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# Polychlorinated naphthalenes in the air over the equatorial Indian Ocean: Occurrence, potential sources, and toxicity



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### ABSTRACT

Monitoring of marine polychlorinated naphthalenes (PCNs) is crucial, as they are considered persistent organic pollutants (POPs) by the Stockholm Convention. Data on PCNs in marine environment are scarce. In this study, 19 air samples were collected during a cruise in the equatorial Indian Ocean on board the Chinese research vessel *Shiyan I* from 4/2011 to 5/2011. PCN concentration of these air samples ranged from 0.033 to 2.56 pg m<sup>-3</sup>, with an average of 0.518 pg m<sup>-3</sup>, equal to or lower than the values reported for other oceans, seas, and lakes worldwide. Tri- and tetra-CNs were the main homologues in most samples. Reemission of Halowax mixtures and incineration processes were the major sources of atmospheric PCNs in the study area. The PCN-corresponding toxic equivalency values ranged from 0 to 0.190 fg m<sup>-3</sup> (average: 0.038 fg m<sup>-3</sup>), falling in the low end of global range.

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## 1. Introduction

Polychlorinated naphthalenes (PCNs) are considered as persistent organic pollutants (POPs) by the Persistent Organic Pollutants Review Committee of United Nations, because of their persistence, long-range transportability, bioaccumulation, and adverse effects on organisms (SCPOP, 2011). PCN congeners are ubiquitous in various environmental media and biota (Bidleman et al., 2010). Technical PCN products had been widely used as insulators, lubricants, flame retardants, paint additives, and so on, until the 1970s/1980s (Falandysz, 1998; Hogarh et al., 2012). Evaporation from the historical residue has been a major pathway of PCNs in air (Harner and Bidleman, 1997). Recently, unintentional emissions of PCNs from combustion processes such as municipal waste incineration and metal smelting (including primary and secondary nonferrous smelting, coking, iron ore sintering, and electric arc furnaces) have been considered more important than ever to atmospheric PCNs (Wang et al., 2012; Liu et al., 2014, 2015).

Oceans and seas are the final sinks of POPs, removing them from the "recyclable pool" in the environment (Dachs et al., 2002). However, oceans might also turn into a secondary source of certain POPs such as dichlorodiphenyltrichloroethane (Stemmler and Lammel, 2009),

alpha-hexachlorocyclohexane (Li and Bidleman, 2003), and polychlorinated biphenyls (PCBs, Zhang and Lohmann, 2010) long after those compounds were banned. Thus, it is important to monitor marine POP pollution status and estimate their sources. Several studies have been carried out to investigate PCN levels in air, sediments, or organisms of the arctic and subarctic oceans and seas (Falandysz and Rappe, 1996; Harner et al., 1998; Lundgren et al., 2002, 2003; Bidleman et al., 2010).

The equatorial Indian Ocean is surrounded by many South Asian countries, including India, Pakistan, Malaysia, Sri Lanka, Vietnam, and the Philippines. Recent studies in India and Pakistan have indicated that atmospheric PCN pollution in South Asia is comparable to or higher than other Asian regions, and is high worldwide (Mahmood et al., 2014; Xu et al., 2014). Our previous study suggested that atmospheric PCNs in the northern South China Sea were influenced by the proximity to source regions and air mass origins, and wood/coal burning and industrial processes were the two major combustion sources of the gaseous PCNs (Li et al., 2012). A similar condition may occur in the equatorial Indian Ocean. However, data on PCNs in the equatorial and adjacent oceans and seas are scarce.

A total of 19 air samples were taken from the equatorial Indian Ocean during the sampling campaign from Malaysia to the south of Bay of Bengal passing by Sri Lanka in 2011 on board the Chinese research vessel *Shiyan I*. In order to understand PCN pollution status in

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the equatorial Indian Ocean, PCN concentrations in the air samples were determined. The composition profiles, spatial distribution, potential sources, and toxicity of PCNs in the air are also analyzed.

