2/10/2001	-0.55	-4.14	0.91	p < 0.001	14.4 ± 3.1
2/25/2001	-0.70	-5.17	0.91	p < 0.001	18.4 ± 5.0
3/9/2001	-0.96	-6.09	0.98	p < 0.001	11.4 ± 4.1
3/24/2001	-0.74	-5.68	0.98	p < 0.001	17.5 ± 3.5
5/14/2001	-0.71	-5.56	0.98	p < 0.001	16.0 ± 4.7
6/9/2001	-0.65	-5.39	0.91	p < 0.001	20.6 ± 4.3
8/17/2001	-0.61	-5.66	0.93	p < 0.001	25.0 ± 5.1
10/7/2001	-0.89	-7.08	0.97	p < 0.001	21.0 ± 4.2
mean	-0.76	-6.03	0.89		18.8
minimum	-1.00	-7.64	0.75		8.5
maximum	-0.55	-4.14	0.98		29.9
confidence level (95.0%)	0.06	0.34	0.03		

in the gas phase had a logK_p value of -3.7 (Table 3), whereas for BaP, mostly found in particles, a logK_p value of -0.66 was determined (Table 3).

When the logK_p of a compound is regressed against its log p_L^o (equation 2) useful information about its partitioning can be extracted from the slope m_r and the intercept b_r of the trend line (18, 20).

$$\log K_p = m_r \log p_L^o + b_r \quad (2)$$

The variation of log K_p relative to log p_L^o for PAHs was studied for all samples collected at Finokalia. The values of p_L^o were adjusted for ambient temperature for all members according to Yamasaki et al. (21). The values of m_r, b_r, and R² for the linear regression log K_p vs. log p_L^o for all samples are presented in Table 4.

The plots of log K_p vs. log p_L^o for all samples gave correlation coefficients R² varying from 0.75 to 0.98 (p < 0.001) (Table 4). The high values determined for all samples imply the agreement of the linear isotherm model, which describes the distribution of semivolatile organic pollutants between gas and particulate phase (18, 22). The slopes m_r varied from -1.0 to -0.55 (mean value -0.76±0.06, confidence level 95%; Table 4). Cotham and Bidleman (11) reported that PAHs collected at a rural site near Lake Michigan (Green Bay, WI) were closer to equilibrium between the gas and particulate phases than PAHs collected at an urban site (Chicago, IL). Thus, they suggested aerosols over Green Bay

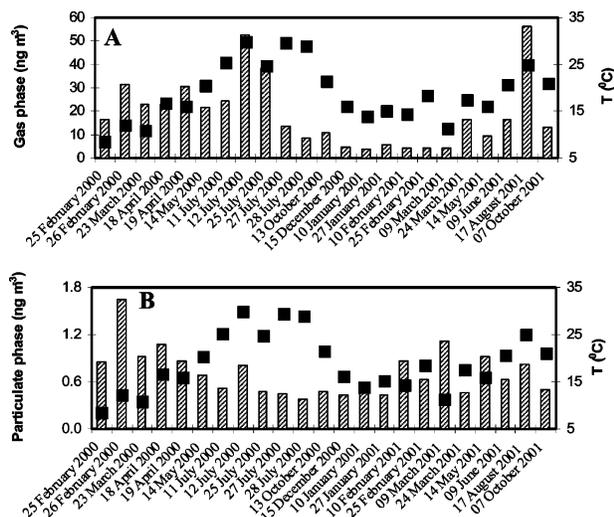


FIGURE 1. Seasonal variation of the total atmospheric concentrations of (A) gas and (B) particulate phases of PAHs detected in Finokalia. Black boxes denote median ambient temperatures for the same period.

had traveled far from their sources, and hence they had enough time to reach equilibrium.

The slopes measured in the urban atmosphere of Heraklion (15) were closer to -1 than the values observed in this study (Table 4). According to Simcik et al. (23) and Goss and Schwarzenbach (20), even if m_r differs from -1 it does not necessarily imply lack of equilibrium. In the above studies (20, 23) it was suggested that slopes m_r can also easily deviate from -1 even if equilibrium sorption processes occur and sampling artifacts are negligible.

