

PAHs in Air and Seawater along a North–South Atlantic Transect: Trends, Processes and Possible Sources

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Received July 14, 2007. Revised manuscript received November 28, 2007. Accepted December 4, 2007.

Polycyclic aromatic hydrocarbons (PAHs) were simultaneously measured in air and surface seawater between 49° N and 25° S in the open Atlantic Ocean. Elevated concentrations of PAHs (Σ_{10} PAHs ≈ 1.4 – 2.5 ng m⁻³ air, and 0.7 – 1 ng L⁻¹ seawater) occurred in the Biscay Bay and off the northwest coast of Africa. The unexpectedly high concentrations off NW Africa were discussed assessing the possible contribution of the emerging oil industry along the African shore, the role of biomass burning and natural sources of PAHs. In the southern Atlantic, concentrations of PAHs were close to detection limits (Σ_{10} PAHs ≈ 0.02 – 0.5 ng m⁻³ air, and 0.06 – 0.5 ng L⁻¹ seawater) and showed decreasing trends with increasing latitudes. Correlations of PAHs' partial pressures versus inverse temperature were not significant, in contrast to results for polychlorinated biphenyls from the same transect. This could have been due to the importance of ongoing primary sources and the shorter atmospheric life-times of PAHs. Air–water fugacity ratios (f_a/f_w) were calculated for selected compounds. They were close to 1 for fluoranthene and pyrene in remote open ocean areas suggesting air–water partitioning near equilibrium. Ratios for anthracene and phenanthrene were <0.3 in the remote tropical Atlantic, suggesting net volatilization.

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Introduction

Global oceans represent a critical compartment affecting the distribution and environmental fate of persistent organic pollutants (POPs) (1). Oceans cover 70% of the planet's surface. Because of their large volume, they can contain a large inventory of POPs (2). Oceanic water bodies can serve as a final sink of these pollutants after undergoing processes such as long-range atmospheric transport, deposition or gaseous exchanges with water, and scavenging to deep waters (1). However, it has been suggested that as primary emissions of POPs are decreasing, a rebalancing of the environmental burden of POPs would result from the rising influence of secondary sources, including a rearrangement of POPs through exchange between air and water (1). Model simulations have been used to illustrate how oceanic biogeochemical processes can control the global dynamics of POPs (1). So far, few studies are available on the global scale to test model predictions. One key factor is understanding the net air–water exchange over the open ocean, yet few data report simultaneous air and water measurements (2). Partitioning of POPs into the water column is also at the base of the accumulation of POPs in aquatic food webs (3), influencing residues in marine biota.

Polycyclic aromatic hydrocarbons (PAHs) are toxic and carcinogenic pollutants resulting from incomplete combustion of carbonaceous materials (4). Although PAHs can have natural sources, anthropogenic combustion (motor vehicles, domestic burning, power generation via combustion of coal and oil, waste incineration, burning of natural gas) dominate their emission scenarios (e.g., (4)). They are present in the atmosphere both in the gas phase and associated with particles (5–8) and can potentially travel long distances reaching remote areas. The main differences between PAHs from other classical POPs are their shorter atmospheric half-lives (range of hours to days) (9), their affinity to soot carbon (5–7) and the influence of ongoing primary sources on their distribution (4, 10). These characteristics make PAHs a complementary group of compounds for investigating the role of atmospheric persistence on the environmental partitioning mechanisms of POPs.

The present study follows previous investigations (10, 11) on a cruise in 2001 along a North–South transect in the Atlantic Ocean, aimed to delineate atmospheric trends for a range of POPs. This time, simultaneous measurements of PAHs were performed in air and seawater along the same cruise track, while adopting measures to check for the occurrence of “ship-made” interferences (12). The main aims of the study were to evaluate concentrations and distributions of PAHs in air and surface seawater and to assess their air–water exchange over the Atlantic Ocean.

