Atmospheric Deposition and Marine Sedimentation Fluxes of Polycyclic Aromatic Hydrocarbons in the Eastern Mediterranean Basin

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Atmospheric input was studied and found to be the major source of PAHs in the eastern Mediterranean open marine ecosystem. Dry and wet atmospheric deposition, air−sea exchange, and sediment trap fluxes of polycyclic aromatic hydrocarbons (PAHs) in the eastern Mediterranean basin were estimated from November 2000 to July 2002. Seven dry and four wet deposition samples were analyzed in total and PAH concentrations were determined. Air−sea exchange fluxes based on air−water concentration gradient were drawn from five air and water samples collected concurrently from a coastal area in the eastern Mediterranean. Total annual average deposition fluxes of dry, wet, and air−sea exchange Σ_{35}PAHs were 58.0, 165.7, and −706.4 μg m^{-2} y^{-1}, respectively. Only 1.1 and 0.7% of the total atmospheric deposition flux of PAHs was measured in the sediment traps at 280 and 1440 m depth, respectively.

Introduction

Land based sources (e.g. refineries, sewage treatment plants, river runoff), tanker oil transportation, shipping, and atmospheric deposition are the most important sources of PAHs in the marine environment (*1*−*3*). Atmospheric deposition was referred to as a significant nonpoint source of PAHs in open sea and remote eastern Mediterranean coastal areas (*4*).

However, the atmospheric deposition of PAHs in the Mediterranean Sea was evaluated in relatively few studies (*5*−*7*), most of which were carried out in the western basin (*5*, *6*). Measurement of dry and wet deposition was the focus of these studies, whereas fluxes of PAHs resulting from air−sea exchange were not studied.

Air−water exchange of semivolatile organic compounds (SOCs) is an important process controlling inflow of these compounds in large aquatic ecosystems such as the North American Great Lakes (*8*−*11*) and marine areas (*12*−*16*). Water absorption of fluorene and phenathrene from the air

in Chesapeake Bay contributed to 93 and 95% of their total atmospheric deposition, respectively (*14*), while significant net annual volatilization rates of PAHs were measured in the Patapsco River (Chesapeake Bay) (*15*).

The extent, to which the atmosphere constitutes an important pathway for persistent organic pollutants from Europe and North Africa to the eastern Mediterranean Sea, remains a matter under investigation. The main objective of this study was to assess PAHs atmospheric deposition impact into the open eastern Mediterranean Sea and their downward fluxes to deep waters. This key objective was achieved through: (1) measurement of dry and wet deposition of PAHs, (2) measurement of PAH exchange in the air−sea system, and (3) measurement of PAHs in settling material delivered to the deep sea ecosystem using sediment traps.

Experimental Section

Study Area and Sampling. Study of depositional fluxes of PAHs in the Eastern Mediterranean was carried out at a background coastal station (Finokalia, 35°19′ N, 25°40′ E, 130 m ASL), 70 km eastward from Heraklion (Island of Crete, Greece; Figure S1). Details about the geography of the area and its meteorological conditions are reported elsewhere (*17*, *18*). Sampling information is presented in Table S1.

Dry Deposition Sampling. Collection of dry deposition samples was achieved using a stainless steel funnel with an area of 0.14 m^2 attached to a glass sample collection container, placed horizontally 1 m above ground level. After remaining exposed for 20−30 days, the funnel surface was rinsed with water, and the sample was transported to the laboratory within 2 h. Seven samples were collected (Table S1).

Wet Deposition Sampling. Wet deposition samples were collected only during rainfall with the same device as above (Table S1). Samples were transported to the laboratory refrigerator (4 °C) and processed within 24 h. Four wet deposition samples were collected in total. To minimize the effect from dry deposition the sampler was installed 1 day before the beginning of each rain event, anticipated with the SKIRON weather forecasting system (htpp://forecast.uoa.gr), which covers the region of Greece.

