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Deposition of polycyclic aromatic hydrocarbons in the North Pacific and the Arctic

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[1] Eighteen polycyclic aromatic hydrocarbons (PAHs) were simultaneously measured in surface seawater and boundary layer air from the North Pacific toward the Arctic Ocean during the Fourth Chinese National Arctic Research Expedition in the summer of 2010. Atmospheric Σ_{18} PAH ranged from 910 to 7400 pg m⁻³, with the highest concentrations observed in the coastal regions of East Asia. Correlations of PAHs' partial pressures versus inverse temperature were not significant, indicating the importance of ongoing primary sources on ambient PAH levels in the remote marine atmosphere. The relatively high atmospheric concentrations observed in the most northerly latitudes of the Arctic Ocean suggest the influence of regional sources. For example, higher levels of particle-bound PAHs were observed in the air of the Arctic Ocean than the North Pacific, indicating forest fire and/or within-Arctic sources. Concentrations of PAHs in surface seawater were within a range of 14–760 pg L⁻¹ and generally decreased with increasing latitude. The observed air-sea gas exchange gradients strongly favored net deposition of PAHs along the entire cruise, with increasing deposition with increasing latitude, while the particle-bound dry deposition fluxes (particularly for the high molecular weight PAH) were highest at sample sites close to East Asia. Based on characteristic PAH ratios, atmospheric PAHs originated from the combustion of biomass or coal, while the ratios observed in seawater reflected a mixture of sources. Given the dominance of primary emissions to the atmosphere and the relatively fast removal of PAHs from the water column, then PAHs will continue to load into the surface waters of the remote marine environment via atmospheric deposition.

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1. Introduction

[2] As a class of semivolatile organic compounds, polycyclic aromatic hydrocarbons (PAHs) are carcinogenic and mutagenic pollutants originating from incomplete combustion and pyrolysis of carbonaceous materials [Ding *et al.*, 2007; Okona-Mensah *et al.*, 2005]. In addition to natural sources, such as oil seeps and forest fires, anthropogenic sources such as fossil fuel and wood combustion still

dominate emissions [Jaward *et al.*, 2004a; Nizzetto *et al.*, 2008; Wild and Jones, 1995]. Another characteristic of PAHs is their sorption to aerosol organic matter, with gas-particle partitioning influencing their atmospheric long-range transport (LRT) and environmental fate [Dachs and Eisenreich, 2000; Lohmann and Lammel, 2004]. Due to direct and indirect photolysis, PAHs are less stable during atmospheric LRT than most other persistent organic pollutant (POPs), which makes them a complementary group of compounds for investigating the role of atmospheric persistence on the presence of POPs in remote oceans [Lohmann *et al.*, 2009].

[3] The Arctic Ocean, for example, receives POPs principally via atmospheric deposition and is no longer a pristine environment free of anthropogenic contaminants [MacDonald *et al.*, 2000]. PAHs have been extensively monitored in ambient air in some Arctic land-based stations (Alert, Yukon, and Zeppelin), and several modeling studies have indicated continental and transoceanic sources of PAHs from midlatitudes [Halsall *et al.*, 1997; Hung *et al.*, 2005; Sofowote *et al.*, 2011; Wang *et al.*, 2010]. It is estimated that the annual (2004) PAH emission from Asian countries contributed ~55% of the global atmospheric emission inventory of PAHs, with the top two emitting countries being China and

Additional supporting information may be found in the online version of this article.

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India, respectively [Zhang and Tao, 2009]. Ice core and surface snow samples from the Greenland ice cap have further demonstrated an increase of anthropogenic PAH deposition over the last 100 years, which correlates strongly with the historical record of world petroleum production. Therefore, current PAH contamination is essentially due to fossil fuel combustion with some inputs from biomass burning [Jaffrezo *et al.*, 1994; Kawamura *et al.*, 1994], and this has been also observed in high-altitude snow/ice cores in the European Alps [Gabrieli *et al.*, 2010].

[4] In addition to the atmospheric LRT process, surface ocean currents are also considered to provide significant transfer routes to the Arctic due to ongoing deposition and gaseous exchange between the atmosphere and seawater [Iwata *et al.*, 1993; Weber *et al.*, 2006]. Simultaneous observations of PAHs in open ocean air and water are rather limited, despite the importance of biological exposure for marine food webs and for controlling the global fate and burden of these chemicals. Moreover, PAHs stored in surface waters may be further controlled by the “biological pump” and undergo uptake into the marine food chain, as well as degradation and removal via carbon export to the deeper oceans, which is traditionally considered as the final sink for organic pollutants [Jaward *et al.*, 2004b]. However, it has been suggested that as primary sources of POPs are reduced, then remote areas like the Arctic Ocean may play a role as a secondary source, resulting in reemission of POPs through exchange between air and water [Cai *et al.*, 2012; Lohmann *et al.*, 2009]. Therefore, for PAHs, the role of oceans as an exchanging compartment with air and/or permanent sink is not fully understood and requires investigation.

