Atmospheric occurrence, transport and gas–particle partitioning of polychlorinated biphenyls over the northwestern Pacific Ocean

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HIGHLIGHTS

- Variation and composition in atmospheric PCBs were closely related to the continental outflow.
- Aerosol phase PCBs were well predicted by the adsorption and absorption model.
- Soot carbon acted as transport medium for the aerosol phase PCBs.
- Transport mass of particulate PCBs into the NWP totaled 2333 kg in the spring.

GRAPHICAL ABSTRACT
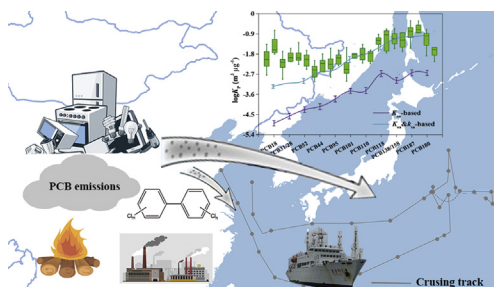
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ABSTRACT

Ship-board air samples were collected during March to May 2015 from the East China Sea (ECS) to the northwestern Pacific Ocean (NWP) to explore the atmospheric occurrence and gas–particle partitioning of polychlorinated biphenyls (PCBs) when the westerly East Asian Monsoon prevailed. Total PCB concentrations in the atmosphere ranged from 56.8 to 261 pg m^{-3}. Higher PCB levels were observed off the coast and minor temperature-induced changes showed that continuous emissions from East Asia remain as an important source to the regional atmosphere. A significant relationship between K_{oa} (octanol–air partition coefficient) and K_P (gas–particle partition coefficient) for PCBs was observed under continental air masses, suggesting that land-derived organic aerosols affected the PCB gas–particle partitioning after long-range transport, while an absence of this correlation was identified in marine air masses. The PCB partitioning cannot be fully explained by the absorptive mechanism as the predicted K_P were found to be 2–3 orders of magnitude lower than the measured K_p, while the prediction was closely matched when soot adsorption was considered. The results suggested the importance of soot carbon as a transport medium for PCBs during their long-range transport and considerable impacts of continental outflows on PCBs across the downwind area. The estimated transport mass of particulate PCBs into the ECS and NWP totals 2333 kg during the spring, constituting ca. 17% of annual emission inventories of unintentionally produced PCB in China.

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1. Introduction

Polychlorinated biphenyls (PCBs), an important class of persistent organic pollutants and known carcinogens and mutagens, are a

group of chlorine substituted aromatic ring substances with extensive commercial and industrial applications (e.g., transformer and capacitor insulating materials, paints, adhesives and surface coatings) (Breivik et al., 2002). Current atmospheric levels of PCBs are closely associated with urban and industrialized source areas (Jaward et al., 2005) and are dominated by advective inputs in the northern hemisphere (Gioia et al., 2011). Although PCBs were prohibited in production industries under national jurisdiction decades ago, they are still widely detected in the atmosphere over different regions especially in East Asia (Hogarh et al., 2013; Liu et al., 2016; Nguyen et al., 2016). It has been reported that diffusive emissions of PCBs associated with their release from industrial and urban sources (intentionally or unintentionally produced PCBs) in East Asia are important sources that continuously contaminate the local atmosphere (Jaward et al., 2005; Hogarh et al., 2012; Cui et al., 2013). Low-level wind recognized as the East Asian monsoon prevails in the westerly direction from the continent in the winter and spring (Verma et al., 2015). Subsequently, PCBs can undergo *trans*-Pacific atmospheric transport from East Asia to North America owing to their semivolatility and extensive range of atmospheric lifetimes (Bailey et al., 2000; Primbs et al., 2007). Model results have demonstrated that East Asian continental outflows of PCBs have a significant impact on the long-range atmospheric transport (LRAT) and cycling of PCBs in the northern hemisphere (Gong et al., 2007; Huang et al., 2007). However, the field monitoring of these chemicals and effects of continental outflows on the neighboring ocean remain elusive.

In this study, PCBs in the air during a research cruise from the East China Sea (ECS) to the northwestern Pacific Ocean (NWP) in the spring of 2015 were investigated. The NWP is positioned within the pathway of East Asian continental outflows, acting as a receptor for PCBs from surrounding countries via the East Asia monsoon. According to latitudinal trends of air PCBs over the investigated oceans, the LRAT controls PCB levels in the remote marine atmosphere (Gioia et al., 2013). Available studies have shown that atmospheric PCB levels over the ocean are closely related to rates of change in PCB emissions from the adjacent land. A minor change in PCB ambient levels was reported for the North Atlantic Ocean characteristics of the dominance of net deposition (Gioia et al., 2008), which could be a response to heavy pollution in the source region. Based on the air sampling of PCBs across European background regions, concentrations are still controlled by continual primary emissions long after restrictions on their usage were first made (Jaward et al., 2004; Gioia et al., 2006). However, the role of primary emissions in dominating the occurrence of atmospheric PCBs over the NWP is still unclear, thus making the NWP an ideal region for studying the PCB from East Asian continental outflows.

