

**PAHs in air and seawater along a North-South Atlantic transect: trends, processes and possible sources**

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# PAHs in air and seawater along a North-South Atlantic transect: trends, processes and possible sources

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## Abstract

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 ( $\Sigma_{10}$  PAHs  $\sim$  1.4-2.5 ng m<sup>-3</sup> air, and 0.7-1 ng L<sup>-1</sup> seawater) occurred in the Biscay Bay and off the north-west 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 ( $\Sigma_{10}$  PAHs  $\sim$  0.02-0.5 ng m<sup>-3</sup> air, and 0.06-0.5 ng L<sup>-1</sup> 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 on-going 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.

## 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 surface. Due to 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

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3 with water and scavenging to deep waters (1). However, it has been suggested that, as  
4 primary emission of POPs are decreasing, a re-balancing of the environmental burden of  
5 POPs would result from the rising influence of secondary sources, including a re-  
6 arrangement of POPs through exchange between air and water (1). Model simulations  
7 have been used to illustrate how oceanic biogeochemical processes can control the global  
8 dynamics of POPs (1). So far, few studies are available on the global scale to test model  
9 predictions. One key factor is understanding the net air-water exchange over the open  
10 ocean, yet few data report simultaneous air and water measurements (2). Partitioning of  
11 POPs into the water column is also at the base of the accumulation of POPs in aquatic  
12 food webs (3), influencing residues in marine biota.

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

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26 The present study follows two previous investigations conducted in 2001 (10) and 2004  
27 (11) along a north-south transect in the Atlantic Ocean, aimed to delineate atmospheric

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3 trends for a range of POPs. This time, simultaneous measurements of PAHs were  
4 performed in air and seawater along the same cruise track, while adopting measures to  
5 check for the occurrence of “ship-made” interferences (12). The main aims of the study  
6 were to evaluate concentrations and distributions of PAHs in air and surface sea water,  
7 and to assess their air-water exchange over the Atlantic Ocean.  
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### 15 16 **Experimental section**

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18 **Sampling:** Sample collection occurred from 13<sup>th</sup> October to 13<sup>th</sup> November 2005 on  
19 board the *RV Polarstern* (Alfred Wegener Institute, Germany) during the Atlantic  
20 transect ANT XXIII. Sampling covered a latitudinal transect of about 74° (~ 8230 km),  
21 from 49° 20' N (Bremerhaven, Germany) to 24° 50' S (Cape Town, South-Africa). Air  
22 samples were collected using a high volume air sampler (Hi-Vol; Tisch Environmental  
23 TE-PNY1123 ACCUVOL MODIFIED PUF SAMPLER, Factory Cleves, OH, USA)  
24 placed windward on the observation deck of the ship (20 m above sea level) to minimize  
25 contamination from the ship. The Hi-Vol operated at an average flow rate of 0.86 m<sup>3</sup> min<sup>-1</sup>.  
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The total sampled air volume averaged 650 – 700 m<sup>3</sup>. The particulate phase was  
collected on a glass fiber filter (GFF) (20 cm x 25 cm, Whatman 934-AH), previously  
baked overnight at 450°C, while 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<sup>-1</sup>. 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° overnight) placed in a stainless steel filter  
holder. GFFs were substituted when the flow rate decreased below 0.8 L min<sup>-1</sup> to avoid

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3 cell breaking. A total of 2-5 GFFs were used to achieve the average sampled volume of  
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5 650 L. A glass column (19 cm length, 3 cm i.d.) filled with 95 mL Amberlite XAD-2  
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7 (Supelco, Bellefonte, PA, USA) was used to trap dissolved PAHs. It was connected to a  
8  
9 filter holder through a glass/PTFE junction. Prior to the cruise, XAD columns were pre-  
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11 extracted with acetone, hexane and dichloromethane (DCM; all solvents Fisher Scientific  
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13 GC-Resolve) and exchanged to pre-extracted milli-Ro water.  
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### 20 **Sample extraction and clean-up.**

