



# Air–sea exchange and gas–particle partitioning of polycyclic aromatic hydrocarbons over the northwestern Pacific Ocean: Role of East Asian continental outflow<sup>☆</sup>



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## ABSTRACT

We measured 15 parent polycyclic aromatic hydrocarbons (PAHs) in atmosphere and water during a research cruise from the East China Sea (ECS) to the northwestern Pacific Ocean (NWP) in the spring of 2015 to investigate the occurrence, air–sea gas exchange, and gas–particle partitioning of PAHs with a particular focus on the influence of East Asian continental outflow. The gaseous PAH composition and identification of sources were consistent with PAHs from the upwind area, indicating that the gaseous PAHs (three- to five-ring PAHs) were influenced by upwind land pollution. In addition, air–sea exchange fluxes of gaseous PAHs were estimated to be  $-54.2$ – $107.4$   $\text{ng m}^{-2} \text{d}^{-1}$ , and was indicative of variations of land-based PAH inputs. The logarithmic gas–particle partition coefficient ( $\log K_p$ ) of PAHs regressed linearly against the logarithmic subcooled liquid vapor pressure ( $\log P_1^0$ ), with a slope of  $-0.25$ . This was significantly larger than the theoretical value ( $-1$ ), implying disequilibrium between the gaseous and particulate PAHs over the NWP. The non-equilibrium of PAH gas–particle partitioning was shielded from the volatilization of three-ring gaseous PAHs from seawater and lower soot concentrations in particular when the oceanic air masses prevailed. Modeling PAH absorption into organic matter and adsorption onto soot carbon revealed that the status of PAH gas–particle partitioning deviated more from the modeling  $K_p$  for oceanic air masses than those for continental air masses, which coincided with higher volatilization of three-ring PAHs and confirmed the influence of air–sea exchange. Meanwhile, significant linear regressions between  $\log K_p$  and  $\log K_{oa}$  ( $\log K_{sa}$ ) for PAHs were observed for continental air masses, suggesting the dominant effect of East Asian continental outflow on atmospheric PAHs over the NWP during the sampling campaign.

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## 1. Introduction

East Asia has experienced rapid industrialization and urbanization, as well as abundant anthropogenic activity. As such, it has been recognized as the predominant emitter of primary aerosols to the northwestern Pacific Ocean (NWP) (Kunwar et al., 2016). The atmospheric circulation of East Asia is dominated by the monsoon

system, characterized by the northerly continental air mass in winter, which shifts seasonally to the prevailing ocean-oriented southerlies in summer (Ding, 1994). Under such conditions, the NWP is prone to receive aerosols via the dominant westerly winds from the surrounding land from mid-autumn to mid-spring (Kawamura et al., 2003; Lin et al., 2011). Studies have reported on the inter-annual and seasonal variations (Liu et al., 2003; Cheng et al., 2016), budgets (Bey et al., 2001), characteristics, and evolution of various substances and chemicals in the outflow region of East Asia (Russo et al., 2003; Matsui et al., 2013; Boreddy and Kawamura, 2015; Verma et al., 2015). However, these studies are mainly model-based or rely on ground measurements at remote

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fixed-point monitoring sites and concentrate on inorganic ions or species (Tang et al., 2004; Boreddy et al., 2014; Kunwar and Kawamura, 2014).

To contribute to our understanding of the export of East Asian emissions and subsequent impacts, additional research is needed on different types of compounds as novel means of quantification. In this study, we used PAHs as a tracer to elucidate the influence of continental outflow to the NWP via long-range atmospheric transport (LRAT). PAHs are semivolatile organic compounds from anthropogenic and natural sources that pose an environmental concern due to their potential toxicity to ecosystems and humans (Hoffman et al., 1984). In addition, numerous studies have examined their chemical properties related to environmental persistence and long-range transport. The semivolatility of PAHs suggests two possible major processes of environmental cycling: gas–particle partitioning in air (Lohmann and Lammel, 2004) and revolatilization from ground and water surfaces (Wania and Mackay, 1993; Semeena and Lammel, 2005). PAHs are partitioned in both the gas and particle phases, and influential factors include ambient temperature, aerosol characteristics, and interactions between aerosols and sorbed chemicals (Pankow, 1994; Lohmann et al., 2000). Further, gas–particle partitioning processes include organic matrix absorption and particle surface adsorption (Pankow, 1994; Finizio et al., 1997; Harner and Bidleman, 1998). Effects of source-dependent aerosol type on PAH partition coefficients have been observed (Harner and Bidleman, 1998), and the properties of particles affected by land can be used to determine the spatial distributions of gas–particle partitioning of pollutants (Gustafson and Dickhut, 1997). The application of organic aerosol-associated absorptive and adsorptive mechanisms of PAHs to atmosphere has been evaluated extensively, especially in heavily impacted source regions (Simcik et al., 1998; Lohmann et al., 2000; Odabasi et al., 2006). Guazzotti et al. (2003) found that up to 75% of carbon-containing particles in downwind marine atmosphere originated from land-based combustion and the strong affinity between PAHs and soot carbon. Thus, its influence on atmospheric PAH distribution, has been evaluated using soot–air partitioning in an adsorption model, in remote regions. Fernández et al. (2002) reported the importance of soot in atmospheric PAH distribution in continental background areas and reflected on the significance of the long-range transportation of soot particles. For gas exchange at the air–sea interface, Gonzalez-Gaya et al. (2016) presented the global air–sea exchange of PAHs, which revealed a larger net atmospheric input supported by land. This was in agreement with a scenario in the tropical Atlantic Ocean, where the air–sea exchange of PAHs was dominated by deposition from primary sources (Lohmann et al., 2013). However, surface seawaters could serve as a buffer and re-supply chemicals back into the boundary atmosphere when a reduction in source emissions occurs (Nizzetto et al., 2010). The transition of air–sea exchange from deposition to volatilization has been detected for several individual PAHs in the Mediterranean Sea (Mulder et al., 2014; Lammel et al., 2016), highlighting the interaction between ongoing continental emissions and secondary release from seawater. However, it is still unclear whether the distribution and fate of atmospheric PAHs over remote oceanic areas are consistent with the dual sorption processes of carbonaceous particles. In particular, it is unknown when remote oceanic areas are characterized by strongly sustained transport of carbonaceous particles from continental outflow and significant volatilization of PAHs from surface seawater, exactly as the atmospheric PAHs from the ECS (East China Sea) to the NWP.