The analysis of gas–particle partitioning can be used to evaluate the LRAT and the fate of PCBs in the atmosphere (Lohmann et al., 2000). The extent of PCB partitioning between gas and particulate phases hinges on particle properties, ambient temperature and interactions between aerosols and sorbed compounds (Pankow and Bidleman, 1991; Pankow, 1994). The partitioning equilibrium of PCBs cannot generally be reached in the field as indicated by the slope of a linear free energy relationship between the partition coefficient (K_P) and sub-cooled liquid vapor pressure levels (P_L^0). This disequilibrium is considered to be source-dependent (Lohmann et al., 2000; Cindoruk and Tasdemir, 2007) or slow kinetics-induced (Simcik et al., 1998; Mandalakis et al., 2002) in cases involving no significant sampling artifacts. East Asia is a major global emitter of organic aerosols derived from biomass burning and industrial and residential emissions (Mochida et al., 2003). Considerable emissions are generated from China, which emits one-fourth of global anthropogenic carbonaceous aerosols and

large quantities of soot aerosols (Kunwar and Kawamura, 2014). The distribution of PCBs between the gas and aerosol phase was investigated in urban areas of East Asia and the sensitivity of PCB partitioning to carbonaceous sorbents in aerosols was alternatively modeled based on octanol–air (K_{oa}) absorption and the Junge–Pankow adsorption model (Kim et al., 2011; Die et al., 2015; Li et al., 2015). Due to the source heterogeneity between PCBs and organic sorbents (e.g., organic matter (OM)) and the significant removal of carbonaceous particles during transport, the applicability of sorption models for the long-range transport of continental PCBs and aerosol particles in relatively remote oceanic areas far from pollution sources remains uncertain. As PCBs are primarily found in the gas phase over the course of their transport, the state of equilibrium partitioning for transported PCBs in the atmosphere over the NWP remains unknown.

To address these gaps, this work investigates the regional concentration and spatial distribution of PCBs in atmosphere to address gas–particle partitioning from the ECS to the NWP in the spring. The partitioning of atmospheric PCBs was explored in marginal sea and open ocean environments; the most suitable sorption models were adopted based on comparisons; and finally, the transport mass of PCBs was estimated. The study results can enhance understanding of the influence of East Asian continental outflows on atmospheric PCBs across this region.

2. Materials and methods

2.1. Sample collection

An air sampling campaign was conducted from the ECS to the NWP (25°N to 38°N and 120°E to 152°E) from March 29, 2015 to May 6, 2015 onboard research vessel Dong Fang Hong 2 of Ocean University of China's (OUC's) using a high-volume air sampler (Guangzhou Mingye Technology Co., Guangzhou, China). The sampler was deployed on the upper-most deck of the ship to prevent possible shipborne contamination and was only operated under favorable conditions with wind traveling from the bow. Air volumes of ca. 412 m^3 were pumped at a constant flow rate of 300 L min^{-1} for roughly 24 h through a quartz fiber filter (QFF, 20 × 25 cm; Pall Gelman, Port Washington, NY, USA) to collect particulate phase PCBs and they were then pumped through a polyurethane foam (PUF) plug (6.5 cm in diameter, 7.5 cm in thickness, and density of 0.030 g cm^{-3}) to trap gaseous PCBs. Preceding sampling, QFF filters were baked at 450 °C for 4 h to remove residual organic contaminants and PUF plugs were precleaned by two successive Soxhlet extractions with acetone and dichloromethane (DCM), each for 48 h and were then dried in a desiccator under vacuum. In total, 26 pairs of air samples were collected. After the sample collection period, loaded QFFs and PUFs were wrapped in prebaked aluminum foil, sealed in double-layered polyethylene bags, and stored in freezers for further analysis.

2.2. Sample processing and analytical procedure

Integrated air samples (QFFs and PUFs) were spiked with recovery standards of a mixture of 2,4,5,6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB 209) and were then Soxhlet extracted separately via DCM for 48 h. The extract was concentrated with a rotary evaporator and solvent-exchanged n-hexane and reduced under a stream of highly purified N$_2$. The concentrated extract was fractionated on a packed alumina/silica column (8 mm internal diameter) with 3% deactivated neutral alumina (3 cm), 3% deactivated neutral silica gel (3 cm), 50% (on a weight basis) sulfuric acid silica (2 cm), and anhydrous sodium sulfate (1 cm) from the bottom to top. PCBs were eluted with 50 mL of DCM/n-hexane (1:1)

and were further concentrated to 200 μL. Pentachloronitrobenzene (PCNB) was added as an internal standard to the concentrates for the quantification of PCBs.

PCBs were determined by an HP-5890 Series II GC coupled to a Ni electron capture detector and chromatographic separation was achieved through an HP-5 capillary column (50 m × 0.25 mm × 0.25 μm). The GC temperature program was applied as follows: an initial temperature of 110 °C was raised to 170 °C at 1.8 °C min^{-1} (3 min hold) and then to 226 °C min^{-1} at 2.5 °C min^{-1}, and it was then ramped to 280 at 40 °C min^{-1} and maintained for 10 min. A total of 21 chromatographic PCB peaks corresponding to 24 individual and co-eluting congeners (i.e., IUPAC PCBs 18, 31/28, 52, 49, 44, 74, 70, 95, 101, 87, 110, 118, 132/153, 138/158, 187, 128, 177, 156, 180, 201, and 205) in air were monitored and quantified.

2.3. Quality control and quality assurance

Five pairs of field blanks (PUF plug + QFF filter) were prepared over the course of the cruise by exposing them to air for a few seconds with no air aspirated through. A laboratory blank (only solvent) and a spiked blank (24 PCB congeners spiked into the solvent) were co-processed using the same method applied to field samples for each batch of six samples. The measured concentrations of field and laboratory blank samples were very low and indicative of minimal contaminations during transport, sampling and processing. The reproducibility of the spiked blanks was acceptable, yielding recoveries of 89.5± 6.4%. The recoveries of TCmX and PCB 209 were 74.8± 8.4% and 85.2± 12.7%, respectively, in the gas phase and were 81.9± 10.5% and 89.6± 13.6% in the particulate phase, respectively. Method detection limits (MDLs) were defined as average values of field blanks with the addition of 3 standard deviations of blank values ranging from values of 0.01–0.05 pg m^{-3} for air samples.

