# Biogeochemical and physical controls on concentrations of polycyclic aromatic hydrocarbons in water and plankton of the Mediterranean and Black Seas

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[1] The Mediterranean and Black Seas are unique marine environments subject to important anthropogenic pressures due to atmospheric and riverine inputs of organic pollutants. They include regions of different physical and trophic characteristics, which allow the studying of the controls on pollutant occurrence and fate under different conditions in terms of particles, plankton biomass, interactions with the atmosphere, biodegradation, and their dependence on the pollutant physical chemical properties. Polycyclic Aromatic Hydrocarbons (PAHs) have been measured in samples of seawater (dissolved and particulate phases) and plankton during two east-west sampling cruises in June 2006 and May 2007. The concentrations of dissolved PAHs were higher in the south-western Black Sea and Eastern Mediterranean than in the Western Mediterranean, reflecting different pollutant loads, trophic conditions and cycling. Particle and plankton phase PAH concentrations were higher when lower concentrations of suspended particles and biomass occurred, with apparent differences due to the PAH physical chemical properties. The surface PAH particle phase concentrations decreased when the total suspended particles (TSP) increased for the higher molecular weight (MW) compounds, consistent with controls due to particle settling depletion of water column compounds and dilution. Conversely, PAH concentrations in plankton decreased at higher biomass only for the low MW PAHs, suggesting that biodegradative processes in the water column are a major driver of their occurrence in the photic zone. The results presented here are the most extensive data set available for the Mediterranean Sea and provide clear evidence of the important physical and biological controls on PAH occurrence and cycling in oceanic regions.

## 1. Introduction

[2] Polycyclic aromatic hydrocarbons (PAHs), arising from incomplete combustion of fossil fuel and from direct spills of oil-derived products are important pollutants in the marine environment. The Mediterranean and Black Sea region, due to its nature of a semi-enclosed basin surrounded by highly populated countries, is an area of special interest in terms of pollutant assessment and research. However, besides some early work on PAHs in the water column, most of the knowledge on PAH occurrence, transport and fate in the Mediterranean basin has been done either in sediments or in local coastal studies [*Lipiatou and Saliot*, 1991; *Yilmaz et al.*, 1991; *Ehrhardt and Petrick*, 1993; *Lipiatou et al.*, 1993; *Kucuksezgin et al.*, 1995; *Dachs et al.*, 1997; *Lipiatou et al.*, 1997; *Maldonado et al.*, 1999; *Gogou et al.*, 2000; *Hatzianestis and Sklivagou*, 2002; *Telli-Karakoç et al.*, 2002; *El Nemr and Abd-Allah.*, 2003; *Tsapakis et al.*, 2003; *Pane et al.*, 2005; *Tsapakis et al.*, 2006]. Since the Mediterranean and Black are unique basins with only one significant entrance of seawater from the Atlantic Ocean through the Gibraltar strait, and it is surrounded by populated regions, both riverine, run-off and atmospheric inputs are important [*Lipiatou et al.*, 1997]. In addition, different sub basins have distinct trophic, physical and bathymetric characteristics that can also exert an influence on pollutant occurrence and sinks. The Mediterranean and Black Seas, besides their intrinsic geographic importance and interest,

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provide a unique ecosystem to assess the major physical and trophic drivers of the oceanic cycling and sinks of PAHs.

[3] There are major gaps in our knowledge of the cycling and factors controlling the occurrence of hydrophobic pollutants such as PAHs and Persistent Organic Pollutants (POPs) in marine waters. Coastal inputs may be certainly important driving the occurrence of pollutants locally, but their influence in open sea waters is small due to the importance of diffuse atmospheric sources. In addition, recent studies relate the levels of POPs, which have similar semi-volatility and hydrophobicity than PAHs, in waters and biota to trophic drivers due to the influence of biomass, settling fluxes, etc. [*Dachs et al.*, 2002; *Nizzetto et al.*, 2008]. However, this knowledge is scarce in general and lacking for the Mediterranean and Black Seas.

[4] Indeed, it is known that biogeochemical cycles, especially those related to organic carbon, affect the POP transport and sinks in the water column. For example, it has been reported that POP concentrations in plankton decrease at higher biomass [*Taylor et al.*, 1991; *Skei et al.*, 2000; *Larsson et al.*, 2000]. This can be due to a dilution of the signal, but also to interactions of phytoplankton uptake and atmospheric deposition [*Dachs et al.*, 1999, 2000]. However, the field evidence of these processes in the marine environment is lacking due to scarce studies with the appropriate sampling strategy. Furthermore, planktonic organisms are the first step of aquatic food webs with concentrations of organic pollutants several orders of magnitude higher than in seawater. Therefore, the understanding of the processes driving the occurrence of PAH and other POP in plankton is essential to comprehend not only the POP fate and behavior in the water column, but also the accumulation of POPs in the trophic web.

[5] The objectives of this work are to i) provide the first extensive study of the occurrence of PAHs in western and eastern Mediterranean Sea and SW Black Sea, ii) assess the biogeochemical and physical drivers of PAH occurrence in seawater and plankton, iii) study the influence of compound's physical-chemical properties on their occurrence and cycling in the marine environment. This study is based on the largest data set available comprising samples from the dissolved phase, the particulate phase and plankton obtained from two sampling cruises. The first campaign was on June 2006 from Barcelona to Istanbul, and the second took place in May 2007 from Barcelona to Alexandria.

## 2. Materials and Methods

### 2.1. Sampling-Site Description

[6] The semi-enclosed Mediterranean Sea is characterized by evaporation exceeding precipitation and river runoff, which is compensated by the input of less saline Atlantic surface waters through the Strait of Gibraltar, leading to an increasing salinity eastwards, up to 10%. At the basin scale, the water masses are dominated by the thermohaline circulation, which at sub-basin has the influence of the heterogeneous bathymetry, atmospheric driven overturning and shelf-slope exchanges. However, there are limited exchanges of coastal waters with open sea surface waters. The Mediterranean can be divided in two sub basins, Western and Eastern basin, both connected though the Channel of Sicily and subdivided in different regions (i.e. North Western

Mediterranean Sea, South Western Mediterranean Sea and Tyrrhenian Sea in the Western basin; Ionian Sea, Central Mediterranean Sea, Levantine Basin and Aegean Sea in the Eastern basin). The Mediterranean exhibits a gradient of increasing oligotrophy from west to east, in terms of nutrient concentration [*Krom et al.*, 1991; *Lasternas et al.*, 2010], primary productivity [*Turley et al.*, 2000; *Regaudie-de-Gioux et al.*, 2009] and autotrophic biomass [*Pitta et al.*, 2001]. During the 2006 cruise, picoplankton was dominated by *Synechoccocus spp* and *Prochlorococcus spp*, while the microplankton was dominated by diatoms except in the SW Black Sea where dinoflagellates and flagellates were the predominant [*Lasternas et al.*, 2010].

[7] The smaller enclosed Black Sea is connected to the Marmara Sea through the Bosporus Strait, which is in turn connected to the eastern Mediterranean through Dardanelles. Unlike the Mediterranean Sea, the Black Sea precipitation and river runoff exceed evaporation, creating strong stratification in the water column in form of a strong halocline at about 100 m depth that separates a surface low-salinity layer from old anoxic waters. The fresher surface water flows out through the narrow and shallow Bosporus and Dardanelles Straits above some saltier incoming Mediterranean waters [*Millot and Taupier-Lestage*, 2005]. In the last three decades, an increasing nutrient supply has produced an increase in the productivity of the phytoplankton in the less saline upper part of the water column of the Black Sea [*Maldonado et al.*, 1999], reducing the biodiversity of its ecosystem to one characterized by frequent and pronounced phytoplankton blooms [*Oguz et al.*, 2001].

[8] Water and plankton samples were collected on board the R/V Garcia del Cid during two sampling cruises made on June 2006 and May 2007, within the framework of the European THRESHOLDS project. In both transects, Barcelona was the initial and final port, with Istanbul and Alexandria being the intermediate stops respectively (Figures 1a and 1b; see also Tables S2a, S2b, and S3a in the auxiliary material).[1]

### 2.2. Sample Collection

[9] Plankton samples (P) were taken at the sampling stations (fixed location) of both sampling cruises using a 50 $\mu$m mesh vertical plankton net tow, from 20 m below the deep chlorophyll maximum (DCM) to surface. The collected material was filtered with GF/D glass fiber Whatman filters (2.7 $\mu$m) to remove the excess water. Filters were frozen ($-18°C$) until the extraction process. In some cases, due to the small amount of the collected material, samples from geographically close stations were combined in order to get levels above detection limits of the used analytical methods. Organic carbon (OC) determination of five plankton samples representative of different biomass amount and regions was performed, giving an average OC content of 44% and ranging from 32.5% to 49.9%. Location of plankton and seawater samples is shown in Figure 1.