[5] To improve the knowledge of the global PAH distribution and the role of atmosphere and ocean on the long-range transport and fate of PAHs, marine boundary layer air and surface seawater samples were collected during the Fourth Chinese National Arctic Research Expedition (CHINARE2010) from East Asia to the High Arctic (35°N–82°N). In this study, the occurrence of 18 PAHs in air and seawater is presented, together with their latitudinal distribution as well as an assessment of their dry deposition and air-water gas exchange along a transect from the North Pacific to the Arctic Ocean.

2. Experimental Section

2.1. Sampling Cruise

[6] Air and seawater samples were taken from the East China Sea to the High Arctic (33.23°N–84.5°N) during an Arctic expedition of the research ice-breaker R/V *Xuelong* (*Snow Dragon*) between June and September 2010. Air samples (~500 m³ per sample, 17 samples) were taken via a high-volume air sampler placed at the front of the ship’s upper deck (20 m, across the bow). The air sampler was well removed from the potential contamination sources such as the ship’s stack/exhaust and only operated under a prevailing headwind. The sample media consisted of a glass fiber filter (GFF) (GF/F, diameter: 135 mm, pore size: 0.7 μm) to trap airborne particles, followed by a self-packed PUF/XAD-2 glass column [1 piece polyurethane slice: 2 cm × Ø5 cm and 35 g XAD-2 resin (particle size: 0.3–1.0 mm)] to collect PAHs in the gaseous phase. The glass columns and filters were stored at –20°C until analysis. Seawater samples

(176–1120 L per sample, 18 samples) were taken using the ship’s intake system (stainless steel pipe line) through a sampler consisting of a GFF (GF/C, 142 mm, pore size: 1.2 μm) followed by a self-packed PAD-3 glass column [length: 250 mm, OD: 30 mm, ID: 25 mm, 30 g PAD-3 resin (particle size: 0.3–1.0)]. The filters were stored at –20°C and the columns at 4°C until analysis. Air and seawater samples were taken together and broadly overlap in both time and space. The dates, positions, temperatures, and wind speeds during the sampling periods are listed in Tables A1 and A2 in the supporting information.

2.2. Material and Reagents

[7] The PAH compounds (Dr. Ehrenstorfer, Germany) measured in this study were as follows (abbreviations in parentheses): naphthalene (Nap), 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), acenaphthylene (Acl), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluor), pyrene (Py), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IP), dibenz[*a,h*]anthracene (DBahA), and benzo[*ghi*]perylene (BghiP). All solvents (methanol, acetone, dichloromethane, and *n*-hexane) were residue grade and were distilled further in an all-glass unit prior to use. All glassware was cleaned with Milli-Q water and acetone and then baked out at 250°C for 10 h.

2.3. Sample Extraction and Cleanup

[8] Extraction and cleanup of the samples was based on our previously published method [Zhong *et al.*, 2012]. Briefly, samples were spiked with internal standards d₁₀-acenaphthene and d₁₂-perylene (10 μL × 1 ng μL⁻¹) prior to extraction, then Soxhlet extracted and purified on a 10% water-deactivated silica column (25 cm × 1 cm ID glass column packed with 2.5 g silica gel + 3 g Na₂SO₄). The first fraction, eluted with 20 ml *n*-hexane, was collected and concentrated to 50 μL. Samples were spiked with an injection standard ¹³C₁₂-PCB-208 (500 pg) prior to gas chromatography–mass spectroscopy (GC-MS) analysis. Analysis was performed on a GC-MS instrument (6890 GC/5975 MSD) operating in electron impact mode. The *m/z* values monitored for quantification and quality control are summarized in Table S3 in the supporting information.

2.4. QA/QC

[9] Sampling columns were preextracted with methanol (48 h), acetone (48 h), and hexane + acetone (1 + 1 v/v) (48 h) in turn. GFFs were baked out at 450°C for 8 h. Na₂SO₄ and silica gel (particle size: 60 mesh) were extracted with dichloromethane for 24 h and then baked out at 450°C for 8 h. The air columns were protected against UV light using aluminum foil to avoid degradation of the target compounds during sampling. Water samples were pumped at 10 m depth (0.5 m beneath the keel of the *Xuelong*). Three PUF/XAD-2 columns, three PAD-3 columns, and five GFF filters were prepared for field blanks on board like handling the sampling material on site. Blank samples were transported together with the samples back to the laboratory (Helmholtz-Centre Geesthacht, Germany). Method detection limits were derived from the mean blank values plus three times the standard deviation (σ) and are summarized