## 2. Materials and methods

#### 2.1. Sampling

On board the Chinese research vessel *Shiyan I* of South China Sea Institute of Oceanology, from 12 April to 4 May 2011, 19 air samples were taken from the equatorial Indian Ocean (0–6°E, 80–98.5°N, Fig.1, Table S1). These samples were taken via a high-volume air sampler placed in the windward on the foredeck of the ship. Approximately 200–500 m<sup>3</sup> of air was drawn through a quartz fiber filter (QFF), and subsequently through a polyurethane foam (PUF) plug (i.d.: 6.5 cm, length: 7.5 cm, density: 0.03 g m<sup>-3</sup>). The PUFs and QFFs were stored at -20 °C until analysis.

## 2.2. Sample preparation and instrumental analysis

The PUF and QFF samples spiked with <sup>13</sup>C-PCB141 as recovery surrogate were Soxhlet-extracted with dichloromethane (DCM) for 36 h and further purified on a column packed with 3-cm neutral alumina (3% deactivated), 3-cm neutral silica gel (3% deactivated), 3-cm sulfuric acid silica gel (50% by mass), and 1-cm anhydrous Na<sub>2</sub>SO<sub>4</sub> from bottom to top (Huang et al., 2013). The column was eluted with 30 mL of DCM/ hexane (1:1) to collect the PCN fraction. The eluted solvent was concentrated and solvent-exchanged to hexane, and then concentrated to approximately 50  $\mu$ L. PCB208 was added as internal standard before instrumental analysis.

The target PCN congeners were measured on an Agilent 7890A/ 5975C GC–MS with a DB-5 ms capillary column (30 m  $\times$  0.25 mm  $\times$  0.25 µm, Agilent, CA, USA). The mass spectrometer was operated with an electron capture negative-ion (ECNI) source in selected ion monitoring (SIM) mode. The initial temperature of the oven was set at 80 °C for 0.5 min, then increased at a rate of 15 °C min<sup>-1</sup> to 160 °C, 2 °C min<sup>-1</sup> to 240 °C, and finally 6 °C min<sup>-1</sup> to 270 °C and held for 2.5 min. The temperatures of the injector interface, transfer line, and ion source were set at 265, 280, and 150 °C, respectively. Trito octa-CNs (tri-CNs: CN19, 24, 14, 15, 16, 17/25, 23; tetra-CNs: CN42, 33/34/37, 47, 36/45, 28/43, 27/30, 39, 32, 35, 38/40, 46; penta-CNs: CN52/60, 58, 61, 50, 51, 54, 57, 62, 53, 59, 49, 56; hexa-CNs: CN66/67, 64/68, 69, 71/72, 63, 65; hepta-CNs: CN73, 74; octa-CN: CN75) were quantified against the technical PCN mixture Halowax 1014 (Xu et al., 2014).

## 2.3. Quality assurance and quality control

Two laboratory blanks, two PUF field blanks, and three QFF field blanks were analyzed. The surrogate recoveries of <sup>13</sup>C-PCB141 were 97  $\pm$  7.2% and 78.1  $\pm$  23.3% for PUF and QFF samples, respectively. The reported PCN concentrations in this study were not recovery-corrected. The instrumental detection limits (IDLs) were calculated from the lowest standard, extrapolating to the corresponding amount of analyte that would generate a signal-to-noise ratio of 3:1. The method detection limits (MDLs) were assigned as average values of blanks plus three times of the standard deviations of blank values. Because target PCN congeners were below the IDLs in the laboratory and field blanks analyzed, the MDLs of measured PCNs were assigned as three times of IDLs, with values ranging from <0.001 to 0.021 pg m<sup>-3</sup>.

Breakthrough of PUF samples was assessed by two consecutive PUF plugs, which were analyzed separately. Target PCN congeners were under MDLs from the subjacent PUF plug, suggesting that these compounds could be effectively collected by the upper PUF plug.

#### 2.4. Air mass back trajectories

NOAA's (National Oceanic and Atmospheric Administration) HYSPLIT model was used to trace the air mass back trajectories of the air samples collected along the sampling cruise (Draxler and Rolph,



Fig. 1. Atmospheric concentrations of PCN homologues and the air mass back trajectories (BTs) during sampling campaign. Three BTs were continental passing over Malaysia and Indonesia (red lines), and the remaining BTs were oceanic passing over the Indian Ocean (green lines).

2010) and 120-h back trajectories were calculated at the beginning and end of each air sampling event in coordinated universal time (UTC) at 10 m above sea level (Fig. 1).