[10] Surface seawater samples (W), as shown in Figure 1b were taken using two similar methodologies. Figure 1b shows in dark blue transects using methodology A, and light blue transects using methodology B. In both cases surface water

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[1]Auxiliary materials are available in the HTML. doi:10.1029/2010GB003775.
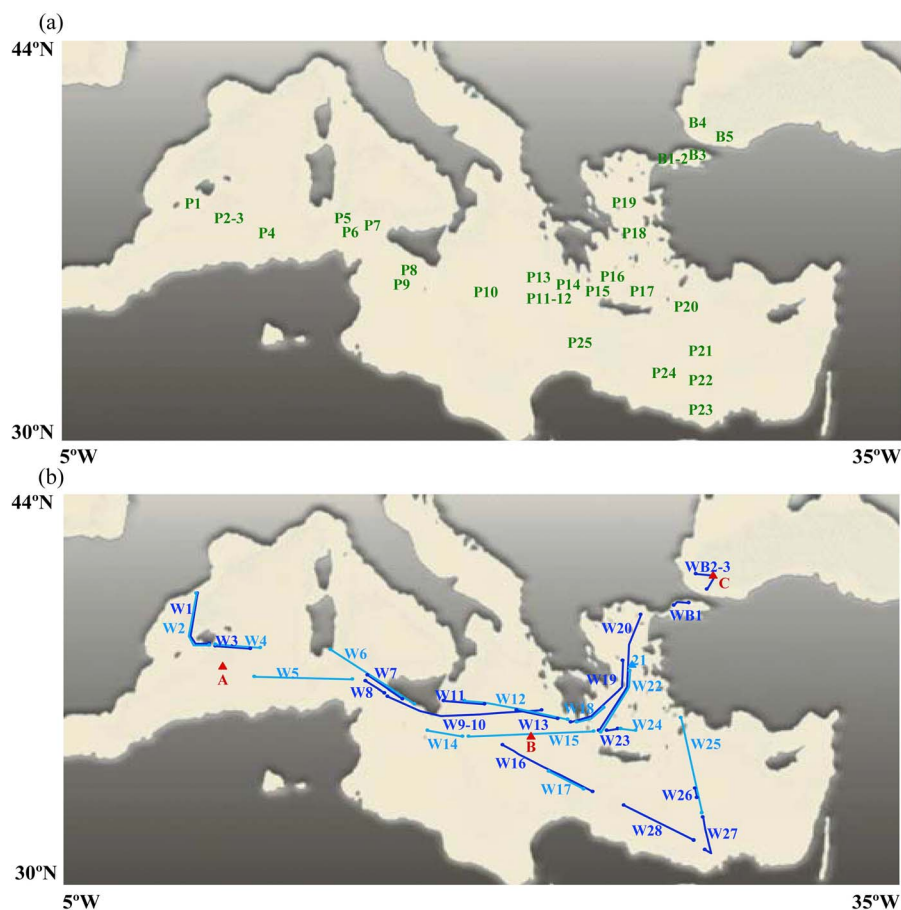
**Figure 1.**  Location of sampling sites for (a) plankton samples integrating the photic zone (P). (b) Surface Water samples (dissolved + particulates (W)) collected during transects (see Section 2 and auxiliary material). Transects in dark blue were those processed using methodology A, and light blue transects are those using methodology B.

was brought on board by using a continuous pumping system consisting of a steel protected Teflon hose connected to a tow fish that navigated at around 2–3 m depth and 3–4 m apart from the boat while travelling. A membrane pump (Wilden Pump & Engineering Co., Grand Terrace, USA) operating at 25 L/min was used to suck the seawater and fill in continuously a 50 L stainless steel overflow container.

[11]  Methodology A for seawater samples: Water samples were taken from the container through PTFE tubes using a peristaltic pump at 30 mL/min flow rate and filtered with glass fiber filters for particle collection before passing through stainless steel columns (2 cm i.d. × 300 mm length) packed with 50 g of Amberlite XAD-2 (Supelco) adsorbent for dissolved PAH sampling. The total volume of the different samples filtered through the system ranged from 90 L to 340 L. Before the sampling campaign, GF/F glass fiber Whatman filters (0.7 $\mu$m particle retention and 47 mm diameter) were pre-weighed and pre-combusted (350°C, 12 h) and the already Soxhlet precleaned adsorbent was sequentially cleaned and conditioned by passing 400 ml methanol and 200 ml dichloromethane through the columns from bottom to top of the column with a 2 ml/min flow rate. The columns were kept at 4°C and were processed within 10 days after the ending of each sampling cruise. Filters

were preserved frozen (−18°C) until chemical analysis. The rest of the analytical methods are shown in the main text of the manuscript, except blanks and recoveries that are shown in Figure S1 and Table S1.

[12]  Methodology B for seawater samples: The sample (250–350 L) was pumped at ca 200 mL/min with a LIQUIPORT ® KNF NF 1.100 FT.18 S PTFE-coated diaphragm pump (KNF FLODOS AG, Switzerland) through 8 mm i.d. PTFE tubing directly from the container over a pre-combusted Whatman GF/F glass fiber filter (0.7 $\mu$m particle retention and 293 mm diameter) and the filtrate extracted online by two 50 g XAD-2 filled stainless steel cartridges (100 mL, Dionex Cooperation, USA) connected in series. XAD-2 polymer was washed with water and pre-cleaned by Soxhlet extraction (methanol, acetone, hexane, acetone, methanol) before transferring into the stainless steel cartridges. Cartridges were cleaned by pressurized liquid extraction (PLE) using a Dionex accelerated solvent extractor (ASE® 300, Dionex Cooperation, USA) with methanol, hexane and methanol again (each 3 cycles with a static time of 5 min at 75°C, heat-up time of 5 min, a flush volume of 100%, a purging time of 60 s and a pressure of 1500 psi) before storing under methanol until sampling. Stainless steel taps were used for closing the cartridges for transport prior and post sampling

for minimizing contact with ambient air. The second XAD cartridge was applied for controlling eventual compound breakthrough. The GF/F filters were transferred for transport and storage in a 500 mL Schott Duran ® borosilicate bottle and frozen until further processing whereas the XAD cartridges were put in a fridge for storage and transport until processing.

[13] Seawater from DCM (WM) was collected at stations using an *in situ* filtration system (Infiltrex, Axys Environmental Systems Ltd, Sidney, Canada) connected to GF/F filters and stainless steel XAD columns.

## 2.3. Chemical Analysis

[14] All samples were analyzed for 19 PAHs: fluorene (Fluo), dibenzonthiophene (DBT), methyldibenzonthiophenes (MethDBT), phenanthrene (Phe), methylphenanthrenes (MethPhe), dimethylphenanthrenes (DimethPhe), anthracene (Anth), fluoranthrene (Flua), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Cry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Per), dibenzo[a,h]anthracene (DBaA), benzo[ghi]perylene (BghiP), indeno[1,2,3-cd]pyrene (InP). A mix containing 4 deuterated PAHs (Acenaphtene-d10, Phe-d10 Cry-d12 and Per-d12, Sigma-Aldrich) was used as surrogate standard.

[15] Dissolved phase samples were analyzed using a slight modification of the method described by *Dachs and Bayona* [1997]. A sequential elution of the XAD-2 columns was performed with 200 ml of methanol followed by 200 ml of dichloromethane from bottom to top of the columns using an axial piston pump with a 2 ml/min flow rate. All used tubes and connections are of stainless steel or PTFE and they were precleaned with acetone prior use in order to avoid contamination. Both extracts were spiked with 50 ng of the mix of surrogates. The methanolic fraction was concentrated by rotary evaporation to half the initial volume and was then submitted to liquid-liquid extraction with 25 ml hexane for three times. The hexane extracts were dried over anhydrous sodium sulphate, combined with the dichloromethane fraction and rotary evaporated for purification on a column filled with 1–2 g of anhydrous sodium sulphate over 3 g of 15% deactivated neutral alumina (aluminium oxide 90, activated at 400°C for 12 h). The elution of the column was made with 5 ml of hexane and 12 ml of hexane/dichloromethane (1:2, v/v) and collected in two separate fractions. The second fraction selected for PAH analysis was concentrated to 0.5 ml by vacuum rotary evaporation, transferred to a 1.7 amber vial with hexane and evaporated to 150 $\mu$l under a nitrogen stream. At this step, 50 ng of the internal standard Anth-d10 was added to the extract.

[16] Water filters containing the particle phase were freeze-dried during 24 h, weighed and Soxhlet extracted with hexane/dichloromethane (1:2, v/v) for 24 h. The extract was rotary evaporated to 2 ml, purified by column chromatography and treated as indicated for dissolved phase samples. Plankton filters were freeze-dried during 24 h, weighed and Soxhlet extracted with hexane/dichloromethane (1:2, v/v) for 24 h. Extracts were rotary evaporated, purified on a column filled with 1–2 g of anhydrous sodium sulphate over 5 g of silica gel (silica 60, 200 mesh, activated at 250°C for 24 h) and 3 g of 3% deactivated neutral alumina (aluminium oxide 90, activated at 250°C for 12 h) and eluted with 50 ml

of hexane/dichloromethane (1:2, v/v). The extract was concentrated to 0.5 ml by vacuum rotary evaporation, transferred to an amber vial and processed as indicated for water samples.