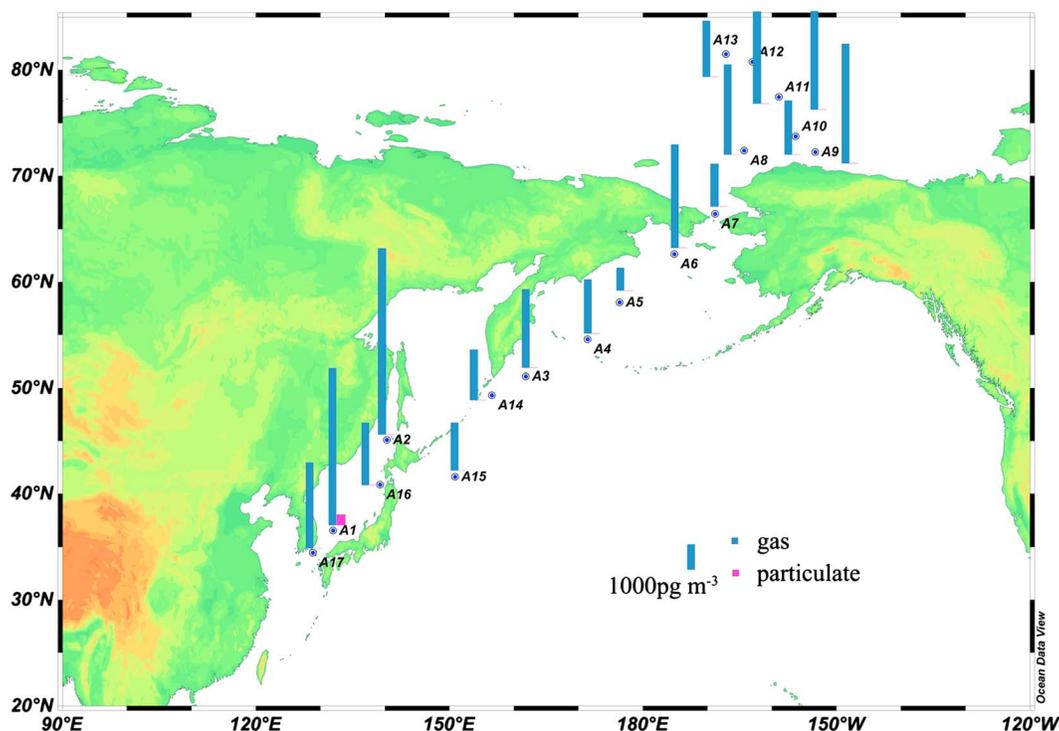


Figure 1. Concentrations of gas- and particulate-phase PAHs in the atmosphere ($\Sigma_{18}[\text{PAHs}]_{\text{atm}}$) along the sampling cruise.

in Table S3 in the supporting information. Recoveries of internal standards d_{10} -acenaphthene and d_{12} -perylene were $77 \pm 16\%$ and $138 \pm 21\%$ in the gaseous phase, $92 \pm 8\%$ and $116 \pm 9\%$ in GFFs, and $93 \pm 15\%$ and $123 \pm 11\%$ in the dissolved phase of water, respectively. Sample results were not corrected for recoveries and blank values.

2.5. Air Mass Back Trajectories

[10] The air mass origins of individual air samples along the cruise were evaluated using air mass back trajectories (BTs) calculated by the NOAA HYSPLIT model [Draxler and Hess, 1997]. Air mass back trajectories (BTs) were calculated in 6 h steps tracing back the air masses for 5 days using the sampling height as the arrival height (see Figure S1 for individual BTs).

3. Results and Discussion

3.1. Atmospheric Concentration Trends

[11] The sums of atmospheric concentrations of 18 PAHs ($\Sigma_{18}[\text{PAHs}]_{\text{atm}}$) ranged from 910 to 7400 pg m^{-3} , with a mean of $3300 \pm 1700 \text{ pg m}^{-3}$ during the entire cruise. The gas-phase PAHs (910–7400 pg m^{-3}) were much higher than those of the particulate phase (0.2–360 pg m^{-3}). Generally, the two- to four-ringed PAHs, from Nap to Py, occurred predominantly in the gas phase (83%–100%); Nap and its alkylated derivatives (1MN and 2MN) contributed >50% to $\Sigma_{18}[\text{PAHs}]_{\text{atm}}$. The heavier compounds (five- to six-ringed PAHs), particularly BbF, BkF, BaP, and BghiP, were mainly detected in the particulate phase (55%–78%, Table S4). The spatial distribution of $\Sigma_{18}[\text{PAHs}]_{\text{atm}}$ (gas + particulate) from 33°N to 84°N is shown in Figure 1. The observed mean

concentrations of $\Sigma_{18}[\text{PAHs}]_{\text{atm}}$ were highest in East Asia (30°N–48°N, 4000 pg m^{-3}), followed by those in the Arctic Ocean (>70°N, 3400 pg m^{-3}) and the North Pacific Ocean (50°N–66°N, 2400 pg m^{-3}). Compared with measurements taken during 2003 in the same regions, our results were significantly lower for both particulate and gas phases [Ding *et al.*, 2007]. Though only a few individual PAHs were reported in a north-south Atlantic transect [Jaward *et al.*, 2004a; Nizzetto *et al.*, 2008], the PAH levels of this study are comparable to these data (Table A6a in the supporting information). Moreover, our results are comparable to the PAHs measured in Lohmann *et al.* (i.e., a west-to-east transect across the tropical Atlantic Ocean) with 10s to 1000s pg m^{-3} for Phe and 10s to 100s pg m^{-3} for Py, Fluro, and Flu [Lohmann *et al.*, 2013]. For this study, comparison of PAH data with those acquired from other remote/marine expeditions is essential. This is because ship-based surveillance for organic compounds, like PAHs, runs the risk of contamination artifacts. For PAHs, both fuel-based evaporation (petrogenic source) and combustion (pyrolytic, e.g., ship's stack) sources may interfere with measurements conducted in background remote/marine air. Importantly, the levels found in our study in the Arctic are comparable to the historic results of the Arctic land-based monitoring stations (e.g., Alert, Tagish, and Dunai during 1992–2000) [Halsall *et al.*, 1997; Hung *et al.*, 2005]. Specifically, compared with recent PAH data acquired at Alert in the summer of 2009, our results are a little higher but are still comparable (Table S6b in the supporting information). Similarly, in comparison with data acquired from a ship-based campaign in the Atlantic/Arctic Ocean area (Table S6b in the supporting information) [Lohmann *et al.*, 2009], our PAH levels are clearly lower. However, in that