#### 3. Results

#### 3.1. PCN concentrations

Target PCN congeners were not detected in the QFF samples, thus PCN concentrations in the PUF samples (gaseous phase) are equivalent to the values in the air over the equatorial Indian Ocean during sampling campaign (Table 1). Among the congeners detected in the air samples, PCN19, 24, 15, 33/34/37, 27/30, and 51 were detectable in all samples, followed by PCN16, 17/25, 52/60, 49, and 64/48, with a detection frequency > 70%. PCN 23, 42, and 50 were detectable in > 50% of samples. The  $\sum$  PCN concentrations ranged from 0.033 to 2.56 pg m<sup>-3</sup>, with an average value of 0.518 pg m<sup>-3</sup> (Table 1). The levels of  $\sum$  PCNs were comparable to the previously detected levels of hexachlorocyclohexanes ( $\sum$  HCHs: 0.76–3.4 pg m<sup>-3</sup>) (Huang et al., 2013), and lower than the levels of polychlorinated biphenyls ( $\sum_{21}$ PCBs: 2.0–29 pg  $m^{-3}$ ) (Huang et al., 2014), hexachlorobenzene (HCB:  $2.2-17 \text{ pg m}^{-3}$ ) (Huang et al., 2014), and dichlorodiphenyltrichloroethane and its metabolites ( $\sum$  DDTs; 2.2–17 pg m<sup>-3</sup>) (Huang et al., 2013) in the same samples.

Data on PCN concentrations in oceanic air are quite limited. The PCN concentrations in the equatorial Indian Ocean are lower than those reported for the air over the north–south Atlantic transect (range: 0.3–86 pg m<sup>-3</sup>, mean: 16 pg m<sup>-3</sup>) (Jaward et al., 2004) and northern South China Sea (mean:  $10.5 \pm 7.16$  pg m<sup>-3</sup>) (Li et al., 2012). Compared with the values in other remote areas, PCN concentrations in this study are comparable to those in the air over the arctic area (<0.01–2.9 pg m<sup>-3</sup>) (Helm et al., 2004) and the Venice Lagoon area (0.19–3.41 pg m<sup>-3</sup>) (Manodori et al., 2006), but lower than those in the air of Great Lakes (0.3–52.1 pg m<sup>-3</sup>) (Harner et al., 2006) and Swedish background areas (1–10 pg m<sup>-3</sup>) (Egebäck et al., 2004). Compared with the values in the air of the adjacent countries, PCN concentrations in this study were one to three orders of magnitude lower than those in India and Pakistan (Mahmood et al., 2014; Xu et al., 2014).

### 3.2. Spatial distribution and compositional profiles of PCNs

The spatial distributions of POPs in the marine atmosphere were influenced by the surrounding land sources and atmospheric transportation (Li et al., 2012). As shown in Fig. 1, sample 1 exhibited high concentration of PCNs. Back-trajectory analysis revealed that continental air masses passing over the land of Indonesia and Malaysia were observed for sample 1, suggesting that the presence of high level of PCNs

T	a	b	l	e	1

PCN concentrations in the air over	the equatorial Indian	Ocean (pg m -	3
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Congeners	Minimum	Maximum	Mean	SD	Median
PCN19	0.002	0.046	0.009	0.010	0.006
PCN24	0.004	0.094	0.018	0.020	0.012
PCN15	0.004	0.076	0.016	0.017	0.011
PCN16	n.d.	0.030	0.011	0.009	0.008
PCN17/25	n.d.	0.127	0.029	0.028	0.021
PCN23	n.d.	0.119	0.025	0.032	0.014
PCN42	n.d.	0.130	0.019	0.033	0.003
PCN33/34/37	0.005	1.09	0.213	0.310	0.024
PCN27/30	0.004	0.142	0.022	0.031	0.013
PCN52/60	n.d.	0.023	0.008	0.006	0.007
PCN50	n.d.	0.016	0.002	0.004	0.001
PCN51	0.005	0.357	0.076	0.096	0.024
PCN49	n.d.	0.154	0.032	0.039	0.016
PCN64/68	n.d.	0.189	0.038	0.055	0.016
$\sum$ PCNs	0.033	2.56	0.518	0.649	0.224

Note: n.d., not detected. SD, standard deviation.

