

Evaluation of atmospheric transport as a nonpoint source of polycyclic aromatic hydrocarbons in marine sediments of the Eastern Mediterranean

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Abstract

Coastal marine sediment, air and seawater samples were collected at six sampling stations in the Eastern Mediterranean Sea distant from pollutant point sources. All sediment samples were analyzed to determine polycyclic aromatic hydrocarbon (PAH), black carbon (BC) and organic carbon (OC) contents. The PAH contents of gaseous and seawater samples of the study were determined in order to evaluate the role of air–sea exchange as PAH nonpoint source to the marine sediments. The average concentration of the total PAHs (Σ PAHs) in the sediments varied from 2.2 to 1056.2 ng g⁻¹ dry weight. The average BC and OC contents varied from 0.3 to 5.6 and from 2.9 to 21.4 mg g⁻¹ dry weight, respectively. Σ PAH concentration in the marine atmosphere varied from 20.0 to 83.2 ng m⁻³. Air–water exchange flux (F_{A-w}) estimation has indicated air transport as a significant source of PAHs to pristine marine sediments of Eastern Mediterranean. In addition, the significant correlation between the PAHs and the organic and soot carbon content further suggests the importance of atmospheric input of PAHs to the sediments.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) can enter the marine environment and be deposited in the sediment through a variety of ways. Atmospheric deposition, municipal treatment discharges and oil

spills are the main pathways. Atmospheric deposition of PAHs in the marine sediment occurs via both dry (gas and particle transfer) and wet flux. In some environments, the role of gas flux is at least as important as the particulate transfer of PAHs into the marine ecosystem (Baker and Eisenreich, 1990; Gustafson and Dickhut, 1997). Indeed, the PAH profiles in the photic zone of the water column are very similar to those found in the gas phase (Baker and Eisenreich, 1990). PAHs in the vapour phase can enter a water body via gas exchange and, due to their high octanol/

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water partition coefficient (K_{ow}) and low solubility, become absorbed into the organic rich particles (e.g. plankton, faecal pellets, colloidal organic particles and flocs) and settle in the marine sediment (Gustafsson et al., 2001a). Nelson et al. (1998) estimated that in Chesapeake Bay the gas absorption contributes 93% and 95% of the total atmospheric loading of fluorene and phenanthrene, respectively. The particulate PAHs via the wet and dry processes can be directly deposited in the sediment (Simcik et al., 1996; Lipiatou et al., 1997).

The partitioning of the PAHs between water and sediment is controlled by the sediment characteristics. The organic content, the black carbon or soot content, the polarity, the aromaticity and the grain size are the parameters most examined (Weber et al., 1992; Gustafsson et al., 1997a; Burgess et al., 2001). Therefore, the accumulation of PAHs is not only determined by the mass flux to the seabed, but also by the sediment characteristics. Furthermore, the fraction of the PAHs associated with the soot content become more resistant to biological recycling.

The coastal ecosystem is an important resource throughout the Mediterranean for commercial as well as recreational purposes. In addition, the contamination of the sediment may pose a high toxic threat to the aquatic fauna, which tend to bioaccumulate the organic pollutants (Baumard et al., 1998). Furthermore, detailed analyses of PAH concentrations and accumulation rates in the northwest Mediterranean basin point out the importance of coastal sediments as a sink of PAHs with about half of the accumulation on the continental shelf (Tolosa et al., 1996; Lipiatou et al., 1997). This may be due to more effective removal in the higher productivity coastal waters as well as to the prevalent circulation pattern with the currents parallel to the coast. Gustafsson et al. (1997b) estimated the vertical fluxes of pyrene in the North East USA to be 2100, 640 and 38 $\text{pmol m}^{-2} \text{day}^{-1}$ for the coastal, shelf and pelagic environments, respectively.

Numerous research studies assessed the PAH inputs in the Northwestern and Central Mediterranean (Tolosa et al., 1996; Lipiatou et al., 1997; Bouloubassi et al., 1997; Benlahcen et al., 1997). Conversely, in the Eastern Mediterranean few data have been published on the presence of PAHs in coastal sediments close to point sources (municipal and river discharges,

etc.), while data are missing for pristine coastal areas (Gogou et al., 2000). The determination of PAHs levels in the Eastern Mediterranean sediment is an important issue for the determination of sediment quality standards. Eljarrat et al. (2001) measured that the toxicity equivalent (TEQ) values of PAHs were several times higher than the TEQ of polychlorinated biphenyls (PCBs) and polychlorinated dioxins/furans (PCDD/Fs), in the sediment from the Catalonian coast, Western Mediterranean.

The goals of this study were as follows. (1) Determine the concentrations of organic and black carbon and of PAHs in superficial sediments, unaffected by point sources, in the Eastern Mediterranean. Organic and black carbon content of these sediments was determined in order to evaluate the importance of their association with PAH sedimentary budget. (2) Determine the concentration of PAHs in the aerosol gas and particulate phase in order to evaluate the role of meso- and long-range atmospheric transport as a nonpoint source of PAHs in the marine environment of Eastern Mediterranean. (3) Determine the concentration of dissolved PAH in seawater in order to estimate the PAH flux into this area due to air–water exchange.

2. Materials and methods

2.1. Study area

Six sampling stations were selected in the Eastern basin of the Mediterranean Sea (Fig. 1). All, except one (S5; Fig. 1), sampling stations were far away from any point sources and atmospheric transport was expected to be the major source of the PAHs to the studied areas. The study sites were selected in different geographical positions in order to have a wide range of the background levels of PAHs in the pristine coastal sediments of the Eastern Mediterranean. In all stations, except for S5, the ship traffic was considered as negligible. Station S5 is close to the main refineries of the country and oil tankers pass by frequently. Information about each station characteristics is presented in Table 1. The depth for all sites varied from 18 to 40 m. The sediment type was silt for S3, S5 and S6 stations and sand for S1, S2 and S4 (Table 1).

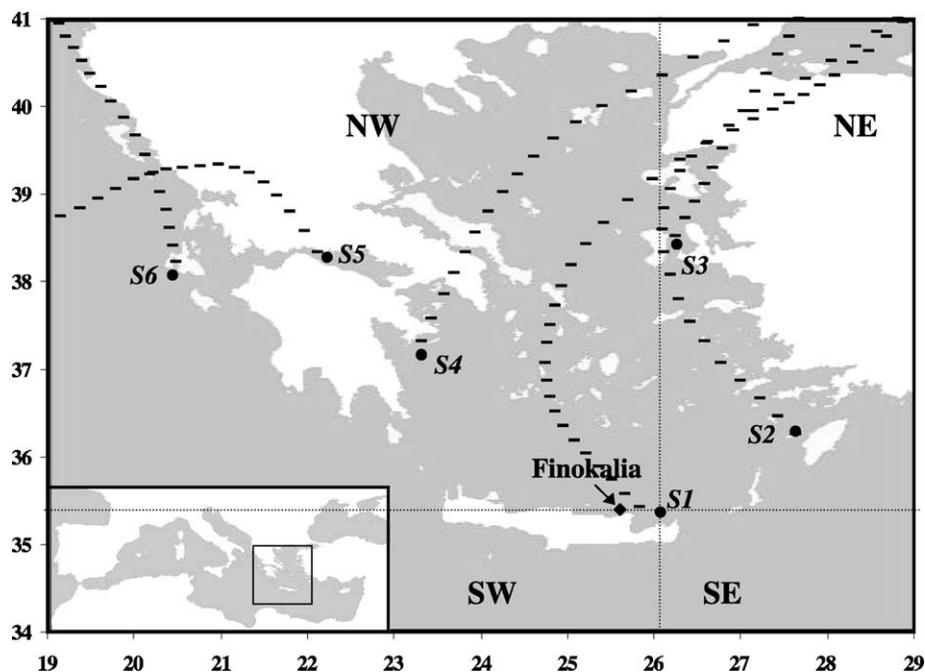


Fig. 1. Map presenting the sampling sites backward air mass trajectories in the Eastern Mediterranean.

