

Levels and spatial distribution of gaseous polychlorinated biphenyls and polychlorinated naphthalenes in the air over the northern South China Sea

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ABSTRACT

Monitoring marine persistent organic pollutants (POPs) is important because oceans play a significant role in the cycling of POPs. The South China Sea (SCS) is surrounded by developing countries in Southeast Asia which are centers of e-waste recycling and the ship dismantling industry. In this study, shipboard air samples collected over the SCS between September 6 and 22, 2005 were analyzed for polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs). The levels of \sum_{12} PCBs ranged from 32.3 to 167 pg m^{-3} , with a mean value of $98.4 \pm 36.0 \text{ pg m}^{-3}$. Tetra-CBs were the predominant congeners. The concentrations of \sum_{18} PCNs ranged from N.D. to 26.0 pg m^{-3} , with a mean value of $10.5 \pm 7.16 \text{ pg m}^{-3}$, and tri-CNPs were predominant. The gaseous concentrations of PCBs and PCNs over the SCS were consistent with those over other seas and oceans. Compared with previous studies, it was found that the concentrations of PCBs exhibited an obviously declining trend. The measured PCB and PCN concentrations in the atmosphere over the SCS were influenced by their proximity to source regions and air mass origins. The highest gaseous PCB and PCN concentrations were found at sampling sites adjacent to the continental South China. E-waste recycling, ship dismantling and combustion in South China and some Southeast Asian countries might contribute PCBs and PCNs to the atmosphere of the SCS.

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1. Introduction

The monitoring of marine persistent organic pollutants (POPs) is of great importance. On the one hand, oceans are believed to be the ultimate sink of POPs (Dachs et al., 2002; Jurado et al., 2004) but they may also turn into a secondary source of particular POPs such as DDTs (Stemmler and Lammel, 2009) and alpha-HCH (Li and Bidleman, 2003) long after those compounds were banned. On the other hand, oceans act as a remote monitoring site of regional/global distribution and time trends of POPs, as the outflow of these pollutants from adjacent land sources carried by monsoon/air masses can travel long distances. Those viewpoints have been confirmed by the occasional observation of some oceans (Ding et al., 2009; Lohmann et al., 2009; Wurl et al., 2006; Zhang et al., 2007).

Polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) are a group of chlorine substituted aromatic ring compounds. Those compounds are widely utilized as insulators,

lubricants, flame retardants and paint additives due to their dielectric, water-repellent, low flammability and fungus-resistant qualities (Jakobsson and Asplund, 2000). Historically, around 130,000 tons of PCBs (Breivik et al., 2002a) and 150,000 tons of PCNs (Falandysz, 1998) have been cumulatively produced around the world. Although the production of PCBs and PCNs has been banned or severely restricted since the 1970s and 1980s, products containing these formulations are still present in the environment (Bidleman et al., 2010; Breivik et al., 2007). In the past two decades, there have been several investigations on the levels, distribution and fate of gaseous PCBs and PCNs in the atmosphere (Falandysz, 1998; Harner et al., 1998; Jaward et al., 2004a; Lee et al., 2007; Mari et al., 2008). The recent researches indicate that historical usage, e-waste and shipwreck are major sources of PCBs (Breivik et al., 2002b; Breivik et al., 2011; Gioia et al., 2011). Meanwhile, PCNs are considered to be released from waste incineration, industrial processes (Bidleman et al., 2010; Jansson et al., 2008; Schneider et al., 1998) and historical usage (Guo et al., 2008; Harner and Bidleman, 1997). Previous studies in remote areas have suggested that those emitted compounds could be transported to regions far from anthropogenic impact via air mass movement (Harner et al., 2006; Helm et al., 2004). The occurrence

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of those pollutants in the marine environment is of concern because they may accumulate in organisms and biomagnified through the food web, and they can be distributed over large areas.