Experimental Section

Sampling. Sample collection occurred from October 13 to November 13, 2005, on board the *RV Polarstern* (Alfred Wegener Institute, Germany) during the Atlantic transect ANT XXIII. Sampling covered a latitudinal transect of about 74° (8230 km), from 49° 20' N (Bremerhaven, Germany) to 24° 50' S (Cape Town, South Africa). Air samples were collected using a high volume air sampler (Hi-Vol; Tisch Environmental TE-PNY123 Accuvol Modified PUF Sampler, Factory Cleves, OH.) placed windward on the observation deck of the ship (20 m above sea level) to minimize contamination from the ship. The Hi-Vol operated at an average flow rate of 0.86 m³ min⁻¹. The total sampled air volume averaged 650 – 700 m³. The particulate phase was

collected on a glass fiber filter (GFF) (20 cm × 25 cm, Whatman 934-AH), previously baked overnight at 450 °C, whereas the gaseous phase was trapped on two polyurethane foam plugs (PUF) (8.6 cm diameter, 7.5 cm length). Surface seawater samples were collected from a stainless steel pipe at 8 m depth using the ship's intake system located in the keel. The initial flow rate was set to 1.2 L min⁻¹. Particle associated compounds were retained on a GFF (Whatman International Ltd., Maidstone-England, diameter 125 mm, nominal pore size 0.7 μm) (backed at 450 °C overnight) placed in a stainless steel filter holder. GFFs were substituted when the flow rate decreased below 0.8 L min⁻¹ to avoid cell breaking. A total of 2–5 GFFs were used to achieve the average sampled volume of 650 L. A glass column (19 cm length, 3 cm i.d.) filled with 95 mL Amberlite XAD-2 (Supelco, Bellefonte, PA) was used to trap dissolved PAHs. It was connected to a filter holder through a glass/PTFE junction. Prior to the cruise, XAD columns were pre-extracted with acetone, hexane and dichloromethane (DCM; all solvents Fisher Scientific GC-Resolve) and exchanged to pre-extracted milli-Ro water.

Sample Extraction and Cleanup. *Air Samples.* GFFs and PUFs were combined and Soxhlet-extracted for 12 h using *n*-hexane. Results from an earlier cruise along the same transect showed that the particle-associated fraction of PAHs was negligible compared to total concentrations (10). Extracts were eluted in glass columns (9 mm i.d.) filled with 1 g of alumina, 2 g of silica gel, and 1 g of sodium sulfate (baked at 450 °C overnight). The extract was concentrated under a gentle stream of N₂ until dryness and immediately rediluted in 100 μL of acetonitrile. Before analysis, the extract was filtered through a syringe filter (Millipore 4 mm Millex-FH, pore size 0.45 μm).

Water Samples. GFFs and XAD columns were analyzed separately. GFFs were Soxhlet extracted for 24 h using 9:1 hexane:acetone. Extracts were dried in a glass column (20 mm i.d.) filled with a 2 cm layer prerinsed NaSO₄. The seawater was drained from the XAD under N₂ pressure and discarded. XADs were extracted with 50 mL methanol followed by 50 mL DCM at a flow of 1 mL min⁻¹. The organic phases were combined in a 500 mL separatory funnel, to which 50 mL of pre-extracted MilliQ water were added. After phase separation, DCM was added three times for manual liquid/liquid extraction. Extracts were concentrated to ~500 μL and fractionated in a glass column (10 mm i.d.) packed with 3 g of activated silica (0.063–0.200 mm mesh, activated at 450 °C for 16 h) and eluted as follows: fraction 1, 32.5 mL of hexane; fraction 2, 15 mL of 1:1 hexane:DCM. Fraction 2, containing the PAHs, was concentrated and filtered as above for the air sample extracts.

Instrumental Analysis. Analysis was performed using a Perkin-Elmer HPLC system with LC250 binary pump, LS40 fluorescence detector and ISS200 autosampler. A PAH Spherisorb column 15 cm × 4.6 mm id (thermostatically controlled) was used to separate PAHs with an acetonitrile/water gradient at a flow rate of 1.5 mL min⁻¹. Acenaphthene (Ace), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[*b*]fluoranthene (B[*b*]F), benzo[*k*]fluoranthene (B[*k*]F), benzo[*a*]pyrene (B[*a*]P), benzo[*ghi*]perylene (B[*ghi*]P), and coronene (Cor) were routinely detected in samples and quantified. Quantification was performed using external calibration curves.