2.2. Sediment sampling

Three replicate sediment samples were collected from each site by means of a Smith McIntype grab (0.1 m²) operated from the research vessel R/V PHILIA on July 2001. The undisturbed sediment surface layer (0–2 cm) was collected and stored at minus 30 °C until analysis.

2.3. Air sampling

Air samples were collected using a high-volume air sampler that was placed at the bow of the research

vessel and samples were collected only when the ship was moving to avoid any contamination from the ship. The air was drawn through a glass fiber filter (GFF) to collect particulate PAHs and then through polyurethane foam (PUF) plug (length 8.0 cm, diameter 7.5 cm) to collect the vapour phase. The duration of sampling was 3–5 h and the volume of the samples was 100–150 m³, approximately. A blank sample with the motor pump closed was collected on the last day and analysis was performed in the same manner as the others. Prior to the sampling, GFFs were heated at 450 °C for 5 h and 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 into vacuum desiccators, placed in glass cylinders and sealed in glass jars. Before and after sampling, the filters were weighed to obtain total suspended particle (TSP) concentrations.

2.4. Water sampling

Two surface water samples (5 l) were collected by means of 5-l Niskin bottles in same month a year later (July 2002) around the station S1 (Fig. 1). Samples

Table 1
Description of the sampling sites

Station	Latitude	Longitude	Depth (m)	Sediment grain facies
S1	35.26619	26.14773	29	fine sand
S2	36.26682	27.63082	39	coarse sand
S3	38.51413	26.2428	40	silt
S4	37.31666	23.31463	33	medium sand
S5	38.33369	22.11675	35	silt
S6	38.21886	20.48153	18	silt

were filtered immediately after collection through precombusted glass fibre filters (Whatman GF/F, 0.7 μm). The filtrates were stored at $-21\text{ }^{\circ}\text{C}$ and transported to laboratory for PAHs analysis.

2.5. Chemical analysis

2.5.1. Organic carbon

The organic content of the sediment was determined using a Perkin Elmer 2400 CHN elemental analyzer according to the method described by [Hedges and Stern \(1984\)](#). Briefly, the sediment was freeze-dried and manually ground. The inorganic material was removed by the addition of HCl 1N.

2.5.2. Black carbon

The content of the black carbon in the sediment was determined according to the method described by [Gustafsson et al. \(1997a, 2001b\)](#). The method is similar to that for organic carbon, except that a pretreatment step was introduced. Prior to acidification, the samples were thermally oxidized at $375\text{ }^{\circ}\text{C}$ for 24 h in an excess of oxygen.

2.5.3. PAH analysis

Freeze-dried sediments (5 g), GFFs and PUFs were spiked with a mixture of three perdeuterated PAHs (d_{10} -phenanthrene, d_{10} -pyrene and d_{12} -perylene) and then extracted in a Soxhlet apparatus for 36 h with dichloromethane (suprasolve grade, Merck). Sea water filtrates after the addition of the internal standards were extracted with *n*-hexane (liquid–liquid extraction). The sample extracts were concentrated by rotary evaporator to 1 ml and analyzed according to [Gogou et al. \(1998\)](#). Briefly, extracts were fractionated on silica column and eluted with 11 ml *n*-hexane and (9.5/5.5) 15 ml *n*-hexane/toluene. The nonpolar aliphatic hydrocarbons were collected in the first fraction and PAHs in the second. Finally, samples were concentrated under a gentle stream of purified nitrogen. Prior to injection, a solution of d_{10} -anthracene was added as a recovery standard.

The GC-MS analysis of polyaromatic hydrocarbons was carried out on a Hewlett-Packard mass-selective detector (5891A) operating in SIM mode. Mass spectrometer was directly coupled with a GC equipped with a $30\text{ m} \times 0.25\text{ mm}$, $0.25\text{-}\mu\text{m}$ thick film, HP-5MS fused silica column.

2.6. Back trajectories

The isobaric backward trajectories (960 hPa) for all stations ([Fig. 1](#)) were calculated using the Hysplit 4 Lagrangian model ([Draxler and Hess, 1997, 1998](#)). A 6-year climatology study of air flows was performed in the study area at Eastern Mediterranean by [Mihalopoulos et al. \(1997\)](#). Contrary to the observations in the Western Mediterranean, Eastern Mediterranean presents a well-defined situation in the origin of air masses. There is a clear seasonal trend in the origin of air masses ([Mihalopoulos et al., 1997](#) and references within). Thus, air masses presented in [Fig. 1](#) fall well within sectors accounting for more than 60% on a yearly basis [Mihalopoulos et al. \(1997\)](#).

3. Results and discussion

3.1. Polycyclic aromatic hydrocarbons (PAHs) in recent marine sediments

Twenty-four (24) PAH members were identified in the marine sediments where important qualitative differences among the different sampling sites were observed ([Table 2](#)). The total (ΣPAHs) mean (and S.D.) concentrations 1056.21 (112.41) and 751.94 (45.51) ng g^{-1} (dry weight) were detected at the stations S5 and S3, respectively ([Table 2](#)). Lower concentrations were detected at the stations S4 and S6 with average values of the PAHs 23.28 (11.79) and 143.38 (24.15) ng g^{-1} , respectively ([Table 2](#)). Stations S1 and S2 exhibited the lowest values 2.22 (0.09) and 6.31 (0.47) ng g^{-1} , respectively ([Table 2](#)). These values are similar to those already published. [Gogou et al. \(2000\)](#) have reported total values for PAHs ($\Sigma 28$ PAHs) in the Cretan Sea between 14.6 and 158.5 ng g^{-1} , while [Baumard et al. \(1998\)](#) have measured total PAHs ($\Sigma 18$ PAHs) from 0.3 to 100 ng g^{-1} in Majorca (Western Mediterranean). Concentrations from 48.1 to 86.5 ng g^{-1} ($\Sigma 14$ PAHs) have been reported for coastal areas in the northwest Mediterranean Sea ([Benlahcen et al., 1997](#)).

The polycyclic aromatic hydrocarbon concentration (PAH) patterns differ according to the emission sources ([Sicre et al., 1987](#); [Rogge et al., 1993a,b,c,d](#); [Benner et al., 1995](#); [Wang et al., 1999](#)) and several PAH concentration diagnostic ratios have been exten-

Table 2
PAH (ng g⁻¹), OC (mg g⁻¹) and BC (mg g⁻¹) concentrations, and PAH diagnostic concentration ratios in Eastern Mediterranean marine sediments