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22 Air samples: GFFs and PUFs were combined and Soxhlet-extracted for 12 hours using  
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24 n-hexane. Results from an earlier cruise along the same transect showed that the particle  
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26 associated fraction of PAHs was negligible compared to total concentrations (10).  
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28 Extracts were eluted in glass columns (9 mm i.d.) filled with 1 g alumina, 2 g silica gel  
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30 and 1 g of sodium sulfate (baked at 450°C overnight). The extract was concentrated  
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32 under a gentle stream of N<sub>2</sub> until dryness and immediately re-diluted in 100 µL  
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34 acetonitrile. Before analysis, the extract was filtered through a syringe filter (Millipore 4  
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36 mm Millex-FH, pore size 0.45 µm).  
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41 Water samples: GFFs and XAD columns were analyzed separately. GFFs were Soxhlet  
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43 extracted for 24 hours using hexane:acetone 9:1. Extracts were dried in a glass column  
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45 (20 mm i.d.) filled with a 2 cm layer pre-rinsed NaSO<sub>4</sub>. The seawater was drained from  
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47 the XAD under N<sub>2</sub> pressure and discarded. XADs were extracted with 50 mL methanol  
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49 followed by 50 mL DCM at a flow of 1 mL min<sup>-1</sup>. The organic phases were combined in  
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51 a 500 mL separatory funnel, to which 50 mL of pre-extracted MilliQ water were added.  
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55 After phase separation, DCM was added three times for manual liquid/liquid extraction.  
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3 Extracts were concentrated to ~ 500  $\mu\text{L}$  and fractionated in a glass column (10 mm i.d.)  
4 packed with 3 g of activated silica (0.063-0.200 mm mesh, activated at 450°C for 16 hrs)  
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6 and eluted as follows: Fraction 1: 32.5 mL hexane; Fraction 2: 15 mL hexane:DCM 1:1.  
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8 Fraction 2, containing the PAHs, was concentrated and filtered as above for the air  
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10 sample extracts.  
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15 **Instrumental Analysis:** Analysis was performed using a Perkin Elmer HPLC system  
16 with LC250 binary pump, LS40 fluorescence detector and ISS200 autosampler. A PAH  
17 Spherisorb column 15 cm x 4.6 mm id (thermostatically controlled) was used to separate  
18 PAHs with an acetonitrile/water gradient at a flow rate of 1.5 mL min<sup>-1</sup>. Acenaphthene  
19 (Ace), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr),  
20 Benzo[*b*]fluoranthene (B[*b*]F), Benzo[*k*]fluoranthene (B[*k*]F) Benzo[*a*]pyrene (B[*a*]P),  
21 Benzo[*ghi*]perylene (B[*ghi*]P) and Coronene (Cor), were routinely detected in samples  
22 and quantified. Quantification was performed using external calibration curves.  
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35 **Quality Assurance/Quality control (QA/QC)** Handling and storage of air samples is  
36 described elsewhere (10). After water sampling, the GFFs were folded and placed in pre-  
37 combusted glass tubes. Tubes were flame sealed and enveloped in solvent rinsed  
38 aluminum foils. GFF containing tubes and XAD column were placed in sealed plastic  
39 bags and stored at 4°C until extraction.  
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46 Sample handling and extraction were performed in a purpose-built clean laboratory at  
47 Lancaster University. Field blanks (pre-extracted PUF plugs, GFFs, and XAD columns, 1  
48 in 5 samples) and lab blanks (1 in 12) were routinely included. The limit of detection  
49 (LOD) was calculated as the mean plus 3 times the standard deviation of the field blanks.  
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56 LODs varied between 1 to 9 pg/m<sup>3</sup> for air samples (considering an average sampled  
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3 volume of 650 m<sup>3</sup>), and 1 to 20 pg/L for water samples (average sampled volume 650 L),  
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5 depending on the PAH. A breakthrough test was performed for the water sample  
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7 collected at the equator by placing 2 GFFs and 2 XAD columns in series. For the particle  
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9 associated fraction, retention on the first filter was between 60 to 70% of the total mass of  
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11 compounds measured on both filters, while for the dissolved fraction, 95-97% of the  
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13 compounds were retained by the first XAD column. Break through correction was  
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15 performed for the particle associated phase when the amount of compound on the second  
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17 filter was above the LOD.  
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22 The quality of the analytical procedure was monitored by adding 1 ng of  
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24 dibenzo[ah]anthracene just before extraction. Analytical response for  
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26 dibenzo[ah]anthracene averaged 99±25% in air samples, and 82±13% and 80±18% for  
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28 particle associated and dissolved phase water samples, respectively. Sample results were  
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30 not corrected for blank values.  
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34 Passive air samplers (PUF disks) were deployed in protective shelters at different  
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36 locations of the ship to measure potential ship-based contamination sources. A detailed  
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38 description of the analytical method adopted for the PUF disks is reported in the  
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40 supplementary information.  
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#### 46 47 **Ancillary data:**

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50 Organic carbon (OC) and elemental carbon (EC): OC and EC concentrations in the  
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52 aerosol were obtained from samples collected onto pre-fired quartz fiber filters with a Hi-  
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54 Volume TSP sampler. Sampling was stopped when wind directions became unfavorable  
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3 and likely to bring ship contamination. Filter samples were analyzed for OC and EC by a  
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5 thermo-optical method (13).  
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9 Meteorological data: Meteorological data were obtained from PODAS (POLarstern DAta  
10 System) on board the vessel, an online management system that collects nautical and  
11 scientific parameters from a multitude of measuring devices installed on the vessel. Air  
12 and water temperature, wind speed and wind direction were averaged from the system  
13 every 5 minutes. NOAA's HYSPLIT model and the NCEP/NCAR Global Reanalysis  
14 dataset were used to calculate back trajectories and atmospheric mixing height. BTs were  
15 traced for 7 days with 1 h steps at 00:00 coordinated universal time (UTC) at 25 m above  
16 sea level, roughly corresponding to the height at which samples were collected.  
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## 31 **Results and discussion**

### 32 **Atmospheric concentration trends**

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36 The sum of atmospheric concentrations of 10 PAHs ( $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$ ) over the Atlantic  
37 Ocean were highly variable (23 - 2560  $\text{pg m}^{-3}$ ; Figure 1a and Table SI 1). Atmospheric  
38 trends and  $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$  measured during this campaign were consistent with previously  
39 reported data (10). Highest  $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$  were measured close to Europe (Biscay Bay,  
40 and Galician coast) and between 20°N and 10°N in proximity of Mauritania, Senegal,  
41 Cape Verde, Guinea Bissau and Guinea.  $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$  were comparable to those reported  
42 for rural areas in Europe (14-16). Lowest  $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$  were recorded between 42° and  
43 27° N and in the Southern Hemisphere (SH), when the air masses came from the open  
44 ocean.  $[\text{PAHs}]_{\text{atm}}$  were close to the LOD at the southern latitudes (0° N to 25° S).  
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3 The relationship between  $[\text{PAHs}]_{\text{atm}}$  and temperature (T) was investigated and  
4 compared between the north and south Atlantic by plotting the natural logarithm of the  
5 PAHs' partial pressure  $\ln P$  (Pa) versus  $1/T$ . A significant correlation between  $\ln P_{\text{PAH}}$   
6 and  $1/T$  indicates conditions close to air-water equilibrium, i.e. that the exchange between  
7 atmosphere and surface water controls atmospheric concentrations (17, 18). Increasing  $P$   
8 with increasing T were observed in the SH, but even for the more volatile PAHs (Phe,  
9 Ant, Fla) the regressions were not significant at 95% (Figure SI\_1). Significant  
10 relationships were observed on this cruise for polychlorinated biphenyls (PCBs) in the  
11 SH (19). The different behavior of the PAHs may be explained by their shorter  
12 atmospheric life-times and the on-going importance of primary sources. In the NH, no  
13 trends were observed even when the high concentrations measured along the NW African  
14 coast were excluded. This may be evidence that  $[\text{PAHs}]_{\text{atm}}$  over the NH Atlantic are  
15 mainly controlled by advection from primary emissions, while in SH air-water  
16 partitioning may have greater influence on the air concentrations. The observed behavior  
17 and concentration differences showed that the inter-tropical convergence zone (ITCZ)  
18 prevented an efficient exchange of PAHs between the two hemispheres across the  
19 Atlantic, thus reducing the exposure of the SH ecosystem to NH emissions.  
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### 46 **Water concentration trends**