Sampling artifacts associated with gas adsorption to QFF filters, the striping of particle phase compounds from filters and break-through losses of volatile PCBs were stringently tested. The ambient temperature varied within a narrow range, contributing to minor effects on striping from the filter. Gas adsorption and gas-phase breakthroughs were assessed via the application of a second filter and split PUF during the cruise period. Based on experiments conducted in our lab, the influence of these artifacts on our analysis of PCB gas–particle partitioning was not expected to be significant, as analyte contents in six backup filter and PUF samples fell below those of the MDLs.

2.4. Air mass back trajectory

Air mass origins were traced by the NOAA's HYSPLIT transport and dispersion model. Air mass trajectories extended back over five days at 6-h intervals were calculated for the beginning of each sampling event in coordinated universal time (UTC) at 100 m above sea level (see supporting information (SI) Fig. S1).

3. Results and discussion

3.1. PCB occurrence

The sum of the 24 measured PCBs ($\sum_{24}$PCBs) in air (both gas and aerosol phase) ranged from 56.8 to 261 pg m^{-3} with an average value of 116 ± 50.1 pg m^{-3}. Atmospheric PCBs mostly existed in the gas phase and varied from 39.8 to 218 pg m^{-3} with a contribution of 77.5± 5.33% (Fig. 1). The sum of ICES-identified congeners ($\sum_{ICES}$PCBs, PCB 31/28, 52, 101, 118, 132/153, 138/158 and 180) ranged between 27.7 and 110 pg m^{-3}, constituting 44.2± 6.30% of

the $\sum_{24}$PCBs. Concentrations of $\sum_{ICES}$PCBs were comparable to or slightly lower than those measured from the west African coast in 2007 (2.1–190 pg m^{-3}) (Gioia et al., 2011), the North Pacific in 2008 (28–103 pg m^{-3}) (Zhang and Lohmann, 2010) and the South Atlantic in 2008 (3.7–220 pg m^{-3}) (Gioia et al., 2008), but they were substantially higher than samples collected over the equatorial Indian Ocean in 2011 (1.4–22 pg m^{-3}) (Huang et al., 2014) and the tropical Atlantic in 2009 (average of 8 ± 3 pg m^{-3}) (Lohmann et al., 2012). Further comparisons focused on the ECS involved available datasets of atmospheric PCBs obtained from different expeditions. Concentrations of total PCBs in the ECS (104–261 pg m^{-3}) compared well to those measured by Iwata et al. (1993) for the ECS in 1989–1990 (62–250 pg m^{-3} for 32 PCBs). Similarly, concentrations of $\sum_{ICES}$PCBs determined from the ECS (43.5–110 pg m^{-3}) were in good agreement with those reported by Gioia et al. (2012) in the East and South China Seas in 2008 (22–122 pg m^{-3}). Field measured atmospheric residence times for ICES PCBs in the East and South China Seas were shorter and the highest average value reached only 61 days for PCB 101 (Gioia et al., 2012). Nonetheless, no obvious differences across the time series in terms of atmospheric levels were observed even though less and more heavily chlorinated congeners ran counter to the rate by which air PCBs decayed in the region. We found no significant decrease in atmospheric PCBs across the ECS despite a long-term ban on their application and production applied in adjacent East Asia. However, concentrations of $\sum_{ICES}$PCBs over the ECS were even 1–2 orders of magnitude greater than those measured for background sites of west-central China (4.0–27.5 pg m^{-3}) (Wu et al., 2011), suggesting that southeast coastal areas of China constitute an important emission source region. This conclusion is supported by model simulations (Hung et al., 2005) and by air monitoring of surrounding countries and especially China where intensifying air PCB burdens have been observed in recent years (Cui et al., 2013).

Spatially, obvious variations in concentrations of total PCBs over the NWP of up to ~5 folds were observed. Higher PCB concentrations were detected in samples A1–A3 from the ECS off the east coast of China (212–261 pg m^{-3}), for which air masses stemmed from China, representing a local hotspot of PCBs in East Asia (Fig. S1). We found several significant PCB loadings for samples gathered from areas close to Japan (A22) and from the west coast of Korea (A26), revealing potential sources of atmospheric PCBs from these countries to the NWP. PCBs in samples A15, A17 and A18 collected from the remote NWP were also found to present elevated concentrations due to the significance of long-range advection input from continental outflows. Air parcels were traced to northern China, traveling over the Korean peninsula and Japan (Fig. S1). Overall, the advection of air masses from heavily polluted land upwind substantially influenced the distribution of atmospheric PCB. An overall decrease in $\sum_{24}$PCBs was found in the open NWP (56.8–137.6 pg m^{-3}, samples A4–A19) due in part to the modulation of dilution and removal processes during LRAT. In addition to the governing role of dominant air mass trajectories, the surface wind field significantly affected PCB levels in the atmosphere. Sampling episodes (A24–A26) measured at sites close to the coast from May were characterized by lower PCB levels in comparison to those of other offshore samples (A1–A3) that could be associated with mitigated land-based inputs restricted by the mounting effects of relatively clean marine air masses supported by the wind field (Fig. S2).

