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Polycyclic aromatic hydrocarbons (PAHs) in the Mediterranean Sea: Atmospheric occurrence, deposition and decoupling with settling fluxes in the water column

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ABSTRACT

\sum_{30} PAH gas phase concentrations (13–86 and 22–40 ng m⁻³ in the Mediterranean and Black Seas, respectively) dominated the atmospheric levels due to the high contribution of phenanthrene, dibenzothiophene and their alkylated derivatives. The high variability of PAH atmospheric concentrations in the different sub-basins is due to several factors (i.e. air-mass trajectory, proximity to sources and losses by deposition). The \sum_{30} PAH atmospheric deposition (dominated by low MW PAH net air–water diffusive fluxes) is estimated to be ~3100 ton y⁻¹ (Mediterranean) and ~500 ton y⁻¹ (Black Sea). Net volatilization for certain PAHs was estimated. Deposition fluxes (1–2 orders of magnitude higher than reported PAH settling fluxes in the water column) confirm an important depletion/sink of water column PAH in the photic zone, especially for low MW PAHs. Degradation processes in the water column may be responsible for this decoupling. Conversely, high MW PAHs dry deposition fluxes are similar to their settling fluxes.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are semi-volatile organic contaminants (SOCs) which are ubiquitous in the environment and may cause a wide range of toxic effects in biota and humans (Menzie et al., 1992). The ubiquity of PAHs in the environment is thought to be dominated by their formation and release to the atmosphere due to the incomplete combustion of coal, oil, petrol and wood (Wild and Jones, 1995), even though natural sources (e.g. forest fires, volcano eruptions, biogenic formation) may also have a significant regional influence on PAH occurrence (Howsam and Jones, 1998; Ravindra et al., 2008). The Mediterranean and Black Sea regions due to their nature of semi-enclosed environments surrounded by highly populated areas (more than 400 million people) are under the influence of large number of organic pollutant sources, including PAHs. However, there is a lack of comprehensive assessment of PAH occurrence and deposition in the Mediterranean region. Existing data is mostly derived from studies performed in coastal sites and lacks from a broad spatial coverage (Lipiatou and Albaigés, 1994; Lipiatou et al., 1997; Pérez et al., 2003; Tsapakis and Stephanou, 2005; Tsapakis et al., 2006). The knowledge of PAH atmospheric levels for the Black sea is even more scarce, and limited to PAH atmospheric

measurements carried out in urban/suburban areas from North-West Turkey (Vardar et al., 2008; Esen et al., 2008) despite less the various studies reporting PAH occurrence in seawater, sediments and biota from the Marmara and Black Seas highlighting their ubiquity and related toxicity (Telli-Karakoc et al., 2002; Readman et al., 2002; Bozcaarmutlu et al., 2009).

The atmosphere is an important vector for PAH inputs to the Mediterranean waters (Tsapakis and Stephanou, 2005; Tsapakis et al., 2006), being atmospheric inputs higher than riverine inputs in some basins, such as the North Western Mediterranean (Lipiatou et al., 1997). In addition, it has been suggested that atmospheric inputs are significantly higher than vertical fluxes of PAHs in the Aegean Sea's water column (Tsapakis et al., 2006). This observation, if confirmed for other marine regions, would have important implications for our knowledge of the environmental fate of PAHs and persistent organic pollutants (POPs). There is compelling evidence of a coupling between the atmospheric inputs and settling fluxes of POPs through air–water exchange linked to phytoplankton uptake and settling of organic matter (Dachs et al., 1999, 2002; Berrojalbiz et al., 2011a). However, it has been suggested that for non-persistent organic pollutants such air–water–plankton coupling is strongly influenced by biotic and abiotic degradation in the water column (Berrojalbiz et al., 2011b). In addition, the influence of water column degradation of organic pollutants on the magnitude of settling fluxes has not been assessed so far.

The overall objectives of this work are: (1) to provide the first comprehensive assessment of PAH gas and aerosol phase

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concentrations in the open Mediterranean Sea and in the Black Sea atmospheric boundary layer; (2) to estimate the dry atmospheric deposition and diffusive air–water exchange of PAHs in the open Mediterranean and Black Seas (3) to investigate how atmospheric inputs relate to reported settling fluxes in order to gain knowledge on the oceanic depletion/sink of PAHs.

2. Materials and methods

2.1. Study area

The Mediterranean and Black Seas are semi-enclosed environments with limited water exchanges. The Mediterranean Sea covers an area of about 2.5×10^6 km² and has connection to the Atlantic Ocean through the strait of Gibraltar that is ~ 14 km wide. A detailed area description has been recently reported elsewhere (Berrojalbiz et al., 2011b). The rapid increase of human activities in the Mediterranean Sea basin, particularly in the fields of industrialization, urbanization and agriculture, and the seasonal increase in coastal tourism is a threat to the environment and biodiversity in the area (UNEP/MAP, 1996). The Black Sea represents an area of 4.2×10^5 km² and its virtually isolated from other Seas. It is connected to the Eastern Mediterranean Sea through the Bosphorus strait. The combination of industrial pressures (offshore oil production and pipeline transport among others) and riverine discharges, mostly from the Danube river (collecting wastewaters from 18 European countries) (Maldonado et al., 1999) endangers the conservation of this ecosystem. In addition, the high contamination potential (both atmospheric emissions and direct spills to waters) derived from the intense maritime traffic from commercial activities in both seas (REMPEC, 1994; Birpınar et al., 2009), contributes to threat of these ecosystems.