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48 PAH concentrations in seawater  $\Sigma_{10}[\text{PAHs}]_{\text{wat}}$  ranged from 58 - 1070  $\text{pg L}^{-1}$  (Table  
49 SI\_2). Most of the PAHs were found in the dissolved phase (Figure SI\_2), which was  
50 dominated by Phe, Fla and Pyr. Highest concentrations in bulk water were observed in  
51 the NH, close to NW African shores (Figure 1b). In these hotspots, PAH concentrations  
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3 and profiles were consistent with those observed in the atmosphere, suggesting that  
4 atmospheric deposition/ air-water exchange exerts a strong influence on  $[\text{PAHs}]_{\text{wat}}$ .  
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8  $[\text{PAHs}]_{\text{wat}}$  in the SH decreased going south, as was observed for  $[\text{PAHs}]_{\text{atm}}$ .  
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10 Concentrations measured in the SH were comparable or lower than previously reported  
11 for remote sub-arctic areas (20). Elevated concentrations of higher molecular weight  
12 (HMW) PAHs, such as B(k)F, B(a)P, B(ghi)P and Cor ( $8.2 - 33.4 \text{ pg L}^{-1}$ ) were measured  
13 in the particle phase in the Biscay Bay (Sample 1). The % PAHs bound to particles was  
14 typically < 20% of the total PAHs in the bulk water, but was about 41 % in Biscay Bay.  
15 This may be related to higher productivity of this area. The Biscay Bay receives a  
16 considerable input of suspended matter and nutrients from several estuaries (21). B(k)F,  
17 B(a)P, B(ghi)P and Cor were also detected in the particle phase close to the African  
18 hotspot. This area is recognized as an important upwelling region (22). In all the other  
19 samples, the HMW PAHs were close to or below the LODs.  
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### 36 **Comments on the high concentrations of North-Western Africa**

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39 Higher  $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$  measured close to west Africa were similar to those observed  
40 close to Europe, but the PAH profile differed. Off Africa, the HMW PAHs were close to  
41 the LOD (Figure 2), while the more volatile Ace, Fla, Pyr and in particular Phe  
42 dominated  $\Sigma_{10}[\text{PAHs}]_{\text{atm}}$ . During this part of the cruise sampling conditions were not  
43 ideal: the relative wind speed was low ( $5 \text{ m s}^{-1}$ ) and the relative wind direction was ~  
44  $230^\circ$ , which could have added ship-based emissions to the sampler (12). However, in the  
45 following we review the evidence suggesting that the elevated  $[\text{PAHs}]_{\text{atm}}$  were real.  
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56 i) *Passive air samplers.* PAHs profiles obtained from the PUF disks deployed on  
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3 the back of the ship, and affected by the ship's emissions were completely  
4 different from those placed on the observation deck (close to the high volume  
5 sampler) (for details, see the SI). The hi-vol sampled elevated concentrations of  
6 Ace, Fla, Pyr, Phe but not of HMW PAHs, which were close to the LOD in this  
7 area. PUF disks analysis showed that the ship stack is a source of HMW PAHs,  
8 which were low in these samples. On the other hand, if the ship was a source of  
9 PAHs from fuel evaporation (a potential source of more volatile PAHs), this  
10 should have also been reflected by the PUF disks deployed on the back of the  
11 ship. Instead these displayed relatively low concentrations of Phe (28 times  
12 lower than High Vol-based results off NW Africa), Ant, Fluor, Pyr (6-8 times)  
13 Ace and Flu (not detected).  
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- 29 ii) *Other samples* Sample 29 was affected by unfavorable wind conditions for a  
30 short while (ca. 7 % of the sampling time). It was collected while the ship was  
31 leaving the high concentration area off Africa; concentrations were only a factor  
32 2 lower than the maximum. If ship-contamination had been the cause of the  
33 high concentrations observed, this sample would have recorded much lower  
34 concentrations.  
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43 iii) *PAHs in the surface ocean* Water concentrations (see above) also showed  
44 relatively high levels in this region for Phe, Fla and Pyr, presumably reflecting  
45 elevated atmospheric concentrations (Figure 1b).  
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51 iv) *Air mass origin* Back trajectory analysis (23) showed that while *RV Polarstern*  
52 was cruising across the hotspot area, the air came from N-NE, moving over the  
53 African coasts before reaching the ship. Then, after crossing the 8° N parallel,  
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3 their provenance changed quickly to the S and low atmospheric concentrations  
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5 were re-established (Figure SI\_4).  
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8 Based on the above, it seems most likely that there is a strong PAH source, probably  
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10 land-based. The high levels measured there are also in agreement with recent  
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12 measurements along two E-W Atlantic transects at 26° and 21° N (24). PAH profiles  
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14 were dominated by Phe. [PAHs]<sub>atm</sub> for individual compounds were 2-4 times higher than  
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16 those measured in this study.  
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### 22 **Estimating the African emission strength**

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

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8 Of the coastal African countries only Senegal, with a population of about 11 million  
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10 inhabitants, has some developed industry including oil extraction. Around 50 extractive  
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12 offshore platforms are documented for Senegal, resulting in an intense international trade  
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14 of crude oil, land base refineries and chemical industries (27). The abundance of more  
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16 volatile PAHs is consistent with the atmospheric fingerprint measured in areas where un-  
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18 combusted fuel, oil spills and potentially gas flaring represent the main source to the  
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20 atmosphere (16, 28, 29). Other ships sailing along this route might have added to the  
21  
22 atmospheric PAHs measured. Biomass burning and natural fires could also have  
23  
24 contributed to the observed concentrations. September - October are periods of peak fire  
25  
26 activity in sub-Saharan and Central Africa (30, 31). Our observed PAH profiles match  
27  
28 those from wood burning, suggesting that biomass burning could have added to the  
29  
30 observed plume (32).  
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36 Natural sources could also contribute to the elevated [PAHs]<sub>atm</sub>. Microbial activity in  
37  
38 tropical soils, especially the anaerobic degradation of organic matter containing pigments,  
39  
40 represents a natural source of PAHs such as Perylene, Phe and Naphtalene (33, 34). The  
41  
42 PAHs could therefore have been transported to the region by atmospheric transport  
43  
44 following volatilization from soils or via run-off and riverine transport of terrestrial  
45  
46 matter. Further work is needed to identify the source(s) of those elevated concentration.  
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### 52 53 **Biogeochemical processes** 54 55 56 57 58 59 60