The temperature dependence of air PCBs was investigated for ICES PCB congeners using the Clausius–Clapeyron (CC) equation, which expresses the linear relationship between the partial vapor pressure of PCBs against the reciprocal temperature. As illustrated in Fig. S4, only PCB 132/153 and PCB 180 generated negative slopes albeit with insignificance at the 95% confidence level. Overall, the
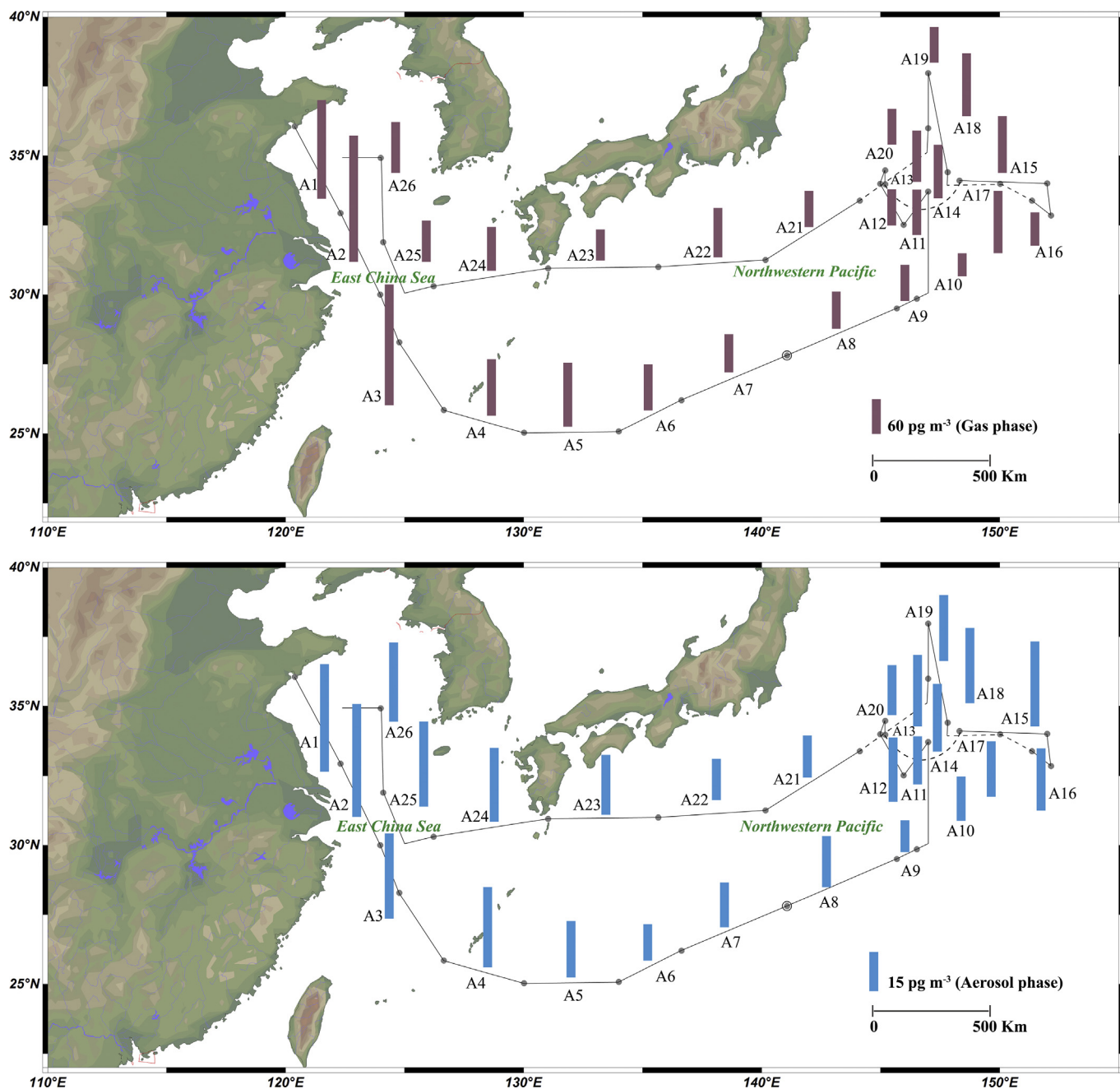
Fig. 1. Spatial distribution of gas (upper panel) and aerosol phases (lower panel) of PCBs during the sampling campaign.

variability of gaseous concentrations of PCBs was not governed by phase exchange thermodynamics and the unexpectedly anomalous existence of positive slopes could not be attributed to the enthalpy of air–surface exchanges. Unlike land-based observations, much greater scatters in CC plots and weaker relationships with air temperatures found in our study are similar to other cruise observations (Gioia et al., 2008; Xu et al., 2012). The absence of temperature dependence found may be attributed to the occurrence of narrow temperature fluctuations (19.5 $\pm$ 3.36 °C).