Compound	S1 (n=3)	S2 (n=3)	S3 (n=3)	S4 (n=3)	S5 (n=3)	S6 (n=3)
Fluorene	0.04 (0.007)	0.46 (0.165)	3.16 (0.167)	0.93 (0.574)	37.58 (7.167)	2.88 (0.371)
Phenanthrene	0.49 (0.119)	2.74 (0.156)	31.41 (3.691)	4.94 (3.459)	127.66 (24.922)	11.25 (0.102)
Anthracene	0.04 (0.001)	0.20 (0.042)	3.57 (0.333)	0.34 (0.223)	4.75 (1.403)	0.90 (0.055)
ΣMethyl-phenanthrenes	0.23 (0.011)	1.01 (0.069)	9.87 (0.827)	2.66 (2.441)	138.82 (18.388)	6.52 (0.671)
Fluoranthrene	0.13 (0.013)	0.14 (0.016)	44.05 (7.692)	0.86 (0.142)	60.86 (1.432)	15.67 (3.524)
ΣDMPs	0.07 (0.007)	0.33 (0.230)	4.43 (0.915)	1.32 (1.216)	84.834 (11.781)	4.52 (1.896)
Pyrene	0.14 (0.011)	0.25 (0.142)	44.51 (7.903)	0.92 (0.028)	60.73 (12.103)	4.22 (0.311)
ΣMethyl-202	0.01 (0.001)	0.01 (0.013)	3.68 (0.206)	0.21 (0.141)	17.41 (2.401)	0.96 (0.147)
Retene	0.01 (0.001)	0.01 (0.004)	0.29 (0.108)	0.04 (0.004)	5.82 (2.241)	0.17 (0.065)
4(<i>H</i>)-cyclo[<i>cd</i>]pyrene	0.02 (0.001)	0.04 (0.022)	13.74 (0.215)	0.18 (0.038)	7.67 (0.682)	1.33 (0.313)
Benzo[<i>a</i>]anthracene	0.03 (0.003)	0.09 (0.033)	93.30 (3.764)	0.49 (0.169)	48.56 (2.319)	7.44 (1.162)
Chrysene/triphenylene	0.09 (0.001)	0.20 (0.093)	109.48 (3.331)	1.32 (0.899)	102.45 (4.892)	10.38 (2.198)
Methylchrysenes	nd ^a	nd	6.69 (0.929)	0.20 (0.205)	19.17 (0.915)	0.63 (0.475)
Benzo[<i>b</i>]fluoranthene	0.05 (0.002)	0.05 (0.052)	72.73 (9.156)	0.89 (0.006)	58.87 (2.811)	10.31 (2.359)
Benzo[<i>k</i>]fluoranthene	0.17 (0.055)	0.13 (0.157)	60.69 (4.991)	0.70 (0.069)	32.19 (1.537)	9.99 (0.225)
Benzo[<i>b</i> / <i>j</i> / <i>k</i>]fluoranthene	0.02 (0.003)	0.02 (0.017)	12.44 (0.525)	0.29 (0.093)	7.81 (0.373)	1.56 (0.167)
Benzo[<i>e</i>]pyrene	0.10 (0.001)	0.03 (0.026)	30.16 (3.27)	0.93 (0.614)	50.22 (2.398)	5.36 (0.493)
Benzo[<i>a</i>]pyrene	0.05 (0.009)	0.03 (0.022)	42.32 (4.595)	0.51 (0.089)	44.12 (5.471)	5.69 (0.392)
Perylene	nd	nd	13.10 (2.398)	0.21 (0.048)	18.12 (0.865)	4.33 (0.526)
Anthranthrene	0.01 (0.009)	0.18 (0.242)	12.38 (0.781)	0.35 (0.051)	9.56 (0.456)	3.65 (0.995)
Indeno[1,2,3- <i>cd</i>]pyrene	0.21 (0.003)	0.18 (0.237)	68.59 (6.189)	1.88 (0.005)	50.10 (4.381)	16.45 (2.923)
Dibenzo[<i>a,h</i>]anthracene	nd	nd	6.89 (0.257)	0.17 (0.047)	4.58 (0.219)	1.44 (0.577)
Benzo[<i>ghi</i>]perylene	0.38 (0.019)	0.22 (0.281)	64.46 (2.251)	2.96 (1.398)	64.33 (3.581)	17.74 (4.208)
Coronene	nd	nd	4.17 (0.613)	0.65 (0.113)	5.97 (0.285)	4.51 (0.945)
ΣPAH	2.22 (0.095)	6.31 (0.466)	751.94 (45.515)	23.28 (11.789)	1056.21 (112.407)	143.38 (24.149)
MP/P	0.5	0.4	0.3	0.5	1.1	0.6
A/178	0.07	0.07	0.10	0.06	0.04	0.07
Fl/[Fl + Py]	0.48	0.36	0.50	0.48	0.5	0.79
IP/[IP + BgP]	0.35	0.46	0.52	0.39	0.44	0.48
TOC	2.9	4.2	21.4	8.5	6.1	17
BC	0.3	0.4	5.6	1.5	0.9	3.2
BC/TOC (%)	10.1	9.8	26.2	17.4	15.2	18.6

^a nd = not detected.

sively used in order to identify and quantify the contribution of each source of contamination to the specific compartments (Bouloubassi et al., 1997; Gogou et al., 2000; Kavouras et al., 2001). The reported ratios should be treated with caution as biogeochemical and physical process may alter the PAH profiles during transport. Differences in reactivity, volatility, water solubility and in sorption rates among the PAHs could lead to the incorrect designation of the sources.

The general distribution of the PAHs in all sediments reflects the high contribution of pyrolytic sources because of the predominance of parent PAHs over their alkylated derivatives (Prah and Carpenter, 1983; Garrigues et al., 1995). The ratio of methyl

phenanthrenes to phenanthrene (MePh/Ph) was <1 for all the stations except for station S5, where almost equal concentrations of parent and methyl substituted phenanthrene were detected (Table 2 and Fig. 2A). For mass 178, an anthracene to anthracene plus phenanthrene (A/178) ratio <0.10 is considered as an indication of fossil fuel inputs while a ratio >0.10 indicates a dominance of combustion (Yunker et al., 2002). For the sediment of station S5, the lowest A/178 ratio (0.04; Table 2) was measured, thus, implying fossil fuel inputs for station S5. Fl/[Fl + Py] ratios obtained in Eastern Mediterranean sediment samples are reported in Table 2. Most of these ratios were ≤ 0.50 and had a mean value of 0.52 (0.14), suggesting for marine aerosols of the same area (see Section

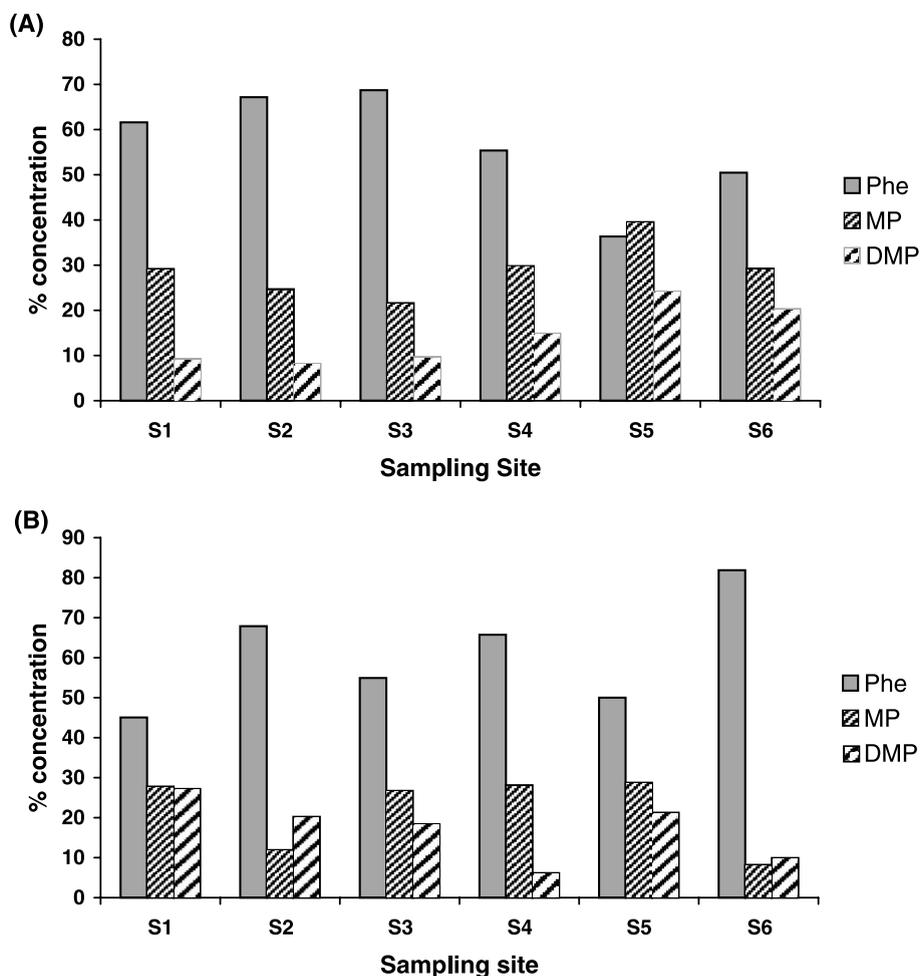


Fig. 2. Concentration distribution (%) of phenanthrene and methylated phenanthrenes in marine sediment (A) and marine aerosol (B) of the Eastern Mediterranean.