As a marginal sea in southeast Asia, the South China Sea (SCS) is surrounded by the regions and countries which are considered as a potential source of PCBs, including southern China, Vietnam and the Philippines (Li et al., 2007). The import and use of PCBs in those countries have generally been official restricted. However, UNEP has pointed that amount of PCBs entering the environment in the region depend largely on disposal of e-waste which containing PCBs (UNEP, 2003). As a global center of e-waste distribution and recycling, the adjacent areas were estimated to receive more than 70% of the world's production of e-waste which could be 20–50 million tons per year (Robinson, 2009). The gross weight of PCBs amounts to nearly 2.1–2.6 tons, and the average PCB concentration that leaked from e-waste was approximately 14 mg kg^{-1} . By the same taken, China, Vietnam and the Philippines have also been major centers of ship-dismantling, which now accounts for more than 14% of the industry, while approximately 0.25–0.8 tons of PCBs are produced by each abandoned ship (Hess et al., 2001). Thus, the prevailing and expanding e-waste recycling and ship-dismantling activities were probably the major sources of PCBs in this region. The SCS has a strong surface current system with warm water from the Pacific entering through the Luzon Strait and then weaving through the complex passages of the Indonesian archipelago to the Indian Ocean, which is a choke-point connecting the tropical Pacific with the Indian Ocean. The surface current system and the monsoon system in the SCS make it possible to transport these compounds to the global environment. Thus, data collected over the SCS will be of primary interest for gaining better insight into the global distribution of POPs.

The collection of atmospheric data for POPs over the open oceans is challenging, and reports in the literature are sparse. The available data for PCB concentrations in the atmosphere over the SCS now date back over a decade (Iwata et al., 1993), and no available data have been found for PCNs. Primary emissions of POPs to the atmosphere have changed over the decades, particularly after the establishment of international regulations on reducing emissions (Wurl et al., 2006). Further research is needed to assess how these toxic chemicals are transported from the surrounding regions to the SCS.

The aim of this study was to determine the concentration levels of PCBs and PCNs in atmospheric samples collected over the SCS in September 2005 and to identify potential sources of atmospheric contaminations of those compounds.

2. Materials and methods

2.1. Sampling

A total of 31 8-h day or night and one 16-h (day and night) air samples were taken from September 6 to September 22, 2005 during a Shiyan III cruise, which circumnavigated the South China Sea in a zigzag pattern from Guangzhou city to the eastern SCS to Hainan island and back to Guangzhou, a distance of approximately 3500 nautical miles (Fig. S1). The sampling route is shown in a previous study (Zhang et al., 2007). A high volume (Hi-Vol) air sampler was placed windward on the uppermost deck of the ship approximately 20 m above the sea level to minimize contamination from the ship's exhaust. Air ($\sim 140 \text{ m}^3$ per sample) was aspirated through a glass fiber filter (GFF) (GF/A, $20.3 \text{ cm} \times 25.4 \text{ cm}$, Whatman) to remove particles from the air stream, and gas-phase compounds were trapped on two polyurethane foam (PUF) plugs (6.5 cm (i.d.) $\times 7.5 \text{ cm}$ (thickness), density 0.030 g cm^{-3}) contained in an aluminum cylinder. Six field blanks were taken during the

whole sampling campaign. Before sampling, PUF plugs were Soxhlet extracted for 48 h with methanol and then acetone for 24 h, followed by two over night extractions using dichloromethane (DCM). GFFs were baked at $450 \text{ }^\circ\text{C}$ for 12 h to remove any organic contaminants. And PUF plugs were dried overnight in a vacuum desiccator and stored in solvent-rinsed glass jars with Teflon lined lids. After sampling, the PUFs and GFFs were transferred into solvent-rinsed glass jars and stored in freezers ($-20 \text{ }^\circ\text{C}$) until analysis.

2.2. Sample extraction and analysis

As the recovery standards for the PCBs and PCNs, 20 ng TCmX, PCB209 and carbon-13 labeled Trans-chlordane were added. The PUFs (filters were not analyzed for POPs) were Soxhlet-extracted with DCM for 48 h, and activated copper was used to remove elemental sulfur. The extract was concentrated and solvent-exchanged to hexane and purified on an 8 mm i.d. alumina/silica column packed, from bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (10 cm, 3% deactivated), 50% sulfuric acid silica (10 cm) and anhydrous sodium sulfate. Neutral alumina, neutral silica gel, and anhydrous sodium sulfate were pre-baked at $450 \text{ }^\circ\text{C}$ for 12 h. The column was eluted with a 50 ml mixture of *n*-hexane and DCM (1:1) to yield the PCBs and PCNs. Finally, the volume was reduced to 200 μL under a gentle nitrogen stream and solvent exchanged into 25 μL of *iso*-octane containing PCB 54 and pentachloronitrobenzene (PCNB) as internal standards, respectively.