study, the authors admitted that their samples were strongly affected by fuel vapors from the ship. In our study, precautions were taken to minimize this artifact by only using data for air samples that were taken under favorable headwind conditions (i.e., at the front of the ship's upper deck, across the bow). The air sampler was also located away from obvious contamination sources like the exhaust stack and fueling systems. In view of the comparable concentrations we observed with the Alert data, we consider that contamination from the ship itself to be negligible.

[12] The gas-phase PAHs showed two very high concentrations over the Sea of Japan (6600 pg m⁻³ at site A1 and 7400 pg m⁻³ at site A2), and the particulate-phase PAHs also displayed one extremely high concentration at site A1 (360 pg m⁻³), in which the air mass mainly originated from the northwest coast of Japan, east coast of Korea, and the close-by terrestrial regions as indicated by the air mass back trajectories (Figure S1 in the supporting information). High PAH levels and emissions have been already observed in East Asian areas [Ohura *et al.*, 2004; Primbs *et al.*, 2007]. It was reported that the ratios of a more reactive PAH to a less reactive PAH, such as Ant/Phe and BaA/Chry, could be used to illustrate whether the air masses collected were fresh or aged [Ding *et al.*, 2007]. These four isomer values and their ratios were particularly high at site A1 (Ant/Phe=0.24, BaA/Chry=1.03; Table S7 in the supporting information), indicating that the air masses sampled at this site were relatively fresh from the adjacent continental source areas.

[13] The natural logarithm of the partial pressure [$\ln P$ (atm)] of more volatile two- to three-ringed PAHs versus $1/T$ was plotted to investigate relationship between [PAHs]_{atm} and ambient temperature (T). It is suggested that a significant correlation would indicate conditions close to air-water equilibrium, in this case, air-water gaseous exchange controlling atmospheric concentrations in the marine environment [Wania *et al.*, 1998]. However, no significant relationships were observed for all two- to three-ringed PAHs along the cruise (Figure S2 in the supporting information). This might be due to the relatively short atmospheric lifetimes of gas-phase PAHs and also demonstrate the importance of their ongoing release from primary sources, whereby PAHs in the marine boundary layer are not in equilibrium with the surface seawater. Nizzetto *et al.* [2008] also found no relationship between $\ln P$ and $1/T$ for PAHs measured along a north-south Atlantic transect. Therefore, this indicates the importance of ongoing release of PAHs from primary sources and indicates continuous atmospheric LRT of volatile PAHs from temperate latitudes to more remote regions.

[14] The spatial distribution of five- to six-ringed PAHs on particles (Σ_6 [PAHs]_{part-atm}, including BbF, BkF, BaP, IP, DBaA, and BghiP) is shown in Figure 2. For most of these heavier compounds, the average fraction in the gas phase was less than 40%. There was a marked decrease in concentrations from East Asia (8.3 pg m⁻³) to the North Pacific (1.9 pg m⁻³), although a slight increase was observed in the Arctic Ocean (3.4 pg m⁻³). A fate model presented by Halsall *et al.* [2001] showed that lighter compounds would be able to reach the Arctic, while most of the heavier compounds (originating from the same source region in NW Europe) would be removed from the atmosphere before reaching the Arctic, either by reaction with OH radicals or by dry and wet deposition along the transport pathway

[Halsall *et al.*, 2001; Hung *et al.*, 2005]. Therefore, the significant decreasing trends of these five- to six-ringed PAHs on particles from East Asia to the North Pacific might be attributed to their lower atmospheric LRT potential. The increase in concentrations in the Arctic indicates the likelihood of other PAH sources within this region. Natural sources, such as summertime forest fires in subarctic parts of Alaska, Canada, Russia, and Siberia, during summer can result in the episodic input of PAHs and other pollutants to the Arctic atmosphere [Becker *et al.*, 2006; Eckhardt *et al.*, 2007; Halsall *et al.*, 1997; Masclet *et al.*, 2000]. It is reported that a series of wildfires broke out in Russia starting in late July 2010 [Mei *et al.*, 2012]. Thus, these regional sources may have affected PAH concentrations in Arctic Ocean air during the cruise period.