Seawater Sampling. Surface seawater was collected by means of a Niskin bottle at a coastal area close to Finokalia station. Samples were analyzed according to the procedure for wet deposition samples. Five water samples were collected on a seasonal basis (Table S1).

Air Sampling. Samples collected simultaneously with seawater samples were processed using a modified high-volume (Hi-Vol) sampler. Details of the sampler efficiency are described elsewhere (*19*). 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 gas phase (Table S1).

Sediment Traps. Three TECNICAP PPS 3/3 cylindroconical sediment traps were deployed at 186, 1426, and 2837 m depth (water depth is 2867 m) in the southern Ionian Sea (20°51′ E−35°08′ N) (Figure S1). The collecting area of traps was 0.125 m^2 (12 receiving cups), and they were programmed on a bimonthly interval. Two 6-month long deployments gave 12 consecutive samples from each deployment period May, 1, 2001−October 15, 2001. Samples were preserved in a 5% formaldehyde solution mixed with seawater and buffered with sodium borate (pH 7.5−8.0). Upon recovery samples were stored in the dark at 2 °C until analysis. Details of sediment trap preparation, deployment, and sample processing have been published elsewhere (*20*).

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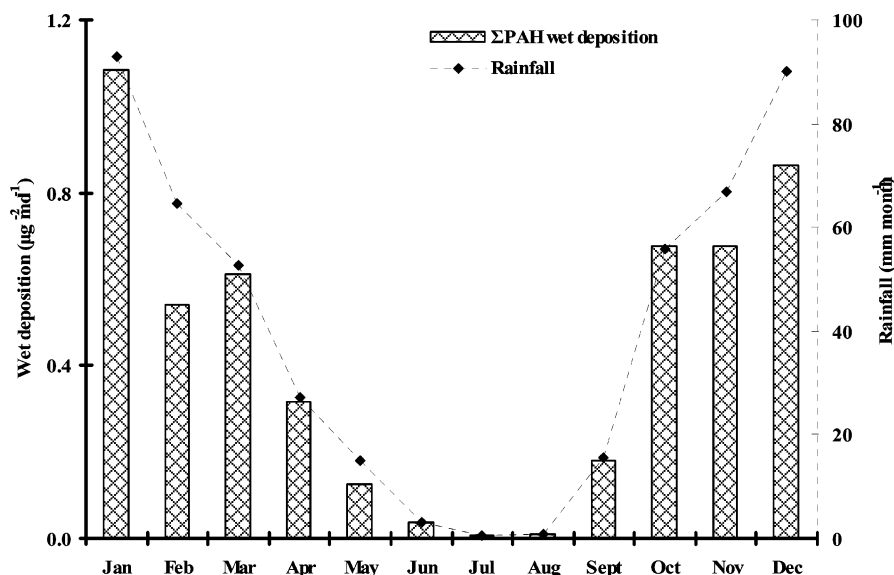
FIGURE 1. Seasonal variation in wet deposition of Σ_{35}PAHs for 2001 (μg m^{-2}d^{-1}).

Chemical Analysis. Settling material and PUF samples were spiked with a mixture of 3 perdeuterated PAHs (d$_{10}$-phenanthrene, d$_{10}$-pyrene, and d$_{12}$-perylene) and then extracted in a Soxhlet apparatus for 24 h with *n*-hexane (Suprasolve grade, Merk). Seawater samples, wet and dry deposition samples, after addition of internal standards, were extracted with *n*-hexane (liquid—liquid extraction). Sample extracts were concentrated to 1 mL with a rotary evaporator. PAHs were isolated from the extracts and analyzed using a gas chromatograph connected to a mass spectrometer according to Tsapakis and Stephanou (*19*).

Quality Assurance. Identification of each compound was based on the use of the mass spectra of reference standards (Dr. Ehrenstrorfer GmbH, Germany). Relative response factors (RRFs) for PAHs were determined prior to sample set analyses by using a standard mixture containing the reported analytes and three internal standards. Relative response factors (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*) is higher than 5, (2) the isotopic ratio of the monitoring and confirmation ion is within ±20% of those observed for reference standards, and (3) the retention time is within ±10 s of those observed for reference standards.