in sample 1 may be related to the reemission of PCNs from historical residues or unintentional release from incineration processes from Indonesia or Malaysia (Helm et al., 2004; Li et al., 2012). Higher levels of PCBs were also measured in the air samples subject to continental air masses (Huang et al., 2014). Although the back trajectory suggested oceanic air masses passing over the equatorial Indian Ocean for samples 11 and 13 (Fig. 1), high concentrations of PCNs were measured in these two samples, with the continental outflow from nearby India or Sri Lanka being the possible sources. The  $\sum$  PCN concentrations (range: 4.9–140 pg m<sup>-3</sup>, average: 28 pg m<sup>-3</sup>) in a previous Indian sampling campaign by PUF disks (Xu et al., 2014) were significantly higher than the values of this study. Similar results have also been found for PCBs in our previous study, where high concentrations of PCBs were observed in samples 13 and 16 with oceanic air masses (Huang et al., 2014).

Overall, tetra- and tri-PCNs were the major homologues in the air samples, with an average contribution of 68.2% to  $\sum$  PCNs, followed by penta-PCNs (23.6%) and hexa-PCNs (8.11%). Similar compositional profiles of PCNs have been found in the air over the northern South China Sea (Li et al., 2012), the Venice Lagoon area (Manodori et al., 2006), the arctic area (Helm et al., 2004), and the Great Lakes area (Harner et al., 2006), for which tri- and tetra-CNs were the predominant homologues. In particular, it was noted that in the samples (1, 3, 5, 7, 9, 11, and 13) with higher concentrations of PCNs (>0.4 pg m<sup>-3</sup>), tetra-CNs were the predominant homologues (53.1–57.4%), with PCN33/34/37 being the most abundant congener (Fig. 2), followed by penta-CNs (20.6–31.7%) and tri-CNs (7.96–19.3%) (Fig. 1). Tri-CNs predominated in most samples with lower PCN concentrations, with PCN17/25 being the major congener, followed by tetra- and penta-PCNs (Fig. 2).

#### 3.3. Potential sources

As the use of technical PCN products has been phased out since the 1970s or 1980s (Hogarh et al., 2012), release of PCNs from historical residues and industrial thermal processes, such as municipal waste incineration, smelting, or coking, was reported to be their main source in the environment (Harner et al., 2006; Li et al., 2012; Wang et al., 2012; Liu et al., 2014). Previous studies suggested that the fraction of combustion-related congeners (e.g., PCN17/25, 36/45, 27/30, 39, 45, 52/60, 50, 51, 54, and 66/67) in  $\sum$  PCNs could be used to identify the importance of combustion source, because these congeners were minor or absent in Halowax and PCB technical formulations compared with incineration or other industrial thermal processes (Helm and Bidleman, 2003; Lee et al., 2007; Wang et al., 2012; Xu et al., 2014).  $\sum_{\text{combustion}} \text{PCNs} / \sum_{\text{PCNs}} \text{PCNs} > 0.5$  indicated emission from combustion, while a value <0.11 was Halowax (Lee et al., 2007). In this study, the combustion-related congeners included PCN17/25, 27/30, 52/60, 50, and 51. The values of  $\sum_{\text{combustion}} \text{PCNs} / \sum_{\text{PCNs}} \text{ in this study varied}$ from 0.213 to 0.451 in most samples with the exception of sample 18 (0.570), indicating both reemissions of Halowax and combustion processes were important sources of the atmospheric PCNs in the



Fig. 2. Compositional patterns of PCNs in the air over the equatorial Indian Ocean.

Table 2		
Correlation matrix for s	ected PCNs, with the data representing the Pearson correlation coe	efficients.

	PCN24	PCN15	PCN17/25	PCN33/34/37	PCN27/30	PCN52/60	PCN51	PCN49	$\sum PCNs$
PCN19 PCN24 PCN15 PCN17/25 PCN33/34/37 PCN27/30 PCN52/60 PCN51 PCN49	0.997**	0.987** 0.989**	0.977** 0.983** 0.986**	0.775** 0.789** 0.751** 0.781**	0.972** 0.972** 0.940** 0.943** 0.851**	$\begin{array}{c} -0.047 \\ -0.01 \\ 0.019 \\ 0.088 \\ 0.288 \\ 0.021 \end{array}$	0.785** 0.798** 0.759** 0.790** 0.993** 0.853** 0.233	0.827** 0.838** 0.805** 0.830** 0.882** 0.887** 0.193 0.992**	0.858** 0.871** 0.836** 0.988** 0.915** 0.242 0.984** 0.986**