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3 Simultaneous air and water sampling was performed in 15 selected areas along the  
4  
5 transect to assess the air-water exchange of PAHs. This is one of the main processes  
6  
7 transferring pollutants between air and water (35, 36). Air-water fugacity ratios (37) were  
8  
9 calculated for PAHs that were routinely detected in both phases as follows:  
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11

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

12  
13 where  $C_a$  is the gaseous concentration ( $\text{mol m}^{-3}$ ),  $C_w$  is the dissolved aqueous  
14  
15 concentration ( $\text{mol m}^{-3}$ ),  $R$  is the gas constant ( $\text{J K}^{-1} \text{mol}^{-1}$ ) and  $H$  is the Henry's law  
16  
17 constant ( $\text{Pa m}^3 \text{mol}^{-1}$ ). Values of  $H$  and their temperature dependence were taken from  
18  
19 Bamford et al. (38) and Shiu and Ma (39) and were corrected for salinity using the  
20  
21 Setshenow equation. Ratios  $> 1$  were observed for Phe, Fla and Pyr in the Biscay Bay  
22  
23 and in the NW African hotspot suggesting net deposition (Figure 3). Fla and Pyr  
24  
25 appeared to be close to equilibrium in all other areas. Ratios  $< 1$  were observed for Phe  
26  
27 and Ant in all locations characterized by low atmospheric concentrations. The calculation  
28  
29 of the fugacity ratios was performed taking into consideration the uncertainty factors  
30  
31 reported by McLeod et al. (40). The uncertainty of air-water exchange is dominated by  
32  
33 accurately knowing  $H$  (95% confidence within a factor  $\sim 3$ ), minimizing the impact of  
34  
35 analytical uncertainties (ca. 30% each for PAHs in atmosphere and water) (41).  $f_a / f_w$  for  
36  
37 Phe and Ant ranged in those areas between 0.04 and 0.36, suggesting the occurrence of  
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39 net (re-)volatilization.  
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48 The following section assesses the factors/processes which could have contributed to  
49  
50 the volatilization of PAHs.  
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3 Net diffusive air-water flux  $F_{a-w}$  ( $\text{ng m}^{-2} \text{d}^{-1}$ ) was calculated for Ant and Phe in regions  
4 where the average  $f_a / f_w < 0.3$ . This threshold reflects the uncertainty of around 3 in  
5 knowing the exact  $f_a / f_w$  (40). Fluxes were estimated using a two resistance model (1, 2):  
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9

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

10  
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14 where  $k_{ol}$  ( $\text{m d}^{-1}$ ) is the overall mass transfer coefficient estimated as described  
15 elsewhere (42). Volatilization fluxes were 70-210 and 3-70  $\text{ng m}^{-2} \text{d}^{-1}$  for Phe and Ant  
16 respectively (Figure 4).  $k_{ol}$  is known within a factor of 3 (40), rendering the uncertainty of  
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 $F_{a-w}$  to be at worst an order of magnitude.

26 Atmospheric degradation plays a key role in the environmental fate of PAHs and  
27 competes with air-water exchange. Atmospheric degradation is mainly due to OH-radical  
28 reactions. The degradation flux  $F_{deg}$  can be estimated as:  
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$$F_{deg} = h \cdot k_{OH} C_{OH} C_a \quad 3)$$

40 where  $h$  (m) is the height of sampling a.s.l.,  $k_{OH}$  ( $\text{cm}^3 \text{molecules}^{-1} \text{d}^{-1}$ ) is the degradation  
41 rate constant, and  $C_{OH}$  ( $\text{molecules cm}^{-3}$ ) is the concentration of OH radicals. These were  
42 calculated as follows:  $h$  was set to 20 m, the height at which the samplers were  
43 positioned;  $k_{OH}$  values were taken from Brubaker and Hites (43);  $C_{OH}$  was estimated from  
44 T (44). OH-radical depletion fluxes were 7-120 and 9-50  $\text{ng m}^{-2} \text{d}^{-1}$  for Phe and Ant,  
45 respectively (Figure 4). The confidence of the estimated  $F_{deg}$  is an order of magnitude,  
46 dominated by the uncertainty of knowing OH concentrations. OH radical depletion fluxes  
47 were comparable in magnitude to the water-to-air fluxes, presumably causing the  
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3 continuous volatilization of PAHs from the water. This raises questions about the  
4 processes which could have supplied sufficient amounts of PAHs to the surface ocean.  
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8 Atmospheric deposition PAH deposition on aerosols was assessed by estimating the  
9 particle bound concentration ( $C_p$ ,  $\text{pg m}^{-3}$  of air) from OC and EC concentrations (6)  
10 details are given in Text SI\_2). The dry deposition flux ( $\text{ng m}^{-2}\text{d}^{-1}$ ) was calculated as:  
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$$F_{DD} = C_p v_D \quad 4)$$