3.2. Composition profiles and sources of PCBs

Chlorination profiles of the homologue basis for all of the samples were statistically similar ($R^2 = 0.80–0.99$, $P < 0.05$),

suggesting that PCB homologue patterns in the atmosphere are less variable from the ECS to the NWP and similar sources. PCBs were characterized by the predominance of tri- and tetra-CBs both in gas and aerosol phases (Fig. S3). On the whole, the relatively high abundance of tri-CBs and tetra-CBs in homologue compositions of PCBs accounted for 35.2$\pm$ 8.80% and 49.6$\pm$ 9.03% of total concentrations, respectively, followed by penta-CBs (12.1$\pm$ 2.96%) along the cruise track. Main components included PCB 31/28 and PCB 52, and concentrations of these congeners amounted to 10.9–64.1 pg m^{-3} and 6.71–52.1 pg m^{-3}, representing 51.2$\pm$ 11.2% and 40.2$\pm$ 11.9% of $\sum_{ICES}$PCBs, respectively. The highly chlorinated congeners with more than 6 chlorine atoms were unanimously detected below 1 pg m^{-3}. The dominance of low chlorinated homologues in the atmospheric profile over the NWP is in line with

those reported for the northern South China Sea (Li et al., 2012) and for adjoining countries such as China (Wu et al., 2011), South Korea (Nguyen et al., 2016) and Japan (Hogarh et al., 2013), revealing the effects of continental outflows on the composition of air PCBs over the remote ocean. These less chlorinated PCBs were found to be released from obsolete electrical transformers and capacitors and/or via unintentional emissions including coking and steel production especially in China (Cui et al., 2013). Additionally, the consistency of compositions was evidenced by the concentration ratios of PCB congeners, as congener ratios in source profiles are not easily distorted (Hogarh et al., 2012). When considering potential degradation during LRAT, heavier PCB congeners with relatively high levels of stability were considered. Ratios of PCB 101/PCB 118 (penta-CBs), PCB 128/PCB 156 (hexa-CBs), and PCB 177/PCB 187 (hepta-CBs) were 2.15 ± 1.01 and 1.73 ± 1.04, 0.73 ± 0.27 and 0.97 ± 0.47, 1.58 ± 1.77 and 1.24 ± 1.47 for land-influenced and marine air masses (A5–A10), respectively, and no distinct difference was found between two types of air masses. The sampling was conducted in the spring when westerly winds prevailed over the NWP, favoring the LRAT of land-based PCB into the NWP, although concentrations varied at different sites.

3.3. Gas–particle partitioning of PCBs using absorptive and adsorptive models

The partitioning of PCBs between the gas and particulate phase is commonly defined as K_p (m³ μg⁻¹), which is given by the concentration ratio of particle-bound and gaseous PCBs (both in pg m⁻³) normalized with total suspended particle concentrations (TSP, μg m⁻³). PCB concentrations falling below detection limits in either phase were not considered in our calculations. The $\log K_p$ values averaged at -1.44 ± 0.42 and -2.01 ± 0.40, -1.91 ± 0.23 and -2.21 ± 0.31, -2.55 ± 0.49 and -2.65 ± 0.36, and -2.53 ± 0.90 and -2.66 ± 0.51 for PCB 18, PCB 31/28, PCB 49 and PCB52 in marine and continentally influenced air masses, respectively. The partitioning of these less chlorinated PCBs to aerosols was slightly stronger for marine air masses. This could be attributed to processes of sea-to-air release when bubbles burst on breaking waves. The period of March to May corresponds to the phytoplankton bloom period of the NWP (Sverdrup, 1953; Obata et al., 1996), during which bubble bursting processes further the transfer of marine biogenic OM in the surface film of the ocean into aerosols (Cavalli et al., 2004). Moreover, higher wind speeds recorded in the open NWP facilitated the production of sea spray aerosols (Woodcock, 1953) with more organic compounds enriching the emitted sub-micrometer fraction (Cochran et al., 2016). The scenario was suggested in Mediterranean coast under different meteorological conditions as well (García-Flor et al., 2009) through atmospheric partitioning analysis. These sprayed OM-containing aerosols contained a certain quantity of less chlorinated PCBs from local marine sources when they were released from water. Then, fresh particles could rapidly absorb volatile PCBs from atmospheric PCBs, resulting in increased K_p values in marine air masses.

Both adsorptive and absorptive processes are expected to be described via $\log K_p$ and $\log P_L^0$ regressions:

$$\log Kp = m \log P_L^0 + b \tag{1}$$

where P_L^0 values were adjusted for the field ambient temperature of each sampling event based on Falconer and Bidleman (1994). The plot of $\log K_p$ and $\log P_L^0$ yields a slope of -0.54 ($R^2 = 0.44$, $P < 0.001$) for all of the samples and Fig. S5 shows that variations in the samples were obtained for regression parameters with slopes (m)

and intercepts (b) ranging from -0.38 to -0.72 and -3.98 to -2.65, respectively ($R^2 = 0.23-0.68$, $P < 0.01$). Slopes shallower than -1 were frequently encountered in urban or regions close to sources of PCBs (Lohmann et al., 2000; Cindoruk and Tasdemir, 2007). These were similarly observed in the marine environment examined in this study. Although these land-derived organic aerosols traveling farther from sources were supposed to undergo long-term adsorptive and absorptive processes, the expected equilibrium of PCB partitioning was still not reached. Slopes far from -1 denote strong inputs from continental outflows. Additionally, on average, shallower slopes of marine air masses ($m = -0.52 \pm 0.11$) than those of continentally influenced air masses ($m = -0.58 \pm 0.09$) were obtained (Fig. 2). Though the difference was not significant, this suggested a partitioning of PCBs further deviating from the theoretical equilibrium under the marine air masses.