The objectives of this study were to reveal the spatial distribution of PAHs influenced by air–sea exchange and gas–particle partitioning in the atmosphere, and to assess the role of the continental outflow on the basis of the mutual relationship between

air–sea exchange and gas–particle partitioning during March 29 to May 6, 2015 along a west-to-east transect from the ECS to the NWP.

## 2. Materials and methods

### 2.1. Sampling

Air and seawater samples were collected from the ECS to the NWP covering an area of 25°N to 38°N in latitude and 120°E to 152°E in longitude on board the research vessel Dong Fang Hong 2 of the Ocean University of China (Fig. 1). Air samples (ca. 412 m<sup>3</sup>) were collected via a high-volume air sampler operated at a constant flow rate of 300 L min<sup>-1</sup> (Guangzhou Mingye Technology Co. Guangzhou, China). The sampler was placed windward on the upper-most deck of the ship to avoid possible contamination from the ship's exhausts and cut off power when the ship stopped. The sampler was equipped with a quartz fiber filter (QFF) held in a metal frame (20 × 25 cm; Pall Gelman, Port Washington, NY, USA) to separate airborne particles from the air stream, followed by a polyurethane foam (PUF) plug (6.5 cm in diameter, 7.5 cm in thickness, density 0.030 g cm<sup>-3</sup>) placed in a glass holder to collect species in the gas phase. Field blank samples were obtained by exposing to air for only a few seconds. The QFF filters were conditioned in a dry box (maintained at 20 °C and 40% relative humidity) before and after sampling to calculate the mass of total suspended particles (see supporting information (SI) Text 2.1 for additional details).

Surface seawater samples (60–100 L/sample) were collected using a seawater-rinsed metal bucket. Particle-bound analytes were captured on a pre-combusted glass fiber filter (142 mm in diameter, bore size 0.7 μm; Whatman, Maidstone, UK) placed in a stainless steel filter holder, while dissolved PAHs were subsequently adsorbed by passing the filtrate through a glass column (25 mm internal diameter, 200 mm in length) packed with Amberlite XAD-2 and XAD-4 resin (1:1 of total 30 g, Sigma-Aldrich, St. Louis, MO, USA) using a peristaltic pump (see SI Text 2.1). In situ meteorology and hydrology data, including wind speed, air and water temperature, and salinity, were also obtained (SI Table S1 and Table S2).

### 2.2. Sample processing and analytical procedure

The PUF plugs and filters spiked with surrogate recovery standards (Ace-d<sub>10</sub>, Phe-d<sub>10</sub>, Chr-d<sub>12</sub>, and Per-d<sub>12</sub>) were Soxhlet-extracted with dichloromethane (DCM) for 48 h. The extract was concentrated by rotary evaporation and solvent-exchanged to n-hexane, and further reduced with a highly purified N<sub>2</sub>. The clean-up and fractionation were performed on a 8 mm i.d. silica/alumina column, packed from the bottom to top, with neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), and anhydrous sodium sulfate (1 cm). Elution of each XAD cartridge was performed with DCM, then ultrasonically extracted (three times) with three 100 mL aliquots of DCM in water bath. A total volume of 300 mL was concentrated and fractionated using the procedure described for air samples. Determination of PAHs was performed on an Agilent 7890A GC equipped with a capillary column (30 m × 0.25 mm × 0.25 μm DB5-MS) coupled to an Agilent 5975C MSD. The temperature of the oven was programmed as follows: initial temperature of 50 °C (8 min hold), then raised to 150 °C at 8 °C min<sup>-1</sup> and held for 3 min and ramped to 290 at 3 °C min<sup>-1</sup>, maintained for 20 min. The abbreviations of the 15 measured PAHs, along with the details of the sample processing and analyses are summarized in SI Text 2.2.

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