[17] PAH analysis was conducted by gas chromatography coupled to a mass spectrometer (Thermo Electron, San Jose, CA, USA) and compounds were quantified by the internal standard procedure. The system was operated in electron impact mode (EI, 70 eV) and with the splitless injection mode. The separation was achieved with a 30 m × 0.25 mm i.d. × 0.25 $\mu$m TRB-5MS capillary column (Teknokroma, Spain). The oven temperature was programmed from 90°C (holding time 1 min) to 175°C at 6°C/min (holding time 4 min) to 235°C at 3°C/min, then to 300°C at 8°C/min (holding time 8 min), and finally to 315°C at 3°C/min keeping the final temperature for 8 min.

[18] The analytical procedure for all sample matrices was validated by determining the recovery rates of the surrogates (see Figure S1). Moreover, field blanks were processed in parallel to the samples (see Table S1 and related information of Text S1 in the auxiliary material).

## 3. Results and Discussion

### 3.1. PAH Occurrence in Seawater

[19] $\Sigma_{19}$ PAH concentration in the dissolved phase ($C_{WD}$) ranged from 158 to 808 pg L$^{-1}$ in the Western Mediterranean, 161 to 8,797 pg L$^{-1}$ in the Eastern Mediterranean and 559 to 2483 pg L$^{-1}$ in the Marmara and Black Seas (Tables 1 and S2c). The highest PAH levels were in samples collected in Marmara and Black Seas, and near the Nile River mouth. These sites are in all cases highly influenced by maritime transport, coastal anthropogenic activity and riverine inputs.

[20] In general, the dissolved PAH concentrations show increasing concentrations from the western towards the eastern basin (Figure 2). Among the factors contributing to this gradient could be mentioned: a) The influence of the Atlantic water inflow [*Dachs et al.*, 1997; *Martí et al.*, 2001] contributing water masses with lower PAH concentrations; b) The hydrogeographic and bathymetric characteristics of enclosed areas of the Eastern Mediterranean such as the Aegean Sea and coastal pollution sources mainly in the Marmara and Black Seas and locally by the Nile river mouth; c) Biogeochemical processes. In the Mediterranean oligotrophic waters, organic carbon and nutrients are remineralized and recycled efficiently within a complex microbial food web [*Siokou-Frangou et al.*, 2002] in the photic zone, thus leading to longer POP residence times and higher concentrations in the water. During the Thresholds cruises there was a trend of higher gross primary productivity in the western basin than in the eastern basin, even though it was not statistically significant, and a general tendency to net heterotrophy [*Regaudie-de-Gioux et al.*, 2009]. In addition, Chlorophyll concentrations at DCM were higher in the western basin than in the eastern Mediterranean. This scenario is consistent with a more efficient recycling of pollutants at the eastern basin and a consequent less effective depletion of dissolved POPs through particle settling and degradation. Besides, higher biomass in the west can lead to deplete $C_{WD}$ due to partitioning to particulate organic matter [*Dachs et al.*, 2002].
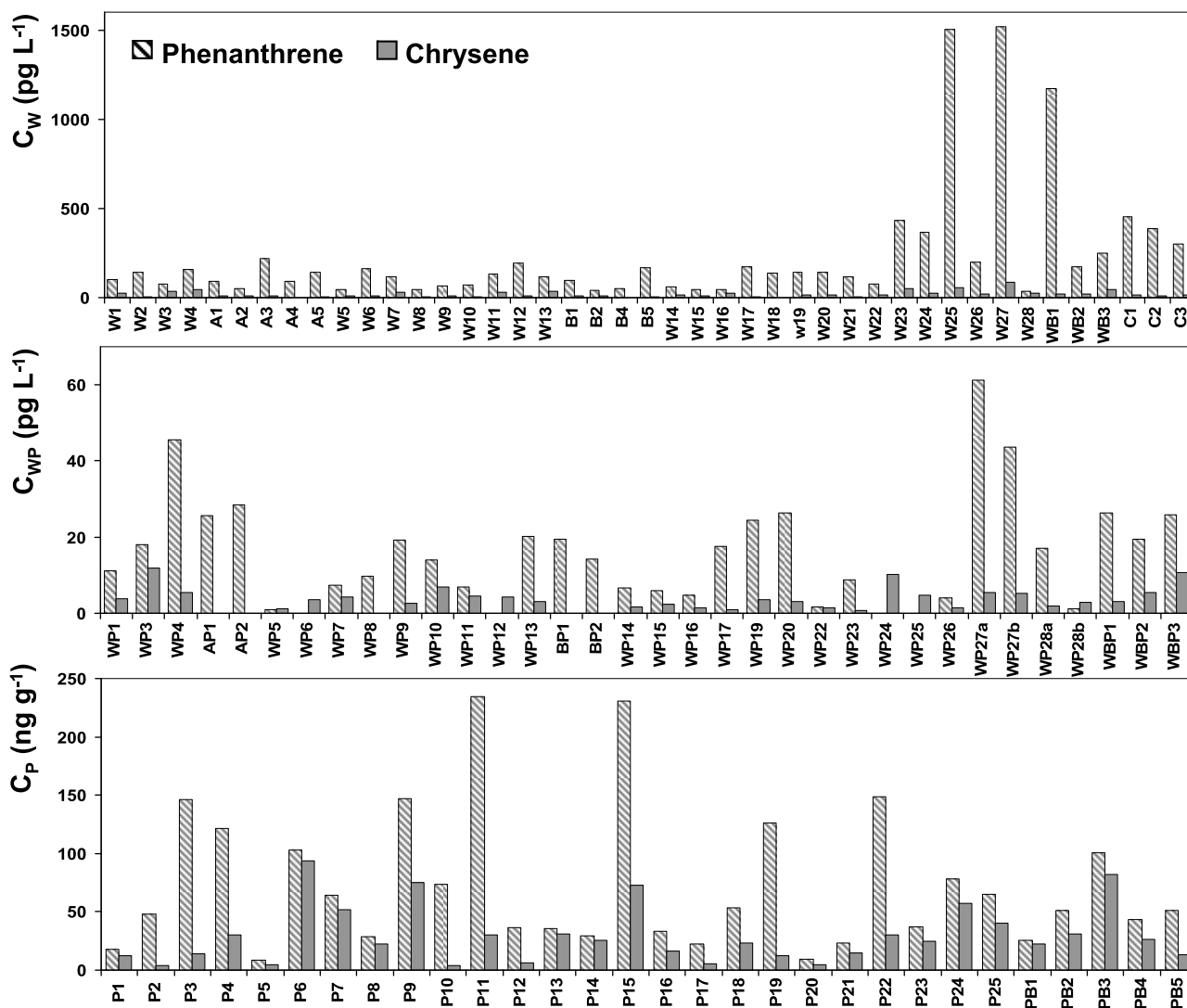
**Figure 2.** Spatial variation of the concentrations of two different PAH in the different samples of (top) dissolved ($C_{WD}$), (middle) particulate ($C_{WPdw}$) and (bottom) plankton phases ($C_P$) (see Figure 1 for location of samples and samples' codes; see also Figure S3 in the auxiliary material).

[21] Among individual PAHs, Phe (phenanthrene) was the most abundant compound, which is in agreement with previous reports [*Ehrhardt and Petrick*, 1993; *Dachs et al.*, 1997; *Tsapakis et al.*, 2006] with a general profile dominated by low molecular weight PAHs (Table 1). The MethPhe (methylphenanthrenes) to Phe ratios (MethPhe/Phe) are useful to provide information on PAH sources (see Figure S2 in the auxiliary material). In general, the predominance of Phe among its alkylated homologues observed in most samples could be attributed to a pyrolytic origin [*Ehrhardt and Petrick*, 1993]. Atmospheric aerosols are a potential important source of pyrolytic PAHs [*Lipiatou et al.*, 1997]. However, local high values of MethPhe to Phe ratios in some samples suggest an additional petrogenic origin due to a probable maritime transport source and cleaning ballast of ship fuel tanks in samples from the 2007 cruise in the E. and SE Mediterranean. PAH concentrations from dissolved phase collected at the DCM ($C_{WM}$) were in all sampling locations higher than the homologous samples collected at surface (see Text S3 in the auxiliary material).