Long-Range Transport vs. Local Sources. The seasonal variation of Σ PAH concentration in gas and particulate phase is presented in Figure 1. The highest gas-phase concentration (56.3 ng m^{-3}) was observed in August 2001, whereas the lowest (3.6 ng m^{-3}) was observed in January 2001 (Figure 1A). Conversely, the highest concentration in the particulate phase (1.6 ng m^{-3}) was observed in February 2000 and the lowest (0.4 ng m^{-3}) was observed in July of the same year (Figure 1B). Even though maximum and minimum concentrations of PAHs in gas and particulate phase appear to have a seasonal variation, this does not apply to the entire set of samples (Figure 1A and B). The variation of PAH concentration in the background marine area of Finokalia is a result of many parameters and the contribution of each one is often difficult to evaluate. Long-range transport, deposition, variation in depth of mixing layer, and physicochemical reactions are the major processes determining the observed concentration of PAHs.

The dependence of semivolatile organics (SOCs) concentration such as PAH on atmospheric temperature has been used for the differentiation of local sources from long-range transport (24). This dependence is described by the Clausius–Clapeyron eq 3

$$\ln P = -a/T + b \quad (3)$$

where P is the partial pressure of SOC gas phase (atm) and T is the ambient temperature (K). The slope a is a good indicator of the importance of SOC transport over long distances (long-range transport). High slopes denote contribution of local sources, whereas low slopes indicate that gas-phase SOC concentration levels are rather determined by long-range transport (24).

In contrast to other categories of chemical compounds (e.g., pesticides and PCBs) the interpretation of Clausius–Clapeyron diagrams is relatively difficult for PAHs (25). PAH

seasonal emission trend, as well their higher chemical activity, might influence the seasonal variation of their atmospheric levels so that variations in concentration cannot be easily attributed to temperature changes. Slope a , correlation coefficient R^2 , and the significant level of the linear regression $\ln P$ vs $1/T$ for the PAH members that showed detectable concentrations in the gas phase are presented in Table S1 (Supporting Information). Only for Fluo (slope -8424) and Py (slope -6311) was the temperature dependence of gas phase concentration statistically significant ($p < 0.05$; Supporting Information, Table S1). For these two compounds it was found that 36 and 21%, respectively, of their concentration variation was due to temperature variation. Conversely, a variation of concentration $< 8\%$, which could be attributed to temperature changes for the other PAHs, suggests that their concentration levels in Finokalia atmosphere were governed by long-range transport.

Similar surveys are sparse in the bibliography (13, 25). Higher slopes, ranging from -1446 to -9600 , were observed by Sofuoglu et al. (25) in the Chicago urban area. At the coastal area of New Jersey, Gigliotti et al. (13) observed that temperature variation was based of a variation of concentration $< 25\%$ for the volatile gaseous PAHs. In contrast, in the Chicago urban atmosphere, temperature was the cause of a 23 to 49% variation of the concentration of volatile PAHs (25).

Long-range transport of pollutants in the atmosphere of Finokalia has been recently reported for PCBs (26). The slope of Clausius–Clapeyron plots observed for PCBs in the study area varied from -4805 to -1812 and the correlation coefficients were not significant for most PCB congeners (26).

To further evaluate the effects of air mass origin on PAH atmospheric concentration levels at Finokalia their backward trajectories were grouped, using their geographic points at 72 h before they reached the sampling station, as follows: NE, northeast of Finokalia; NW, northwest of Finokalia; and S, south of Finokalia (Figure 2A). During most of the sampling days, air masses originated from northeast and northwest Europe (Figure 2A). This is in agreement with the normal circulation standards of air masses in the Eastern Mediterranean basin (4). The analysis of atmospheric circulation patterns in the atmosphere of Finokalia, for a large time interval, has shown that the area was influenced to a great extent ($> 61\%$) by air masses from the north or the northwest (4), while air masses from the southwest and the southeast have shown a firm seasonal pattern during spring (4). We observed two extreme cases of samples, namely those with concentrations higher than the average concentration (19.2 ng m^{-3}) plus the standard deviation (SD, 13.1 ng m^{-3}) and those with concentrations lower than the average concentration minus the SD. Σ PAHs concentrations in four samples were higher than the average plus SD and varied from 33.0 to 57.2 ng m^{-3} (26/02/00, 12/07/00, 25/07/00, 17/08/01) (Figure 2A). All these samples originated from Northeastern and Central Europe (Figure 2A). This particular area is characterized by higher emissions of PAHs in the atmosphere (5). In five samples the measured concentrations were found to be lower than the average concentration minus the SD (4.1 – 5.3 ng m^{-3}). Four of these originated from the south (27/01/01, 25/02/01) or had traveled a long distance over the sea (15/12/00, 09/03/00) (Figure 2A).