3.3) combustion of liquid fossil fuels as a major PAH source for Eastern Mediterranean marine sediments. IP/[IP+BgP] ratios obtained for Eastern Mediterranean sediments ranged from 0.35 to 0.52 (Table 2), suggesting combustion of liquid fossil fuels as a major source of PAHs also for the marine sediment. Retene, a PAH associated with forest fires, was present in all sediment samples in concentrations varying from 0.01 (stations S1 and S2) up to 5.82 (station S5) ng g^{-1} (Table 2). In a previous study, Gogou et al. (2000) determined the occurrence of retene in the sediment of the same area (S1; Fig. 1) and related its presence related with an atmospheric transport mechanism.

3.2. Organic and black (soot) carbon in recent marine sediments. Correlation with PAHs

The concentration of total organic carbon (OC) and black carbon (BC or soot) in the superficial sediment of the six selected sites was determined (Table 2). For station S3, the highest values for OC and BC, 21.4 and 5.6 mg g^{-1} dry weight, respectively (Table 2), were determined. Conversely, for station S1, the lowest concentrations for OC and BC, 2.9 and 0.3 mg g^{-1} , respectively (Table 2), were determined. These data are similar with OC (3.1–19.2 mg g^{-1} , Karakassis et al., 2000; 3.0–8.2 mg g^{-1} , Gogou et al., 2000) and BC (1.42 mg g^{-1} , Middelburg et al., 1999)

concentrations determined in other sites at the Eastern Mediterranean.

The soot component is a direct indicator of the anthropogenic combustion sources. The ratio BC to OC, i.e. in atmospheric aerosols, was found to vary with the distance of the sources. Thus, Heintzenberg (1989) measured the aerosol compositions in different regions of the troposphere and the percent ratio BC/OC were 2.7%, 20.8% and 29.0% for the remote, nonurban continental and urban areas, respectively.

Although the organic carbon component in the marine sediments is a consequence of the contribution from both autochthonous (e.g. produced by photosynthesis) and allochthonous carbon (e.g. atmospheric deposition), the BC/OC ratio in marine sediments might be used as useful tool to identify the relative contribution of the combustion sources (Bird and Cali, 1998).

Stations S1 and S2 exhibited the lowest values of the percent ratio of BC to OC at 10.1% and 9.8%, respectively; while the contribution of the anthropogenic sources in these stations is also illustrated by the low PAH concentration (Σ PAHs 2.22 and 6.31 ng g⁻¹, respectively; Table 2). Conversely, station S3 close to the populated west coast of Turkey (Fig. 1), exhibited a BC/OC ratio of 26.2% (Table 2) and a higher PAH concentration (Σ PAHs 751.94 ng g⁻¹; Table 2). The BC/OC ratio, determined in the sediment of S3, is similar to that found for urban aerosol (29.0%; Heintzenberg, 1989). Stations S4, S5 and S6 exhibited, for the BC/OC ratio, intermediate values of 17.4%, 15.2% and 18.6%, respectively. A high correlation (R^2) was determined between BC/OC ratio, the concentration of total PAHs (expressed as log(Σ PAHs); $R^2=0.92$ with $p<0.001$) in the marine sediments of the Eastern Mediterranean (Fig. 3A). The concentrations of OC and BC were well correlated with log(Σ PAHs (Fig. 3B and C, respectively) at all sites (except S5). All the stations exhibited a high correlation ($R^2=0.98$ with $p<0.001$; Fig. 3B) between OC concentration and the log(Σ PAHs, and BC concentration and the log(Σ PAHs ($R^2=0.95$ with $p<0.001$; Fig. 3C). The above correlations imply common sources for OC, BC and PAHs in Eastern Mediterranean sediments, and most probably common input path of the above chemical parameters into the marine environment of this area. Different models have been used to interpret the partitioning of PAHs and other nonpolar organic com-

pounds between the sediment and pore water. In these models, the sedimentary organic carbon (OC) was considered as the sorption phase (Karickhoff et al., 1979). It was suggested (Karickhoff et al., 1979) that an increase of the amount of sediment organic content should imply an increase for the amount of the hydrophobic compounds. More recent studies have proposed that other sediment characteristics such as the polarity and the aromaticity of organic matter, the grain size and the soot content may influence partitioning (Burgess et al., 2001; Huang et al., 1997; Huang and Weber, 1997; Rutherford et al., 1992). Station S5 deviated substantially from the above regression lines and the measured concentration of PAHs was higher than that one could predict on the basis of OC and BC sedimentary concentrations. Different sorption mechanism, different sediment characteristics and nonequilibrium conditions between the sediment and the pore water could account for this deviation. Station S5 is close to the main refineries of Greece and the fossil character (MePh/Ph > 1) of their inputs illustrated in Fig. 2A and Table 2 (see Section 3.1), imply other PAHs input pathways than atmospheric inputs and, thus, explaining the higher amount of PAHs in the sediment in relation to OC and BC contents.

A higher dependence of the PAH concentrations in marine sediment from the BC vs. OC content is shown in Fig. 3B and C. The regression slope between the log(Σ PAHs and BC concentration was 0.45 (Fig. 3C), while the slope between the log(Σ PAHs and OC concentration was 0.12 (Fig. 3B). These results are in agreement with the higher BC–water than OC–water distribution coefficients (Gustafsson et al., 1997a; Bucheli and Gustafsson, 2000). The higher dependence of pyrogenic vs. fossil PAHs concentration in relation to sedimentary BC content is shown in Fig. 4A. Pyrogenic PAHs in the sediment were more strongly associated (Σ pyrPAHs, $R^2=0.94$, slope = 0.51; Fig. 4A) with sedimentary soot (BC; Fig. 4A) than the fossil ones (Σ mePAHs, $R^2=0.84$, slope 0.31 Fig. 4A). This observation is similar, although not so pronounced, with that which Simo et al. (1997) found in marine aerosol.