Significant correlations of $\log K_p$ values for ICES PCB congeners and corresponding aerosol-associated concentrations (given as pg mg⁻¹) were found (Fig. S6), revealing the influence of organic constituents of aerosols on PCB gas–particle partitioning. K_{oa} is perceived to be an alternative descriptor provided that absorptive partitioning into organic film coating particles dominates and sorbing properties of sampled aerosols equate to those of octanol. Temperature-corrected K_{oa} values were achieved based on Harner and Bidleman (1996) and Kömp and McLachlan (1997). Linear regressions of $\log K_{oa}$ and $\log K_p$ for the sampling period are presented in Fig. 3. Significant correlations of $\log K_{oa}$ and $\log K_p$ were found for air samples collected in proximity to land or substantially impacted by continental outflows. Even for the furthermost sites measured during the cruise period, $\log K_{oa}$ and $\log K_p$ relationships remained strong for samples A15, A17 and A18 for the remote NWP ($R^2 = 0.42 \pm 0.17$, $P = 0.03 \pm 0.02$), revealing strong effects of land-derived organic aerosols on PCB gas–particle partitioning after long-range transport (Fig. S7). Regarding air samples of marine origin (A5–A10) in the open NWP, an absence of this correlation was identified except for A7 ($R^2 = 0.36$, $P = 0.03$). As compared to the more continentally influenced samples with significant relationships, relatively lower aerosol phase concentrations and K_p values for highly chlorinated congeners were showed in marine air masses and thereby less strong gas-to-particle partitioning of these PCB members was supposed to elevate the lower left end of the plot of $\log K_p$ versus $\log K_{oa}$ for air masses of marine origin (Fig. 3b).

With the use of mass fractions of OM (f_{OM}) in particles and K_{oa}, the role of absorption into organic matrixes was evaluated using the following relation:

$$\log K_p = \log K_{oa} + \log f_{OM} - 11.91 \tag{2}$$

Parameterization for OM absorption modeling was described in SI Text 1. The results of the absorption model show an overall underestimation of the selected congeners as is illustrated in Fig. 4. It was found that differences between the measured and predicted K_p values were smaller from three to seven-chlorine substituted members, and they were 2.56 ± 0.55, 1.76 ± 0.64, 1.29 ± 0.45, 1.70 ± 0.37 and 1.50 ± 0.49 log unites for tri-CBs, tetra-CBs, penta-CBs, hexa-CBs and hepta-CBs, respectively. This possibly indicated the increasing absorption of heavily chlorinated PCBs into OM. However, the overall underprediction found did not result from the introduction of f_{OM} value, as the term $\log f_{OM}$ cannot create 2 orders of magnitude of difference. This deviation could be attributed to the oxidative attack of OH radicals during LRAT, but this pattern of depletion is typical for gaseous low chlorinated PCBs, enlarging field K_p values (Anderson and Hites, 1996). Slopes of significant relationships of $\log K_{oa}$ and $\log K_p$ were commonly shallower than $+1$ (Fig. S7), suggesting that absorptive partitioning equilibrium was not reached and that the gas–particle partitioning of PCBs
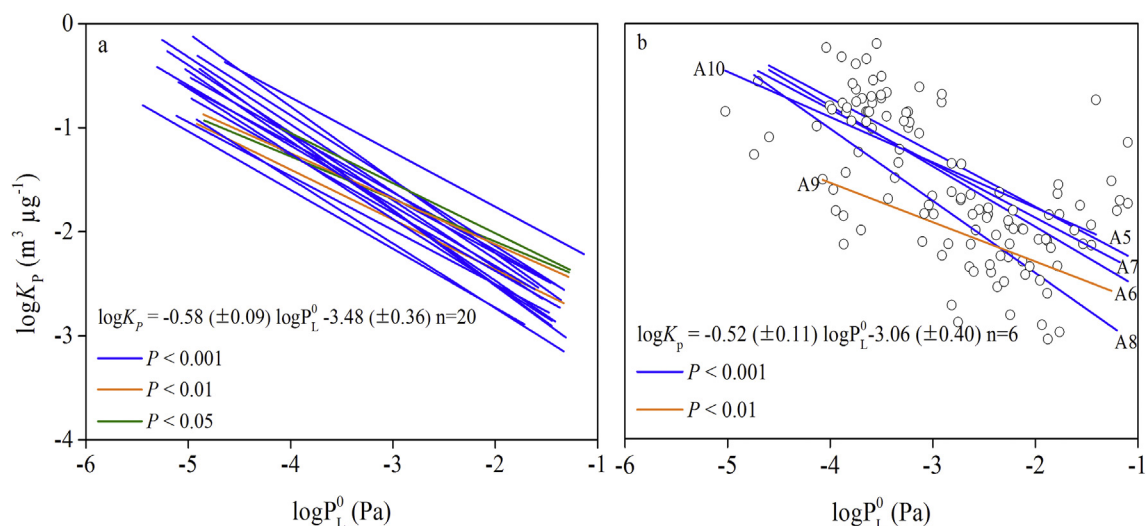
Fig. 2. Linear correlations of $\log K_p$ versus $\log P_L^0$ for continentally influenced air masses (a) and marine air masses (b) over the ECS and NWP.
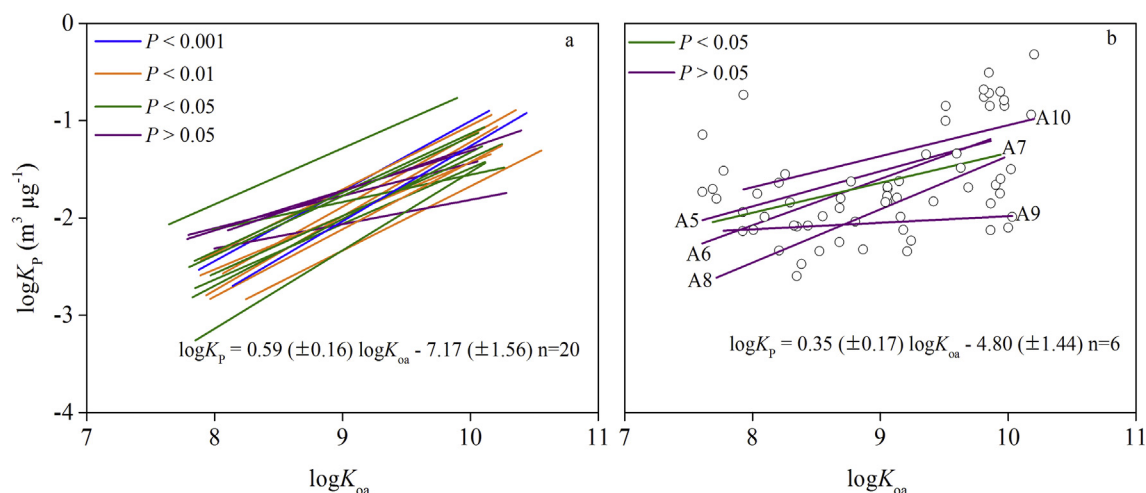