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18 where  $v_D$  ( $\text{m d}^{-1}$ ) is the particles' deposition velocity. Values of  $v_D$  were taken from Del  
19 Vento and Dachs (24), using on-board measurements from a different cruise.  $F_{DD}$ s for  
20 Phe and Ant were 0.002-0.120 and 0.006-0.340  $\text{ng m}^{-2}\text{d}^{-1}$  respectively; 3 - 4 orders of  
21 magnitude lower than  $F_{a-w}$  and  $F_{deg}$  (Figure 4), ruling out a significant contribution to the  
22 relatively high fugacity of surface water, even considering an uncertainty of 1 order of  
23 magnitude. Wet deposition, finally, does not appear to significantly contribute in adding  
24 PAHs to the surface ocean either in this region. Jurado et al. (35) showed that wet  
25 deposition fluxes are important during the rain event itself but they lose their importance  
26 over longer time scales. During the cruise, especially in the SH, no significant rain events  
27 were recorded.  
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42 The lowest fugacity ratios were observed in tropical/ subtropical latitudes. These regions  
43 have no marked seasonality, so changes in T, water productivity etc. should not affect the  
44 fugacity ratio in this area much. In any case, biological productivity would affect PAHs  
45 with higher  $K_{OW}$  values, such as Fla and Pyr, which were close to equilibrium. It is also  
46 unlikely that short time scale fluctuations (days-weeks) in the advective fluxes could  
47 generate the observed behavior, given the distance from the land and the constant pattern  
48 of the air masses coming from the open ocean. This was confirmed through back  
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3 trajectory analysis (23), at least for all the sites in the SH, by following their air mass  
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5 origin during the week before the sampling.  
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8 Taken together, atmospheric deposition alone cannot account for the observed net  
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10 volatilization flux of PAHs, suggesting that there is an additional source of PAHs in the  
11  
12 surface water. One hypothesis could be the existence of natural sources for Phe and Ant  
13  
14 in the water column, following what was observed in tropical soils (33, 34). The fast  
15  
16 turnover of organic matter and the rapid degradation of pigments carrying aromatic  
17  
18 structures could be the driving process. Elevated water temperature and the scarcity of  
19  
20 nutrients, typical of the NH and SH gyres, promote the rapid recycling of almost all Fe, C  
21  
22 and N early in the surface waters (45). This, together with the absence of significant  
23  
24 vertical removal processes (low export rate (1)), would enhance PAH fugacity in water,  
25  
26 supporting their net volatilization. If they exist, such sources would also release PAHs in  
27  
28 other regions, such as the NW African hot spot, contributing to the high concentrations  
29  
30 measured there in both water and air. If present, natural PAH sources in the oceans could  
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32 be more easily detected in remote and oligotrophic areas such as the northern and  
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34 southern gyres, under stable conditions removed from anthropogenic sources. This  
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36 hypothesis needs further investigation, since anthropogenic sources are generally  
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38 considered to dominate the regional/global inventories of PAHs.  
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49  
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51  
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54 support.  
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## Supporting Information

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

## REFERENCES

1) Dachs, J., Lohmann, R., Ockenden W. A., Mejanelle, L., Eisenreich, S.J., Jones, K. C., Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. *Environ. Sci. Technol.*, **2002**, 36, 4229-4237.

2) Iwata, H., Tanabe, S., Sakal, N., Tatsukawa, R., Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate, *Environ. Sci. Technol.*, **1993**, 27, 1080-1098.

3) Dachs, J., Eisenreich, S. J., Baker, J. E., Ko, F. C., Jeremiason, J. D., Coupling of phytoplankton uptake and air-water exchange of persistent organic pollutants, *Environ. Sci. Technol.*, **1999**, 33, 3653-3660.

4) Wild, S. R., Jones, K. C., Polynuclear aromatic hydrocarbons in the United Kingdom environment, *Environ. Pollut.*, **1995**, 88, 91-108.

5) Dachs, J., Eisenreich, S. J., Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, **2000**, 34, 3690-3697.

1  
2  
3 6) Lohmann, R., Lammel, G., Adsorptive and absorptive contributions to the gas-  
4 particle partitioning of polycyclic aromatic hydrocarbons: state of the knowledge and  
5 recommended parametrization for modeling, *Environ. Sci. Technol.*, **2004**, 38, 3793-  
6 3803.  
7

8  
9  
10  
11  
12  
13 7) Mader, B. T., Pankow J. F., Study of the effects of particle-phase carbon on the  
14 gas/particle partitioning of semivolatile organic compounds in the atmosphere using  
15 controlled field experiments. *Environ. Sci. Technol.* **2002**, **36**, 5218-5228.  
16  
17

18  
19  
20  
21 8) Pankow, J. F. and T. F. Bidleman (1991). "Effects of Temperature, Tsp and Per Cent  
22 Nonexchangeable Material in Determining the Gas Particle Partitioning of Organic-  
23 Compounds." *Atmos. Environ. Part A* **25**(10): 2241-2249.  
24  
25  
26

27  
28  
29 9) Mackay, D., Shiu, Y.W., Ma, K.C. *Illustrated handbook of physical-chemical*  
30 *properties and environmental fate for organic chemicals*, Lewis Publisher, **1992**, Boca  
31 Raton  
32  
33  
34  
35

36  
37  
38 10) Jaward, F. M., Barber, J.L., Booij, K., Jones, K.C., Spatial distribution of  
39 atmospheric PAHs and PCNs along a north-south Atlantic transect, *Environ. Pollut.*,  
40 **2004**, 132, 173-181.  
41  
42  
43

44  
45  
46 11) Jaward, F. M., Barber, J.L., Booij, K., Dachs, J., Lohmann, R., Jones, K.C.,  
47 Evidence for dynamic air-water coupling and cycling of persistent organic pollutants over  
48 open Atlantic Ocean, *Environ. Sci. Technol.*, **2004**, 38, 2617-2625.  
49  
50  
51

52  
53 12) Lohmann, R., Jaward, F.M., Durham, L., Barber, J.L., Ockenden, W., Jones, K.C.,  
54 Bruhn, R., Lakashus, S., Dachs, J., Booij, K., Potential contamination of shipboard air  
55  
56  
57  
58  
59  
60

1  
2  
3 samples by diffusive emissions of PCBs and other organic pollutants: implications and  
4 solutions, *Environ. Sci. Technol.*, **2004**, 38, 3965-3970.  
5  
6

7  
8  
9 13) Birch, M., Cary, R. A., Elemental carbon-based method for monitoring  
10 occupational exposure to particulate diesel exhaust, *Aerosol Sci. Technol.*, **1996**, 25,  
11 221-241.  
12  
13  
14

15  
16  
17 14) Dorr, G., Hippelein, M., Hutzinger, O., Baseline contamination assessment for a  
18 new resource recovery facility in Germany, part V: levels and profiles of polycyclic  
19 aromatic hydrocarbons (PAH) in ambient air, *Chemosphere*, **1996**, 33, 1569-1578.  
20  
21  
22

23  
24  
25 15) Ravindra, K., Mittal, A.K., Van Grieken, R., Health risk assessment of urban  
26 suspended particulate matter with special reference to polycyclic aromatic hydrocarbons:  
27 a review, *Rev. Environ. Health.*, **2001**, 16, 169-189.  
28  
29  
30

31  
32  
33 16) Ravindra K., Bencs, L., Wauters, E., de Hoog, J., Deutsch, F., Roekens, E., Bleux,  
34 N., Berghams, P., Van Grieken, R., Seasonal and site-specific variation in vapour and  
35 aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic  
36 activities, *Atmos. Environ.*, **2006**, 40, 771-785.  
37  
38  
39