3.3. PAH in aerosol gas and particle phases

Twenty-four (24) parent and substituted polycyclic aromatic hydrocarbons with a molecular mass

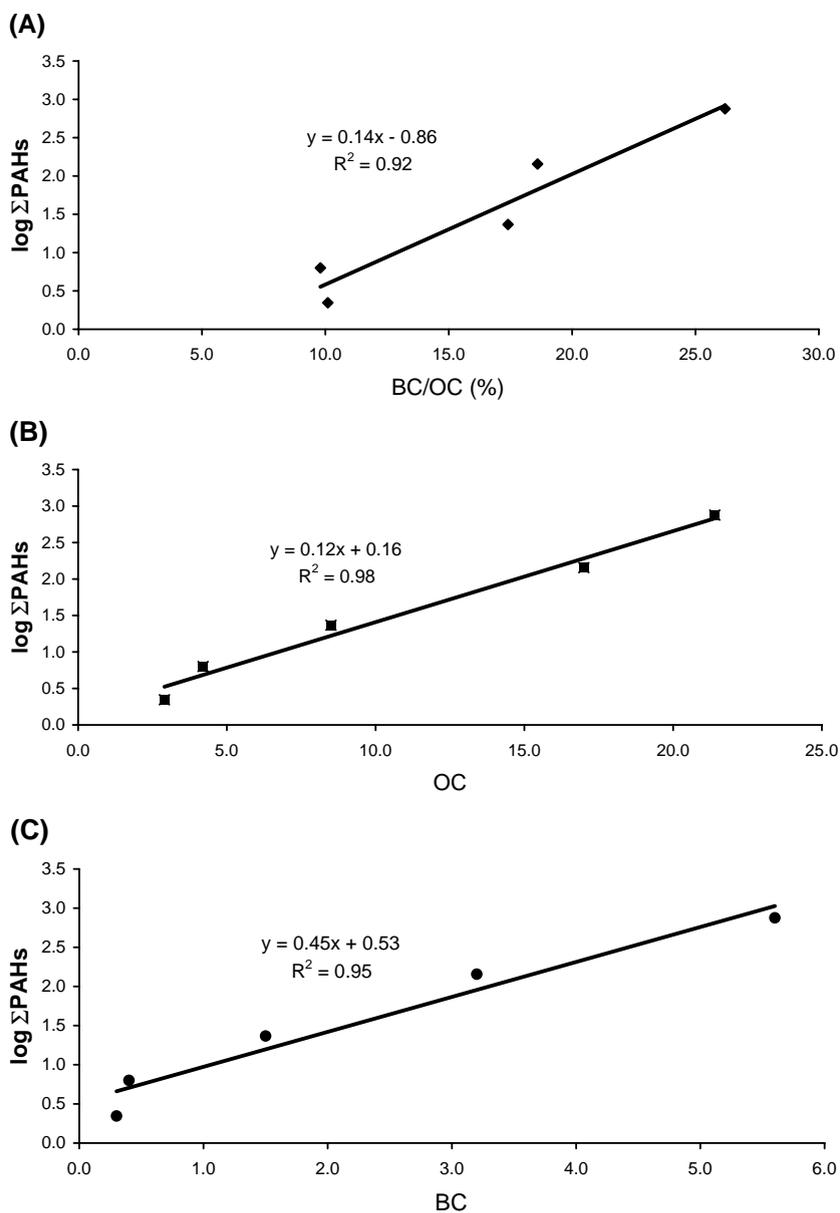


Fig. 3. Correlation of black carbon (BC) and organic carbon (OC) ratio (BC/OC) (A), OC concentration (mg g^{-1}) (B) and BC concentration (mg g^{-1}) (C) with the log of total PAH concentration in Eastern Mediterranean marine sediments.

from 166 to 300 were detected in the particulate phase, while 18 PAHs with a molecular mass varying from 166 to 252 were identified in the gas phase of Eastern Mediterranean aerosol samples. The most abundant PAHs in all the samples were phenanthrene, pyrene and fluoranthene (Table 3). Pyrogenic

hydrocarbons consisted of benz[*a*]anthracene, benzo-fluoranthenes, benz[*e*]pyrene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, and benzo[*ghi*]perylene (Table 3) generated during the combustion of both fresh and fossil organic matter. Fossil fuel hydrocarbons consisted of methylated phenanthrenes and

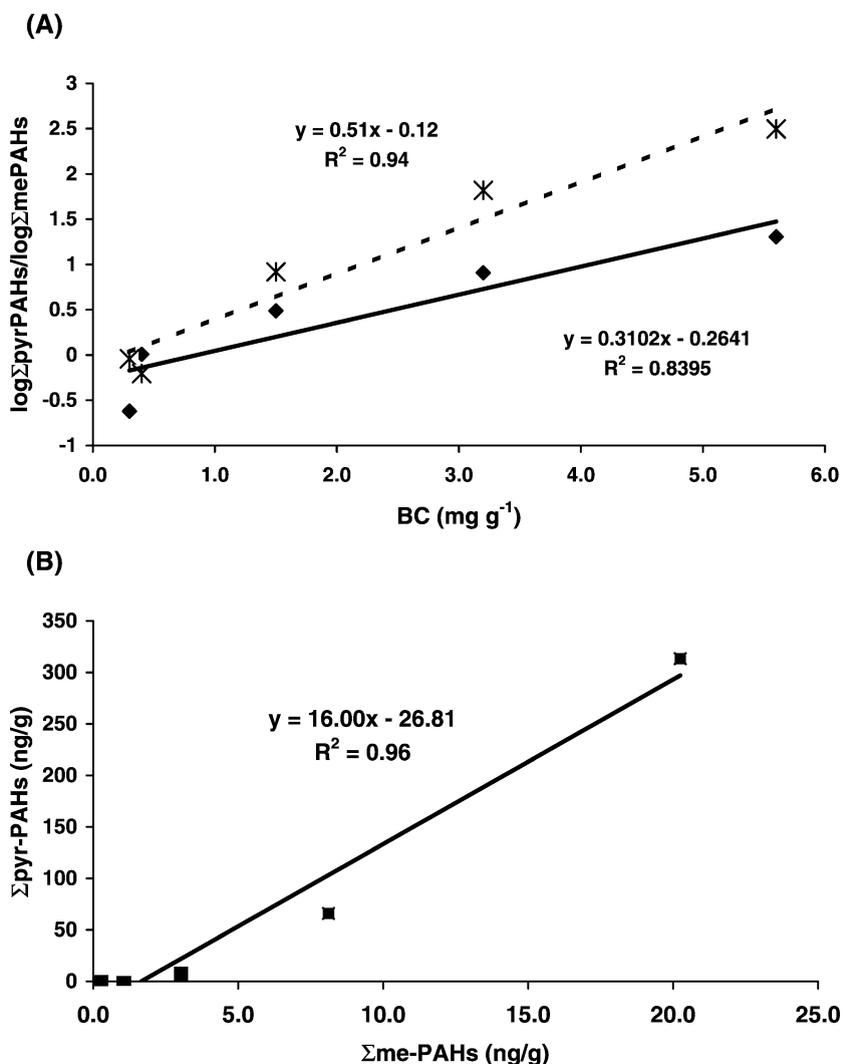


Fig. 4. Correlation of black carbon (BC) concentration (mg g^{-1}) with the log of pyrogenic PAH (ΣpyrPAH) and petrogenic PAH (ΣmePAH) concentration in Eastern Mediterranean marine sediments (A). Correlation of pyrogenic PAH (ΣpyrPAH) with the petrogenic PAH (ΣmePAH) concentration (ng g^{-1}) in Eastern Mediterranean marine sediments (B).

pyrenes (Table 3) highly abundant in fossil fuels (Yunker et al., 2002). Retene also occurred in the aerosol collected at all sites (Fig. 1 and Table 3). Retene's presence has been also confirmed in a previous study (Gogou et al., 1996) in air particles collected on a land based sampling station (Finokalia; Fig. 1) near S1.

Total PAH concentration (ΣPAHs) was higher ($19.65\text{--}75.95 \text{ ng m}^{-3}$; Table 3) in the gas phase than in the particulate one ($0.25\text{--}7.27 \text{ ng m}^{-3}$; Table 3).