The PCBs were analyzed by an Agilent-5975 GC-MSD system with a Varian CP-Sil8 CB capillary column (50 m length \times 0.25 mm i.d., 0.25 μm film thickness). The initial oven temperature was set at $150 \text{ }^\circ\text{C}$ for 3 min and raised to $290 \text{ }^\circ\text{C}$ at a rate of $4 \text{ }^\circ\text{C min}^{-1}$, then held for 10 min. The injector and detector temperatures were set at 250 and $230 \text{ }^\circ\text{C}$, respectively. The mixed standard including 33 congeners was applied to quantify PCBs, and there were 12 congeners detected: 28 (tri-CBs); 49, 52, 60, 66, 70, 74 (tetra-CBs); 99, 101, 118 (penta-CBs); 153, 158 (hexa-CBs). The total PCBs quoted in this paper are a sum of the detectable congeners of those PCBs.

The PCNs were detected using an Agilent 7890-5975C (GC-MSD), which was operated in electron capture negative ion (ECNI). A DB-5MS column (30 m length \times 0.25 mm i.d., 0.25 μm film thickness) was used for the separation. The temperature program was as follows: the initial temperature of $80 \text{ }^\circ\text{C}$ was held for 0.5 min, increased to $160 \text{ }^\circ\text{C}$ at a rate of $15 \text{ }^\circ\text{C min}^{-1}$, then increased to $240 \text{ }^\circ\text{C}$ at a rate of $3 \text{ }^\circ\text{C min}^{-1}$, and then increased to $270 \text{ }^\circ\text{C}$ at a rate of $6 \text{ }^\circ\text{C min}^{-1}$ and held for 2 min. The injector and detector temperatures were set at 260 and $150 \text{ }^\circ\text{C}$, respectively. The monomer mass fraction of the results was corrected using Halowax1014. The individual and coelute congeners of PCNs were quantified by standard, and 18 congeners were detected: CN 19, 24 (tri-CN); CN 42, 33/34/37, 47, 36/45, 28/43, 27/30, 38/40, 46 (tetra-CN); CN 52/60, 61, 50, 57, 49 (penta-CN); CN 64/68, 69, 71/72 (hexa-CN). The total PCNs quoted are a sum of the detectable congeners of these PCNs.

2.3. Quality assurance and quality control

Recovery standards were added to the samples, laboratory blanks and field blanks prior to extraction to monitor the extraction and cleanup procedures. The average recoveries were $76.0 \pm 11.0\%$, $85.0 \pm 7.10\%$ and $81.8 \pm 12.5\%$ for TCmX, PCB209 and carbon-13 labeled Trans-chlordane, respectively. The method detection limits (MDLs) were assigned as average values of field blanks plus 3 standard deviations of field blank values. When compounds were

not found in the field blanks, the MDLs were calculated as 3 times the instrumental detection limits (IDLs). The IDL values were calculated from the lowest standards, extrapolating to the corresponding amount of analyte that would generate a signal-to-noise ratio of 3:1. The target compounds were below the IDLs in the field and lab blanks. The MDLs of the individual compounds are listed in Table 1. Instrumental performance was checked by quality control standards every eight samples. The reported data on PCBs and PCNs in this study were not corrected for the surrogate recoveries.

The breakthrough of PUF samples was tested by two consecutive PUF plugs. The results indicated that the target compounds were under the MDLs from the subjacent PUF plug.

2.4. Back trajectories

Air mass origins were calculated for the cruise samples by the HYSPLIT transport and dispersion model from the NOAA Air Resources Laboratory (Draxler and Rolph, 2010). Back trajectories (BTs) were traced for 5 days with 3 h intervals from 00:00 coordinated universal time (UTC) to 9:00 UTC during day sampling and from 12:00 to 21:00 UTC during night time sampling at 100, 500 and 1000 m above sea level (Fig. S2). Meteorological data were attained from an online detection system on the vessel, which collected air and water temperature, wind speed and direction, atmospheric pressure and humidity.

3. Results and discussion

The atmospheric temperature was approximately 28 °C during the sampling, and the PCBs and PCNs in the atmosphere would have been mainly in gaseous form (He and Balasubramanian, 2009; Jaward et al., 2004b). Therefore, the results of gaseous PCBs and PCNs basically reflect the actual situation of those compounds in the atmosphere, but they could skew the data on the individual high-chlorine congeners.

Table 1
Gaseous concentrations of PCBs and PCNs (pg m^{-3}) over the northern SCS.