[22] Regarding the particulate fraction collected simultaneously with the dissolved phase, the $\Sigma_{19}$ PAH concentrations ($C_{WP}$) ranged from 33 to 369 pg L$^{-1}$ in the Western Mediterranean, 33 to 319 pg L$^{-1}$ in the Eastern Mediterranean and 122 to 105 pg L$^{-1}$ in the Marmara and Black Seas (Tables 1 and S2d). The highest values in concentrations of PAHs in particles were measured near Mallorca's coast in May 2007 (W3) and in the surroundings of the Nile River (W27a, W27b). Concentrations of PAHs in particles collected at DCM are also shown in Text S3 in the auxiliary material (Table S3b). Particle phase concentrations can also be given as dry weight concentrations ($C_{WPdw}$), which are shown in Figure 3. This figure shows that for the compounds with mid-high hydrophobicities (up to five aromatic rings) there is a decrease of these concentrations when TSP concentrations are high (see discussion below), while they are fairly constant for the lower MW compounds.

[23] The PAH profiles in the particulate fraction were different than those found for the dissolved fraction. The predominant individual PAHs were MethPhe (36%), fol-

**Table 1.** PAH Concentrations (Mean and Range) in the Different Matrices (Dissolved, Particulate, and Plankton)

| Compound | Dissolved Phase (pg L$^{-1}$) | | | | Particulate Phase (pg L$^{-1}$) | | | | Plankton Samples (ng g$^{-1}$ Dry Weight Basis) | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Mediterranean Sea (n = 35)[a] | | Black Sea and Marmara Sea (n = 6) | | Mediterranean Sea (n = 20)[a] | | Black Sea and Marmara Sea (n = 3) | | Mediterranean Sea (n = 35) | | Black Sea and Marmara Sea (n = 6) | |
| | Mean | Range | Mean | Range | Mean | Range | Mean | Range | Mean | Range | Mean | Range |
| Fluorene | 82.24 | (9.80–584.27) | 289.06 | (64.35–495.70) | 13.80 | (2.68–45.99) | 17.59 | (8.09–25.38) | 17.39 | (0.00–49.65) | 14.51 | (4.80–25.86) |
| DBT | 12.55 | (0.00–57.33) | 67.45 | (0.00–254.40) | 3.77 | (0.08–28.85) | 2.22 | (0.00–2.62) | 8.63 | (0.00–38.91) | 1.73 | (0.00–6.31) |
| ∑MethylDBT | 22.61 | (0.00–230.86) | 43.95 | (0.00–178.20) | 4.28 | (0.00–18.23) | 1.92 | (0.00–3.37) | 19.92 | (0.00–97.39) | 3.77 | (0.00–14.77) |
| Anthracene | 7.26 | (0.00–36.70) | 13.07 | (4.88–22.58) | 0.50 | (0.00–2.29) | 1.66 | (0.00–1.66) | 8.49 | (0.00–42.25) | 2.30 | (0.00–6.92) |
| Phenanthrene | 163.43 | (38.19–1504.7) | 456.07 | (174.53–1172.13) | 16.22 | (1.12–43.65) | 23.91 | (19.48–26.37) | 77.33 | (8.88–234.52) | 54.45 | (25.29–100.57) |
| ∑MethylPhe | 82.83 | (0.00–1287.16) | 74.90 | (0.00–311.02) | 44.25 | (3.54–157.90) | 14.85 | (6.64–24.38) | 106.16 | (6.25–447.73) | 60.47 | (29.51–122.58) |
| ∑DimethylPhe | 64.16 | (0.00–888.58) | 39.25 | (0.00–132.27) | 6.73 | (0.00–44.78) | 4.77 | (3.17–7.40) | 87.24 | (4.19–417.87) | 52.54 | (12.33–142.97) |
| Fluoranthene | 62.26 | (13.00–198.94) | 174.95 | (89.41–237.66) | 4.92 | (0.77–16.55) | 8.16 | (4.02–12.35) | 31.89 | (4.46–224.20) | 43.33 | (24.83–109.81) |
| Pyrene | 59.68 | (7.78–387.43) | 31.66 | (9.22–73.02) | 8.49 | (0.64–32.74) | 8.00 | (4.73–13.75) | 36.60 | (1.91–251.42) | 37.18 | (17.42–90.95) |
| Benzo[a]anthracene | 4.78 | (0.00–43.04) | 1.58 | (0.74–3.85) | 0.82 | (0.00–6.98) | - | | 8.84 | (1.39–29.57) | 11.48 | (5.71–23.42) |
| Crysene | 16.85 | (1.83–54.65) | 22.36 | (12.56–47.73) | 3.79 | (0.77–11.78) | 6.43 | (3.17–10.72) | 27.79 | (3.79–93.45) | 35.09 | (13.38–81.70) |
| Benzo[b]fluoranthene | 5.92 | (0.00–73.33) | 7.24 | (3.11–13.14) | 3.80 | (0.00–23.22) | 5.85 | (3.98–6.93) | 23.23 | (0.00–117.48) | 66.83 | (0.00–147.74) |
| Benzo[e]pyrene | 5.32 | (0.00–29.41) | 2.96 | (0.96–5.33) | 2.70 | (0.43–7.16) | 3.97 | (2.66–5.09) | 7.65 | (0.00–42.20) | 10.97 | (0.00–29.16) |
| Benzo[a]pyrene | 3.13 | (0.00–43.27) | 0.44 | (0.10–1.02) | 2.52 | (0.00–11.77) | 4.47 | (3.10–6.45) | 7.94 | (0.00–33.99) | 6.74 | (0.00–11.55) |
| Perylene | 1.59 | (0.00–11.70) | 0.10 | (0.00–0.31) | 5.93 | (0.23–12.52) | 8.58 | (5.60–10.15) | 3.82 | (0.00–12.41) | 10.16 | (0.00–29.16) |
| Dibenzo[a,h]anthracene | 3.44 | (0.00–28.78) | 3.21 | (0.00–5.34) | 2.52 | (0.00–6.22) | 4.11 | (0.00–4.11) | 4.15 | (0.00–27.03) | 2.00 | (0.00–7.47) |
| Benzo[ghi]perylene | 3.14 | (0.00–15.78) | 0.82 | (0.00–3.35) | 0.07 | (0.00–0.79) | - | | 0.20 | (0.00–4.69) | 0.92 | (0.00–4.62) |
| Indeno[1,2,3-cd]pyrene | 4.08 | (0.00–28.53) | 1.43 | (0.50–1.76) | 12.93 | (0.00–50.54) | 3.22 | (0.00–3.94) | 3.89 | (0.00–16.03) | 5.31 | (0.00–22.03) |
| ∑ PAHs | 605.28 | (158.3–3655.9) | 1230.51 | (559.94–2483.14) | 129.11 | (33.34–380.26) | 114.04 | (121.89–105.01) | 605.28 | (158.36–3655.96) | 1230.5 | (559.94–2483.14) |

[a]Values corresponding to the water (W$_{27}$ and W$_{27a}$) collected near the Nile River mouth are not included.

lowed by Phe and DimethPhe (dimethylphenanthrenes), accounting for 10% and 4% of the total amount of PAHs in total suspended particles (TSP), respectively. In addition, the abundance of mid and high MW PAHs is also higher in the particle phase than in the dissolved phase. This distribution is consistent with what was found in previous studies along the Mediterranean Sea [*Dachs et al.*, 1997; *Martí et al.*, 2001]. In general, MethPhe to Phe ratios indicate an uncombusted fossil fuel origin (see Figure S2b) although other biogeochemical factors such as preferential accumulation in plankton [*Berrojalbiz et al.*, 2009] and biogenic sources occurring in the water column [*Nizzetto et al.*, 2008] could explain the high abundance of methylated PAHs in water particles.

[24] The comparison of the concentrations in dissolved and particle phase for the two sampling cruises shows no significant differences in parent concentrations of PAHs, while the 2007 samples showed higher predominance of methylated PAHs, but this could be due to the influence of an important variability in these compounds due to occasional inputs from ship ballasts, etc. In this sense, alkylated PAHs may be more affected by recent sources (spills, biogenic…) while parent PAHs show less inter-annual variability.

## 3.2. PAH Occurrence in Plankton

[25] $\Sigma_{19}$ PAH concentrations in plankton samples ($C_P$) ranged from 57 to 831 ng g$^{-1}$ (dry weight basis) in the Western Mediterranean and from 548 to 1903 ng g$^{-1}$ in the Eastern Mediterranean (Tables 1 and S2e). The highest levels have been found in the sample taken in 2006 in the outer part of the Aegean Sea (P15) and in plankton corresponding to the sampling located at 20 km from Nile River mouth (P22). The latter is in agreement with the high concentrations found in the dissolved phase at this coastal region. In the Marmara and Black Seas, $C_P$ ranged from 560 to 2486 ng g$^{-1}$, being these concentrations similar than in the eastern Mediterranean.