\*\* *p* < 0.01.

equatorial Indian Ocean. In particular, the values of  $\sum_{combustion} PCNs/$  $\sum PCNs$  were 0–0.405 and 0.031–0.49, respectively, for tri- and tetra-CNs. Higher combustion values (0.017–0.608) were observed for penta-CNs, with combustion values >0.5 in six air samples, suggesting that combustion emission significantly contributed to penta-CNs in the air. We also analyzed the Pearson correlations among the PCN congeners with detection frequency > 80%. The results suggested that significant correlations occurred for most PCN congeners (Table 2). Although PCN52/60 was suggested as indicator congeners of combustion-related sources (Liu et al., 2015) and combustion source as a major contributor to the atmospheric PCNs in this study as indicated earlier, no significant correlation was observed between PCN52/ 60 and other congeners, even the combustion-related ones (Table 2). This might be due to the reemission of Halowax and the different transport path of PCN52/60 from other congeners.

Besides, as by-products of PCB technical mixtures, PCNs will also be emitted from PCB sources (Harner and Bidleman, 1997; Xu et al., 2014). The previously detected concentrations of  $\sum_{21}$ PCBs (average: 12 pg m<sup>-3</sup>) and  $\sum_{\text{ICES}}$ PCBs (average: 8.1 pg m<sup>-3</sup>) (Huang et al., 2014) in the air over the equatorial Indian Ocean were approximately 20 times higher than that of  $\sum$  PCNs. Furthermore, no significant correlation was observed between the concentrations of  $\sum$  PCNs and those of  $\sum_{\text{ICES}}$ PCBs or  $\sum_{21}$ PCBs (r < 0.5, p > 0.05), indicating insignificant volatilization of PCNs from historical PCB residues (Gevao et al., 2000; Xu et al., 2014).

### 3.4. Potential toxicity

PCNs exhibit dioxin-like toxicity, because they have a planar structure similar to dioxins (Blankenship et al., 2000; Lin et al., 2013). 2,3,7,8-tetrachlorodibenzo-p-dioxin relative potency factors (RPFs) of CN congeners could be used to estimate the PCN-corresponding toxic equivalency (TEQ) values (Wang et al., 2012). In this study, TEQ values of PCN52/60, PCN50, and PCN64/68 were calculated based on the available RPFs reported by Helm et al. (2004) and Noma et al. (2004). The total TEQ in air ranged from 0 to 0.190 fg  $m^{-3}$ , with an average of  $0.038 \text{ fg m}^{-3}$ . Being consistent to the spatial pattern of PCN concentrations, TEQ values of samples 11 and 13 were higher than others. Compared with other studies, TEQs were slightly higher than those in the arctic air monitoring stations (0.0001–0.0455 fg m<sup>-3</sup>) (Helm et al., 2004), and considerably lower than those reported for the Barents Sea (0.99 fg m<sup>-3</sup>), the Norwegian Sea (0.36 fg m<sup>-3</sup>), and the eastern Arctic Ocean (0.548 fg m<sup>-3</sup>) (Harner et al., 1998). Much higher TEQ values have been estimated for the air in adjacent countries such as Pakistan and India (Mahmood et al., 2014; Xu et al., 2014).

## 4. Conclusion

Although the equatorial Indian Ocean is adjacent to the South Asian continent with relatively high atmospheric PCN levels, no significantly higher PCN concentration was observed in this area than those reported for other oceans and seas. However, it is noteworthy that air masses were seldom from the continents during the sampling period. Further study on PCNs in the air of the equatorial Indian Ocean during winter when the wind blows southward off the South Asian continent would be valuable to obtain a complete understanding of PCN pollution and fate in this area. Our results suggest that unintentional emission from incineration processes is an important source of PCNs in the studied area. As chemical products containing PCNs have been phased out in many countries worldwide, continuous PCN pollution due to unintentional emission deserves close attention.

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.marpolbul.2016.03.065.