Quality Assurance/Quality Control (QA/QC). Handling and storage of air samples is described elsewhere (10). After water sampling, the GFFs were folded and placed in precombusted glass tubes. Tubes were flame sealed and enveloped in solvent rinsed aluminum foils. Test tubes containing GFFs and XAD columns were placed in sealed plastic bags and stored at 4 °C until extraction.

Sample handling and extraction were performed in a purpose-built clean laboratory at Lancaster University. Field

blanks (pre-extracted PUF plugs, GFFs, and XAD columns, 1 in 5 samples) and laboratory blanks (1 in 12) were routinely included. The limit of detection (LOD) was calculated as the mean plus 3 times the standard deviation of the field blanks. LODs varied between 1 and 9 pg m⁻³ for air samples (considering an average sampled volume of 650 m³), and 1 and 20 pg L⁻¹ for water samples (average sampled volume 650 L), depending on the PAH. A breakthrough test was performed for the water sample collected at the equator by placing 2 GFFs and 2 XAD columns in series. For the particle associated fraction, retention on the first filter was between 60 and 70% of the total mass of compounds measured on both filters, while for the dissolved fraction, 95–97% of the compounds were retained by the first XAD column. Break through correction was performed for the particle associated phase when the amount of compound on the second filter was above the LOD.

The quality of the analytical procedure was monitored by adding 1 ng of dibenzo[*ah*]anthracene just before extraction. Analytical response for dibenzo[*ah*]anthracene averaged 99 ± 25% in air samples, and 82 ± 13 and 80 ± 18% for particle-associated and dissolved phase water samples, respectively. Sample results were not corrected for blank values.

Passive air samplers (PUF disks) were deployed in protective shelters at different locations of the ship to measure potential ship-based contamination sources. A detailed description of the analytical method adopted for the PUF disks is reported in the Supporting Information.

Ancillary Data. *Organic Carbon (OC) and Elemental Carbon (EC).* OC and EC concentrations in the aerosol were obtained from samples collected onto prefired quartz fiber filters with a Hi-Volume TSP sampler. Sampling was stopped when wind directions became unfavorable and likely to bring ship contamination. Filter samples were analyzed for OC and EC by a thermo-optical method (13).

Meteorological Data. Meteorological data were obtained from PODAS (Polarstern Data System) on board the vessel, an online management system that collects nautical and scientific parameters from a multitude of measuring devices installed on the vessel. Air and water temperature, wind speed, and wind direction were averaged from the system every 5 min. NOAA's HYSPLIT model and the NCEP/NCAR Global Reanalysis data set were used to calculate back trajectories and atmospheric mixing height. BTs were traced for 7 days with 1 h steps at 00:00 coordinated universal time (UTC) at 25 m above sea level, roughly corresponding to the height at which samples were collected.

Results and Discussion

Atmospheric Concentration Trends. The sums of atmospheric concentrations of 10 PAHs (Σ₁₀[PAHs]_{atm}) over the Atlantic Ocean were highly variable (23–2560 pg m⁻³; Figure 1a and the Supporting Information, Table SI 1). Atmospheric trends and Σ₁₀[PAHs]_{atm} measured during this campaign were consistent with previously reported data (10). Highest Σ₁₀[PAHs]_{atm} were measured close to Europe (Biscay Bay and Galician coast) and between 20°N and 10°N in proximity of Mauritania, Senegal, Cape Verde, Guinea Bissau and Guinea. Σ₁₀[PAHs]_{atm} were comparable to those reported for rural areas in Europe (14–16). Lowest Σ₁₀[PAHs]_{atm} were recorded between 42 and 27° N and in the Southern hemisphere (SH), when the air masses came from the open ocean. [PAHs]_{atm} were close to the LOD at the southern latitudes (0° N to 25° S).