Compound	Mean	Maximum	Minimum	Median	MDL ^A	n
PCB 28	39.5 ± 20.1	84.1	11.3	34.2	–	32
PCB 49	24.3 ± 11.4	51.5	12.1	21.9	1.11	31
PCB 52	12.6 ± 7.40	28.5	7.47	13.1	1.11	28
PCB 60	1.57 ± 1.56	7.60	1.38	5.25	0.43	4
PCB 66	9.27 ± 8.76	35.1	2.55	6.47	1.11	28
PCB 70	3.24 ± 2.03	8.22	1.38	3.39	1.11	24
PCB 99	1.17 ± 1.54	7.32	2.19	3.61	0.78	6
PCB 101	2.92 ± 1.67	6.80	2.19	2.81	1.11	27
PCB 118	0.82 ± 0.69	3.16	0.69	2.12	0.56	6
PCB 153	1.23 ± 0.99	3.55	1.27	2.38	0.78	13
PCB 158	0.67 ± 0.42	2.21	1.68	1.89	1.11	3
Σ_{12} PCBs	94.4 ± 36.3	167	32.3	94.2	–	32
PCN19	0.54 ± 0.55	2.27	0.28	0.81	0.003	20
PCN24	2.95 ± 2.25	9.93	0.92	2.71	0.01	28
PCN42	0.10 ± 0.07	0.26	0.03	0.10	<0.001	28
PCN33/34/37	0.85 ± 0.56	2.08	0.32	0.94	0.002	28
PCN47	0.24 ± 0.16	0.61	0.08	0.23	<0.001	28
PCN36/45	0.15 ± 0.11	0.40	0.05	0.12	<0.001	28
PCN28/43	0.36 ± 0.49	1.52	0.29	0.88	0.004	13
PCN27/30	0.17 ± 0.12	0.43	0.07	0.17	<0.001	27
PCN38/40	1.62 ± 1.89	6.43	0.36	1.60	0.02	23
PCN46	0.02 ± 0.08	0.37	0.10	0.25	<0.001	3
PCN52/60	0.40 ± 0.46	1.49	0.07	0.22	0.001	28
PCN50	1.80 ± 2.44	8.40	0.23	0.87	<0.001	29
PCN57	0.13 ± 0.48	2.27	1.55	1.91	0.02	2
Σ_{18} PCNs	10.5 ± 7.16	26.0	N.D.	9.04	–	29

Note: PCB 74 was only detected in sample 30; PCN 49, 69 and 71/72 were only detected in sample 1; PCN 61 was only detected in sample 31; PCN 64/68 was only detected in sample 8; N.D. means no detection; A: Sampling volume was 140.57 m^3 .

3.1. Atmospheric concentrations of PCBs

The following 12 PCBs were routinely detected in the 32 air samples: PCB 28 (tri-CBs); PCB 49, 52, 60, 66, 70, and 74 (tetra-CBs); PCB 99, 101, and 118 (penta-CBs); PCB 153, and 158 (hexa-CBs). The detailed gaseous concentrations of individual PCB congeners from the SCS are given in Table 1. The concentrations of total PCBs in the atmosphere ranged from 32.3 to 167 pg m^{-3} . It is noteworthy that PCB 28 was the dominant congener, accounting for $41.4 \pm 11.3\%$ of the total PCBs, followed by PCB 49 and PCB 52, which accounted for $28.0 \pm 11.3\%$ and $15.2 \pm 7.50\%$, respectively.

The compositional profiles of the PCBs of each sample are illustrated in Fig. 1. The results indicate that the tetra- and tri-CBs were the major components, constituting 31.6–82.7% and 11.5–59.8% of the total concentrations (Σ_{12} PCBs), respectively. For high molecular weight PCBs (penta- and hexa-CBs), the relative contributions ranged from no detection to 10.7% and from no detection to 4.50% to the Σ_{12} PCB air concentrations, respectively. This notable composition pattern was dominated by tetra-CBs, a result that is slightly different from those of other regions (Bruhn et al., 2003; Jaward et al., 2004a; Manodori et al., 2007; Sundqvist et al., 2004; Zhang and Lohmann, 2010), where tri-CBs were the dominant congener. However, this pattern is consistent with the composition characteristics of PCBs in the atmosphere of the East Asia (Jaward et al., 2005). The explanation of the observed composition pattern is probably related to the following factors. First among these factors is the emission from sources related to the production and consumption history of PCBs from the neighboring countries, taking Vietnam, Thailand, the Philippines and China as examples (UNEP, 2003; Xing et al., 2005). Second among these factors are the different physical and chemical properties of each congener. Tetra-CBs possess relatively lower degradation rates than tri-CBs and higher vapor pressure than penta- and hexa-CBs, which guarantees that they could travel over long distances during atmospheric transport (Shen et al., 2006).