The average concentrations for the studied basin for gaseous ΣPAHs equaled 44 ± 20 and $2 \pm 3 \text{ ng m}^{-3}$ for the particulate ones. The gas phase concentration was in the same order of magnitude with those measured at Chesapeake Bay ($5\text{--}42 \text{ ng m}^{-3}$; Bamford et al., 1999). As less PAH members (13) were measured at Chesapeake Bay (Nelson et al., 1998), we compared the concentration of specific compounds determined in Eastern Mediterranean such as phenanthrene (7.83 ng m^{-3} (S1) up to 26.50 ng m^{-3} (S6);

Table 3
Concentration (ng m⁻³) of PAH in particulate (P) and in the gas (G) phase in Eastern Mediterranean marine atmosphere

	S1		S2		S3		S4		S5		S6	
	P	G	P	G	P	G	P	G	P	G	P	G
Fluorene	0.003	1.904	0.003	1.525	0.005	6.129	0.022	2.220	0.010	1.947	0.003	11.769
Phenanthrene	0.013	7.830	0.020	9.029	0.045	18.375	0.057	22.273	0.290	22.990	0.028	26.501
Anthracene	0.001	0.730	0.001	1.146	0.003	2.860	0.004	3.054	0.054	3.236	0.001	2.114
ΣMethyl-phenanthrenes ^a	0.008	4.827	0.013	1.584	0.027	8.935	0.076	9.527	0.156	13.214	0.017	2.657
Fluoranthene	0.019	2.856	0.016	0.830	0.048	2.774	0.096	0.740	0.188	7.267	0.010	1.900
ΣDMPs ^a	0.007	4.723	0.008	2.688	0.028	6.144	0.077	2.083	0.113	9.771	0.014	3.210
Pyrene	0.022	1.084	0.022	1.482	0.032	2.553	0.058	1.395	0.272	10.020	0.012	2.545
ΣMethyl-202 ^a	0.007	0.328	0.004	0.331	0.010	0.517	0.044	0.542	0.050	1.278	0.003	0.351
Retene	0.001	0.072	0.002	0.099	0.003	0.251	0.007	0.000	0.007	0.683	0.003	0.122
4(<i>H</i>)-cyclo[<i>cd</i>]pyrene	0.011	0.019	0.009	0.022	0.009	0.024	0.006	0.024	0.475	2.151	0.003	0.013
Benzo[<i>a</i>]anthracene	0.010	0.011	0.010	0.011	0.014	0.029	0.025	0.070	0.304	0.758	0.002	0.016
Chrysene/triphenylene	0.047	0.056	0.042	0.045	0.071	0.108	0.039	0.226	0.825	1.810	0.009	0.041
Methylchrysenes ^a	0.003	0.002	0.005	0.003	0.007	0.012	0.153	0.011	0.096	0.144	0.001	0.006
Benzo[<i>b</i>]fluoranthene ^b	0.017	0.005	0.026	0.005	0.034	0.012	0.012	0.000	0.584	0.133	0.007	0.007
Benzo[<i>k</i>]fluoranthene ^b	0.010	0.003	0.022	0.005	0.029	0.007	0.022	0.000	0.761	0.086	0.012	0.007
Benzo[<i>b</i> / <i>j</i> / <i>k</i>]fluoranthene ^b	0.001	0.001	0.003	0.000	0.004	0.002	0.256	0.010	0.078	0.014	0.002	0.002
Benzo[<i>e</i>]pyrene ^b	0.012	0.004	0.024	0.003	0.028	0.014	0.096	0.038	0.888	0.147	0.010	0.016
Benzo[<i>a</i>]pyrene	0.006	0.002	0.011	0.001	0.016	0.010	0.060	0.006	0.363	0.041	0.004	0.012
Perylene	0.001	0.001	0.001	0.000	0.004	0.003	0.009	0.004	0.080	0.000	0.000	0.000
Anthranthrene	0.006	0.000	0.013	0.000	0.015	0.000	0.020	0.000	0.224	0.000	0.008	0.000
Indeno[1,2,3- <i>cd</i>]pyrene ^b	0.020	0.000	0.031	0.000	0.050	0.000	0.052	0.000	0.529	0.004	0.014	0.000
Dibenzo[<i>a,h</i>]anthracene	0.001	0.000	0.002	0.000	0.003	0.000	0.003	0.000	0.016	0.000	0.000	0.000
Benzo[<i>ghi</i>]perylene ^b	0.021	0.000	0.051	0.000	0.073	0.000	0.069	0.000	0.899	0.011	0.031	0.000
Coronene ^b	0.003	0.000	0.012	0.000	0.009	0.000	0.008	0.000	0.009	0.000	0.002	0.000
ΣPAH	0.25	24.95	0.35	19.65	0.56	49.78	1.27	42.55	7.27	75.95	0.20	52.26
ΣmePAH	0.02	9.88	0.03	4.61	0.07	15.61	0.35	12.16	0.41	24.41	0.03	6.22
ΣpyrPAH	0.08	0.01	0.17	0.01	0.23	0.04	0.51	0.05	3.75	0.40	0.08	0.03
Fl/[Fl + Py]	0.72		0.36		0.52		0.370		0.420		0.430	
IP/[IP + BgP]	0.48		0.38		0.41		0.430		0.370		0.310	

^a Petrogenic PAH (ΣmePAH).

^b Pyrogenic PAH (ΣpyrPAH; according to Simo et al., 1997).

Table 3) and fluoranthene (0.74 ng m⁻³ (S4) up to 7.27 ng m⁻³ (S5); Table 3) with the concentration of the same compounds determined at Chesapeake Bay. The concentrations determined in the present study were higher than those determined by Nelson et al. (1998) in Chesapeake Bay: 0.36–10.8 and 0.07–1.90 ng m⁻³, for phenanthrene and fluoranthene respectively.

The sites with the highest ΣPAHs (gas and particulate) concentration were S5 (83.22 ng m⁻³), S6 (52.46 ng m⁻³), S3 (50.34 ng m⁻³) and S4 (43.82 ng m⁻³). Some of these sites are near urban centers (S4 and S5; Fig. 1). At sites S4 and S5 (Fig. 1), the highest concentrations of gaseous fossil (ΣmePAHs; 12.16 and 24.41 ng m⁻³; Table 3) and particulate pyrogenic (ΣpyrPAHs; 0.51 and 3.75 ng m⁻³; Table

3) PAHs were also measured. A substantial decline in the particulate concentration of the PAHs associated to the increasing distance of the sampling sites from urban centers was observed. The highest concentrations in the particulate phase 7.27 and 1.27 ng m⁻³ (Table 3) were measured at the sampling stations S5 (Fig. 1) and S4 (Fig. 1), respectively. During the sampling time, station S5 was influenced by air masses passing over the central and west part of Greece where major urban centers exist, and station S4 by air masses passing over the Athens metropolitan area (Fig. 1). The lowest concentrations were measured at stations S6, S2 and S1 (Table 3). The air masses before reaching these sites had traveled a long distance (>100 km) over the sea (Fig. 1) and the deposition processes (wet and/or dry) might have

removed the major fraction of the particles from the atmosphere. The concentration of PAHs in the gas phase ranged from 19.65 ng m⁻³, at station S2, to 75.95 ng m⁻³ at station S5 (Table 3). A lower variation in the gas phase PAH concentration (compared with the corresponding particulate one) was observed among the stations of the studied area. The ratio between the highest to the lowest ΣPAHs concentration in the gas phase was 3.9 whereas the corresponding value in the particulate phase was 37.1. This difference is probably due to the fact that removal processes of the PAHs in the particulate phase (e.g. wet and dry deposition) are faster than in the gas phase (Halsall et al., 2001).