Correlation between the Concentrations of PAHs and Ozone. A recent study has shown that ozone concentrations at Finokalia exhibit a well-defined seasonal cycle with a maximum during the summer months (7). The ozone concentration in the Eastern Mediterranean basin was found to be influenced by the air mass origin reaching the area (7). The lowest values were systematically associated with the south/southwest sector and the highest values were associated with the north/northwest sector (7). The high ozone

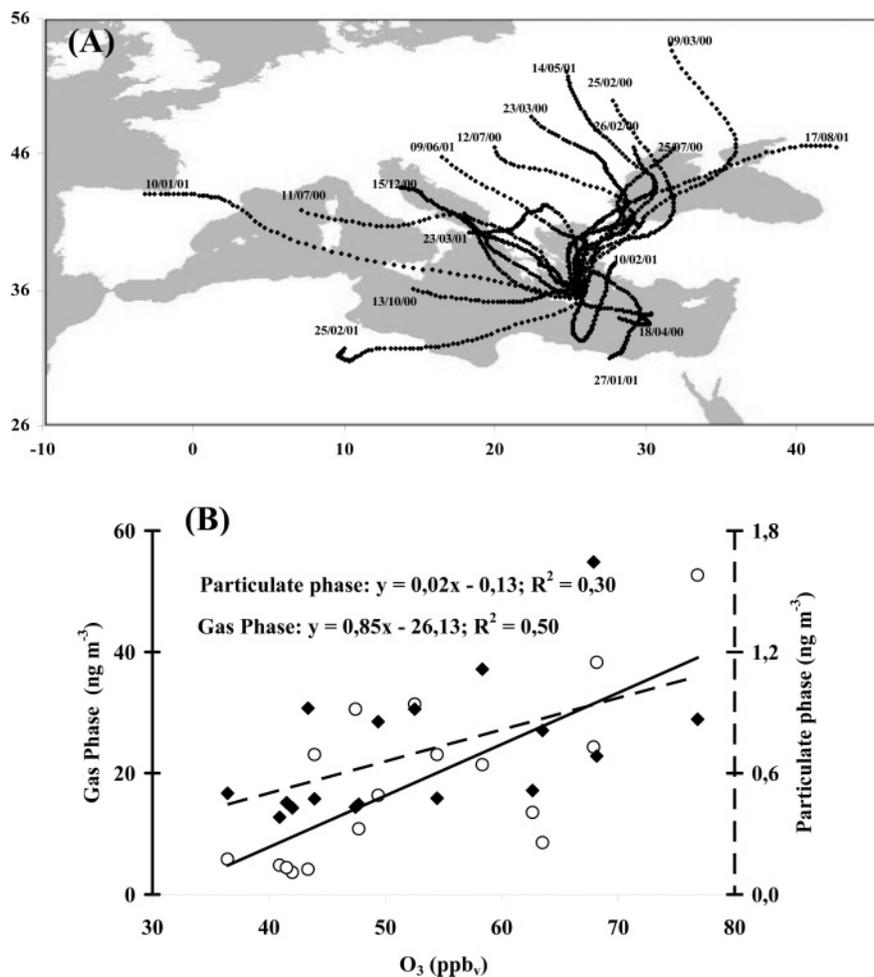


FIGURE 2. (A) 72-h backward trajectories during sampling days at Finokalia. Each point corresponds to 1 h back. (B) Correlation of gas and particulate phase PAHs with ozone in Finokalia atmosphere (empty circles, particulate phase; filled lozenges, gas phase).

concentrations during north/northwest winds resulted from buildup of photooxidants during transport from urban areas of Europe (7).