The relationship between [PAHs]_{atm} and temperature (T) was investigated and compared between the north and south Atlantic by plotting the natural logarithm of the PAHs' partial pressure in *P* (Pa) versus 1/*T*. A significant correlation between ln *P*_{PAH} and 1/*T* indicates conditions close to

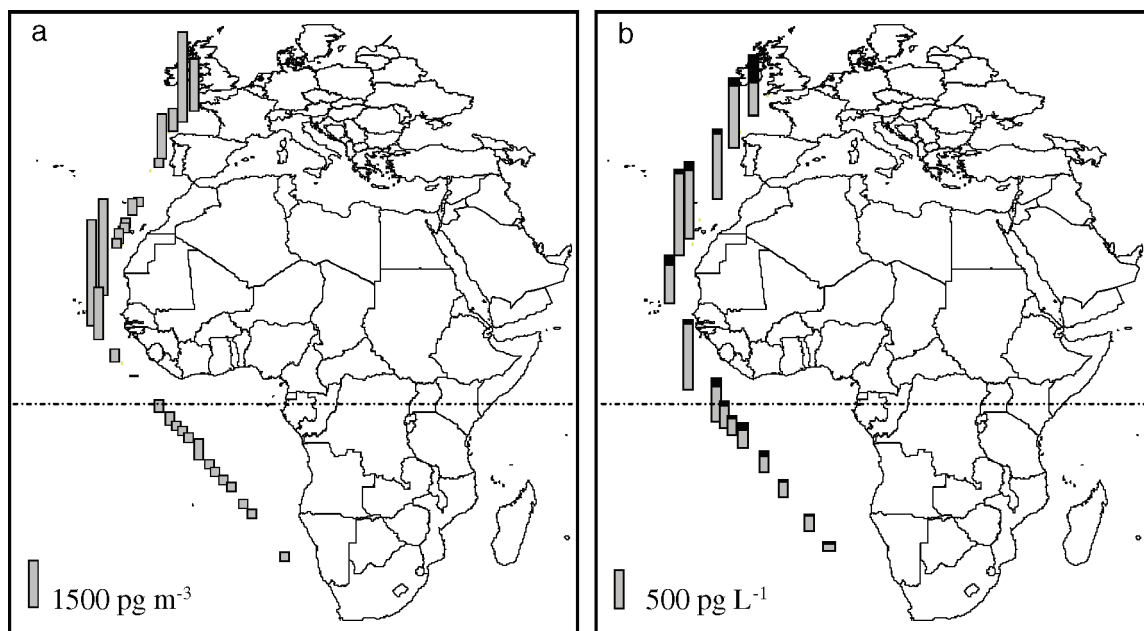


FIGURE 1. Latitudinal distribution of Σ_{10} PAHs in (a) air, and (b) water (grey represents the dissolved fraction and black the particle associated fraction).

air–water equilibrium, i.e., that the exchange between atmosphere and surface water controls atmospheric concentrations (17, 18). Increasing P with increasing T was observed in the SH, but even for the more volatile PAHs (Phe, Ant, Fla), the regressions were not significant at 95% (see the Supporting Information, Figure SI 1). Significant relationships were observed on this cruise for polychlorinated biphenyls (PCBs) in the SH (19). The different behavior of the PAHs may be explained by their shorter atmospheric life-times and the ongoing importance of primary sources. In the NH, no trends were observed even when the high concentrations measured along the NW African coast were excluded. This may be evidence that $[\text{PAHs}]_{\text{atm}}$ over the NH Atlantic are mainly controlled by advection from primary emissions, while in SH air–water partitioning may have greater influence on the air concentrations. The observed behavior and concentration differences showed that the intertropical convergence zone (ITCZ) prevented an efficient exchange of PAHs between the two hemispheres across the Atlantic, thus reducing the exposure of the SH ecosystem to NH emissions.

Water Concentration Trends. PAH concentrations in seawater $\Sigma_{10}[\text{PAHs}]_{\text{wat}}$ ranged from 58 to 1070 pg L^{-1} (see the Supporting Information, Table SI 2). Most of the PAHs were found in the dissolved phase (see the Supporting Information, Figure SI 2), which was dominated by Phe, Fla, and Pyr. Highest concentrations in bulk water were observed in the NH, close to NW African shores (Figure 1b). In these hotspots, PAH concentrations and profiles were consistent with those observed in the atmosphere, suggesting that atmospheric deposition/air–water exchange exerts a strong influence on $[\text{PAHs}]_{\text{wat}}$.