Field and laboratory blank samples were routinely analyzed in order to evaluate analytical bias and precision. The detection limits were set at three times the mean blank concentration for each PAH. 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, dissolved, and sinking material). PAH concentration (Σ_{35}, Table S2) varied from 1.5 to 12.5 pg m^{-3} in the vapor phase, from 0.02 to 0.9 ng L^{-1} in the dissolved phase, and from 0.3 to 10 ng g^{-1} in the sinking material.

Calculations

Wet Deposition. PAH flux was calculated based on four rainfall events, according to

$$F_{w} = \frac{C_{w}*R}{D} \tag{1}$$

where F_{w} is the wet deposition flux (μg m^{-2} d^{-1}), C_{w} is the rain analyte concentration (μg L^{-1}), R is the rainfall (mm), and D is the number of sampling periods weighted to the annual rainfall intensity.

Wet deposition flux was estimated on an annual basis by taking into account that the concentration of PAHs in rainwater (Table S2) and the atmosphere of the study area (*21*) did not exhibit a seasonal variation. For the months in which sampling was not carried out, the wet deposition flux was calculated by using the mean concentration of PAHs during rainfall (343.2 ng L^{-1}; Table S2).

Air—Sea Exchange. Gas transfer of PAHs across the air—sea interface was calculated using a modified two-layer resistance model. The overall flux is defined by

$$F = K_{OL}\left(C_{dis} - \frac{C_{gas}}{H}\right) \tag{2}$$

where F is the overall mass flux (ng m^{-2} d^{-1}), and ($C_{dis} - C_{gas}/H'$) describes the concentration gradient (ng m^{-3}). C_{dis} and C_{gas} describe the dissolved and gas concentrations, respectively. H' is the dimensionless Henry's low constant. The overall mass transfer coefficient, K_{OL}, takes into account the resistance to transfer across the water and gas layer. The H' and K_{OL} coefficients were calculated according to ref *13*.

Results and Discussion

Wet and Dry Deposition. The range of total (dissolved plus particulate) concentration in rain for Σ_{35}PAHs was 322—366 ng L^{-1} (Table S2). Comparable total PAH concentrations in rain were also measured at sampling stations in northern Greece (143—1397 ng L^{-1} (*22*)), Hungarian agricultural areas (164—1993 ng L^{-1} (*23*)), and France (1.5—130 ng L^{-1} (*24*)). Higher concentrations, attributed to the proximity of sampling sites (~15 km) to the Boston urban area, were measured in Massachusetts (550—47 730 ng L^{-1}) and Maine (690—48 460 ng L^{-1}) (*25*). The absence of a seasonal trend in the concentration of PAHs in the rain, we observed, is in agreement with the results of a previous study in the same area for PCBs (*26*). However, in other studies (*22, 24, 27*), higher concentrations of PAHs were reported for the winter, due to higher emissions from domestic heating.

The highest wet deposition flux for Σ_{35}PAHs (1.1 μg m^{-2} d^{-1}) occurred in January (rainfall 92.9 mm) whereas the lowest (0.01 μg m^{-2} d^{-1}) in August (rainfall 0.74 mm) (Figure 1). The annual precipitation intensity was 480 mm which was very close to the mean annual average value (438 mm) for the period 1995—2000 (*26*). The mean wet deposition flux of Σ_{35}PAHs was 0.45 μg m^{-2} d^{-1} for the year 2001. Despite the low rainfall and the absence of local PAHs emission sources

TABLE 1. Atmospheric Gas, Dissolved (Seawater) PAH Concentrations (ng m^{-3}), and Meteorological Parameters.