3.2. Spatial Distribution of PAHs in Surface Seawater

[15] PAHs concentrations in seawater (Σ_{18} [PAHs]_{wat}) ranged from 14 to 760 pg L⁻¹ (dissolved + particulate) and showed a lower frequency of detection compared to the atmosphere. Most of the PAHs were found in the dissolved phase (Table S5 in the supporting information), which was dominated by the lower molecular weight (MW) compounds of 2MN, Phe, and Py, contributing about 50% to the dissolved Σ_{18} [PAHs]_{wat}. Concentrations of five- to six-ringed PAH species were extremely low, with average concentrations ≤ 1 pg L⁻¹. Compared with the north-south transect of the eastern Atlantic Ocean, our reported concentrations were lower than those detected in the Northern Hemisphere of the eastern Atlantic Ocean (670–1000 pg L⁻¹) and were comparable to the levels found in the Southern Hemisphere (58–400 pg L⁻¹) [Nizzetto *et al.*, 2008], but higher than those previously observed in remote subarctic areas (<5.0–65 pg L⁻¹) [Schulz-Bull *et al.*, 1998].

[16] Figure 3 shows the spatial distribution of Σ_{18} [PAHs]_{wat} (dissolved + particulate) from East Asia to the Arctic Ocean (33°N–84°N). Generally, we observed a decrease in Σ_{18} [PAHs]_{wat} with increasing northerly latitude. The observed mean concentrations of Σ_{18} [PAHs]_{wat} were 150 ± 270 pg L⁻¹ in East Asia (35°N–48°N), 76 ± 46 pg L⁻¹ in the North Pacific Ocean (50°N–68°N), and 37 ± 18 pg L⁻¹ in the Arctic Ocean (>70°N). These trends indicate that PAHs are effectively removed by biogeochemical processes in the water column. The highest concentrations in bulk water were observed in East Asia, at site W1 in the vicinity of Korea and Japan. The high PAH levels in these “hot spots” were consistent with those observed in the atmosphere, suggesting that atmospheric deposition/air-water exchange exerts a strong influence on PAHs in seawater. Meanwhile, for certain PAHs, additional sources to seawater might also exist, such as river outflow and potential point sources such as coastal wastewater treatment plants (WWTPs) and ship ballast. Another relatively high concentration was observed near Russia (140 pg L⁻¹ at site W2), although the sampling location was well removed from the coastline.

3.3. Source Identification

[17] Two different molecular diagnostic ratios (MDRs) were calculated to estimate the influence of potential sources, but these should be interpreted with caution due to different environmental processing of the isomers during transport processes [Galarneau, 2008]. As shown in Figure 4, the

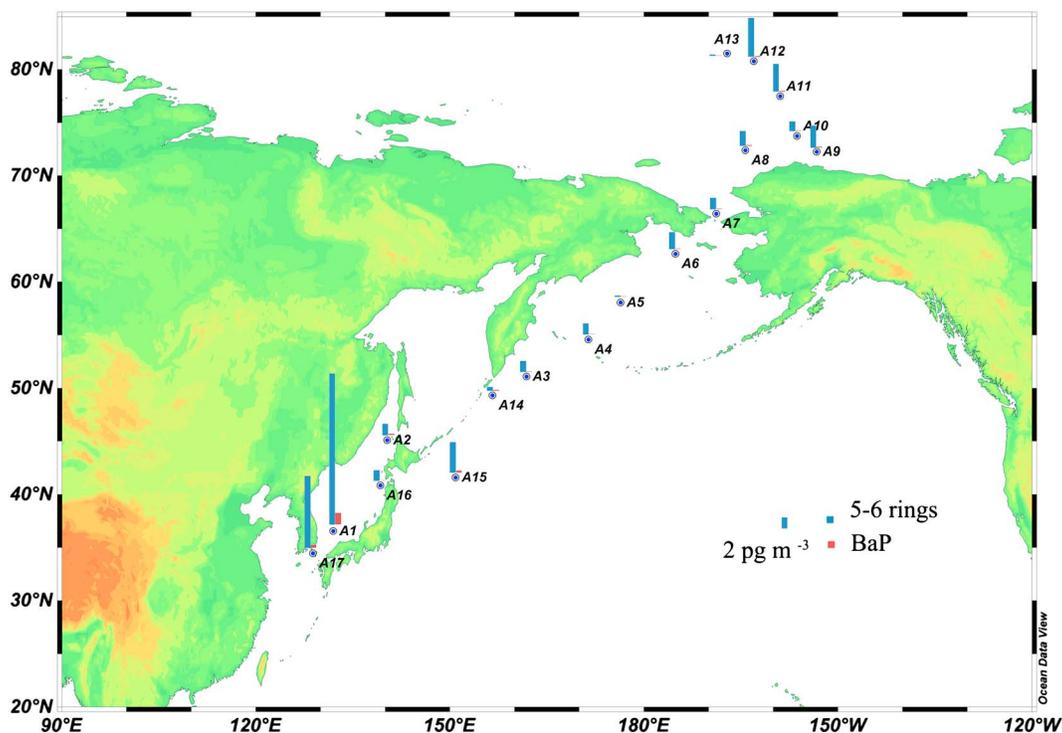


Figure 2. Concentrations of five- to six-ringed particulate-phase PAHs and BaP in the atmosphere along the sampling cruise.