2.2. Sampling

Simultaneous air and surface seawater samples were collected during two surveys performed on June 2006 and May 2007 on board of the *R/V García del Cid* (CSIC). The campaigns started and finished in Barcelona, with Istanbul and Alexandria being the intermediate stops, respectively. Transects encompassing all Mediterranean basins, the Marmara Sea and the South West Black Sea were gathered within a year of difference allowing a good spatial coverage (Figs. S1 and S2 and Text S1; Table S1–S3 for sample details, Supporting information, SI). Briefly, air samples were taken by using high volume samplers. Aerosol phase (i.e. air particulate phase) collection was performed on quartz fibre filters (QFFs) whereas gas phase trapping was achieved by using polyurethane foams (PUFs). Sampling volumes varied for most of the samples from 150 to 950 m³ and additional higher volume samples (300–1600 m³) were also collected for aerosols. Water samples were collected as reported elsewhere (Berrojalbiz et al., 2011b). Briefly, seawater was pumped on board (from 2 to 3 m depth) into a stainless steel overflow container from where samples (90–350 L) were taken. Retention of the particulate water phase was performed on glass fibre filters (GFFs), whereas the dissolved water phase was sampled by using XAD columns. For the purpose of this study only those dissolved phase samples simultaneously collected with gas phase samples are considered. A total of 66 atmospheric samples (gas + aerosol phases) and 43 dissolved water phase samples were collected.

2.3. Analysis

Details on the PAH extraction and analytical procedures are presented in Text S2 (SI). Briefly, PUF and QFF were spiked with PAH labelled standards before Soxhlet extraction (24 h). Extract volumes were generally reduced and fractionated on alumina columns, and PAHs were eluted in the second fraction with hexane/dichloromethane. Extracts were then concentrated to 50–150 μ L under gentle nitrogen flow. Prior to injection, syringe labelled PAHs were added to the extracts. PAH analysis was performed by high resolution gas chromatography–low resolution mass spectrometry (HRGC–LRMS). Samples were analysed for the following PAHs: Fluorene (FL), phenanthrene (PHE), anthracene (AN), dibenzothiophene (DBT), sum of methyl-dibenzothiophenes (Σ MeDBT), sum of methyl-phenanthrenes (Σ MePhe), sum of dimethyl-phenanthrenes (Σ DimePhe), fluoranthrene (FA), pyrene (PY), chrysene (CHR), benzo(a)anthracene (BaAN), benzo(b)fluoranthene (BbFA), benzo(j)fluoranthene (BjFA), benzo(k)fluoranthene (BkFA), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), perylene (PE), dibenzo(a,h)anthracene (DBaA), benzo(g,h,i)perylene (BghiP) and, indeno(1,2,3-cd)pyrene (IP).

2.4. Quality assurance/Quality control (QA/QC)

The QA/QC procedures are detailed in Text S3 (SI). Summarizing, field and procedural blanks (for sampling and analysis) were collected and analysed with the samples. Aerosol phase blank values (QFF blanks) were at the limit of detection (LOD) levels so no blank correction of the results was performed, whereas air gas phase blank levels (PUF blanks) exceeded LODs for low MW compounds. Results were corrected by blanks levels in those cases. Blank values for individual PAH in

both gas and aerosol phases are presented in Tables S4 and S5, respectively (SI). Procedural blanks showed similar levels to field blanks so no contamination of samples during manipulation or processing occurred. An air sampling reproducibility study was carried out for selected aerosol samples by operating two samplers (A and B) simultaneously during the 2007 cruise (T6–T9) with significant correlation ($p < 0.001$) between results from the two sampling devices (Table S6 and Fig. S3), so mean concentrations for each PAH in transects T6, T7, T8 and T9 were considered for further calculations and discussion.

Standards (natives + labelled compounds) were introduced in the chromatographic sequence to evaluate possible variations during the time of analyses. Chromatographic peaks of target compounds were only considered when their abundance was at least 3 times higher than the noise. LODs were calculated as blank + 3 standard deviation (SD) (therefore taking into account the influence of both processing and analytical steps). LODs ranged from 0.03 to 10.5 pg m⁻³ for air gas phase samples and from 0.01 to 4.3 pg m⁻³ in aerosols depending on the PAH and sample analysed. Average method recoveries (extraction–cleanup–analysis) in gas and aerosol phases were of 60% and 97%, respectively. Results were corrected by recoveries. QA/QC details for water samples have been reported elsewhere (Berrojalbiz et al., 2011b).

2.5. Atmospheric deposition fluxes

Since both sampling cruises were performed in summer or late spring/summer, in the absence of precipitation events, the atmospheric deposition was considered to be represented by the air–water diffusive and the dry deposition fluxes. Diffusive air–water exchange was calculated by determining the PAHs absorption (F_{AWAbs} , ng m⁻² d⁻¹) and volatilization (F_{AWVol} , ng m⁻² d⁻¹) fluxes as:

$$F_{AWAbs} = -10^{-3} k_{AW} C_g / H' \quad [1]$$

$$F_{AWVol} = -10^{-3} k_{AW} C_w \quad [2]$$

Where k_{AW} is the air–water mass transfer coefficient (m d⁻¹), C_g (pg m⁻³) and C_w (pg m⁻³) are the pollutant concentration in the gas and dissolved phases, respectively, and H' the dimensionless Henry's law constant. H' values and their temperature dependence as well as k_{AW} values have been estimated as explained elsewhere (Bamford et al., 1999; Jurado et al., 2004). The nonlinear influence of wind speed has been taken into account by correcting the water-side mass transfer coefficient considering a Weibull distribution of wind speeds (Nightingale et al., 2000; Jurado et al., 2004) (Text S4, SI).