40  
41  
42  
43 17) Simcik, M. F., Basu, I., Sweet, C. W., Hites, R. A., Temperature dependence and  
44 temporal trends of polychlorinated biphenyl congeners in the great lakes, *Environ. Sci.*  
45  
46  
47  
48  
49  
50

51 18) Wania, F.; Haugen, J.-E.; Lei, Y. D.; Mackay, D. Temperature dependence of  
52 atmospheric concentrations of semivolatile organic compounds. *Environ. Sci. Technol.*  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 19) Gioia, R., Nizzetto, L., Lohmann, R., Dachs, J., Jones, K.C., Polychlorinated  
4 biphenyls (PCBs) in air and seawater of the Atlantic Ocean. *Environ. Sci. Technol.*, in  
5  
6  
7  
8 *press*.

9  
10  
11 20) Schulz-Bull, D. E., Petrick, G., Bruhn, R., Duinker, J. C. Chlorobiphenyls (PCB)  
12 and PAHs in water masses of the northern North Atlantic, *Marine Chem.*, **1998**, 61, 101-  
13  
14  
15  
16 114.

17  
18  
19 21) Loyer, S., Lampert, L., Menesguen, A., Cann, P., Labasque, T., Seasonal evolution  
20 of the nutrient pattern on Biscay Bay continental shelf over the years 1999-2000, *Scientia*  
21  
22  
23  
24 *Marina*, **2002**, 70, 31-46.

25  
26  
27 22) Wooster, W. S., Bakun, A., McLain, D. R., The seasonal upwelling cycle along the  
28 eastern boundary of the North Atlantic, *J. Marine Res.*, 1976, 34, 131-141.

29  
30  
31  
32 23) NOAA ARL HYSPLIT Model. <http://www.arl.noaa.gov/ready/Hysplit4.html>.

33  
34  
35  
36 24) Del Vento, S., Dachs, J., Atmospheric occurrence and deposition of polycyclic  
37 aromatic hydrocarbons in the north-east tropical and subtropical atlantic ocean, *Environ.*  
38  
39  
40  
41 *Sci. Technol.*, **2007**, 41, 5608-5613.

42  
43  
44 25) Lee, R. G. M., Coleman, P., Jones, J. L., Jones, K. C., Lohmann, R., Emission  
45 factors and importance of PCDD/Fs, PCBs, PCNs, PAHs and PM10 from the domestic  
46  
47  
48  
49 burning of coal and wood in the UK, *Environ. Sci. Technol.*, **2005**, 39, 1436-1447.

50  
51  
52 26) Lobsheid, A. B., McKone, T. E., Constraining uncertainties about the sources and  
53  
54  
55  
56  
57  
58  
59  
60 magnitude of polycyclic aromatic hydrocarbon (PAH) levels in ambient air: the state of  
Minnesota as a case study, *Atmos. Environ.*, **2004**, 38, 5501-5515.

1  
2  
3  
4  
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6  
7  
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52  
53  
54  
55  
56  
57  
58  
59  
60

27) <http://www.mbendi.co.za/land/af/sn/p0005.htm>

28) Gevao, B., Al-Omair, A., Al-Ali, L., Al-Bahloul, M., Helaleh, M., Zafar, J., Passive sampler-derived air concentrations for polybrominated diphenylethers and polycyclic hydrocarbons in Kuwait, *Environ. Toxicol. Chem.*, **2006**, 25, 1496-1502.

29) Strosher, M. T., Characterization of emissions from diffusion flare systems. *J. Air Waste Management Association*, **2000**, 50, 1723-1733.

30) Csiszar, I., Denis, L., Giglio, L., Justice, C. O., Hewson, J., Global fire activity from two years of MODIS data, *Int. J. Wildland Fire*, **2005**, 14, 117-130

31) Edwards, D. P., Emmons, L. K., Gille, J. C., Chu, A., Attié, J. L., Giglio, L., Wood, S. W., Haywood, J., Deeter, M. N., Massie, S. T., Ziskin, D. C., Drummond, J. R., Satellite-observed pollution from Southern Hemisphere biomass burning, *J. Geophys. Res.*, **2006**, 111, D14312.

32) Oros, D.R., Simoneit, B.R.T., Identification and emission factors of molecular tracers in organic aerosols from biomass burning. Part 1. Temperature climate conifers. *Appl Geochem.*, **2001**, 16, 1513–1544.

33) Wilcke, W., Krauss, M., Amelung, W., Carbon isotope signature of Polynuclear aromatic hydrocarbons (PAHs): evidence for different sources in tropical and temperate environments? *Environ. Sci. Technol.*, **2002**, 36, 3530-3535.

34) Chen, J., Henderson, G., Grimm, C. C., Lloyd, S. W., Laine, R. A., Termites fumigate their nests with naphthalene, *Nature*, **1998**, 392, 558.

1  
2  
3 35) Jurado, E., Jaward, F., Lohmann, R., Jones, K. C., Simoa, R., Dachs, J., Wet  
4 deposition of persistent organic pollutants to the global ocean. *Environ. Sci. Technol.*,  
5  
6 **2005**, 39, 2426-2435.  
7  
8

9  
10  
11 36) Jurado, E., Jaward, F., Lohmann, R., Jones, K. C., Simoa, R., Dachs, J.,  
12 Atmospheric dry deposition to the Atlantic and interferences for the global ocean,  
13  
14 *Environ. Sci. Technol.*, **2004**, 38, 5505-5513.  
15  
16

17  
18  
19 37) Mackay, D, Finding fugacity feasible. *Environ. Sci. Technol.* **1979**, 13: 1218-1223.  
20  
21

22  
23 38) Bamford, H. A., Poster, D. L., Baker, J. E., Temperature dependence of Henry's  
24 law constants of thirteen polycyclic aromatic hydrocarbons between 4°C and 31°C,  
25  
26 *Environ. Toxic. Chem.*, **1999**, 18, 1905-1912.  
27  
28