ratios of Fluor/(Fluor+Py) and InP/(BghiP+InP) in the atmosphere ranged from 0.50 to 0.76 and from 0.47 to 0.85, respectively, indicating a combustion of biomass or coal origin [Yunker *et al.*, 2002]. This conclusion is consistent with

observations over the same water body as our study during the CHINARE2003 cruise [Ding *et al.*, 2007]. Compared with other regions investigating the sources of PAHs, a mixed combustion of biomass and fossil fuel was also suggested as

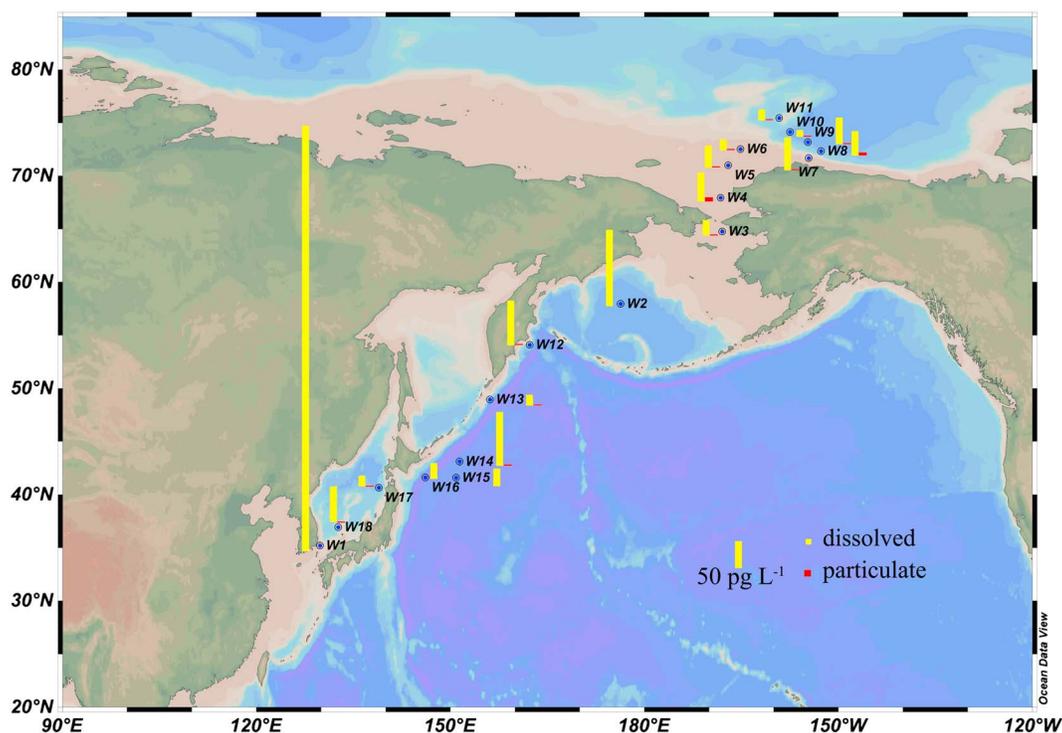


Figure 3. Concentrations of dissolved- and particulate-phase PAHs in seawater ($\Sigma_{18}[\text{PAHs}]_{\text{wat}}$) along the sampling cruise.

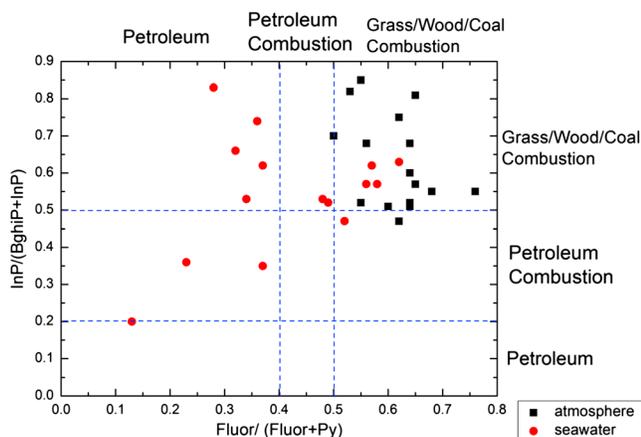


Figure 4. Ratios of $\text{InP}/(\text{BghiP} + \text{InP})$ versus $\text{Fluor}/(\text{Fluor} + \text{Py})$ in the atmosphere and seawater.

a source of PAHs observed in the atmosphere of the northern Indian Ocean as well as surface snow on the Greenland ice cap [Crimmins *et al.*, 2004; Jaffrezo *et al.*, 1994]. However, in the North Atlantic Ocean, a petrogenic source has been suggested [Lohmann *et al.*, 2009]. Nonetheless, for seawater, these two ratios, as shown in Figure 4, show a good deal of scatter. Specifically, the ratios of $\text{Fluor}/(\text{Fluor} + \text{Py})$ and $\text{InP}/(\text{BghiP} + \text{InP})$ in the seawater ranged from 0.13 to 0.62 and from 0.20 to 0.83, respectively, suggesting a well-mixed source profile of petrogenic, biomass combustion as well as coal and liquid fossil fuel origin. Hence, part of the seawater and atmospheric PAHs share the same source profile, which to some extent might be due to air-sea gas exchange and deposition, while part of the potential source of PAHs in the surface water and atmosphere were uncoupled. Studies in the North Atlantic Ocean implied a pyrogenic origin [with $\text{Fluor}/(\text{Fluor} + \text{Py})$ of 0.9–1.0 and about 0.6] [Lohmann *et al.*, 2009; Schulz-Bull *et al.*, 1998], while in a recent cruise following a west-to-east transect across the tropical Atlantic Ocean, traffic emissions and petroleum products were implied through the use of MDR [with $\text{Fluor}/(\text{Fluor} + \text{Py})$ ratios of 0.1–0.5] [Lohmann *et al.*, 2013].