[26] In general, PAH concentrations in plankton samples were dominated by Phe, representing a mean of 16% of the total PAHs and its alkylated homologues, MethPhe and DimethPhe (21% and 17% respectively). As mentioned above for particle phase PAHs, MethPhe to Phe relative abundance and ratios are different than in the dissolved phase due to: i) higher microbial degradation of methylated PAHs than parent compounds as suggested elsewhere [*Lipiatou et al.*, 1993; *Dachs et al.*, 1997]; ii) the higher accumulation potential of alkylated PAH in phytoplankton and zooplankton [*Berrojalbiz et al.*, 2009]. *Nizzetto et al.* [2008] suggested a potential biological origin of low MW PAHs. However, in our data set, no single PAH concentration increased at higher biomass or higher chlorophyll concentration, so these biogenic sources, if exist, are masked by the other processes.

[27] The regional variability in the PAH concentration in plankton samples does not exhibit the clear increasing tendency that could be observed in seawater from western to eastern Mediterranean basin. Indeed, with the exception of the sample taken in Bosporus Strait near the city of Istanbul (PB3) where total PAH concentrations in plankton are higher presumably due to the influence of the urban/industrial activity and intense maritime transport, PAH concentrations in plankton samples from Marmara and Black Seas are similar in quantity to those found in Aegean Sea. Nevertheless, the

$C_P$ (Table S2e and Figure 4) shows a tendency for higher concentrations at low biomass (B) for some PAH, where B is the dry weight of samples recovered from the nets. This sampled biomass approximately equals organic matter since the average organic carbon content of plankton samples was of 44%. Therefore, for both PAHs in particles and plankton, there is a dependence of dry weight concentrations on TSP or biomass, but there are significant differences between surface particulates and integrated photic zone plankton. Before these differential behavior is commented, it is necessary to review the current knowledge on the factors driving PAH occurrence in particles and plankton.

## 3.3. PAH Concentration Dependence on the Amount of Particles and Plankton Biomass

### 3.3.1. Theoretical Considerations

[28] It is important to gain knowledge on the role that biogeochemical and physical controls play on the occurrence of PAHs in seawater and their accumulation in plankton since they are key processes affecting the cycling and impact of these compounds in oceans. Figure 5 shows the dominant processes influencing the occurrence of PAH in surface particulates and plankton from the photic zone. Among them, it could be distinguished between i) physical processes such as water column mixing and atmosphere-ocean exchange of PAHs, and ii) processes with a biogeochemical nature due to the close relationship between PAH and organic matter cycles such as: uptake and depuration in phytoplankton and bacteria, accumulation in zooplankton, biodegradative activity in bacteria and zooplankton, sorption to the different pools of particle matter (organic carbon, soot carbon,…) and settling to deeper waters. The relationship between PAH concentrations and plankton biomass can be derived theoretically by considering four extreme cases of environmental behavior following the processes shown in Figure 5 and considering the type of sample; superficial TSP or plankton samples integrated for the photic zone.

### 3.3.1.1. Case A

[29] Given a hypothetical water volume that contains a constant amount of chemical ($C_{Total}$ pg L$^{-1}$), with no inputs and losses, then the chemical will partition between the dissolved and particulate or plankton phase. Assuming that the mass of PAHs is constant per unit of volume of water, and equals $C_{Total}$, then $C_{Total} = C_{WD} + C_{WP}$ where $C_{WD}$ and $C_{WP}$ are the PAH concentrations (ng L$^{-1}$) in the dissolved and particulate phases respectively, and $K_P$ is the particle-water partition coefficient,
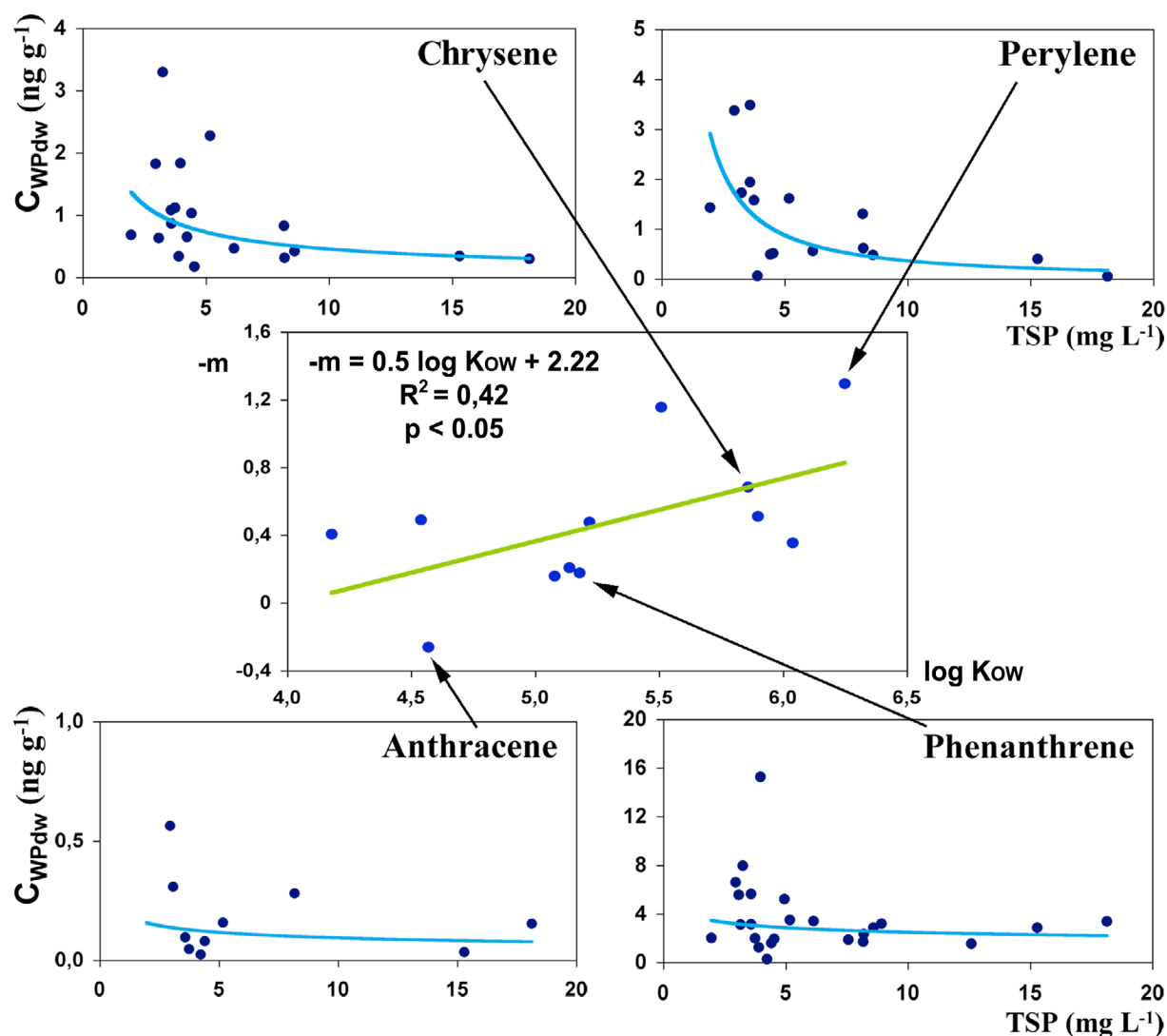
$$K_P = \frac{C_{WP}}{C_{WD} \cdot TSP} \tag{1}$$

where TSP is the total suspended particles (g L$^{-1}$). Then:

$$C_{Total} = \frac{C_{WP}}{K_P \cdot TSP} + C_{WP} = C_{WP} \cdot \left( \frac{1}{K_P \cdot TSP} + 1 \right). \tag{2}$$

[30] Correcting $C_{WP}$ by the concentration of particles, we obtain $C_{WPdw} = C_{WP}/TSP$, which is the dry weight particle phase concentrations, then it is derived that

$$C_{WPdw} = C_{Total} \cdot \frac{K_P}{1 + TSP \cdot K_P} \tag{3}$$

**Figure 3.** Concentrations of four individual PAHs in particle matter ($C_{WPdw}$) versus TSP. The center plot shows the values of the slope ($m$) for each individual PAH versus $K_{OW}$.

Analogously, and by defining the BCF as

$$BCF = \frac{C_P}{C_{WD} \cdot Biomass} \qquad (4)$$

We derive that:

$$C_P = C_{Total} \cdot \frac{BCF}{1 + Biomass \cdot BCF}. \qquad (5)$$

[31] Therefore, depending on whether the factor ($TSP \times K_P$) or ($Biomass \times BCF$) is significantly higher than unity the dry weight concentrations will be inversely correlated to TSP or biomass, due to dilution effect (Figure 6a), or on the contrary, they will be constant. This process will gain importance during phytoplankton blooms when phytoplankton biomass could be the predominant process explaining dilution. In addition, BCF are lower during periods of intensive phytoplankton growth [*Del Vento and Dachs*, 2002].