Dry deposition fluxes (F_{DD} , ng m⁻² d⁻¹) were calculated as:

$$F_{DD} = v_d C_A \quad [3]$$

where C_A is the volumetric concentration of PAHs in the aerosol phase (ng m⁻³) and v_d is the deposition velocity of particles. There are very few field measurements of v_d for the Mediterranean region, and these are limited to coastal sites with v_d ranging between 0.3 and 0.5 cm s⁻¹ for the North Western Mediterranean (Del Vento and Dachs, 2007a). However, the only available direct measurements of dry deposition fluxes performed over the oceans (Del Vento and Dachs, 2007b) reported lower values of v_d , ranging from 0.1 to 0.3 cm s⁻¹, with enhanced v_d values at high wind speeds. Here, a value of 0.2 cm s⁻¹ for v_d has been chosen as representative of marine aerosols at high sea, since wind speeds were usually low (average of 5 m s⁻¹). However, a degree of uncertainty (factor of two–three) is associated to this calculation due to the lack of measurements of v_d during the cruises.

3. Results and discussion

3.1. Gas phase occurrence of PAHs

PAH atmospheric concentrations were dominated by gas phase levels due to the high abundance of <4 aromatic ring PAHs. Σ_{30} PAH gas phase concentrations over the Mediterranean Sea ranged from 13 to 86 ng m⁻³. Concentrations measured in the Black Sea (22–40 ng m⁻³) were within the range of those in the Mediterranean Sea. Results for individual PAH in all transects are presented in Table S7 (SI). Gas phase pattern was dominated by DBT (57 \pm 5%), followed by PHE (20 \pm 2%) and Σ MeDBTs (12 \pm 4%) (Fig. S4A, SI). Other studies have already reported the predominance of DBT, PHE and MePHE in the coastal and marine atmosphere (Gigliotti et al., 2000; Del Vento and Dachs, 2007b).

All previous studies of PAHs in Mediterranean atmosphere and seawater only report concentrations from one sub-basin (for example, NW Mediterranean or Aegean Sea), thus we divided the study area into five regions, named (A) Western Mediterranean, (B)

Ionian Sea–Sicily, (C) South-East Mediterranean, (D) Aegean Sea and (E) Marmara–Black Sea (Fig. S1, SI). Mean values and range of atmospheric concentrations measured in each region are presented in Table 1. The highest \sum_{30} PAH concentration was measured in the Western Mediterranean (26–86 ng m⁻³), whereas the lowest levels were measured in the SE Mediterranean (13–28 ng m⁻³). Nevertheless, there was an important variability even when sub-basins are considered, due to different processes affecting the atmospheric levels of PAHs. For example, FA, CHR and \sum MePHE exhibited a different spatial distribution, not always presenting same concentration peaks within basins (Fig. S5, SI). FA's highest concentration was measured at G1 (Western Mediterranean), whereas levels for CHR at G1 were among the lowest. FA and CHR peaked at G8 (Ionian Sea/Sicily) whereas \sum MePHE exhibited the lowest concentration at the same G8 transect. A further example is given by comparison of individual PAH gas phase concentrations during transect G6 (W Mediterranean) and G17 (SE Mediterranean) which are the samples with the highest and lowest \sum_{30} PAH concentrations, respectively (Fig. S6a, SI). Individual PAH gas phase concentrations were from 5 to 30 fold-times higher in Western Mediterranean. Forty eight hours air mass back trajectories at 15 and 500 m over sea surface were calculated for these samples by using the HYSPLIT model (Draxler and Rolph, 2011). Air masses were circulating close to the north African coast in the sample collected in the Western Mediterranean (G6), whereas a general open sea circulation of air masses was computed for the sample collected in the SE Mediterranean (G17), corresponding to lower gas phase concentrations (Fig. S7, SI). This fact may explain the higher PAH levels measured in the Western Mediterranean and highlights the potential PAH sources of north Africa, and other coastal areas, to the Mediterranean open sea atmosphere. Higher levels of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) over the Mediterranean Sea open waters when air masses coming from NW Africa have also been reported (Castro-Jiménez et al., 2010)

3.2. Aerosol phase occurrence of PAHs

\sum_{30} PAH concentrations varied from 0.5 to 3 ng m⁻³ in the Mediterranean Sea. Levels measured in the Marmara and Black Sea are within this range (0.8–2.6 ng m⁻³). Results for PAH mean concentrations in the five sub-basins are presented in Table 2, whereas values for all transects are reported in Table S8 (SI). A more evenly distributed pattern was observed for the aerosol phase, dominated by the methylated PAHs (DimePHE: 25 ± 7%; MePHE:

14 ± 4% and MeDBT: 14 ± 6% of the sum of PAHs) (Fig. S4B, SI). Similar range of \sum_{30} PAH aerosol concentrations was measured in the five sub-basins, showing a high within basin variability. PAHs also showed differences in their spatial distribution. Generally, higher MW PAH exhibited higher concentrations in the SE Mediterranean and the Black Sea (such is the case for PE, BghiP, BkFA, BaP and BeP) (Fig. S8A, SI), but not for low-mid MW PAH (FA and PY for example) (Fig. S8B, SI). Individual PAH aerosol phase concentrations were from 4 to 8 fold-times higher in P18 transect (highest \sum_{30} PAH concentrations) in comparison to P20 transect (lowest \sum_{30} PAH concentrations) both samples collected in SE Mediterranean, (Fig. S6B). Since there was no major difference in the air mass back trajectories corresponding to those samples (Fig. S7, SI), this higher value may be explained in part by the proximity to the Nile delta and Alexandria urban area (around 4 million inhabitants), which proximate samples (P17–P19) exhibiting \sum_{30} PAH concentrations from 2 to 6 fold-time higher than the rest of the SE Mediterranean (P14, P15 and P20) (Fig. S2, SI). In addition, some PAHs correlated with the organic carbon (OC) and soot carbon (EC) content of aerosols (which were determined for a few samples during both cruises) and both aerosol fractions, although clearly linked, were very variable (also within basins). Therefore, the variability of PAH concentrations in the aerosol phase is most probably due to a combined effect of the continuous emissions of these chemicals, the coastal urban influence, the high maritime traffic in this region and to the overall variability of the OC and specially EC concentrations.