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#### References

- Bidleman, T.F., Helm, P.A., Braune, B.M., Gabrielsen, G.W., 2010. Polychlorinated naphthalenes in polar environments-a review. Sci. Total Environ. 408, 2919–2935.
- Blankenship, A.L., Kannan, K., Villalobos, S.A., Villeneuve, D.L., Falandysz, J., Imagawa, T., Jakobsson, E., Giesy, J.P., 2000. Relative potencies of individual polychlorinated naphthalenes and Halowax mixtures to induce Ah receptor-mediated responses. Environ. Sci. Technol. 34, 3153–3158.
- Dachs, J., Lohmann, R., Ockenden, W.A., Mejanelle, L., Eisenreich, S.J., Jones, K.C., 2002. Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. Environ. Sci. Technol. 36, 4229–4237.
- Draxler, R.R., Rolph, G.D., 2010. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY. NOAA Air Resources Laboratory, Silver Spring, MD. Websitehttp://ready.arl.noaa.gov/HYSPLIT.php.
- Egebäck, A.-L., Wideqvist, U., Järnberg, U., Asplund, L., 2004. Polychlorinated naphthalenes in Swedish background air. Environ. Sci. Technol. 38, 4913–4920.
- Falandysz, J., 1998. Polychlorinated naphthalenes: an environmental update. Environ. Pollut. 101, 77–90.
- Falandysz, J., Rappe, C., 1996. Spatial distribution in plankton and bioaccumulation features of polychlorinated naphthalenes in a pelagic food chain in the southern part of the Baltic Sea. Environ. Sci. Technol. 30, 3362–3370.
- Gevao, B., Harner, T., Jones, K.C., 2000. Sedimentary record of polychlorinated naphthalene concentrations and deposition fluxes in a dated lake core. Environ. Sci. Technol. 34, 33–38.
- Harner, T., Bidleman, T.F., 1997. Polychlorinated naphthalenes in urban air. Atmos. Environ. 31, 4009–4016.
- Harner, T., Kylin, H., Bidleman, T.F., Halsall, C., Barrie, L.A., Strachan, W.M.J., 1998. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in arctic air. Environ. Sci. Technol. 32, 3257–3265.
- Harner, T., Shoeib, M., Gouin, T., Blanchard, P., 2006. Polychlorinated naphthalenes in Great Lakes air: assessing spatial trends and combustion inputs using PUF disk passive air samplers. Environ. Sci. Technol. 40, 5333–5339.
- Helm, P.A., Bidleman, T.F., 2003. Current combustion-related sources contribute to polychlorinated naphthalene and dioxin-like polychlorinated biphenyl levels and profiles in air in Toronto. Canada. Environ. Sci. Technol. 37, 1075–1082.

- Helm, P.A., Bidleman, T.F., Li, H.H., Fellin, P., 2004. Seasonal and spatial variation of polychlorinated naphthalenes and non-/mono-ortho-substituted polychlorinated biphenyls in arctic air. Environ. Sci. Technol. 38, 5514–5521.
- Hogarh, J.N., Seike, N., Kobara, Y., Habib, A., Nam, J.-J., Lee, J.-S., Li, Q., Liu, X., Li, J., Zhang, G., Masunaga, S., 2012. Passive air monitoring of PCBs and PCNs across East Asia: a comprehensive congener evaluation for source characterization. Chemosphere 86, 718–726.
- Huang, Y., Xu, Y., Li, J., Xu, W., Zhang, G., Cheng, Z., Liu, J., Wang, Y., Tian, C., 2013. Organochlorine pesticides in the atmosphere and surface water from the equatorial Indian Ocean: enantiomeric signatures, sources and fate. Environ. Sci. Technol. 47, 13395–13403.
- Huang, Y., Li, J., Xu, Y., Xu, W., Cheng, Z., Liu, J., Wang, W., Tian, C., Luo, C., Zhang, G., 2014. Polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) in the equatorial Indian Ocean: temporal trend, continental outflow and air-water exchange. Mar. Pollut. Bull. 80, 194–199.
- Jaward, F.M., Barber, J.L., Booij, K., Jones, K.C., 2004. Spatial distribution of atmospheric PAHs and PCNs along a north–South Atlantic transect. Environ. Pollut. 132, 173–181.
- Lee, S.C., Harner, T., Pozo, K., Shoeib, M., Wania, F., Muir, D.C.G., Barrie, L.A., Jones, K.C., 2007. Polychlorinated naphthalenes in the global atmospheric passive sampling (GAPS) study. Environ. Sci. Technol. 41, 2680–2687.
- Li, Y.F., Bidleman, T.F., 2003. Correlation between global emissions of αhexachlorocyclohexane and its concentrations in the arctic air. J. Environ. Inform. 1, 52–57.
- Li, Q., Xu, Y., Li, J., Pan, X., Liu, X., Zhang, G., 2012. Levels and spatial distribution of gaseous polychlorinated biphenyls and polychlorinated naphthalenes in the air over the northern South China Sea. Atmos. Environ. 56, 228–235.
- Lin, Y., Zhao, Y., Qiu, X., Ma, J., Yang, Q., Shao, M., Zhu, T., 2013. Spatial distribution of polychlorinated naphthalenes in the atmosphere across North China based on gridded field observations. Environ. Pollut. 180, 27–33.
- Liu, G., Lv, P., Jiang, X., Nie, Z., Zheng, M., 2014. Identifying iron foundries as a new source of unintentional polychlorinated naphthalenes and characterizing their emission profiles. Environ. Sci. Technol. 48, 13165–13172.