### 3.3.1.2. Case B

[32] Air-water exchange is one of the main pathways for entry and loss of POPs in the ocean compartment [*Dachs et al.*, 2002, 1999]. If PAHs in gas phase are equilibrated with the dissolved phase which in turn is equilibrated with particles or plankton, for a given gas phase concentration, PAH dry weight concentrations ($C_{WPdw}$ or $C_P$) will be independent of TSP or B (Figure 6b) and will be given by:

$$C_{WPDW} = \frac{C_{Gas} \cdot K_P}{H'} \qquad (6)$$

$$C_P = \frac{C_{Gas} \cdot BCF}{H'} \qquad (7)$$

where H′ is the dimensionless Henry's Law constant corrected for temperature and the salting out effect. This process should gain importance in the surface ocean mix layer which is directly affected by atmosphere-ocean diffusive exchange and in conditions favoring a fast air-water equil-
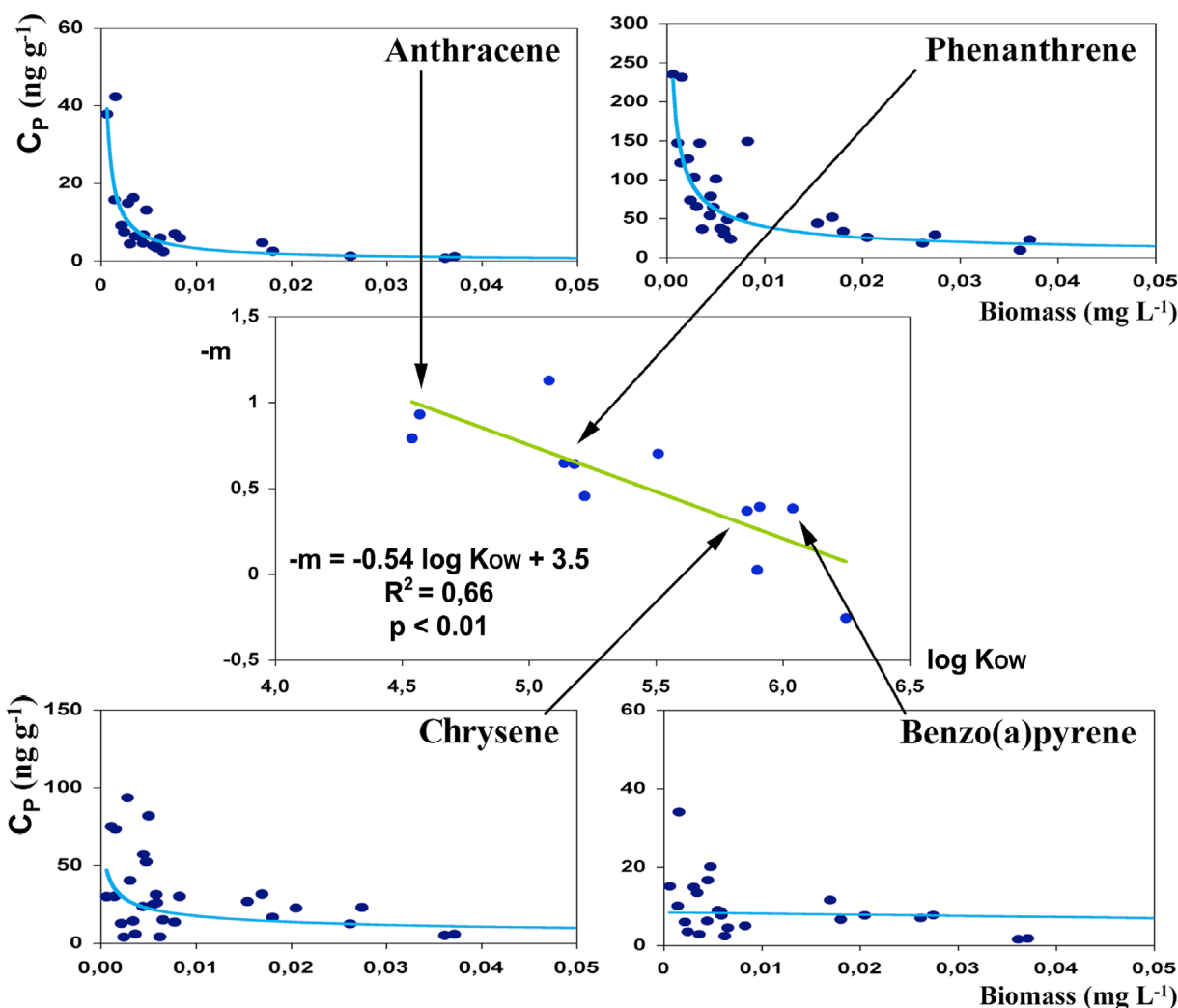
**Figure 4.** Concentrations of four individual PAHs in the plankton phase ($C_P$) versus biomass (B). The center plot shows the values of the slope ($m$) for each individual PAH versus $K_{OW}$.

ibration (high wind speeds). Therefore, this process can have an effect for the particle phase samples since these were taken at 2–3 m depth, but on the contrarily, since most phytoplankton was below the thermocline during the THRESHOLDS sampling cruises (see chlorophyll profiles in the auxiliary material), then most biomass is not permanently in contact with the atmosphere.

#### 3.3.1.3. Case C

[33] Another extreme hypothetical case is when settling fluxes are important and losses associated to sinking organic matter or soot carbon are faster than air-water-plankton transfer. In this case, concentrations in particles or plankton will decrease at higher TSP or B (due to settling of particles) following a non-linear behavior, as has been reported elsewhere [*Dachs et al.*, 1999, 2000, 2002]. This effect will be more important for the more hydrophobic pollutants, and not significant for the chemicals with low hydrophobicities (Figure 6c).

#### 3.3.1.4. Case D

[34] The fourth extreme scenario considers the losses of the chemical associated with degradation processes in the photic zone due to bacteria, zooplankton or photodegradation. The concentration of PAH in plankton ($C_P$) reported here are a combination of concentrations in zooplankton and phytoplankton. In this sense, it is important to consider food chain transfer of PAHs to zooplankton and how zooplankton processes PAHs. While in simpler organisms such as bacteria or phytoplankton the accumulation is characterized by simple passive diffusion (bioconcentration mechanism controlled by passive diffusion to/within the cell) [*Bouloubassi et al.*, 2006], for zooplankton, the accumulation of PAH, depends on different processes modeled by [*Berrojalbiz et al.*, 2009]:

$$\frac{dC_{Zoo}}{dt} = k_u \cdot C_W + k_{Food} \cdot C_W - k_d \cdot C_{Zoo} - k_{Eg} \cdot C_{Zoo} - k_{Met} \cdot C_{Zoo}$$

$$(8)$$

where $C_{Zoo}$ is the PAH concentration in zooplankton (ng kg$^{-1}$), $k_u$ is the uptake constant due to diffusive uptake (m$^3$ kg$^{-1}$ d$^{-1}$), $k_{Food}$ is the uptake constant due to feeding on phytoplankton (m$^3$ kg$^{-1}$ d$^{-1}$), $k_d$ is the diffusive depuration constant (d$^{-1}$), $k_{Eg}$ is the depuration due to eges-
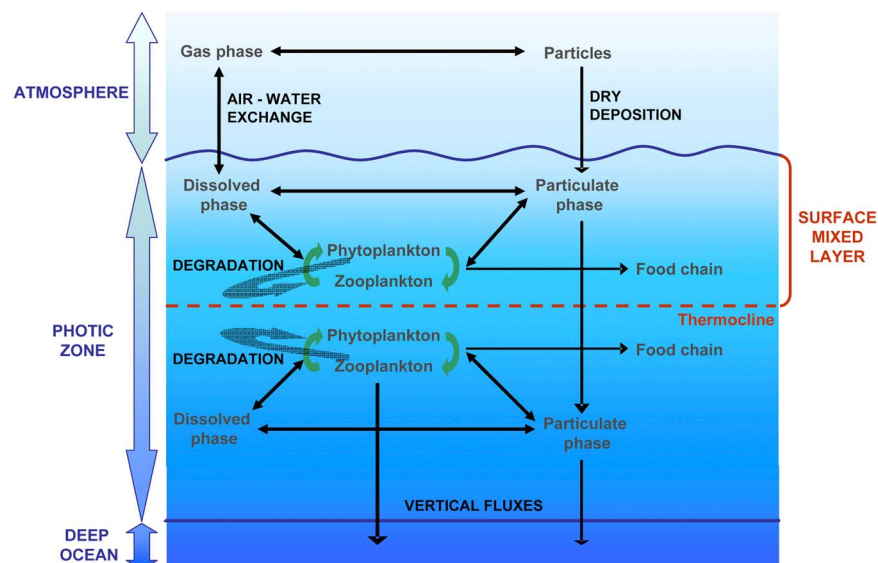
**Figure 5.** Schematics of the physical and biogeochemical processes affecting surface concentrations of dissolved and particle phase PAHs and plankton PAHs in the photic zone.

tion of fecal pellets and laying of eggs ($d^{-1}$), and $k_{Met}$ is the depuration due to metabolization of PAHs ($d^{-1}$). *Berrojalbiz et al.* [2009] have shown that for low MW PAHs, for which metabolization is an important loss process, PAH plankton phase concentrations are inversely related to the biomass (Figure 6d) [see *Berrojalbiz et al.*, 2009, equation 23 and Figure S5]. It is noteworthy that even though in equations (4), (5), and (7) we used the BCF, the accumulation of PAHs in zooplankton from feeding on phytoplankton is feasible [*Berrojalbiz et al.*, 2009], then the bioaccumulation factor (BAF) could have been used in equations (4), (5), and (7).