Fig. 3. Linear correlations of $\log K_p$ versus $\log K_{oa}$ for continentally influenced air masses (a) and marine air masses (b) over the ECS and NWP.

could not be fully explained by the absorptive mechanism. Other sorbents (e.g., soot carbon) should be present in aerosols, accounting for additional particulate PCBs.

In view of the strong soot-PCBs interactions found in aquatic environments (Jonker et al., 2004), the sorption behavior of air PCBs over the NWP should be influenced by gas-to-particle conversions resulting from the transport of polluted air mass carrying high levels of soot-like organic carbon in aerosols over long distances. The soot–air partitioning of PCBs is thus extended in the sorption model (Dachs and Eisenreich, 2000).

$$K_p = f_{OM} \frac{\zeta_{OCT}}{\zeta_{OM}\rho_{OCT}} \frac{MW_{OCT}}{MW_{OM}10^{12}} K_{oa} + f_{EC} \frac{\partial_{EC}}{\partial_{AC}10^{12}} K_{sa} \qquad (3)$$

where f_{EC} is the mass fraction of elemental carbon (EC) in the TSP, ∂_{EC} and ∂_{AC} are the specific surface areas of EC and activated carbon, respectively, ζ_{OCT} and ζ_{OM} are activity coefficients of PCBs in octanol and OM, respectively, MW_{OCT} and MW_{OM} are the molecular masses of octanol and OM, respectively, K_{sa} is the soot–air partition coefficient, and ρ_{OCT} is octanol density (0.82 kg L^{-1}). Ratios of $\partial_{EC}/\partial_{AC}$, ζ_{OCT}/ζ_{OM} and MW_{OCT}/MW_{OM} were assumed to be 1. The

parameters applied in Eq. (3) were given in SI Text 1. No experimentally derived K_{sa} have so far been covered for PCBs. The estimation of K_{sa} was determined as the ratio of soot–water (K_{sw}) and air–water partition coefficients (H') (Table S4). The obtained K_{sa} values were further compared with those derived from a thermodynamically based model. van Noort (2003) introduced this alternative estimation for adsorption of PCBs by soot based on relationships with $\log K_{oa}$ (or $\log P_L^0$) and soot-specific surface area (A_{sc}). Assumed values of 100 and 370 m^2 g^{-1} for A_{sc}, as reported in previous studies (e.g., Ludwig and Schmidt, 1990; Bucheli and Gustafsson, 2000), were applied. The predictions from thermodynamic model assuming A_{sc} of 370 m^2 g^{-1} were slightly below those estimated from K_{sw} and H' (less than 1 log unit), however, the difference as much as one order of magnitude was observed for PCB18, PCB101 and PCB 118 between the different prediction approaches if A_{EC} of 100 m^2 g^{-1} was taken (Table S5). A_{sc} values vary with the soot aerosol types and environmental conditions during transport of soot carbon. The applicability of predictions based on K_{sw} and H' was further suggested, given the uncertainty in A_{EC} and less discrepancies between predicted and field measured K_p using K_{sw} and H'-derived K_{sa}; the simulations deviated from the field
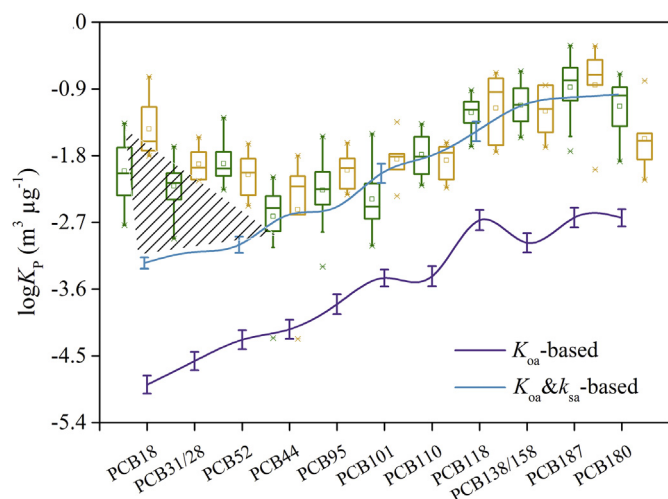
Fig. 4. Derived K_p for selected PCBs based on the K_{oa} (purple) and dual K_{oa} and K_{sa} (blue). Box plots of field K_p values in green and orange represent continentally influenced air masses and marine air masses, respectively. Curved lines with error bars correspond to mean ± standard deviations of the modeling values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

measurements by 1.37 ± 0.50, 1.06 ± 0.31, 0.23 ± 0.49, and 0.22 ± 0.37 log units for PCB 18, PCB 52, PCB 101 and PCB 118, respectively. The fit to the field K_p values is consistently low for less chlorinated PCBs as the K_{oa}-based model. The positive deviations (denoted by the shaded area in Fig. 4) could be partially attributed to the uncertainty in affinity to OM relative to octanol, as indicated by Berrojalbiz et al. (2014). However, the activity coefficients of non-polar or weakly polar compounds in various liquid aerosols are fairly constant especially in the combustion aerosols (Chandramouli et al., 2003), which means a minor influence of the term ζ_{OCT}/ζ_{OM} on the determination of predicted K_p.