compound	September 2001		October 2001		February 2002		April 2002		July 2002	
	gas	dissolved	gas	dissolved	gas	dissolved	gas	dissolved	gas	dissolved
fluorene	1.37	160	1.20	280	0.15	170	0.84	50	1.67	240
phenanthrene	5.23	360	2.77	720	1.75	480	7.78	230	6.39	470
antrhacene	0.47	50	0.40	40	0.12	70	1.31	10	0.77	60
Σ methyl-phenanthrenes	0.94	330	2.81	420	1.93	170	3.35	20	2.21	440
fluoranthene	1.69	110	0.80	160	0.12	120	0.69	130	0.79	210
pyrene	0.97	90	0.38	150	0.14	130	0.92	70	0.84	170
benzo[*a*]antrhacene	0.09	40	0.01	40	0.01	30	0.11	30	0.03	60
chrysene/triphenylene	0.33	80	0.06	130	0.06	410	0.26	80	0.17	140
surface skin temperature (K)	293.65		291.95		286.55		291.65		298.8	
mean wind speed (m/s)	6.6		3.6		4.2		2.9		5.9	

TABLE 2. Mean Annual Atmospheric Fluxes (μg m^{-2} y^{-1}) of PAHs

compound	wet deposition	dry deposition	air–sea exchange
fluorene (Fl)	1.5	2.2	−21.4
phenanthrene (Phe)	29.4	7.7	−336.1
anthracene (An)	3.9	1.5	−32.5
Σ methyl-phenanthrenes (ΣC1–Phe)	12.9	0.7	−135.9
fluoranthene (Fluo)	28.6	6.6	−87.3
Σ dimethyl-phenanthrenes (Σ DMPs)	8.3	2.2	nc[a]
pyrene (Py)	15.1	3.3	−68.4
Σ methyl-fluoranthene/pyrene (ΣC1–202)	1.7	0.7	nc[a]
retene (Ret)	0.4	0.4	nc[a]
4(H)-cyclo[cd]pyrene (4H–CY)	6.1	2.2	nc[a]
benzo[*a*]antrhacene (BaA)	3.9	4.0	−3.5
chrysene/triphenylene (Chr/T)	22.5	9.5	−21.2
Σ methyl-chrysenes (ΣC1-Chr)	0.8	0.4	nc[a]
benzo[*b*]fluoranthene (BbF)	6.8	5.1	nc[a]
benzo[*k*]fluoranthene (BkF)	7.6	2.9	nc[a]
benzo[b/j/k]fluoranthene (BbjkF)	0.6	0.4	nc[a]
benzo[*e*]pyrene (BeP)	5.2	2.9	nc[a]
benzo[*a*]pyrene (BaP)	2.2	1.8	nc[a]
perylene (Per)	0.9	1.5	nc[a]
anthranthrene (Anthr)	1.8	0.4	nc[a]
indeno[1,2,3-cd]pyrene (IP)	3.0	0.7	nc[a]
dibenzo[a,h]anthracene (DBA)	0.1	0.4	nc[a]
benzo[ghi]perylene (BghiP)	2.4	0.7	nc[a]
coronene (Cor)			
Σ_{35}PAH	165.7	58.0	−706.4

[a] nc: not calculated.

in the study area, the observed wet deposition flux is similar to corresponding fluxes measured in other nonurban areas. PAH fluxes varying from 0.082 to 0.16 μg m^{-2} d^{-1} were reported for the western Mediterranean (*6*), while in Chesapeake Bay (1990–1991) (*28*) and in Galveston Bay (*29*) the corresponding fluxes were 0.21 μg m^{-2} d^{-1} and 0.36 μg m^{-2} d^{-1}, respectively.

The dry deposition rates for Σ_{35}PAHs (0.025–0.48 μg m^{-2} d^{-1}, Table S3) measured in the present study were similar with those measured earlier in the same study area (0.10–0.15 μg m^{-2} d^{-1} (*7*)). In the western Mediterranean, by using cascade impactor data, dry deposition rates of Σ_{11}-PAH were calculated and reported to range from 0.026 to 0.081 μg m^{-2} d^{-1} (*5*) and from 0.033 to 0.081 (*6*).