[35] These four scenarios are the dominant known interactions of physical and biogeochemical processes affecting PAHs in the water column. It is possible that there are other relevant processes, but that are yet poorly understood. One of these could be the influence of soot carbon on PAH cycling in the water column. Briefly, there are two competing relevant phases in the water column, the organic carbon and the soot carbon. The particle-water partitioning can be described by:

$$K_P = \frac{f_{OC} \cdot K_{OW}}{d_{Oct}} + f_{EC} \cdot K_{SW} \qquad (9)$$

where $f_{OC}$ and $f_{EC}$ are the fractions of organic carbon and soot carbon, respectively, $K_{OW}$ and $K_{SW}$ are the octanol-water and soot-water partition coefficients, and $d_{Oct}$ is the density of octanol [*Gustafsson et al.*, 1996]. If $f_{OC}$ is high, then the overall partitioning will be dominated by the organic carbon since the ratio $f_{OC} K_{OW}/(d_{Oct} f_{EC} K_{SW})$ will be higher than unity. However, if $f_{OC}$ is small, then the influence of partitioning to soot will have a bigger relevance. Analogous reasoning has been used for assessing the relative importance of soot and organic carbon in gas-particle partitioning and its implications for the fate of deposited aerosol bound PAHs to the marine environment [*Dachs and Eisenreich*,

2000]. In fact, for PAHs with more than five aromatic rings, dry soot aerosol deposition is the predominant source to the water column, and due to the strong PAH-soot adsorption, it is possible that these chemicals are barely available for phytoplankton.

[36] It should be envisaged that due to the complex environmental processes (see Figure 5) all scenarios with interactions between these four cases are possible and thus situations in the middle than those shown in Figure 6 can occur. Therefore, the predicted relationship between particle and plankton phase concentration could be fitted to the power law equations:

$$C_{WPdw} = a \, TSP^{-m} \qquad (10)$$

$$C_P = a \, B^{-m} \qquad (11)$$

being the slope $m$ between zero and unity when fitted to field data sets.

### 3.3.2. Extent of Apparent Dilution Effect in the Field Data

[37] Measured particle and plankton phases PAH concentrations versus TSP and B, respectively, are shown for several representative PAHs in Figures 3 and 4 (see also Figure S4 in the auxiliary material). After regression analysis, it is found that $C_{WPdw}$ (ng $g^{-1}$) decreased with increasing TSP (mg $L^{-1}$) following equation (10) where $a$ and $m$ are constants depending on the individual PAHs properties (Figure 3). The slope $m$ was significantly different than zero for most PAHs with four or more aromatic rings. Similarly, PAH concentrations in plankton ($C_P$ [ng $g^{-1}$]) correlate with planktonic B (mg $L^{-1}$) following equation (11) (Figure 4). Thus, the PAH concentration decreases as TSP or B increase although the $m$ value depends on the compound physical-chemical properties. As an additional confirmation of the key importance of B and $K_{OW}$ as the variables explaining the variability of plankton phase PAH, principal component
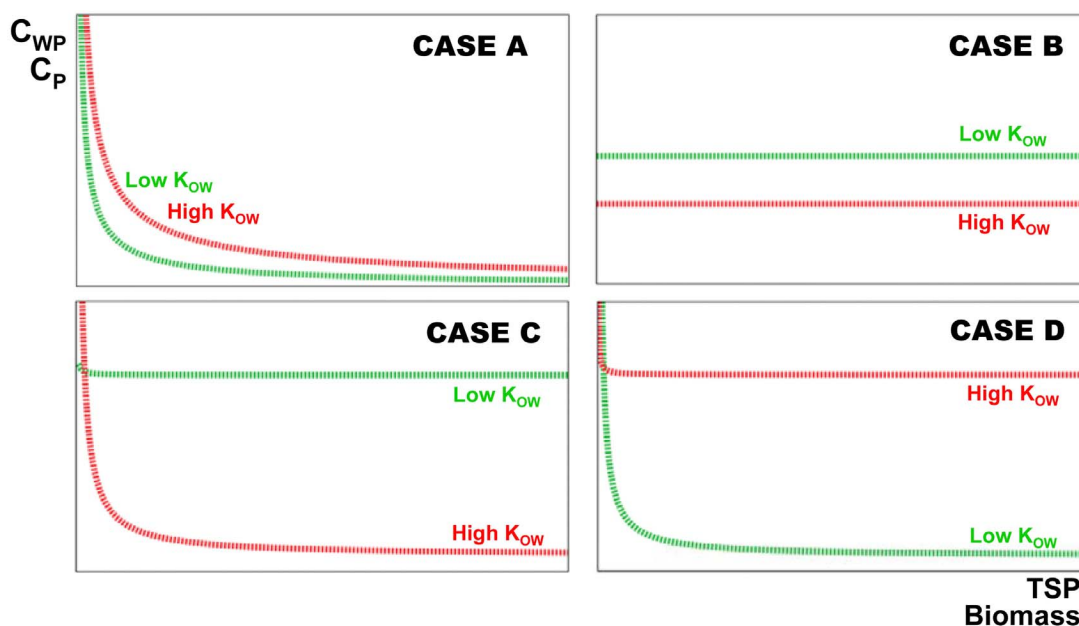
**Figure 6.** Qualitative prediction of the dependence of particulate or plankton phase PAH concentrations ($C_{WP}$ and $C_P$ respectively) versus TSP of B for (a) biodilution, (b) air-water-plankton equilibrium, (c) water column depleted concentrations due to settling fluxes, and (d) degradative processes.

analysis (PCA) was performed on the field concentrations (see Text S4 in the auxiliary material). After a pre-treatment of the plankton phase concentrations by subtracting the mean and normalizing by the standard deviation, the PCA showed that the first two principal components (PC1 and PC2) explained 51 and 21%, respectively, of the variability of the data set (see auxiliary material for related PCA analysis). Exploratory analysis of the factors correlated with the two principal components showed (Figure 7) that PC1 is correlated with B while PC2 is correlated with $K_{OW}$. Similar results can be obtained by performing the PCA of particle phase PAH concentrations, where the first component is correlated to TSP. These finding are in agreement with what was found by Taylor and co-workers in Lakes of Canada [*Taylor et al.*, 1991] who described that particle phase PCB concentrations decreased at high biomass.

[38] The value of *m* is indicative of the influence of the extent of the decrease of the concentrations of a particular compound at high TSP or B. Therefore, higher *m* values would suggest a higher influence of the particle load on the chemical concentration, while lower *m* values imply that PAH concentrations are independent of TSP or B. PCA analysis suggested that $K_{OW}$ is a key physical chemical property affecting the extent of the dilution effect. Likewise, it is well known that $K_{OW}$ is a descriptor of partitioning processes of organic matter. Thus, *m* values for each compound were plotted against the corresponding $K_{OW}$. Figures 3 and 4 show the results for particles and plankton samples, respectively. While Figure 3 (middle) shows higher *m* values as the compounds hydrophobicity increases ($R^2 = 0.41$; $p < 0.05$), Figure 4, showing the results for plankton, indicates a decrease of *m* with increasing $K_{OW}$ ($R^2 = 0.66$; $p < 0.01$) hence suggesting a decrease in the influence of biomass for the more hydrophobic compounds (up to five aromatic rings).

[39] The different behavior of individual PAHs depending on the particle amount (TSP or B) is to great extent related to the nature of the samples and to the fact that TSP was collected at the surface (2 m depth) while plankton corresponds to integrated samples for the photic zone. In addition, TSP is collected on GFF filters (mesh size of 0.7 $\mu$m), while plankton samples were collected with 50 $\mu$m nets, even though smaller material can also be collected. In addition, the OC content of plankton samples is high 44%, while that of TSP is significantly lower. Small particles are composed mainly by inorganic material, detritus, phytoplankton organisms and maybe some bacterial influence, in bigger particles phytoplankton aggregates and small zooplankton species dominate [*Valiela*, 1995]. Taking into account the nature of the samples (Figure 5), it is then possible to discuss the biogeochemical and physical drivers of the occurrence of PAH in particles and plankton by considering the four cases or extreme scenarios pointed out before.