The predicted K_p values for selected PCBs based on Eq. (3) were 1−2 orders of magnitude greater than those derived from Eq. (2), confirming a strong affinity between PCBs and soot. Compared to the K_{oa}-based model, the dual K_{oa} and K_{sa} simulations resemble field measurements for marine air and land-influenced air masses with estimated K_p values increasing by 1.57 ± 0.06 and 1.46 ± 0.07, 1.18 ± 0.05 and 1.10 ± 0.05, 1.29 ± 0.02 and 1.27 ± 0.02, and 1.08 ± 0.04 and 1.01 ± 0.04 log units on average for PCB 18, PCB 52, PCB 101 and PCB 118, respectively, in these two types of air masses. This implies that the soot adsorption of PCBs plays a key role in partitioning to aerosols and overwhelms OM absorption even when atmospheric soot levels are low. The differences for PCB 18 and PCB 52 may be reflective of primary contributions of exchangeable PCBs adsorbed on soot. East Asia is the source region of soot carbon in the NWP (Zhang et al., 2015; Kanaya et al., 2016) and anthropogenic contributions measured in the spring was considerable for East Asia such as coal burning (Kunwar et al., 2016) and oil combustion (Shimada et al., 2015). A majority of trajectories show that air masses passing over the East Asian continent prior to arrival at the NWP should have been enriched with continental soot (Fig. S1). Besides, open biomass burning levels are significant in the spring in this study region, thus making greater contributions to soot components in aerosols (Zhang and Cao, 2015); PCBs can be re-volatilized from residuals in soil and then adsorbed onto soot carbon (Eckhardt et al., 2007). Meanwhile, emission factors of PCBs show that PCBs and tetra-CBs, in particular, can be generated during the combustion of coal and wood fuels (Lee et al., 2005). These combustion-derived or accidentally released PCBs would

subsequently partition to the exchangeable fraction of formed soot aerosols during the LRAT to the NWP.

3.4. Implications for the importance of continental outflow

The transport mass of PCBs in the aerosol phase (M_{PCB}) from China to the NWP was estimated using Eq. (4) based on the modeled eastward soot carbon flux (F_{EC}) of 13.3 kg s^{-1} into the NWP in the spring (Matsui et al., 2013) and the matched value of f_{EC} derived from Eq. (3).

$$MPCB = \frac{C_P}{f_{EC} \times TSP} \times F_{EC} \times t \qquad (4)$$

where C_p is the concentration of PCBs in the aerosol phase (pg m^{-3}) and t is the time interval for estimation (day). Based on the matched model of dual OM and soot sorption (Eq. (3)), the f_{EC} value of 0.03 was used to estimate M_{PCB} in Eq. (4). The f_{EC} value is comparable to land-based measurements for China (Cao et al., 2007), suggesting their high levels of stability in the atmosphere. Based on a dynamic model, Huang et al. (2007) found a net flux of 3 PCBs (CB-28, 153, and 180) that included gas and aerosol phases of 1048 kg per year in the atmosphere of the North Pacific Ocean. In comparison, the transport mass of 24 particulate PCBs reached up to 1011 kg over the course of our cruise (39 days) and 2333 kg in the spring of 2015 (90 days). As estimated by Cui et al. (2013), intentionally produced emissions for 22 selected PCBs from 1960 to 2010 reached 172.2 t and are comparable to those of unintentionally produced PCBs (UP-PCBs: byproducts of emissions containing PCBs during combustion or other industrial activities, 146.1 t). However, UP-PCB emissions in China have been constantly augmented in recent years and have represented the majority of total PCB emissions since 1990. The emissions inventory of UP-PCBs exceeded 14,000 kg in 2010, of which densely emitted UP-PCBs occurred in eastern and southern China (Cui et al., 2013). It is estimated that transported aerosol phase PCB loadings for the spring over the NWP account for ca. 17% of the yearly UP-PCB emission mass. Westerly winds prevailed in the winter and spring in East Asia when PCB outflows from source regions were substantial. The eastward soot carbon mass exported from China to the NWP in this spring reached 103 Gg, representing 5% of soot emissions over China (1957 Gg per year) (Wang et al., 2012). Though removal processes accompanied the eastward LRAT of the PCBs, abundant supplies of PCBs mainly from eastern China confirm the presence of particle-bound PCBs over the NWP during the spring under the influence of strong East Asian Monsoon.

4. Conclusions

This study was to provide new information on the occurrence and gas−particle partitioning of air PCBs over the NWP. The spatial variability of atmospheric PCBs was consistent with the air mass origins of long-range advective transport from the East Asian Continent, as further evidenced by concordant composition profiles of PCBs from the ECS to the NWP. The predicted K_P based on the dual absorption and adsorption model was found to be 1−2 orders of magnitude higher than those by the absorptive mechanism, and the former prediction closely matched with the measured K_P, suggesting the importance of soot carbon as a transport medium for PCBs under the influence of continental outflow. The estimated eastward PCB flux of 2333 kg for in the studying area suggested the continental outflow from the southeast China was an important source over the NWP.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.08.056.

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