Air–Sea Exchange. The concentrations of eight PAH members in the gas and dissolved phases, the sea surface skin temperature, and the wind speed are presented in Table 1. Phenanthrene was the most abundant PAH member both in the gas and dissolved phases, ranging from 1.75 to 7.78 ng m^{-3} (gas) and from 230 to 720 ng m^{-3} (dissolved) (Table 1).

Negative values for the flux F (see Calculations in the Experimental Section) indicated that PAH absorption into the water column was the dominant exchange process. In this study, total exchange flux of gaseous PAHs varied from −870 (ng m^{-2} d^{-1}) to −3580 (ng m^{-2} d^{-1}), while the mean flux

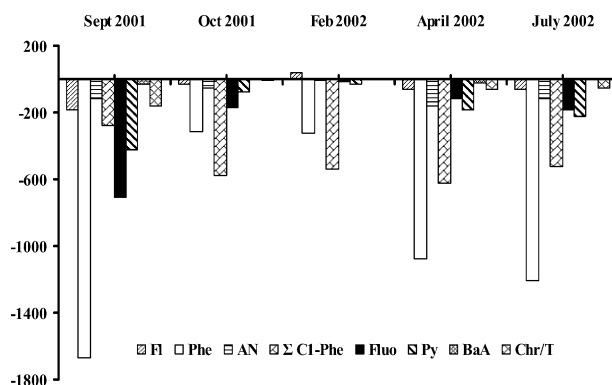**FIGURE 2. Air–sea exchange fluxes (ng m^{-2} d^{-1}) of PAHs in the eastern Mediterranean: (−) flux reflects net absorption and (+) reflects net volatilization.**