### 3.3.3. Drivers of PAH Occurrence in Particles

[40] If case A (dilution effect) was explaining the dependence of PAH concentration in TSP, then the value of *m* would be the same for all compounds, but conversely, the decrease of concentrations is only observed as the compounds hydrophobicity increases. Therefore, case C is the most suitable candidate to explain the observed trends. In this scenario, there is a depletion of concentrations due to airwater disequilibria driven by particulate settling fluxes for most hydrophobic PAHs (Figure 6c). On the contrary, for less hydrophobic compounds, there are conditions close to air-water-particle equilibrium (Figure 6c).

[41] The partitioning between particulate and dissolved phase PAH ($K_P = C_{WPdw}/C_{WD}$) shows a correlation with $K_{OW}$ which means that the more hydrophobic PAH have higher fractions of sorbed chemical (see Text S5 in the
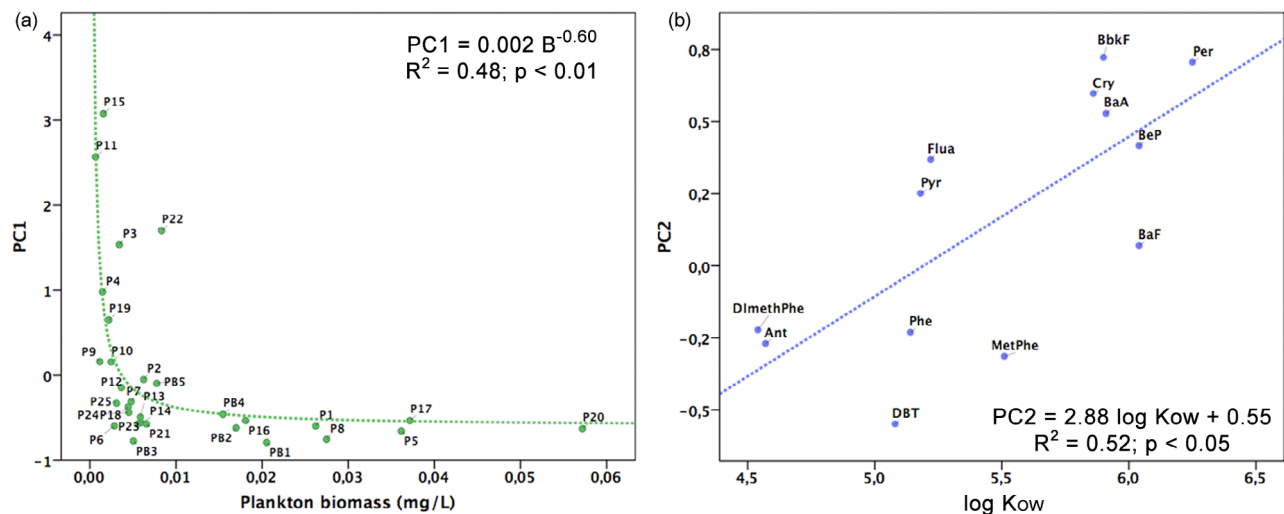
**Figure 7.** Results of Principal component Analyses (PCA) for PAH concentrations in plankton ($C_P$). (a) PC1 versus biomass, B, and (b) PC2 versus $K_{OW}$.

auxiliary material). When the amount of particles is higher, enhanced settling fluxes induce a depletion of PAHs in the water column [*Dachs et al.*, 2000] by scavenging and thus depleting the water concentrations of the more hydrophobic compounds. On the contrary, for less hydrophobic PAHs, any potential depletion of dissolved phase PAH is compensated due to a faster air-water exchange [*Dachs et al.*, 2002, 2000]. *Tsapakis et al.* have shown that absorption of PAHs in seawater is a major inflow process in the eastern Mediterranean basin [*Tsapakis et al.*, 2006] and may be the dominant input in all the open Mediterranean Sea. In this scenario, it is unclear which could be the influence of soot carbon. Unfortunately, the spatial variability and cycling of soot carbon in the water column is unknown due to lack of appropriate methods for soot determination in dilute water samples. However, as commented above, when the amount of particles is high, presumably the influence of soot carbon is negligible [*Dachs and Eisenreich*, 2000]. Case C scenario also implies lower dissolve phase concentration due to depletion of the water column by sinking fluxes [*Dachs et al.*, 2000]. In fact, $C_{WD}$ concentrations showed lower averages and variability at high TSP values than at low TSPs (see auxiliary material).

[42] The dynamic coupling between air-water exchange and particle settling may only affect the top meters of the water column, not below the thermocline [*Jurado et al.*, 2007; *Dachs et al.*, 2002]. Therefore, this coupling is not an effective phenomena affecting the PAH concentrations in the plankton phase, since most plankton was sampled below the thermocline where the phytoplankton biomass was located (see Figure S8 in the auxiliary material).

### 3.3.4. Drivers of PAH Occurrence in Plankton

[43] The *m* values when fitting equation (11) to field data are lower when increasing $K_{OW}$ (Figure 4, middle) and thus it differs from PAHs in superficial TSP. *m* values are higher for the low MW PAHs, contrarily to that predicted by equation (5) for the dilution effect. In addition, the OC content of plankton samples is not correlated with B, suggesting that results shown in Figure 4 are not induced by

differences in OC content. Several studies have shown various processes that can lead to an enhanced dilution for the more hydrophobic compounds (case C or A). However, the trend reported here is not consistent with that described by others [*Taylor et al.*, 1991; *Larsson et al.*, 2000; *Dachs et al.*, 2000] since in our case the effect is more pronounced for the less hydrophobic compounds. The only known process capable of leading to the observed trends is the scenario considered in case D where PAH degradation processes gain importance. Several studies have reported evidence for important losses, presumably due to degradation, of PAHs in the marine environment. *Lipiatou et al.* [1993] described selective degradation of low MW PAHs such as methylphentrenes in settling particles during vertical transport., Likewise, *Dachs et al.* showed a more efficient degradation of low MW PAHs than high MW PAHs in vertical profiles of particle-bound PAHs [*Dachs et al.*, 1997]. In addition, other studies have revealed that PAH atmospheric inputs are two orders of magnitude higher than settling fluxes, suggesting important losses in the water column [*Tsapakis et al.*, 2006]. Recently, it has been shown that zooplankton degrades PAHs with higher degradation rates for the low MW PAHs such as phenanthrene and methylphenanthrenes [*Berrojalbiz et al.*, 2009]. The signal we see in our plankton samples is the result and confirmation of all these observations, with lower concentrations of lighter PAHs at high biomass. This degradation occurs along the entire photic zone, so that the effects of this process only could be observed in the results for planktonic samples but not in the particles collected at 2 meters depth as the later ones are highly influenced by atmospheric inputs (case C), while most plankton lied below the thermocline in late spring, and thus not directly coupled to atmospheric levels (see Figure S8 in the auxiliary material). Nevertheless, PAH degradation activity is presumably the result of different contributions: i) Bacteria are susceptible to be able to degrade certain POPs by means of exoenzymes that could degrade the chemicals on the cellular surface [*Del Vento and Dachs*, 2002]. ii) Phytoplankton detoxification processes [*Semple et al.*, 1999; *Lei et al.*, 2002, 2007;

*Haritash and Kaushik*, 2009]; iii) Zooplankton metabolization of low MW PAHs [*Berrojalbiz et al.*, 2009] and iv) photodegradation.

## 4. Conclusions and Implications for PAH Occurrence and Cycling in the Open Oceans

[44] The present study provides important information on the major physical and biogeochemical controls of PAH occurrence in the Mediterranean, which are likely to be important in other oceanic regions. The dependence of PAH occurrence on particle and plankton concentrations suggests that background levels of PAHs are controlled by cycling processes in the water column, and to certain extent, independent of proximity to sources. Levels of PAH in particles above the thermocline are driven by air-water-particle interactions with concentrations independent of TSP for low MW PAHs, but with a decrease of high MW PAHs at high TSP. These trends are consistent with the case C scenario. Results for plankton samples, mainly collected below the thermocline, provide the evidence of the presence of important removal process of the low MW PAHs, presumably due to biodegradation by bacteria and zooplankton. This is consistent with case D scenario. In the case of the Mediterranean Sea, there were few samples affected by coastal pressures, either riverine inputs or enhanced atmospheric deposition events. Thus high concentrations were found close to Nile River and Marmara Sea. However, during the Thresholds cruises, very few coastal sites were sampled, and thus it is possible that other coastal regions shown an influence of adjacent source areas. In the Mediterranean Sea, there is limited exchange between coastal waters and open sea surface waters since most coastal currents are along the coast. Therefore, open sea pollution is more affected by air-water interactions and water column biogeochemical cycles modulating the concentrations than by proximity to sources, as pointed out by the database shown in Figures 3 and 4. These trends observed in the Mediterranean provide important clues on the processes driving PAH in other oceanic regions, where the gradients in biomass and other environmental variables can be larger than in the Mediterranean. In any case, further research is needed on methodological approaches and biogeochemical processes affecting the fate, cycling and sinks of PAHs and other organic pollutants in the photic zone of the water column.

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