Figure 2B presents the correlation of total PAH concentration in gas and particulate phases with the atmospheric concentration of ozone, both measured at Finokalia in the present study. A maximum in ozone concentration at Finokalia was observed when the air mass had a north-northwestern origin whereas a minimum was observed when air masses originated from south-southeastern areas (7). A significant correlation ($R^2 = 0.5$, $P < 0.001$) was observed between the concentration of gaseous PAHs and the corresponding concentration of ozone. Conversely, the linear regression between particulate PAHs and ozone was not significantly correlated ($R^2 = 0.3$, $P < 0.01$). The interpretation we propose for this observation is that the two pollutants are in different phases and their deposition mechanisms during transport differ. In addition, the heterogeneous chemical reactions of particulate PAHs and ozone, which are considered to be an important mechanism for their degradation, should also be taken into account to interpret our observation (27).

PAH Distribution and Removal Rate over the Eastern Mediterranean. The spatial variation of PAH concentration in gas and particulate phase over the Eastern Mediterranean area is presented in Figure 3 panels A and B, respectively. A slight variation was observed in the total concentration of gas-phase PAHs over the sea surface between sampling stations. The concentration of gaseous PAHs varied from 15.0 up to 25.0 ng m⁻³, with a mean concentration of 19.0

ng m⁻³, which was similar to the total mean concentration of gas-phase PAHs at Finokalia (18.8 ng m⁻³; Figure 3A). Higher concentrations of particulate PAHs were determined at sampling stations adjacent to the urban area of Athens (Figure 3C). The mean concentration of particulate PAHs sampled at a distance of <80 km from Athens was 1.2 ng m⁻³, whereas the mean concentration over the sea area between continental Greece and Finokalia was 0.3 ng m⁻³ (Figure 3B). A number of studies reported a dependence of PAH deposition fluxes on their distance from urban centers (28). A rapid drop in fluxes has been observed at port, coastal, and open ocean areas (28). For example, Py fluxes dropped significantly (>20 times) at a distance of 100 km from urban centers (28). This result is in agreement with our observations for particulate PAHs in the Eastern Mediterranean atmosphere. Differences observed between the spatial variations of particulate and gaseous PAHs in the Eastern Mediterranean are probably due to their different atmospheric removal rates. It is well-documented that deposition rates of particles are much higher than those for gases (1, 29). Thus, a rapid decline of particulate PAH concentrations in the atmosphere at sites distant from their emission source (e.g., urban centers), observed in the study herein, should be expected (Figure 3B). Conversely, the gas-phase PAH concentration exhibited a more uniform spatial distribution in the Eastern Mediterranean atmosphere (Figure 3B). Although a clear seasonal variation was not observed for the gaseous PAHs (Figure 3A), a diurnal variation was observed during summer (30). Gas-phase PAH concentration was higher during the day than during the night (30). This observation is suggesting that the