Both PAH gas and aerosol phase concentrations reported in this work are in agreement with cruise measurements of atmospheric PAHs performed in the Easter Mediterranean in summer 2001 when \sum_{18-24} PAH concentrations ranging from 20 to 76 ng m⁻³ in the gas phase and from 0.2 to 7 ng m⁻³ in the aerosol were reported (Tsapakis et al., 2003). However, PAH levels in the Mediterranean were higher than those reported for cruise measurements performed in late autumn/winter 2005 in the Atlantic Ocean (0.02–2.5 ng m⁻³ for \sum_{10} PAHs sum of gas and aerosol phases) (Nizzetto et al., 2008). \sum_{30} PAH (gas + aerosol) concentrations measured in Black Sea (23–43 ng m⁻³) were in agreement with those reported for \sum_{14-15} PAH (gas + aerosol) in suburban areas from Bursa (Turkey) in summer 2004, around 200 km south west from our sampling sites (9–45 ng m⁻³) (Vardar et al., 2008).

3.3. Source indication by PAH molecular ratios

In order to have an estimation of potential sources of PAH in the atmosphere over the Mediterranean and Black Seas we

Table 1
PAH gas phase concentration (ng m⁻³, mean and range) in the different Mediterranean sub-basins and in the SW Black Sea.

Compound	Western Mediterranean		Ionian Sea-Sicily		South-East Mediterranean		Aegean Sea		Black Sea	
	Mean (N = 7)	Range	Mean (N = 6)	Range	Mean (N = 4)	Range	Mean (N = 3)	Range	Mean (N = 3)	Range
Fluorene	1.94	(0.64–3.29)	2.25	(1.27–5.65)	0.69	(0.36–1.23)	1.22	(0.79–1.49)	1.72	(1.11–2.44)
Phenanthrene	7.69	(0.20–18.90)	7.00	(3.52–15.45)	3.94	(2.50–6.35)	4.28	(3.46–5.37)	5.69	(3.89–7.67)
Anthracene	0.39	(0.20–0.83)	0.37	(0.18–0.55)	0.20	(0.16–0.30)	0.22	(0.18–0.25)	0.27	(0.21–0.31)
Dibenzothiophene	21.51	(11.84–50.61)	18.91	(9.16–34.24)	11.14	(8.02–17.18)	13.28	(10.58–14.79)	19.01	(13.14–25.97)
\sum MethDBT ^a	5.01	(3.10–9.02)	3.41	(2.61–4.44)	2.55	(1.29–3.53)	2.42	(1.77–2.85)	3.02	(2.13–4.02)
\sum MePhe ^b	1.51	(0.67–3.63)	1.14	(0.89–1.49)	0.58	(0.19–0.78)	0.61	(0.41–0.78)	0.82	(0.57–1.04)
\sum DimePhe ^c	0.22	(0.05–0.55)	0.21	(0.13–0.31)	0.05	(0.02–0.07)	0.09	(0.07–0.10)	0.14	(0.09–0.17)
Fluoranthrene	0.04	(0.01–0.09)	0.05	(0.02–0.07)	0.007	(0.003–0.011)	0.01	(0.01–0.02)	0.02	(0.01–0.03)
Pyrene	0.03	(0.01–0.07)	0.04	(0.02–0.06)	0.006	(0.003–0.009)	0.013	(0.012–0.014)	0.02	(0.01–0.02)
Chrysene	0.06	(0.03–0.17)	0.09	(0.03–0.23)	0.03	(0.02–0.05)	0.05	(0.04–0.07)	0.05	(0.04–0.07)
\sum_{30} PAHs ^d	38.38	(25.84–86.47)	33.45	(19.10–60.11)	19.19	(12.60–28.36)	22.21	(17.33–25.52)	30.76	(21.71–40.40)

^a Sum of two PAHs.

^b Sum of four PAHs.

^c Sum of seven PAHs.

^d HMW PAHs (from BbFA to BghiP) were not detected in the gas phase.

Table 2
PAH aerosol concentration (pg m^{-3} , mean and range) in the different Mediterranean sub-basins and in the SW Black Sea.