29  
30 39) Shiu, W. Y., Ma, K. C., Temperature dependence of Physical-Chemical properties  
31 of selected chemicals of environmental interest. I. Mononuclear and polynuclear aromatic  
32 hydrocarbons, *J. Phys. Chem. Ref. Data*, **2000**, 29, 41-130.  
33  
34  
35

36  
37  
38 40) MacLeod, M., Fraser, A. J., Mackay, D., Evaluating and expressing the propagation  
39 of uncertainty in chemical fate and bioaccumulation models, *Environ. Toxicol. Chem.*,  
40  
41 **2002**, 21, 700-709.  
42  
43

44  
45  
46 41) Bruhn, R., Lakaschus, S., McLachlan, M. S., Air/sea gas exchange of PCBs in the  
47 southern Baltic Sea, *Atmos. Env.*, **2003**, 37, 3445-3454.  
48  
49

50  
51  
52 42) Schwarzenbach, R. P., Gschwend, P. M., Imboden, D. M., **2003**. Environmental  
53 Organic Chemistry, 2nd ed. . " John Wiley, New York, NY, USA. .  
54  
55



1  
2  
3 43) Brubaker, W. W., Hites, R., OH reaction kinetics of polycyclic aromatic  
4 hydrocarbon and polychlorinated dibenzo-p-dioxins and dibenzofurans, *J. Phys. Chem. A*,  
5  
6 **1998**, 102, 915-921.  
7  
8

9  
10  
11 44) Beyer, A., Wania, F., Gouin, T., Mackay, D., Matthies, M., Temperature  
12 dependence of the characteristic travel distance, 2003, *Environ. Sci. Technol.*, **2003**, 37,  
13  
14 766-771.  
15  
16

17  
18  
19 45) Thomalla, S., Turnewitsch, R., Lucas, M., Poulton, A., Particulate organic carbon  
20 export from the North and South Atlantic gyres: the  $^{234}\text{Th}/^{238}\text{U}$  disequilibrium approach,  
21  
22 *Deep Sea Res. Part II*, **2006**, 53, 1629-1648.  
23  
24  
25  
26  
27  
28  
29  
30  
31  
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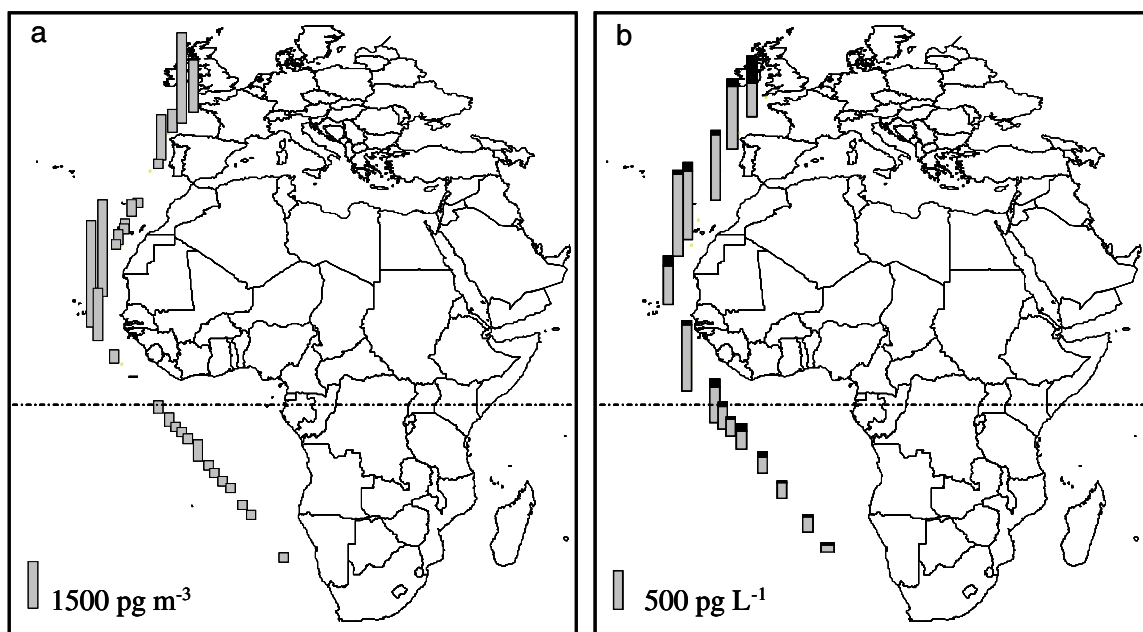


Figure 1. Latitudinal distribution of  $\Sigma_{10}$ PAHs in a: Air, b: Water (grey represents the dissolved fraction and black the particle associated fraction).