was −1940 (ng m^{-2} d^{-1}). The magnitude of ΣPAHs fluxes varied on a seasonal scale (Figure 2). Wind speed, surface skin temperature, and the air–water concentration gradient strongly influenced the direction and magnitude of PAH fluxes. Even though high surface skin temperature induces evaporation from the sea to the atmosphere, we observed the largest net absorption rates in September 2001 and in April and July 2002. Conversely, lower fluxes were observed
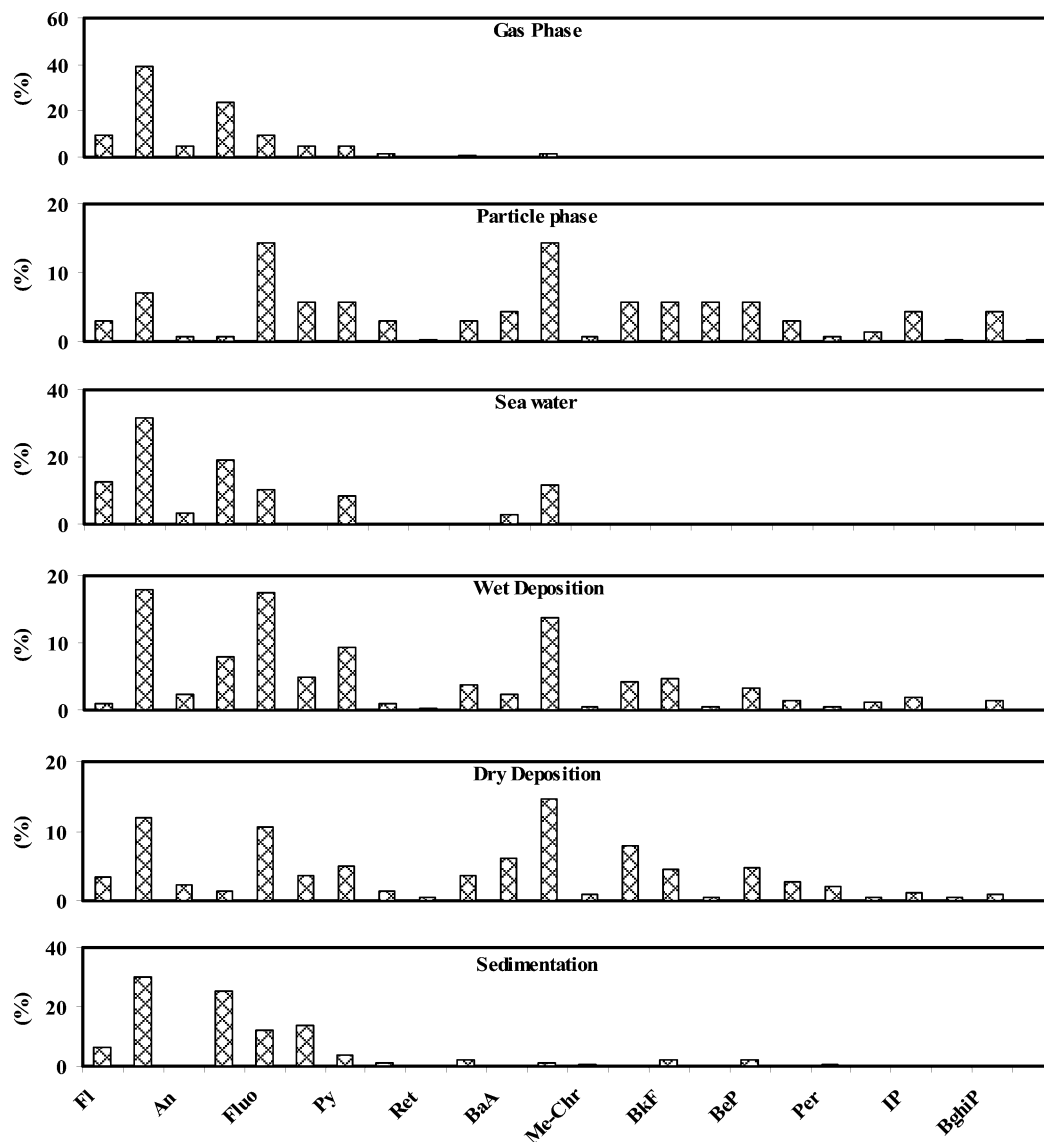
FIGURE 3. PAH concentration profiles among gas, particle and dissolved seawater phases, wet and dry deposition, and sedimentation flux.

in October 2001 and February 2002 (Figure 2). It should be stressed that during sampling in September 2001 and July 2002, we recorded the highest wind speeds (6.6 and 5.9 m/s, respectively) (Table 1). The highest air−water gradient was measured in April 2002 (Table 1). Phenathrene, Σmethyl-fluoranthene/pyrene, and fluoranthene fluxes were the highest for all samplings (Figure 2). A similar observation concerning the above fluxes was reported for Chesapeake Bay and the New York Bight (14).

Relative Contribution of Deposition Processes. Average total annual flux of wet deposition, dry deposition, and air−sea exchange were 165.7, 58.0, and −706.4 μg m^{-2} y^{-1}, respectively (Table 2). Dry and wet deposition are key processes of SOCs atmospheric deposition in aquatic ecosystems located in areas with high rainfall and near urban centers with high concentrations of particulate material (30). In remote areas, PAH wet deposition exceeds the corresponding dry deposition (6, 31).

Absorption of PAH in the seawater is the most important inflow process in the eastern Mediterranean marine ecosystem, introducing 4 and 11 times the corresponding quantity introduced through wet and dry deposition, respectively (Table 2). Our results are in good agreement with

similar studies carried out in many aquatic ecosystems (12, 14).

Atmospheric deposition of low molecular weight PAHs is dominated by diffusive exchange. For example, gas absorption contributes to 86 and 91% of the total net flux for fluorene and phenanthrene, respectively. Dry particle deposition and wet deposition are not important for the above compounds. This observation is similar to that reported for the Chesapeake Bay (U.S.A.) system, where absorption contributed to 93 and 95% of the net atmospheric flux of fluorene and phenanthrene, respectively (14). Conversely, PAHs with high molecular weight are introduced in the marine environment primarily through dry and wet deposition (Table 2).