Compound	Western Mediterranean		Ionian Sea-Sicily		South-East Mediterranean		Aegean Sea		Black Sea	
	Mean (N = 10)	Range	Mean (N = 8)	Range	Mean (N = 9)	Range	Mean (N = 6)	Range	Mean (N = 6)	Range
Fluorene	3.15	(1.34–4.14)	1.37	(0.86–1.87)	1.34	(1.14–1.55)	4.82	(4.64–5.00)	11.93	(11.93–11.93)
Phenanthrene	53.25	(11.72–102.13)	56.84	(14.39–120.17)	40.21	(11.39–134.85)	49.08	(22.15–78.36)	78.06	(45.82–123.76)
Antrathene	9.61	(0.59–19.07)	7.23	(0.89–12.92)	8.82	(0.68–22.50)	10.76	(5.52–16.12)	11.84	(7.28–18.40)
DBT	55.11	(2.57–135.04)	7.80	(2.26–13.32)	14.98	(1.96–42.96)	33.08	(1.41–103.04)	10.40	(1.91–17.69)
Σ MeDBT	251.42	(87.44–340.62)	152.28	(68.95–255.93)	196.40	(62.73–474.13)	165.84	(35.02–212.78)	141.81	(53.39–192.35)
Σ MePhe	237.41	(149.50–311.94)	227.05	(90.91–351.86)	270.38	(48.36–299.71)	173.95	(155.87–190.21)	164.83	(144.70–203.16)
Σ DimePhe	428.86	(256.92–620.65)	349.74	(119.62–522.24)	294.34	(124.71–474.54)	279.40	(212.19–334.90)	231.30	(190.09–330.87)
Fluoranthrene	62.38	(11.80–124.30)	98.69	(13.39–185.55)	49.39	(11.48–118.27)	82.93	(32.18–189.74)	170.35	(62.29–226.91)
Pyrene	72.59	(12.22–140.26)	108.71	(16.08–216.06)	57.21	(12.06–141.62)	78.12	(26.94–165.69)	157.38	(54.84–218.86)
Benzo(a)anthracene	14.46	(3.44–25.28)	13.28	(6.09–23.89)	18.08	(4.19–45.62)	15.00	(7.69–22.48)	29.45	(12.04–67.95)
Chrysene	47.35	(7.93–118.46)	44.28	(12.81–81.11)	43.25	(11.52–100.68)	46.97	(23.04–64.48)	90.89	(45.08–177.77)
Benzo(b)fluoranthene	12.92	(9.61–20.95)	28.84	(12.02–45.44)	32.63	(10.16–59.78)	29.21	(18.43–39.26)	78.13	(22.95–178.19)
Benzo(j)fluoranthene	5.86	(4.99–7.23)	15.26	(4.06–16.46)	9.57	(8.40–10.74)	11.94	(9.09–14.79)	20.63	(20.63–20.63)
Benzo(k)fluoranthene	9.05	(0.35–36.22)	14.74	(5.39–26.54)	88.77	(5.11–333.43)	34.84	(11.48–107.79)	52.00	(13.56–140.69)
Benzo(a)pyrene	9.67	(3.72–20.13)	9.31	(4.20–16.61)	34.37	(5.00–80.57)	17.04	(12.88–26.31)	42.33	(14.47–105.95)
Benzo(e)pyrene	17.69	(12.65–24.32)	29.96	(17.11–46.53)	46.32	(17.06–92.74)	28.29	(19.85–33.85)	72.64	(24.50–188.81)
Pyrene	2.20	(0.15–9.47)	2.24	(0.48–4.42)	24.61	(0.10–68.01)	2.06	(1.43–2.65)	5.66	(2.73–13.93)
Indeno(1,2,3-cd)pyrene	7.91	(1.91–12.81)	18.32	(5.57–31.55)	8.59	(1.79–12.95)	23.97	(18.28–28.70)	68.38	(18.19–192.68)
Dibenzof(a,h)anthracene	1.27	(1.05–1.48)	4.84	(2.76–6.91)	32.03	(1.40–94.20)	2.72	(2.09–3.34)	7.54	(7.54–7.54)
Benzo(ghi)perylene	15.45	(8.03–29.23)	25.64	(16.68–41.64)	81.17	(11.71–210.02)	26.49	(18.58–33.38)	65.42	(22.79–176.40)
Σ_{20} PAHs	1362.29	(881.74–1843.30)	1286.17	(691.70–1908.30)	1261.24	(509.89–3057.94)	1136.94	(1078.15–1192.26)	1553.37	(941.13–2448.14)

investigated two different molecular diagnostic ratios (MDR) (Yunker et al., 2002). The ratios FA/FA + PY and Phe/ Σ MePhe provide clues whether the PAHs stem from petroleum spills (petrogenic origin) or combustion of fossil fuels (pyrolytic origin) (Lohmann et al., 2011). FA/FA + PY > 0.5 and Phe/ Σ MePhe > 1.0 (Fig. S9, SI) were obtained for gas phase concentrations indicating a pyrogenic origin (Yunker et al., 2002; Lohmann et al., 2011). However, same ratios derived from aerosol phase concentrations (FA/FA + PY = 0.4–0.5 and Phe/ Σ MePhe = 0.2–0.8) pointed to a combined situation where both petrogenic and pyrogenic origins seem to be possible. In addition the pyrogenic character of the PAH measured in the atmosphere seem to increase eastwards (Fig. S9B, SI). However, MDR ratios must be carefully interpreted in atmospheric samples. Some authors have recently reported contradictory results when performing source apportionment by using MDRs and do not recommend their use for samples collecting far from strong and defined sources (Katsoyiannis et al., 2011; Dvorská et al., 2011). We believe that in our case (mainly open sea) they reflect a mixture of sources.

3.4. Atmospheric deposition of PAHs to the Mediterranean and Black Seas

Fig. 1 presents PAH average net air–water diffusive and dry deposition fluxes for each study region as estimated using equations [1–3]. Average net air–water diffusive fluxes are dominated by same PAH in all basins, named DBT, Phe, and Σ MeDBT, ranging from 1400 to 1980 $\text{ng m}^{-2} \text{d}^{-1}$, from 570 to 810 $\text{ng m}^{-2} \text{d}^{-1}$, and from 240 to 540 $\text{ng m}^{-2} \text{d}^{-1}$, respectively (Fig. 1A). Fig. 2 and Table S9 (SI) present the individual PAH net diffusive fluxes for each transect. Two situations were found: (a) Net absorption for a certain number of PAHs (i.e. PHE, DBT, Σ MeDBT, AN and CHR) was observed in all transects; (b) Net volatilization for other PAHs (i.e. FL, Σ MePhe, Σ DimePhe, FA and, PY) was observed in part of the transects. FA exhibit the widest spatial extension in volatilization fluxes but with lower intensity (1–41 $\text{ng m}^{-2} \text{d}^{-1}$). However, volatilization fluxes of alkyl-Phe, although more regionally focussed, were higher ranging from 60 to 1650 and from 2 to 1445 $\text{ng m}^{-2} \text{d}^{-1}$ for Σ MePhe and Σ DimePhe, respectively. The highest volatilization fluxes were registered in the SE Mediterranean, in particular in samples collected in the vicinity of Alexandria and the Nile delta (G16A and G16B) (Fig. S10, SI). Water samples collected in this area have been reported to exhibit the highest PAH water dissolved phase concentrations in the Mediterranean Sea due to proximity to Alexandria and the Nile delta (Berrojalbiz et al., 2011b). The large volatilization fluxes (in particular those of FA and alkyl-Phe) are the result of low gas phase concentrations (see discussion above) and high water dissolved phase PAHs. The effect of higher volatilization from coastal waters with high PAH concentrations has been recently reported in other impacted regions such as Narragasset Bay (USA) (Lohmann et al., 2011). In addition, these high volatilization fluxes could be due to enhanced seawater concentrations due to ship ballast (200,000 vessels have been estimated to cross the Mediterranean annually) (REMPEC, 1994). Net volatilization for some PAHs (i.e. Phe: 70–210 $\text{ng m}^{-2} \text{d}^{-1}$ and AN: 3–70 $\text{ng m}^{-2} \text{d}^{-1}$) have also been reported for the Atlantic open waters (Nizzetto et al., 2008). The volatilization fluxes for FL in the Mediterranean Sea (40–735 $\text{ng m}^{-2} \text{d}^{-1}$) are within the range of those reported in the Atlantic Ocean.