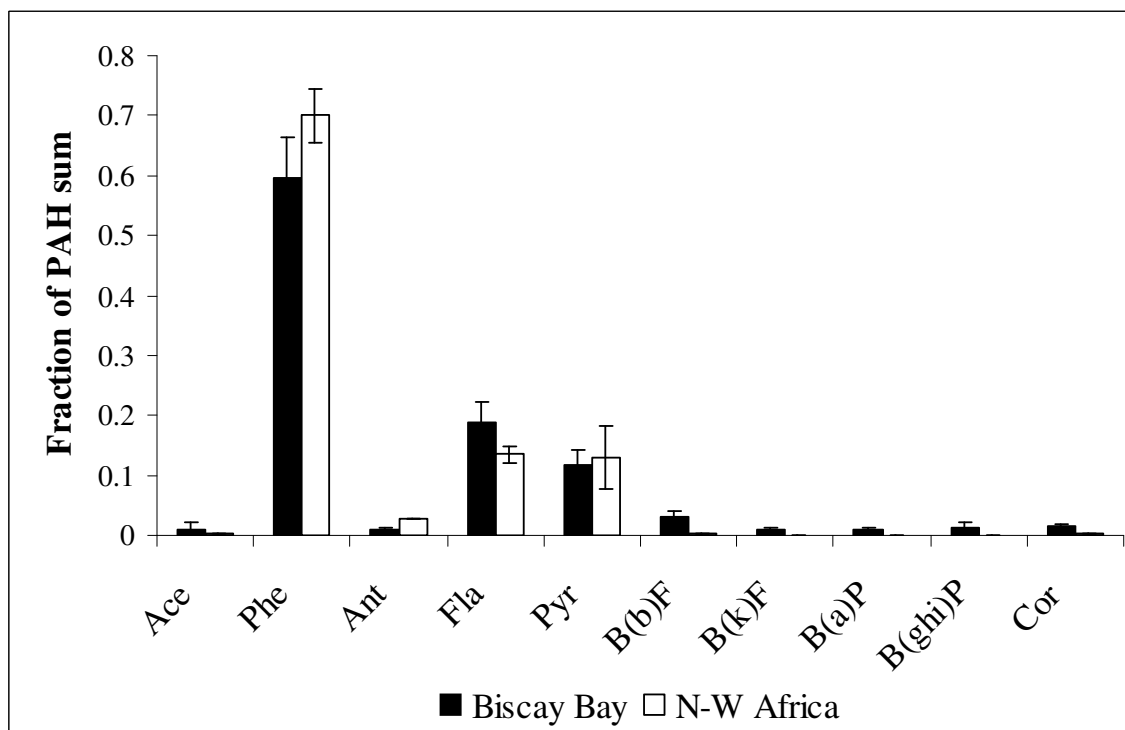


Figure 2. Comparison of the average atmospheric PAH profile in the Biscay Bay and in N-W Africa. Error bars represent 1 standard deviation.

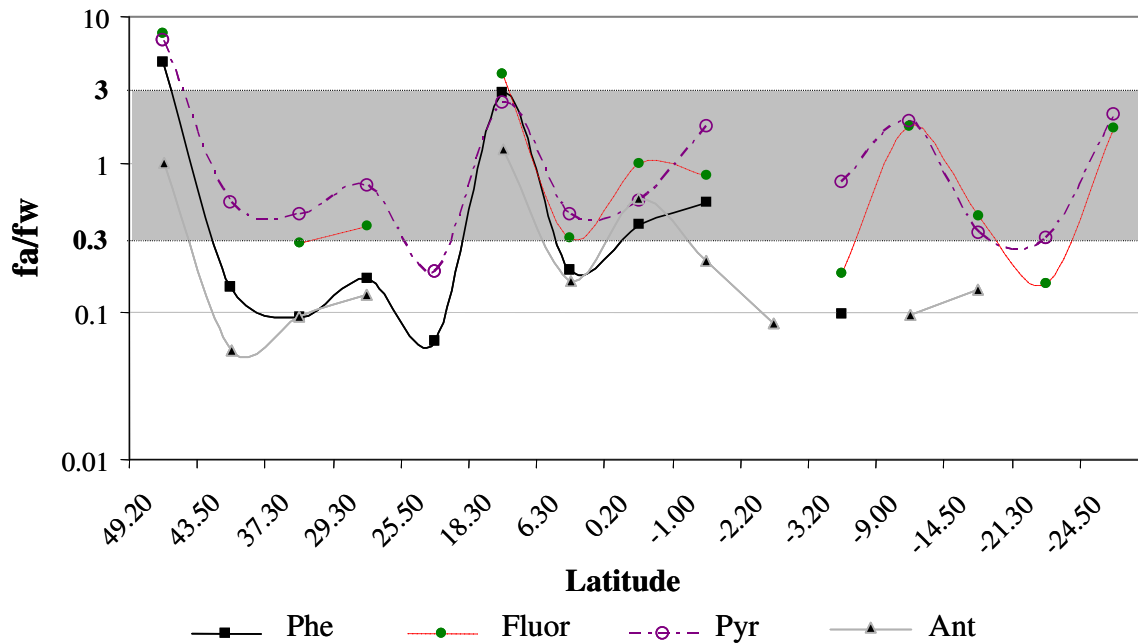


Figure 3: Fugacity ratios of selected PAHs. The grey area shows the uncertainty of air-water equilibrium; ratios outside suggest PAHs not at air-water equilibrium.

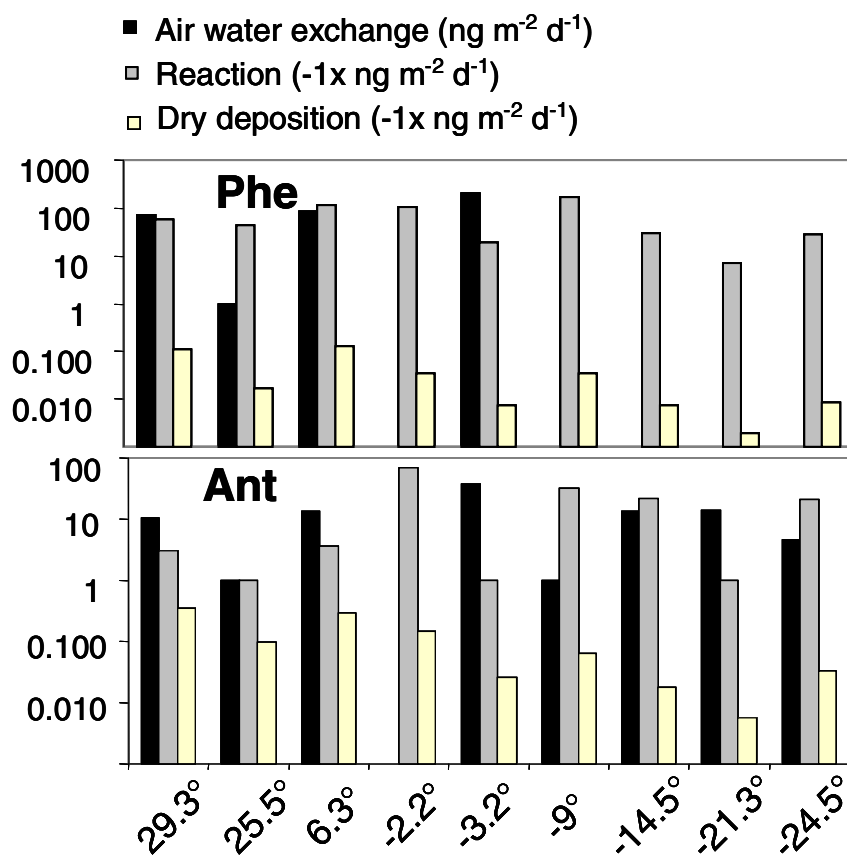


Figure 4. Calculated inter-compartmental fluxes of phenanthrene and anthracene in areas with  $f_d/f_w < 0.3$