Sedimentation in the Water Column. The concentration of Σ_{35}PAHs in settling material at 250 and 1440 m depth was 468 and 259 ng g^{-1} (dry weight), respectively (Table 3). Due to analytical problems PAH concentrations in the 2820 m trap are not reported. Phenanthrene was the most abundant PAH at both depths. At 250 m the concentration of phenanthrene was 141 ng g^{-1} and at 1440 m 92 ng g^{-1}. The fluxes of Σ_{35}PAHs at the two depths (250 and 1440 m) were 28.2 ng m^{-2} d^{-1} and 22.7 ng m^{-2} d^{-1}, respectively (Table 3). Although only 14 f PAH members were measured, higher fluxes were

TABLE 3. Settling Particle Fluxes (ng m^{-2} d^{-1}) of PAHs at 250 and 1440 m Depth

compound	250 m	1440 m
Fl	1.74	0.60
Phe	8.49	8.01
An	nd[a]	nd[a]
Σ C1–Phe	7.11	2.38
Fluo	3.37	2.34
Σ DMPs	3.82	0.80
Py	1.03	1.38
Σ C1–202	0.34	0.06
4H–CY	0.58	0.06
BaA	0.35	1.03
Chr/T	0.09	nd[a]
Σ C1-Chr	nd[a]	nd[a]
BbF	nd[a]	nd[a]
BkF	0.55	0.62
B bjkF	nd[a]	nd[a]
BeP	0.58	0.34
BaP	nd[a]	nd[a]
Per	0.16	nd[a]
Anthr	nd[a]	nd[a]
IP	nd[a]	nd[a]
DBA	nd[a]	nd[a]
BghiP	nd[a]	nd[a]
Cor	nd[a]	nd[a]
Σ_{35}PAH	28.20	22.66

[a] nd: not detected. For compound abbreviations see Table 2.

FIGURE 4. Estimated PAH fluxes in the Eastern Mediterranean.

estimated for the western Mediterranean: The sedimentation fluxes of Σ_{14}PAHs ranged from 220 ng m^{-2} d^{-1} to 240 ng m^{-2} d^{-1} in the Alboran Sea (3) and 670 to 910 ng m^{-2} d^{-1} in the northwestern Mediterranean (32). The observed differences between the PAH settling fluxes in the western and eastern Mediterranean basins likely result from enhancement of air–water exchange and vertical sinking fluxes due to the higher primary production in the western Mediterranean (33, 34).

PAH Profiles in Deposition Samples. PAHs with two and three aromatic rings were the dominant species in the gas phase of the atmosphere, the dissolved phase of seawater, and settling material (Figure 3). Conversely, PAHs with at least four rings were the prevailing compounds in atmospheric particles and wet and dry deposition samples (Figure 3). Atmospheric particles PAH profiles were found to be significantly correlated with those of wet ($R^2 = 0.77$, $p < 0.0001$) and dry ($R^2 = 0.84$, $p < 0.0001$) deposition, implying efficient particle removal. The atmospheric particle and wet deposition significant correlation suggests the efficient scavenging of particulate PAHs during precipitation, as it has been also reported in previous studies (35). The correlation between profiles of PAHs in the gas and the seawater dissolved phase was statistically significant ($R^2 = 0.94$, $p < 0.0001$) indicating that the air and seawater compartments are closely coupled. A similar coupling ($r^2 = 0.90$, $p < 0.01$) was reported for the New York–New Jersey harbor estuary (13). The profiles of PAHs in gas phase and settling particles were also significantly correlated ($R^2 = 0.94$, $p < 0.0001$) supporting that air–sea exchange is a significant factor of PAH transport to deep-sea ecosystems.