There is an important uncertainty in diffusive fluxes, mainly due to the uncertainty associated to Henry's law constants and truly dissolved concentrations. The significance of the net flux direction can be evaluated using the ratios of fugacity in air over fugacity in water (f_g/f_w). When f_g/f_w ranges from 0.3 to 3, gas and dissolved phases can be assumed close to equilibrium, when $f_g/f_w > 3$ there is a net absorption and when $f_g/f_w < 0.3$ there is a net volatilization

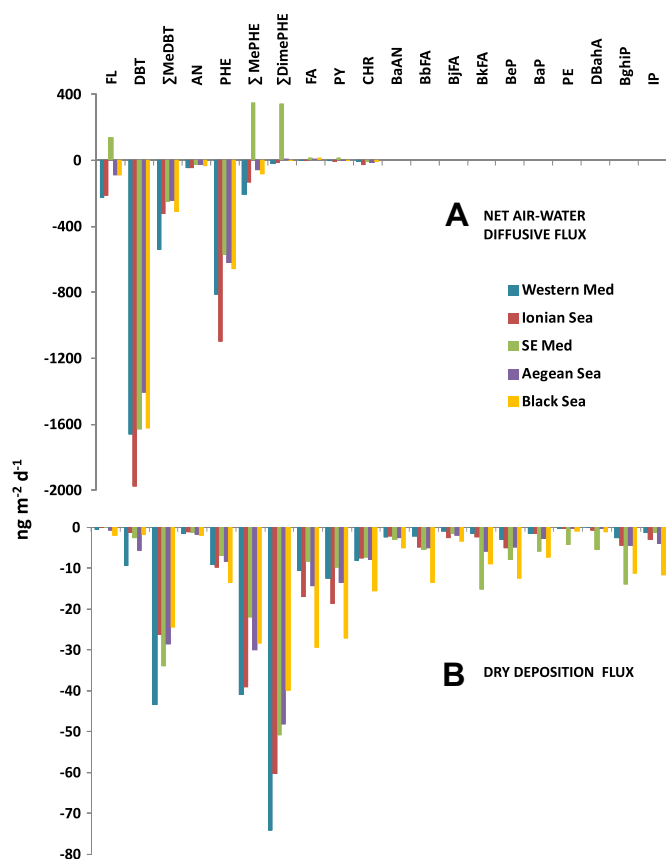


Fig. 1. PAH average net air–water diffusive (A) and dry deposition (B) fluxes in the different Mediterranean Sea basins and in the Black Sea. Positive values are volatilization fluxes whereas negative values are deposition fluxes (see Materials and method Section for PAH acronym identification).

(see Text S5, SI). Table S10 (SI) shows the fugacity ratios for PAHs in all samples. Fugacity ratios were higher than 3 for the lower MW PAHs (FL to Σ MePHE) and for CHR except for the three samples in SE Mediterranean exhibiting in general equilibrium conditions

($f_g/f_w = 0.3-3$), pointing to a significant net absorption flux. Conversely, fugacity ratios for Σ DimePhe, FA and PY were at equilibrium or below 0.3 in particular in the SE Mediterranean, confirming the tendency for net volatilization fluxes in this region.

Atmospheric dry deposition over the Mediterranean and the Black Seas is dominated by alkyl-PAHs (Fig. 1B), being predominant in all basins. The average dry deposition fluxes varied from 10 to 40 and from 20 to 60 $\text{ng m}^{-2} \text{d}^{-1}$ for Σ MePhe and Σ DimePhe, respectively and from 25 to 40 $\text{ng m}^{-2} \text{d}^{-1}$ for Σ MeDBT. Dry deposition fluxes and spatial distribution for individual PAH in all samples are shown in Table S11 and Fig. S11 (SI), respectively. Due to the assumptions in the dry deposition estimations these fluxes follow the pattern of PAH aerosol phase concentrations.

3.5. Net inputs of PAHs to open waters

Based on the average net diffusive and dry deposition fluxes calculated for each basin an estimation of the total yearly inputs (net air–water diffusive flux + dry deposition flux) as sum of PAHs was performed per each basin. The highest atmospheric inputs (Σ_{30} PAHs) were estimated for the Western Mediterranean (1170 ton y^{-1} , considering a surface of $8.5 \times 10^{11} \text{m}^2$) and the Ionian Sea-Sicily region (1110 ton y^{-1} , considering a surface of $7.5 \times 10^{11} \text{m}^2$). The lowest average inputs were estimated for the Aegean Sea (210 ton y^{-1} considering a surface of $2.1 \times 10^{11} \text{m}^2$). The estimated atmospheric inputs in the SE Mediterranean (645 ton y^{-1} considering a surface of $9.6 \times 10^{11} \text{m}^2$) were in between and more in the range of those from the Black Sea (490 ton y^{-1} considering a surface of $4.4 \times 10^{11} \text{m}^2$). Mediterranean Sea open waters receive therefore ~ 3100 tons of PAHs (as sum of 30 compounds) each year from the atmosphere.