- Liu, G., Cai, Z., Zheng, M., Jiang, X., Nie, Z., Wang, M., 2015. Identification of indicator congeners and evaluation of emission pattern of polychlorinated naphthalenes in industrial stack gas emissions by statistical analyses. Chemosphere 118, 194–200.
- Lundgren, K., Tysklind, M., Ishaq, R., Broman, D., VanBavel, B., 2002. Polychlorinated naphthalene levels, distribution and biomagnification in a benthic food chain in the Baltic Sea. Environ. Sci. Technol. 36, 5005–5013.
- Lundgren, K., Tysklind, M., Ishaq, R., Broman, D., Van Bavel, B., 2003. Flux estimates and sedimentation of polychlorinated naphthalene the north part of the Baltic Sea. Environ. Pollut. 126, 93–105.
- Mahmood, A., Malik, R.N., Li, J., Zhang, G., Jones, K.C., 2014. PCNs (polychlorinated naphthalenes): dietary exposure via cereal crops, distribution and screening-level risk assessment in wheat, rice, soil and air along two tributaries of the River Chenab. Pakistan. Sci. Total Environ. 481, 409–417.
- Manodori, L., Gambaro, A., Zangrando, R., Turetta, C., Cescon, P., 2006. Polychlorinated naphthalenes in the gas-phase of the Venice Lagoon atmosphere. Atmos. Environ. 40, 2020–2029.
- Noma, Y., Yamamoto, T., Sakai, S.-I., 2004. Congener-specific composition of polychlorinated naphthalenes, coplanar PCBs, dibenzo-p-dioxins, and dibenzofurans in the Halowax series. Environ. Sci. Technol. 38, 1675–1680.
- SCPOP (Stockholm Conventionon Persistent OrganicPollutants), 2011). http://chm.pops. int/TheConvention/POPsReviewCommittee/POPRCRecommendations/tabid/243/ctl/ Download/mid/10484/Default.aspx?id=5&ObjID=11956 (accessed on 2015-05-06).
- Stemmler, I., Lammel, G., 2009. Cycling of DDT in the global environment 1950–2002: world ocean returns the pollutant. Geophys. Res. Lett. 36, L24602.
- Wang, Y., Li, Q., Xu, Y., Luo, C., Liu, X., Li, J., Zhang, G., 2012. Improved correction method for using passive air samplers to assess the distribution of PCNs in the Dongjiang River basin of the Pearl River Delta, South China. Atmos. Environ. 54, 700–705.
- Xu, Y., Li, J., Chakraborty, P., Syed, J.H., Malik, R.N., Wang, Y., Tian, C., Luo, C., Zhang, G., Jones, K.C., 2014. Atmospheric polychlorinated naphthalenes (PCNs) in India and Pakistan. Sci. Total Environ. 466–467, 1030–1036.
- Zhang, L., Lohmann, R., 2010. Cycling of PCBs and HCB in the surface ocean-lower atmosphere of the open ocean. Environ. Sci. Technol. 44, 3832–3838.