$[\text{PAHs}]_{\text{wat}}$ in the SH decreased going south, as was observed for $[\text{PAHs}]_{\text{atm}}$. Concentrations measured in the SH were comparable or lower than previously reported for remote subarctic areas (20). Elevated concentrations of higher-molecular-weight (HMW) PAHs, such as B(k)F, B(a)P, B(ghi)P, and Cor ($8.2\text{--}33.4 \text{ pg L}^{-1}$) were measured in the particle phase in the Biscay Bay (sample 1). The % PAHs bound to particles was typically <20% of the total PAHs in the bulk water, but was about 41% in Biscay Bay. This may be related to higher productivity of this area. The Biscay Bay receives a considerable input of suspended matter and nutrients from several

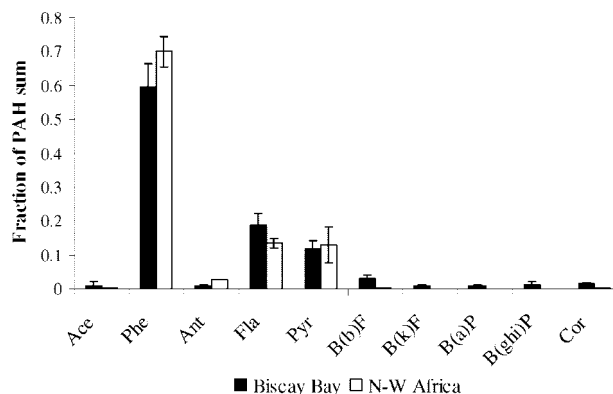


FIGURE 2. Comparison of the average atmospheric PAH profile in the Biscay Bay and in NW Africa. Error bars represent 1 standard deviation.

estuaries (21). B(k)F, B(a)P, B(ghi)P, and Cor were also detected in the particle phase close to the African hotspot. This area is recognized as an important upwelling region (22). In all the other samples, the HMW PAHs were close to or below the LODs.

Comments on the High Concentrations of Northwestern Africa. Higher $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$ measured close to west Africa were similar to those observed close to Europe, but the PAH profile differed. Off Africa, the HMW PAHs were close to the LOD (Figure 2), while the more volatile Ace, Fla, Pyr and in particular Phe dominated $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$. During this part of the cruise, sampling conditions were not ideal: the relative wind speed was low (5 m s^{-1}) and the relative wind direction was $\sim 230^\circ$, which could have added ship-based emissions to the sampler (12). However, in the following we review the evidence suggesting that the elevated $[\text{PAHs}]_{\text{atm}}$ were real.

(i) Passive Air Samplers. PAHs profiles obtained from the PUF disks deployed on the back of the ship, and affected by the ship's emissions were completely different from those placed on the observation deck (close to the high volume sampler) (for details, see the Supporting Information). The hi-vol sampled elevated concentrations of Ace, Fla, Pyr, Phe but not of HMW PAHs, which were close to the LOD in this area. PUF disks analysis showed that the ship stack is

a source of HMW PAHs, which were low in these samples. On the other hand, if the ship was a source of PAHs from fuel evaporation (a potential source of more volatile PAHs), this should have also been reflected by the PUF disks deployed on the back of the ship. Instead these displayed relatively low concentrations of Phe (28 times lower than High Vol-based results off NW Africa), Ant, Fluor, Pyr (6–8 times) Ace, and Flu (not detected).

(ii) *Other Samples.* Sample 29 was affected by unfavorable wind conditions for a short while (ca. 7% of the sampling time). It was collected while the ship was leaving the high concentration area off Africa; concentrations were only a factor 2 lower than the maximum. If ship-contamination had been the cause of the high concentrations observed, this sample would have recorded much lower concentrations.

(iii) *PAHs in the Surface Ocean.* Water concentrations (see above) also showed relatively high levels in this region for Phe, Fla, and Pyr, presumably reflecting elevated atmospheric concentrations (Figure 1b).