Σ_{30} PAH average dry deposition accounted for the 5–11% (15–70 ton y^{-1}) of the average total annual inputs in the Mediterranean depending on the basins, and the 8% (40 ton y^{-1}) of the average annual total inputs in the Black Sea. However, dry deposition accounts for 100% of the total deposition of high MW PAHs. The dry deposition fluxes estimated for the Western Mediterranean in the present work (50–100 ton y^{-1}) are in agreement with the atmospheric inputs (wet + dry deposition) for Σ_{15} PAHs reported by Lipiatou et al. (1997) in the same basin (35–70 ton y^{-1}). A study performed in the Eastern Mediterranean in

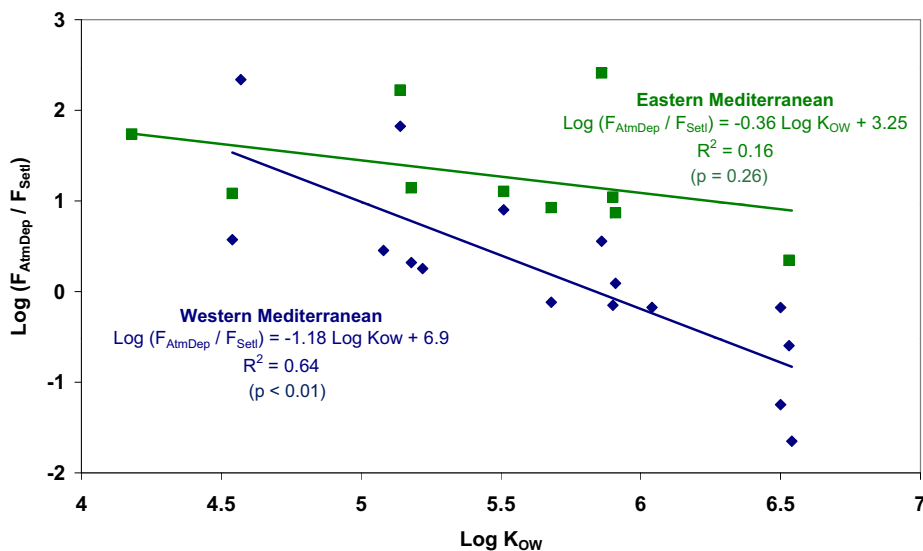


Fig. 2. Ratio of atmospheric deposition flux (net diffusive + dry deposition) and settling fluxes in the water column versus $\log K_{ow}$ for PAHs in the Western and Eastern Mediterranean. The atmospheric deposition fluxes are those estimated here. The settling fluxes are those reported by Tsapakis et al. (2006) for the Eastern Mediterranean and the average of those reported by Bouloubassi et al. (2006) and Dachs et al. (1996) for the Western Mediterranean.

a remote site 70 km eastward from Heraklion (Greece) (Tsapakis et al., 2006) reported average net diffusive absorption fluxes for Phe (324 ton y⁻¹), AN (30 ton y⁻¹) and CHR (20 ton y⁻¹) among others which are within the same range of those estimated in the present work (Phe: 200 ton y⁻¹; AN: 10 ton y⁻¹ and CHR: 3 ton y⁻¹). The same study also reported \sum_{35} PAH average dry deposition fluxes ranging from 10 to 170 ton y⁻¹ which are also in good agreement with our dry deposition estimations for \sum_{30} PAH (20–185 ton y⁻¹) in the SE Mediterranean region.

3.6. Atmospheric deposition versus settling of PAH in the water column

The Mediterranean sea is an environment rich in sediment trap studies reporting PAH settling fluxes at various depths, in particular in the Western basin (Tsapakis et al., 2006; Lipiatou et al., 1993, 1997; Dachs et al., 1996; Raoux et al., 1999; Bouloubassi et al., 2006; Deyme et al., 2011). Table 3 present a summary of PAH settling fluxes (ton y⁻¹) derived from available sediments trap studies together with the average annual depositional fluxes (net diffusive and dry deposition) estimated in this work for comparison. Reported settling fluxes of PHE (7–43 ng m⁻² d⁻¹) and DBT (19 ng m⁻² d⁻¹) accounted for the 1–5% and the 1%, respectively of the average diffusive fluxes estimated for the same pollutants in the present work (786 and 1695 ng m⁻² d⁻¹, respectively). The same differences between settling and atmospheric deposition fluxes are found for most PAHs (Fig. S12, SI). This fact suggests an important PAH depletion occurring in the photic zone of the Mediterranean Sea open waters, in particular for low MW PAHs. This observation is in agreement with results from a mass balance performed in the Eastern Mediterranean (Tsapakis et al., 2006), where PAH settling fluxes accounted only for a tiny fraction of atmospheric inputs (~1%). Conversely, settling fluxes are not significantly different (factor of 2–3) from the atmospheric dry deposition fluxes (dominated by the contribution of high MW PAHs).

Current knowledge derived for POPs suggest that after organic compounds enter the water column by diffusive exchange, they sorb to the dominant organic matter pools and a fraction of it settles out of the photic zone, being atmospheric inputs similar in magnitude with settling fluxes (Dachs et al., 1999, 2002; Berrojalbiz et al., 2011a). However, this air–water–settling coupling (which is the biological pump) has not been evaluated previously for non-persistent organic compounds such PAHs. For the more hydrophobic compounds (higher *K_{OW}*), settling fluxes induce a depletion of water

concentrations, but in any case the atmospheric inputs would remain similar in magnitude to those of the settling fluxes (Dachs et al., 2002). Fig. 2 shows that the ratio of the atmospheric deposition flux (net diffusive + dry deposition) to settling flux of PAHs in the water column is significantly correlated with the PAHs log *K_{OW}* for the Western Mediterranean but not for the Eastern Mediterranean. However, in the latter, the ratio of fluxes is even higher than in the Western Mediterranean.