The distribution of PAHs between the gas (A) and the particulate (F) phase is an important factor affecting their removal mechanism and residence time in the atmosphere (Pankow and Bidleman, 1992). The partitioning of PAHs was parameterized using the partitioning coefficient, K_p (m³ μg⁻¹) according to the following relationship (Yamasaki et al., 1982):

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

where TSP is the concentration of total suspended particulate matter (μg m⁻³), and F and A are the analyte concentrations of the particulate and gas phases, respectively. Measured partition coefficients, K_p , correlated with the subcooled vapor pressure (p_1^0) of the pure PAHs according to the equation:

$$\log K_p = m_r \log p_1^0 + b_r \quad (2)$$

where m_r and b_r are the slope and the intercept of the regression, respectively. The plots of $\log K_p$ vs. $\log p_1^0$, for all samples, gave correlation coefficients R^2 (with $p < 0.001$) varying from 0.88 to 0.98. The slopes m_r varied from -0.73 to -0.96 . Regarding the slopes, two groups of stations could be discerned. The observed differences are most probably due to the history of air masses reaching the sampling stations. Stations S1 and S2, where the air masses had traveled a long distance (Fig. 1), showed slopes of -0.90 and -0.96 respectively, indicating a closer to equilibrium ($m_r = -1$; Yamasaki et al., 1982; Pankow and Bidleman, 1992) situation. On the contrary, the S3, S4, S5 and S6 (closer to urban centres) exhibited slopes of -0.74 , -0.88 , -0.73 and -0.81 , respectively.

Cotham and Bidleman (1995) have reported that PAHs collected at a rural site near Lake Michigan (Green Bay) were closer to equilibrium between the gas and particulate phases than PAHs collected at an urban site (Chicago). Cotham and Bidleman suggested that the aerosols over Green Bay had travelled far from their sources, hence, they had enough time to reach equilibrium.

PAHs of molecular mass 178 and 202 have been used to distinguish between pyrogenic (combustion of fossil fuels) and fossil (unburned fuels) emission sources (Sicre et al., 1987; Gogou et al., 1996). Phenanthrene alkyl homologue series maximizing at C1 (methyl-phenanthrene, MP) or/and C2 (dimethyl-phenanthrene, DMP) can be taken as a sign of fossil PAH emissions, while a maximum at the parent compound phenanthrene (molecular mass 178) usually indicates combustion (Sicre et al., 1987; Gogou et al., 1996). In Fig. 2B, the percent concentration distributions of phenanthrene and its alkyl homologues are shown. All aerosol samples collected at the sampling stations of Eastern Mediterranean demonstrated a pyrogenic pattern, with the parent phenanthrene being in higher proportion than its alkylated derivatives. Simo et al. (1997) reported similar observations. In their study, the relative concentration of alkylated derivatives of phenanthrene was found to decrease, from near combustion sources to remote marine samples, during atmospheric transport (Simo et al., 1997). Fluoranthene (Fl), pyrene (Py) (molecular mass 202) and indeno[1,2,3-*cd*]pyrene (IP), benzo[ghi]perylene (Bgp) (molecular mass 278) degrade photolytically at comparable rates (Behymer and Hites, 1988), suggesting that the original composition information is preserved during atmospheric transport. For Fl/[Fl+Py], the petroleum boundary ratio is close to 0.40 and ratios between 0.40 and 0.50 are characteristic of liquid fossil fuel combustion (Yunker et al., 2002). Fl/[Fl+Py] ratios obtained in our aerosol samples are reported in Table 3. Most of these ratios were < 0.50 and had a mean value of 0.47 (0.13), suggesting combustion of liquid fossil fuels as a major PAH source for Eastern Mediterranean aerosol. According to Yunker et al. (2002), IP/[IP+Bgp] ratios < 0.20 imply fossil inputs, while ratios between 0.20 and 0.50 imply combustion of liquid fossil fuels. The IP/[IP+Bgp] ratios obtained for Eastern Mediterranean aerosol ranged from 0.31 to 0.48 (Table 3),

also suggesting combustion of liquid fossil fuels as major emission source of PAHs.

Simo et al. (1997) considered the total concentration of alkylated polycyclic aromatic hydrocarbons (Σ mePAHs: methyl-phenanthrenes + methyl-pyrenes + methyl-chrysenes) as an indicator for fossil PAHs and the total concentration of pyrogenic polycyclic aromatic hydrocarbons (Σ pyrPAHs: benzo[*b*]fluoranthene + benzo[*k*]fluoranthene + benzo[*bjk*]fluoranthene + benzo[*e*]pyrene + indeno[1,2,3-*cd*]pyrene + benzo[*ghi*]perylene + coronene) as an indicator of the pyrogenic polycyclic aromatic hydrocarbons. Pyrogenic PAHs generally associate with soot-rich particles, which protect them from degradation in the atmosphere and as well as in the water column and sediments (Simo et al., 1997). Gogou (1998) determined a strong correlation ($R^2=0.753$, $p<0.001$) between pyrogenic PAHs and soot content in Eastern Mediterranean (Cretan Sea) marine aerosols collected at a coastal site on the island of Crete near the sampling station S1 (Fig. 1). Simo et al. (1997) found a different correlation of pyrogenic and fossil PAHs to black carbon marine aerosol content and suggested that these PAH categories present a decoupled association to soot.

3.4. Estimate of PAH air–sea exchange. Transfer of PAHs to the marine sediment

To estimate the role of atmospheric transport as a PAHs nonpoint source into the marine sediments of the Eastern Mediterranean, we only used the data acquired from five stations, namely S1, S2, S3, S4 and S6. As mentioned above, station S5 is very close to local sources such as refineries. The fossil inputs from the surrounding sources have been confirmed through the sediment PAH composition (see Section 3.1). Several studies pointed out the dependence of PAHs fluxes on the distance from the urban centres. A rapid fall-off in PAHs fluxes over harbour, coastal, continental shelf and open-ocean distances has been reported. A >20-fold reduction in pyrene fluxes at a 100-km distance from the urban centres was found by Gustafsson et al. (1997b, and references within). Mldonado et al. (1999) also observed a predominance of fossil PAHs in the suspended particulate matter of Northwestern Black Sea water near the coast, whereas a decrease of the fossil to pyrolytic PAH ratio was

observed with coast distance. These observations are in agreement with our results: Station S3, which is influenced by the densely populated west coast of Turkey, exhibited a 30-fold higher concentration of the PAHs in marine sediment compared to the corresponding concentrations of the S1 and S2 stations, which are far away from any point sources (Table 2). This is due to the substantial decline in the particulate concentration of the PAHs with the increased travelling distance of the air masses from the urban centres (see Section 3.2).

Air–sea exchange of semi-volatile organic compounds (SOCs) plays an important role in the mass balancing of inputs in large water body systems such as the Great Lakes (Mackay et al., 1986; Baker and Eisenreich, 1990; Achman et al., 1993; Hombuckle et al., 1994; Totten et al., 2001) and the world's ocean (GESAMP, 1989; Iwata et al., 1993). Sampling station S1 is away from any point sources and atmospheric transport is expected to be the major source of the PAHs to this area (Gogou et al., 1996). In addition, the air masses reaching Eastern Mediterranean present a well-defined seasonal trend as it has been shown by Mihalopoulos et al. (1997). Thus, the air samples collected during this study can be considered as representative for predominant air mass transport occurring in this area. During the collection of air and sediment samples, simultaneous collection of water samples (to determine dissolved PAHs) was not possible. In order to evaluate PAH flux, due to air–sea exchange, in the study area, we used the results of PAH analysis in water samples collected in July 2002 around station S1 (Fig. 1). The results of seawater analysis are reported in Table 4. To our best knowledge, reports on dissolved PAH concentration in the broader Mediterranean area are very rare. Erhardt and Petrick (1993) reported higher dissolved PAHs concentration, than ours, especially for phenanthrene ($11\text{--}13\text{ ng l}^{-1}$) for the central Mediterranean basin.