(iv) *Air Mass Origin.* Back trajectory analysis (23) showed that while *RV Polarstern* was cruising across the hotspot area, the air came from N-NE, moving over the African coasts before reaching the ship. Then, after crossing the 8° N parallel, their provenance changed quickly to the S and low atmospheric concentrations were re-established (see the Supporting Information, Figure SI 4).

Based on the above, it seems most likely that there is a strong PAH source, probably land-based. The high levels measured there are also in agreement with recent measurements along two E-W Atlantic transects at 26° and 21° N (24). PAH profiles were dominated by Phe. $[\text{PAHs}]_{\text{atm}}$ for individual compounds were 2–4 times higher than those measured in this study.

Estimating the African Emission Strength. In the following we estimate the necessary strength of a hypothetical source located on the African coast. The “hotspot” area covered a 1500 km long N-S transect as the ship traveled at an average distance of ca. 400 km from the coast. The Atmospheric Boundary Layer (ABL) was about 200 m during this cruise track (23). The wind speed in the area was between 4 and 8 m s⁻¹. Considering the back trajectories (see the Supporting Information, Figure SI 3) and wind direction, we estimate an average atmospheric residence time of 36–96 h in the volume delimited by the coast line, the cruise track and the ABL (120 000 km³). For Phe, the most abundant PAH, average concentrations were 1600 pg m⁻³. Considering the North–South wind direction, the advective flux of Phe out of the southern section area (delimited by the distance from the coast and the ABL (~80 km²)), was 1.8–3.6 kg h⁻¹. Net air-to-water exchange was calculated as 129 and 332 ng m⁻² d⁻¹ for an average wind speed of 4 and 8 m s⁻¹, respectively. This implies a flux of Phe into the water of 1.3–4.3 kg h⁻¹. It is estimated that OH-radical reaction would have depleted a further 0.8–2.2 kg h⁻¹ (averaged over 24 h). In total, a hypothetical coast-based source would need to emit 4–10 kg h⁻¹ of Phe, a value comparable to mean emission rates of Phe for the U.K. (25) or Minnesota (26).

Of the coastal African countries, only Senegal, with a population of about 11 million inhabitants, has some developed industry including oil extraction. Around 50 extractive offshore platforms are documented for Senegal, resulting in an intense international trade of crude oil, land base refineries and chemical industries (27). The abundance of more volatile PAHs is consistent with the atmospheric fingerprint measured in areas where uncombusted fuel, oil spills, and potentially gas flaring represent the main source to the atmosphere (16, 28, 29). Other ships sailing along this route might have added to the atmospheric PAHs measured. Biomass burning and natural fires could also have contributed to the observed concentrations. September–October are

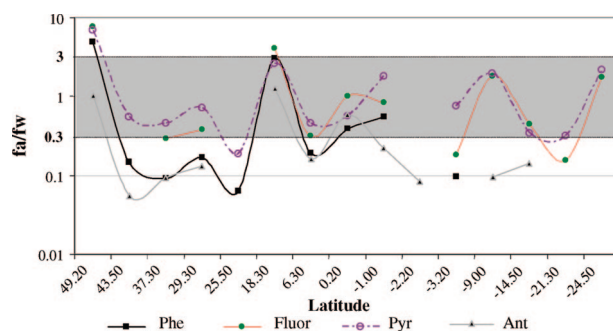


FIGURE 3. Fugacity ratios of selected PAHs. The grey area shows the uncertainty of air–water equilibrium; ratios outside suggest PAHs not at air–water equilibrium.

periods of peak fire activity in sub-Saharan and Central Africa (30, 31). Our observed PAH profiles match those from wood burning, suggesting that biomass burning could have added to the observed plume (32).

Natural sources could also contribute to the elevated $[\text{PAHs}]_{\text{atm}}$. Microbial activity in tropical soils, especially the anaerobic degradation of organic matter containing pigments, represents a natural source of PAHs such as Perylene, Phe and Naphtalene (33, 34). The PAHs could therefore have been transported to the region by atmospheric transport following volatilization from soils or via runoff and riverine transport of terrestrial matter. Further work is needed to identify the source(s) of those elevated concentration.