3.4. Atmospheric Deposition

[18] To estimate the influence of air-seawater coupling and the atmospheric input of PAHs into the ocean, we calculated the air-seawater gas exchange and estimated the particle-bound dry deposition fluxes of PAHs into the ocean. To estimate the direction (or equilibrium status) of the air-sea gas exchange of PAHs (particularly for the low MW two- to three-ringed PAHs), the fugacity ratio (FR) f_a/f_w was calculated, and the exchange flux (F_{aw}) was estimated with the modified version of the Whitman two-film resistance model (the calculation details are provided in the supporting information) [Bamford *et al.*, 2002; Schwarzenbach *et al.*, 2003]. Results of calculated FR values at different latitudes are shown in Table S8 in the supporting information. Slight volatilization trends were observed for 2MN, 1MN, and Ace at site W1 in the vicinity of coastal regions of Korea and Japan. Water samples collected in this area exhibited the highest PAH levels during the entire cruise. The effect of volatilization from coastal waters with high PAH levels has been recently reported in other PAH-impacted regions

such as Narragansett Bay (USA) and the southeast Mediterranean [Castro-Jimenez *et al.*, 2012; Lohmann *et al.*, 2011]. Such slight volatilization trends might indicate the existence of some additional sources of PAHs to seawater, such as riverine runoff, ship ballast, and potential point sources such as WWTPs. With the exception of 2MN, 1MN, and Ace at site W1, air-sea gas exchange of all PAHs was strongly dominated by net deposition along the entire transect (note that for BaA, Chry, and the five- to six-ringed PAHs, the fugacity ratios are largely hypothetical as the gas phase is negligible). Similarly, PAHs were observed to be mostly undergoing net deposition across the tropical Atlantic Ocean during the summer of 2009 [Lohmann *et al.*, 2013].

[19] The estimated air-sea gas exchange fluxes are shown in Table S8 in the supporting information. Generally, the two- to four-ringed PAHs nearly accounted for all the fluxes (>99%), consistent with their dominant contribution to the gas phase $\Sigma_{18}[\text{PAHs}]$. On the whole, the highest deposition fluxes were observed in the Arctic region, with the average individual deposition flux ranging from $0.14 \pm 0.071 \text{ ng m}^{-2} \text{ d}^{-1}$ for BaP to $300 \pm 180 \text{ ng m}^{-2} \text{ d}^{-1}$ for 2MN, which might be driven by relatively low seawater concentrations and high atmospheric gas concentrations (Figure 5). It is noteworthy that some three- and four-ringed compounds (MW 166–202) all exhibited extremely high deposition fluxes at site W1, even higher than the northernmost site of W11. The notably high atmospheric concentrations at this site will contribute to such high deposition.

[20] To investigate the particle-bound deposition flux of PAHs, we estimated the dry particle-bound deposition flux using deposition velocities of 0.3 cm s^{-1} for the East Asia region and 0.1 cm s^{-1} for both North Pacific Ocean and the Arctic based on summertime particle size distributions observed in these different geographical regions (see the supporting information for details). The dry deposition flux is shown in Table A9 in the supporting information and Figure 6. Precipitation was not encountered during the cruise period, so wet deposition was not considered. Generally, the dry deposition fluxes were significantly lower than the air-sea gas exchange fluxes but are likely to be more relevant given the low gas-phase fraction for some chemicals. Unlike the gaseous deposition, the highest dry particle deposition fluxes for all PAH species were observed

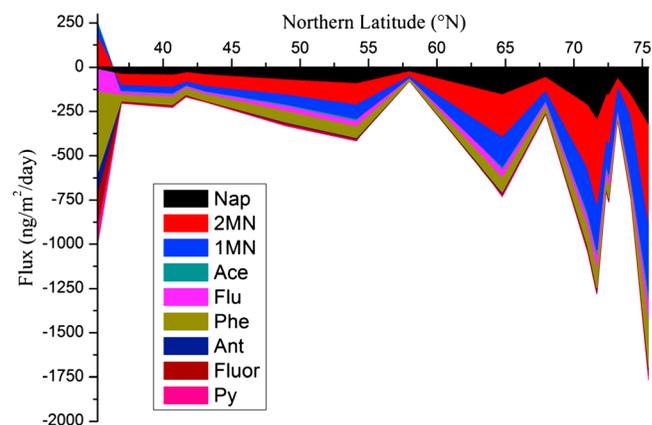


Figure 5. Accumulated (sum) air-sea gas exchange fluxes of top nine PAHs versus latitude along the sampling transect. Negative (–) flux indicates deposition into the water column.