Advection out of the Mediterranean can not account for this depletion of water column concentrations because the only exchange is through the Gibraltar Strait resulting in a net income of PAHs (Dachs et al., 1997). Transport to deep waters due to vertical turbulent diffusivity may remove PAHs from the photic zone, but it is difficult to estimate due to uncertainties in the eddy diffusion coefficient, but usually assumed small, if not negligible, comparison to settling fluxes of POPs bounded to organic matter. Another process could be the transfer to higher trophic levels. PAHs do not bioaccumulate in zooplankton and fish due to an efficient metabolism. In addition, microbial degradation of lower MW PAHs is thought to be an efficient process. Indeed, low MW PAH concentration depletion with depth has been attributed to possible degradation processes when observing a decrease of low MW PAH with depth in settling and suspended particles in studies conducted in the Western Mediterranean (Lipiatou et al., 1993; Dachs et al., 1997). Berrojalbiz and co-workers recently proved that low MW PAH can be efficiently metabolized by zooplankton, suggesting this process as an important sink of PAH in open seas (Berrojalbiz et al., 2009). In a further study by Berrojalbiz et al. (2011b) degradation of low MW PAHs by zooplankton and bacteria has been suggested to play an important role driving the water column PAH concentrations. Therefore, the strong decoupling of atmospheric deposition and settling fluxes (Fig. 2) may be the result of efficient degradation in the water column which is more efficient for the low MW PAHs, because they are easily degraded in comparison to high MW PAHs, but also, because they enter the water column predominantly as dissolved and not sorbed to aerosol soot carbon. The Eastern Mediterranean is highly oligotrophic, thus with lower settling fluxes of organic matter, increasing the residence times of PAHs in the photic zone, leading to greater potential for degradation.

Conversely, high MW PAH do not effectively degrade in the water column, which can be due to their strong association to soot particles, which may even prevent their effective water particle partitioning because high MW PAH are in part encapsulated inside carbonaceous particles. This leads to similar high MW PAH concentrations in

Table 3
Atmospheric deposition fluxes calculated in the present study and settling fluxes from sediment trap studies in the Mediterranean Sea.

Study basin	Site description	Sampling period	Trap depth	Compounds	Flux (ton y ⁻¹) ^e	Reference
Atmospheric inputs						
Western Med	Open waters	May/Jun/July 2006, 2007	/	Σ_{30} PAHs	1100 (net diffusive) 70 (dry)	This study
South-Eastern Med	Open waters	May/Jun/July 2006, 2007	/	Σ_{30} PAHs	570 (net diffusive) 70 (dry)	This study
Sediment trap studies (settling fluxes)						
Western Med	Ligurian Sea ^a	Mar–Jun 1987	200 m	Σ_{15} PAHs	30–90	Lipiatou et al., 1993
Western Med	Coastal site (Monaco) ^c	Jan 1988–Aug 1990	80 m	Σ_{30} PAHs	40–3260	Raoux et al., 1999
Western Med	Alboran Sea ^b	Feb–May 1992	250 m	Σ_{14} PAHs	45–50	Dachs et al., 1996
Western Med	Sardinia ^c	April 2001–May 2002	250 m	Σ_{13} PAHs	3–55	Bouloubassi et al., 2006
Western Med	Ligurian Sea ^a	Nov 2000–July 2002	200 m	Σ_{13} PAHs	0.3–30	Deyme et al., 2011
Eastern Med	Finokalia ^d	May–Oct 2001	250 m	Σ_{35} PAHs	10	Tsapakis et al., 2006

^a Ligurian Sea surface: 2.8×10^{11} m².

^b Alboran Sea surface: 5.7×10^{11} m².

^c Western Mediterranean surface: 8.5×10^{11} m².

^d Southern-East Mediterranean surface: 9.6×10^{11} m².

^e Average flux.

surface water particles than deep water particles. Therefore, the similar atmospheric deposition and settling fluxes (Dachs et al., 1997; Dachs and Eisenreich, 2000) for mid-high MW PAHs (Fig. 2) would be consistent with a coupling of dry deposition and settling fluxes without an efficient degradation in the photic zone.

4. Conclusions

The first comprehensive assessment of gas and aerosol phase PAH concentrations and deposition fluxes across the Mediterranean Sea and in the South West Black Sea is presented. PAH atmospheric concentrations exhibited a high variability in the different Mediterranean sub-basins due to the interplay of several factors such as air-mass trajectory, proximity to potential coastal sources, intense maritime traffic in the region and losses by deposition. The origin of PAHs in the atmospheric boundary layer over the Mediterranean Sea seem to be related to a mixture of sources as indicated by molecular diagnostic ratios. Low molecular weight PAH net air–water diffusive fluxes dominated the atmospheric deposition to the Mediterranean and Black Seas. In addition, evidence of net volatilization for certain PAHs were found. Atmospheric deposition fluxes are 1–2 orders of magnitude higher than reported PAH settling fluxes in the water column, confirming the existence of an important depletion/sink of water column PAH concentrations in the photic zone, especially for low MW PAHs. This decoupling may be ubiquitous in the ocean, since low MW PAH abundance reported for oceanic sediments is lower than that observed in surface waters and the atmosphere (Nizzetto et al., 2008; Lohmann et al., 2009). Conversely, high MW PAH which enter the ocean through dry deposition are ultimately transferred to deep waters and sediments. Further research is needed concerning the evaluation of photo- and bio-degradation processes in the water column and the role that soot carbon plays on the availability of PAHs and their transport in the water column.

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.envpol.2012.03.003.

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