Biogeochemical Processes. Simultaneous air and water sampling was performed in 15 selected areas along the transect to assess the air–water exchange of PAHs. This is one of the main processes transferring pollutants between air and water (35, 36). Air–water fugacity ratios (37) were calculated for PAHs that were routinely detected in both phases as follows:

$$f_a/f_w = (C_a RT)/(C_w H) \quad (1)$$

where C_a is the gaseous concentration (mol m⁻³), C_w is the dissolved aqueous concentration (mol m⁻³), R is the gas constant (J K⁻¹ mol⁻¹), and H is the Henry's law constant (Pa m³ mol⁻¹). Values of H and their temperature dependence were taken from Bamford et al. (38) and Shiu and Ma (39) and were corrected for salinity using the Setshenow equation. Ratios >1 were observed for Phe, Fla and Pyr in the Biscay Bay and in the NW African hotspot suggesting net deposition (Figure 3). Fla and Pyr appeared to be close to equilibrium in all other areas. Ratios <1 were observed for Phe and Ant in all locations characterized by low atmospheric concentrations. The calculation of the fugacity ratios was performed taking into consideration the uncertainty factors reported by McLeod et al. (40). The uncertainty of air–water exchange is dominated by accurately knowing H (95% confidence within a factor ~3), minimizing the impact of analytical uncertainties (ca. 30% each for PAHs in atmosphere and water) (41). f_a/f_w for Phe and Ant ranged in those areas between 0.04 and 0.36, suggesting the occurrence of net (re)volatilization.

The following section assesses the factors/processes which could have contributed to the volatilization of PAHs.

Net Diffusive Air–Water Flux. F_{a-w} (ng m⁻² day⁻¹) was calculated for Ant and Phe in regions where the average $f_a/f_w < 0.3$. This threshold reflects the uncertainty of around 3 in knowing the exact f_a/f_w (40). Fluxes were estimated using a two resistance model (1, 2)

$$F_{a-w} = k_{ol} \left(C_w - \frac{C_a RT}{H} \right) \quad (2)$$

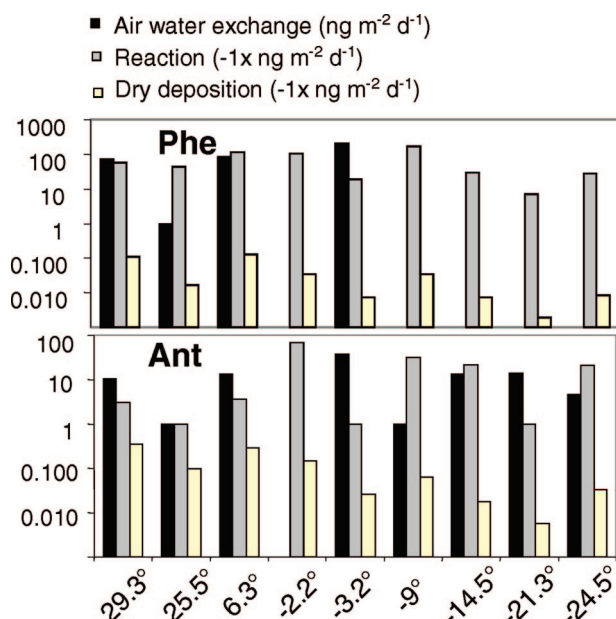


FIGURE 4. Calculated intercompartmental fluxes of phenanthrene and anthracene in areas with $f_a/f_w < 0.3$.

where k_{ol} (m day^{-1}) is the overall mass transfer coefficient estimated as described elsewhere (42). Volatilization fluxes were 70–210 and 3–70 $\text{ng m}^{-2} \text{day}^{-1}$ for Phe and Ant, respectively (Figure 4). k_{ol} is known within a factor of 3 (40), rendering the uncertainty of F_{a-w} to be at worst an order of magnitude.