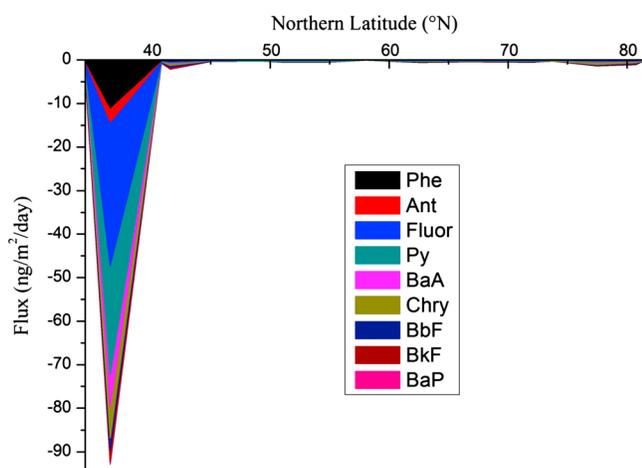


Figure 6. Accumulated (sum) particle-bound dry deposition fluxes of top eight PAHs and BaP versus latitude along the sampling transect. Negative (–) flux indicates deposition into the water column.

in the East Asia region, especially at site A1 due to the high particle-bound concentrations (from 0.1 pg m^{-3} for Acl to 127 pg m^{-3} for Fluor), with the individual deposition fluxes ranging from $0.05 \text{ ng m}^{-2} \text{ d}^{-1}$ for Acl to $33 \text{ ng m}^{-2} \text{ d}^{-1}$ for Fluor. Moreover, the dry deposition fluxes in the Arctic were higher than those in the North Pacific regions. Meanwhile, the dry particle deposition fluxes dominated for the heavier four- to five-ringed PAHs, contributing $>90\%$ to the overall depositional flux. As compared with other studies, both the air-sea gas exchange and dry deposition fluxes of our study were higher than those determined along a north-south Atlantic transect [Nizzetto *et al.*, 2008] but lower than the Mediterranean Sea [Castro-Jimenez *et al.*, 2012].

[21] In the remote marine environment, the net flux of POPs is typically of the route air–surface waters–deeper waters, where the deep ocean serves as the oceanic sink [Jaward *et al.*, 2004b]. For halogenated POPs such as the organochlorine pesticides, then air–water transfer is driven by a concentration gradient that favors either net deposition, equilibrium, or net volatilization. In the case of α -HCH, for example, net deposition in northerly latitudes like the Arctic has been reversed in recent years due to the decline in concentrations in the atmosphere [Dachs *et al.*, 2002; Lohmann *et al.*, 2009]. In the same cruise of this study, we discovered that α -HCH underwent an iterative process consisting of deposition, volatilization into the atmosphere, and redeposition against a background of reducing primary emissions and climate change [Cai *et al.*, 2012]. However, for the nonpersistent organic compounds, such as PAHs, such a phenomenon has not been reported. In our study, strong net deposition dominated the marine transect from East Asia to the Arctic. If there was substantial reemission from the surface water to the atmosphere, then a relationship with ambient temperature should exist [Jaward *et al.*, 2004a], and yet in our results, no significant relationships between any volatile PAHs in the atmosphere and ambient temperature were evident (Figure S2 in the supporting information). Rather, proximity to potential continental source regions like East Asia, where high PAH concentrations were observed, and the influence of seasonal and regional sources (i.e., forest fires) in the Arctic appear to be the controlling

factors. Hence, primary sources, rather than secondary sources, broadly control the ambient PAH concentrations over the entire cruise. In addition to high atmospheric concentrations, relatively low PAH concentrations in the surface water will also drive a concentration gradient that favors gas-phase deposition. Phytoplankton blooms followed by the growing of zooplankton take place during spring and summer across the study region, which will result in an enhanced vertical transport of dead planktonic algae down the water column. The large quantity of settling particulate matter is likely to strip sparingly soluble PAHs from surface waters to deeper waters [Witt, 2002]. Furthermore, growing biomass might also lead to higher biodegradation rates of PAHs present in surface waters. PAHs do not bioaccumulate in zooplankton due to efficient metabolism, especially for the lower MW PAHs. Berrojalbiz *et al.* [2011] have recently demonstrated that low MW PAHs can be efficiently metabolized by zooplankton, suggesting that this process is an important sink for PAHs in the pelagic environment [Berrojalbiz *et al.*, 2009, 2011]. Depletion of low MW PAHs in the water column has been observed in studies conducted in the Mediterranean Sea, which was attributed to possible degradation processes [Dachs *et al.*, 1997]. Thus, once atmospheric PAHs are deposited into surface seawater, both physical and biological removal processes in the water column will influence air–water transfer. The relatively high atmospheric concentrations near temperate primary source regions and the low surface seawater concentrations induced strong deposition of gas-phase PAHs in our study area. It is therefore likely that PAHs will continue to load into surface seawater in the remote pelagic environment with particle deposition of the higher MW PAHs relatively more significant near temperate source regions.

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