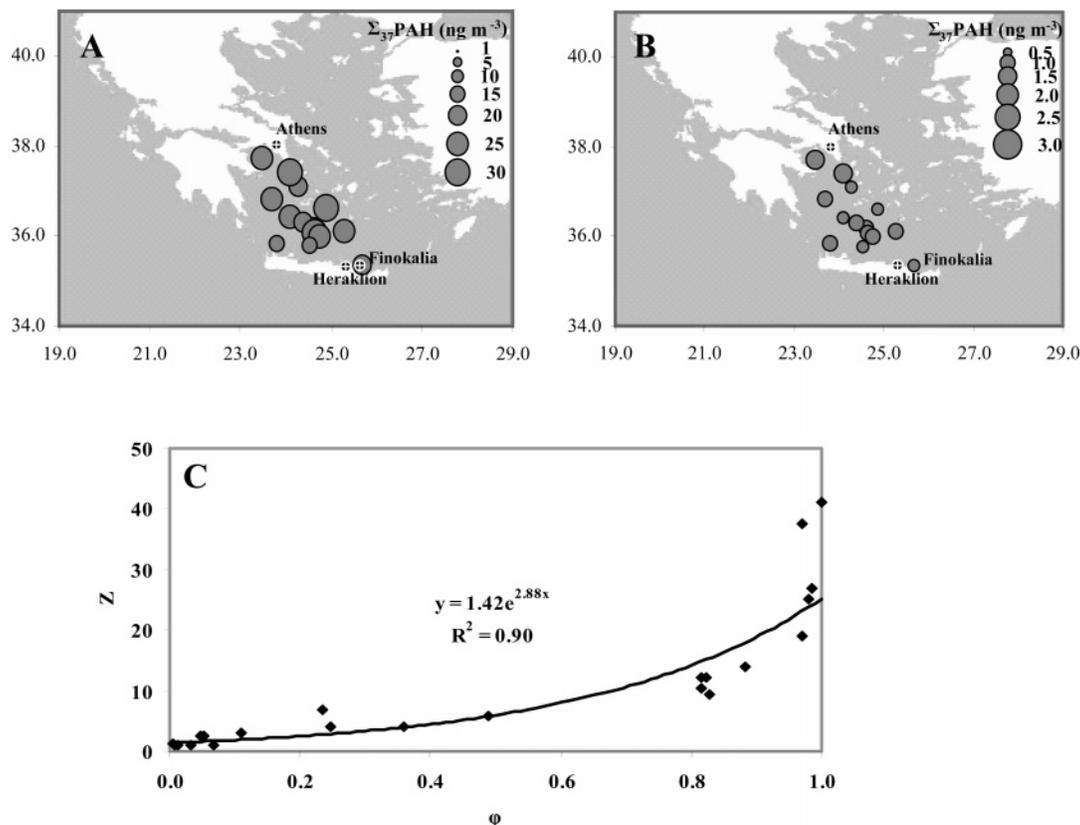


FIGURE 3. Spatial distribution of PAHs in (A) gas and (B) particulate phase over the Eastern Mediterranean. (C) Dispersal diagram of removal factor Z relative of distribution ratio ϕ (fraction of particulate over total concentration of each compound in Finokalia atmosphere).

surrounding waters might also buffer the concentration of light PAHs contributing thus to their observed uniform levels over the Eastern Mediterranean. Simcik et al. (31) also observed that the ratio of the average concentration of particulate PAHs measured in the Chicago urban area and over Lake Michigan was approximately 300, while the corresponding ratio for gaseous PAHs was approximately 10.

The removal rate of PAHs depends on their physico-chemical behavior during air mass transport. Particularly, the gas-to-particle ratio and the particle size distribution determine their deposition rate (29). The relative rate of PAH removal was studied by using their total (gaseous and particulate) atmospheric concentrations observed at Finokalia (this study) and the urban area of Heraklion (Island of Crete, Greece) (15). The urban site (Heraklion) was selected as a representative location where the presence of PAHs is directly related to local sources and the background site (Finokalia) as one in which PAHs occurrence is related to long-range transport from remote emission sources. Phe, which is the most abundant member in all samples, was used as the reference compound. For each PAH member we define a removal factor Z_i calculated as follows:

$$Z_i = (C_i/C_{\text{phe}})_{\text{Heraklion}} / (C_i/C_{\text{phe}})_{\text{Finokalia}} \quad (4)$$

where C_i and C_{phe} are the total (gaseous and particulate) concentrations of PAH member i and Phe, respectively.

If Z_i is greater than 1, the rate of removal of this element is larger than the rate of removal of Phe. Values for Z_i were greater than 1 for all studied PAHs (Supporting Information, Table S2). Phe exists almost exclusively in the gas phase, and its deposition rates (wet and dry) are not expected to be significant (29). The reaction of volatile PAHs with OH radicals is their most important atmospheric degradation mechanism (12). Phe decay resulting from reaction with OH radicals in

the gas phase is less efficient in comparison to that of other volatile PAHs (12). Phe half-life was estimated to be 11.2 h, whereas considerably shorter half-lives (<9.1 h) have been calculated for other compounds (12). Significantly higher rates of removal were observed for PAHs with 5 and 6 aromatic rings (Supporting Information, Table S2). For example, BghiP and Cor are removed 37.5 and 41.1 times faster, respectively, than Phe. A strong exponential correlation ($R^2 = 0.9$) was observed between factor Z and the fraction of particulate PAH over their total concentration in the atmosphere of Finokalia (Figure 3C). Halsall et al. (1) used a simulation model for the atmospheric PAH transport from the United Kingdom to the North Pole and predicted that the half-life of residual BaP during its transport in the atmosphere was 3–4 times lower than the corresponding value for Phe. The PAH members almost exclusively associated with particles are rapidly removed via dry and wet deposition. Thus, PAH distribution between particulate and gas phase appears to be the most important parameter determining their removal rate from the atmosphere.

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Supporting Information Available

Table of parameters of the Clausius–Clapeyron equation and table of average PAH concentrations in Heraklion and Finokalia atmosphere. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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