Atmospheric Degradation. Atmospheric degradation plays a key role in the environmental fate of PAHs and competes with air–water exchange. Atmospheric degradation is mainly due to OH radical reactions. The degradation flux F_{deg} can be estimated as:

$$F_{deg} = h k_{OH} C_{OH} C_a \quad (3)$$

where h (m) is the height of sampling a.s.l., k_{OH} ($\text{cm}^3 \text{molecules}^{-1} \text{day}^{-1}$) is the degradation rate constant, and C_{OH} (molecules cm^{-3}) is the concentration of OH radicals. These were calculated as follows: h was set to 20 m, the height at which the samplers were positioned; k_{OH} values were taken from Brubaker and Hites (43); C_{OH} was estimated from T (44). OH-radical depletion fluxes were 7–120 and 9–50 $\text{ng m}^{-2} \text{day}^{-1}$ for Phe and Ant, respectively (Figure 4). The confidence of the estimated F_{deg} is an order of magnitude, dominated by the uncertainty of knowing OH concentrations. OH radical depletion fluxes were comparable in magnitude to the water-to-air fluxes, presumably causing the continuous volatilization of PAHs from the water. This raises questions about the processes which could have supplied sufficient amounts of PAHs to the surface ocean.

Atmospheric Deposition. PAH deposition on aerosols was assessed by estimating the particle bound concentration (C_p , pg m^{-3} of air) from OC and EC concentrations (6) details are given in Text SI_2). The dry deposition flux ($\text{ng m}^{-2} \text{d}^{-1}$) was calculated as:

$$F_{DD} = C_p v_D \quad (4)$$

where v_D (m d^{-1}) is the particles' deposition velocity. Values of v_D were taken from Del Vento and Dachs (24), using on-board measurements from a different cruise. F_{DD} s for Phe and Ant were 0.002–0.120 and 0.006–0.340 $\text{ng m}^{-2} \text{day}^{-1}$ respectively; 3–4 orders of magnitude lower than F_{a-w} and F_{deg} (Figure 4), ruling out a significant contribution to the relatively high fugacity of surface water, even considering an uncertainty of 1 order of magnitude. Wet deposition, finally,

does not appear to significantly contribute to adding PAHs to the surface ocean either in this region. Jurado et al. (35) showed that wet deposition fluxes are important during the rain event itself but they lose their importance over longer time scales. During the cruise, especially in the SH, no significant rain events were recorded.

The lowest fugacity ratios were observed in tropical/subtropical latitudes. These regions have no marked seasonality, so changes in T , water productivity etc. should not affect the fugacity ratio in this area much. In any case, biological productivity would affect PAHs with higher K_{OW} values, such as Fla and Pyr, which were close to equilibrium. It is also unlikely that short time scale fluctuations (days–weeks) in the advective fluxes could generate the observed behavior, given the distance from the land and the constant pattern of the air masses coming from the open ocean. This was confirmed through back trajectory analysis (23), at least for all the sites in the SH, by following their air mass origin during the week before the sampling.

Taken together, atmospheric deposition alone cannot account for the observed net volatilization flux of PAHs, suggesting that there is an additional source of PAHs to the surface water. One hypothesis could be the existence of natural sources for Phe and Ant in the water column, following what was observed in tropical soils (33, 34). The fast turnover of organic matter and the rapid degradation of pigments carrying aromatic structures could be the driving process. Elevated water temperature and the scarcity of nutrients, typical of the NH and SH gyres, promote the rapid recycling of almost all Fe, C, and N in the surface waters (45). This, together with the absence of significant vertical removal processes (low export rate (1)), would enhance PAH fugacity in water, supporting their net volatilization. If they exist, such sources would also release PAHs in other regions, such as the NW African hot spot, contributing to the high concentrations measured there in both water and air. If present, natural PAH sources in the oceans could be more easily detected in remote and oligotrophic areas such as the northern and southern gyres, under stable conditions removed from anthropogenic sources. This hypothesis needs further investigation, since anthropogenic sources are generally considered to dominate the regional/global inventories of PAHs.

Acknowledgments

The *RV Polarstern* crew is acknowledged for their competent and professional assistance during sampling, and Armando Caba (GKSS) is thanked for his technical and logistical support.

Supporting Information Available

Additional figures and tables detailing sample concentrations and conditions, estimated particle fractions, and passive sampler results (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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ES0717414