The model, mostly used to describe the transfer of organic compounds across the air–water interface, has been reported by Liss and Slater (1974) and is presented below:

$$F_{A-W} = K_{ol}(C_W - C_A/H')$$

F_{A-W} is the air–water exchange flux, C_A and C_W are the concentrations of the PAH member in air (ng

Table 4

Dissolved PAH seawater concentration (pg l^{-1}), PAH vapor concentration (ng m^{-3}), PAH flux through air–water exchange (F_{A-w}) ($\text{ng m}^{-2} \text{day}^{-1}$) and total deposition (wet and dry) ($\text{ng m}^{-2} \text{day}^{-1}$) in Eastern Mediterranean

	Dissolved (pg l^{-1}) ^a	Vapor (ng m^{-3}) ^a	K_{ol} ($T=21.2$ °C, $V=3.3$ m/s) ^b	H ($T=21.2$ °C) ($\text{Pa m}^{-3} \text{mol}^{-1}$)	F_{A-w} ^a ($\text{ng m}^{-2} \text{day}^{-1}$)	Total deposition ($\text{ng m}^{-2} \text{day}^{-1}$) ^c	Percent contribution of F_{A-w}
Fluorene	240	1.90	0.299	5.62	− 173.8	12.1	93.5
Phenanthrene	470	7.83	0.195	2.31	− 1513.3	43.8	97.2
Anthracene	60	0.73	0.219	2.81	− 124.7	54.8	69.5
Fluoranthene	210	2.86	0.086	0.73	− 791.9	124.9	86.4
Pyrene	170	1.08	0.078	0.65	− 299.9	208.5	59.0
Benzo[<i>a</i>]anthracene	60	0.01	0.051	0.41	− 0.3	27.3	1.2
Chrysene/triphenylene	140	0.06	0.006	0.46	− 0.9	28.5	3.1
Total					− 2905	500	

K_{ol} is the mass transfer coefficient and H is the Henry constant.

^a This study.

^b Nelson et al., 1998.

^c (Wet and dry) mean value for July 1997 and July 1998 (Hatzara, 1999).

m^{-3}) and in water (ng m^{-3}), respectively. H' is the dimensionless Henry's low constant corrected for temperature and K_{ol} is the overall mass-transfer coefficient with units of velocity (m day^{-1}). The value of K_{ol} depends on the physical and chemical properties of the compound as well as on the environmental parameters (e.g. wind velocity). We utilized PAH seawater concentrations, reported in Table 4, to calculate F_{A-w} . The temperature correction of the PAH Henry constants (H in Table 4) was achieved by using the equation published by Tateya et al. (1988). In addition, we used K_{ol} values (Table 4) reported by Nelson et al. (1998) for the corresponding temperature (21.5 °C) and wind speed (3.3 m/s). The calculated F_{A-w} values varied for the different PAHs ($-0.3 \text{ ng m}^{-2} \text{day}^{-1}$ for benzo[*a*]anthracene up to $-1513.3 \text{ ng m}^{-2} \text{day}^{-1}$ for phenanthrene; Table 4). The estimated air–water exchange flux values have shown an absorptive deposition trend to the seawater of the study for reported PAHs (S1, Fig. 1). High loadings -173.8 and $-1513.3 \text{ ng m}^{-2} \text{day}^{-1}$ were determined for the more volatile PAHs, fluorene and phenanthrene, respectively (Table 4). These fluxes, due to gas absorption, are substantially higher than the corresponding fluxes due to atmospheric deposition (wet and dry; Table 4; Hatzara, 1999), measured from 1997 to 1998, at the coastal marine station of Finokalia in the vicinity of sampling area (Fig. 1). The contribution of the air–water exchange was calculated to represent the 93.5% for fluorene and 97.2% for

phenanthrene total input (Table 4) in the study area. On the other hand, the contribution of this process for the heavier PAHs such as benzo[*a*]anthracene ($-0.3 \text{ ng m}^{-2} \text{day}^{-1}$; Table 4) and chrysene ($-0.9 \text{ ng m}^{-2} \text{day}^{-1}$; Table 4) should be negligible. According to Nelson et al. (1998), for Chesapeake Bay, gas absorption was evaluated to contribute 93% and 95% of the total atmospheric loading of fluorene and phenanthrene, respectively. Henry's low constants of organic compounds increase with the salinity, i.e. PAH Henry constants determined in saline water are higher by ca. 10–50% when compared with those determined in pure water (Schwarzenbach et al., 1993). Due to the high salinity (39.2–39.4‰) of the seawater in the Eastern Mediterranean, the calculated gas absorption is expected to be overestimated (Nelson et al., 1998). Nevertheless, air–sea exchange is still an important input mechanism for the more volatile PAHs in Eastern Mediterranean.

Despite the time scale difference between the different processes, PAH relative composition in marine sediments and in marine atmosphere may suggest their deposition process. Phenanthrene proportion to the total PAHs measured in the sediment was 43.4% and 21.9% at stations S2 and S1, respectively (Table 3). This observation strongly supports the importance of volatile PAHs absorption by the surface waters in the Eastern Mediterranean. Conversely, the percent contribution of phenanthrene to the total PAHs inputs through wet and dry deposition varied from 1% up to

3%, during 1997–1998 (Hatzara, 1998), at the same area (Finokalia, Fig. 1). As mentioned above, Nelson et al. (1998) observed a similar contribution for these compounds in the Chesapeake Bay. Thus, wet and dry deposition processes alone could not justify the observed phenanthrene high concentration in the marine sediments collected in areas distant from point sources (e.g. S1, S2 and S6; Fig. 1).

The contribution of phenanthrene to the total PAHs measured in the sediment was 43.4%, 21.9% and 21.2% at the S2, S1 and S4 stations, respectively (Table 2). Lower values 4.2%, 12.1% and 7.9% were observed for the S3, S5 and S6 stations, respectively. Phenanthrene, compared to the other PAHs, is relatively volatile ($p_1^0 = 8 \cdot 10^{-4}$ Torr at 25 °C) and relatively soluble in the water (1.10 mg/l at 25 °C) and its high abundance in the marine sediments is characteristic of the importance of the gas flux of PAHs in the marine environment for the remote areas. In addition, if for pyrogenic PAHs (Σ pyrPAHs; Table 3) the atmospheric deposition is established as the main input mechanism to the remote marine sediments, their high correlation ($R^2 = 0.97$; Fig. 4B) with the fossil components (Σ mePAHs) mostly found in the gas phase (Table 3), is showing their common origin namely atmospheric transfer.

4. Conclusion

A high variation of the particulate concentration of the PAHs in the marine atmosphere of the Eastern Mediterranean was observed. The concentration was substantially higher for the stations close to the urban centres than the remote areas. The PAHs in the gas phase exhibited an almost equal distribution over the sea. The partitioning of the PAHs in the gas and particulate phase is an important parameter affecting the PAH deposition from the atmosphere and the consequent accumulation in the marine sediment. Coastal marine sediments close to the continental shelf showed a higher amount of PAHs. This was due to the concentration of the PAHs in the particulate phase, which was higher close to the urban areas. Gas transfer of PAHs from the atmosphere into the marine environment is an important process for the remote areas.

A significant correlation between the PAHs and the organic and soot carbon content was observed for the

sites receiving PAHs mostly through atmospheric input. The PAHs in the sediment were more sensitive to changes in the soot content than in the organic content probably due to the higher water–soot than water–organic partitioning coefficients.

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