Comparison of Fluxes of PAHs in Eastern Mediterranean. The different fluxes of PAHs for the eastern Mediterranean (on the basis of the above results) are summarized in Figure 4. The total annual average (min-max) dry and wet deposition was 58 (9.1–177.0) μg m^{-2} y^{-1} and 165 (154.7–176.0) μg m^{-2} y^{-1}, respectively. The net air–sea exchange was 706 μg m^{-2} y^{-1} (318.0–1310.6 μg m^{-2} y^{-1}). The atmospheric gaseous exchange process primarily introduces PAHs of lower molecular weight, whereas dry and wet atmospheric deposition introduces PAHs with primarily five or more aromatic rings. The total atmospheric deposition of Σ_{35}PAH
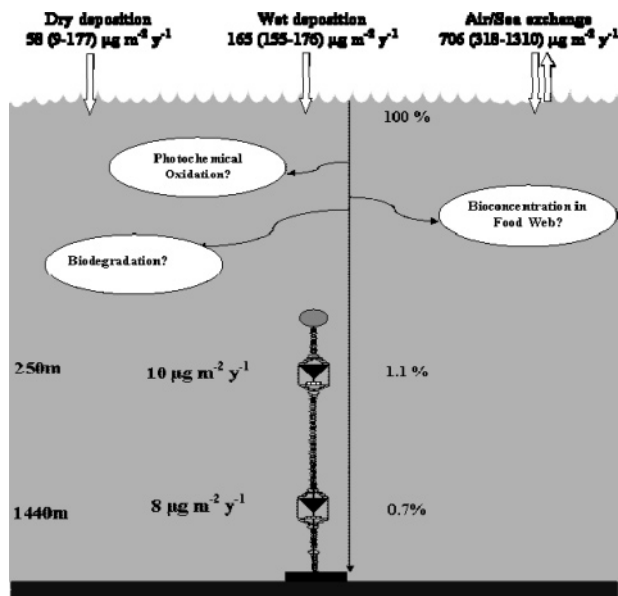
in the eastern Mediterranean was 959 μg m^{-2} y^{-1}. PAH sedimentary fluxes were considerably lower within the water column: At 250 m the sedimentation flux was 10 μg m^{-2} y^{-1}, corresponding to the 1.1% of total atmospheric deposition, and at 1440 m the flux was 8 μg m^{-2} y^{-1} corresponding to the 0.7% of the total atmospheric deposition (Figure 4). These data imply that the majority of atmospheric PAHs introduced to the eastern Mediterranean Sea remains in the euphotic zone. Dachs et al. (3) measured total sedimentation flux of PAHs ranging from 80.3 to 87.6 μg m^{-2} y^{-1} using sediment trap data. Atmospheric deposition fluxes in the same area ranged from 1.83 to 10.22 μg m^{-2} y^{-1} (3). However, it should be noted that air–sea exchange was not considered in Dachs et al. study (3).

Transport of persistent organic pollutants (POPs) to deeper layers of the water column is largely determined by biological characteristics of marine ecosystems (34). Flux of organic matter in deeper layers has been observed to be higher in eutrophic areas relative to oligotrophic areas (36). Additionally, POPs flux was found to be higher in areas with elevated chlorophyll concentrations (34).

The well-layered oligotrophic eastern Mediterranean is characterized from a trophic chain composed of picoplankton and a potentially dominant microbial loop. This has a negative effect on energy transport in deeper water layers and benthos. Tselepides et al. (37) estimated carbon fluxes based sediment traps deployed in the same area. They reported that only 2.8-4.8% of primary production found its way into the particulate organic carbon (POC) flux out of the surface mixed layer. These observations support the low PAHs percentage transported to deep marine ecosystems, determined in our study. A major fraction of PAHs introduced in the marine ecosystem might bioconcentrate on the food web or might be biodegraded or photochemically oxidized. However data on these processes are limited at the present time, and further research effort is needed to be more conclusive.

Supporting Information Available

Tables (Tables S1−S3) containing the sampling information and a map (Figure S1) showing the sampling area. This material is available free of charge via the Internet at http://pubs.acs.org.

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