Compared with the concentrations of PCBs in other seas or oceans of the world (Table S4), the concentrations of PCBs in the SCS were similar to the reported data in the Vince Lagoon (Manodori et al., 2007), the Atlantic Ocean (Gioia et al., 2008) and the Pacific Ocean (Zhang and Lohmann, 2010), but higher than that in the Kattegat Sea (Sundqvist et al., 2004). These trends are probably due to the relatively high atmospheric concentrations of PCBs in most countries around the SCS caused by tens of millions of tons of electrical and electronic equipment disposal (Terazono et al., 2006) and the booming ship-breaking industry (Hess et al., 2001). The atmospheric concentrations of developed areas such as North America and Europe (Shen et al., 2006) have proved to be high because of the extensive historical use of PCBs (Jaward et al., 2005). However, some recent studies have suggested that the atmospheric concentrations of PCBs have been constantly declining since the 1990s (Wania and Daly, 2002). The present study is also consistent with those conclusions. Compared with the previous study in the SCS (Iwata et al., 1993), the concentration levels of Σ PCBs decreased to some extent over the past 20 years. This declining trend is probably attributable to the successive banning of PCBs by many countries in this area (UNEP, 2003).

3.2. Atmospheric concentrations of PCNs

Table 1 also shows the mean, maximum, minimum, and median gaseous concentrations of individual PCN congeners over the SCS. The concentrations of Σ_{18} PCNs in the air widely ranged from no detection (sample 11, 16 and 19) to 26.0 pg m^{-3} (sample 27) with a mean value of 10.5 pg m^{-3} . In all 18 congeners, PCN 24 was the major contributor to the total PCNs. The average concentration of

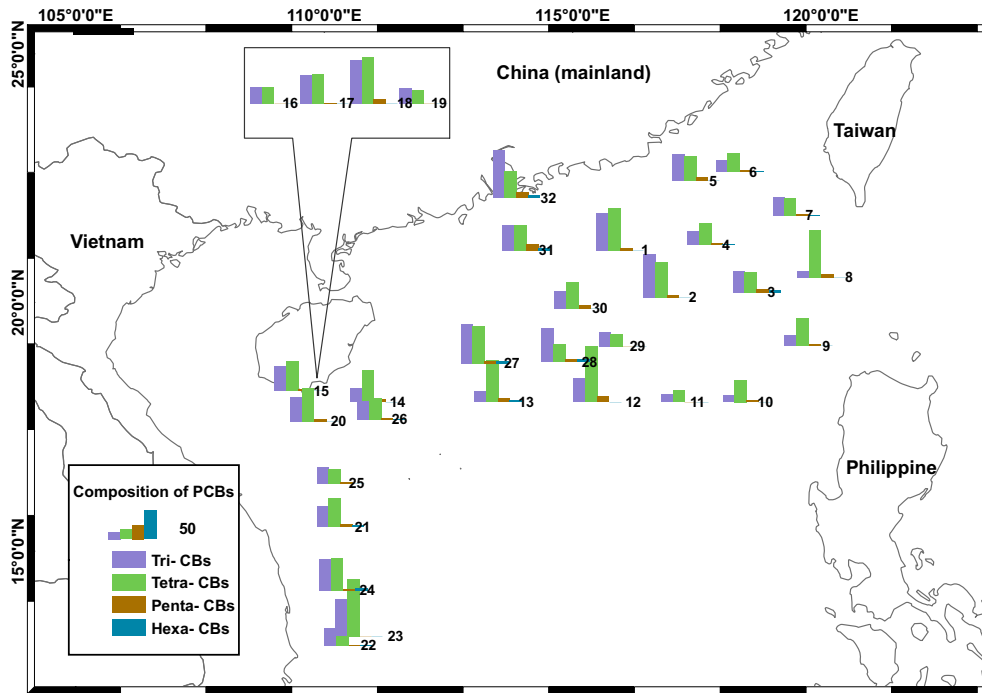


Fig. 1. Concentrations of each composition PCB (pg m^{-3}) in the atmosphere (gas phase) over the SCS.

PCN 24 was 2.95 pg m^{-3} , accounting for $31.9 \pm 12.6\%$ of the total PCNs. The heavier congeners were seldom detected, possibly due to the relatively low vapor pressure of highly chlorinated PCNs, making them difficult to transfer to areas far from the point source.

The compositional profiles of PCNs in the air over the SCS are presented in Fig. 2. Tri-CNs (PCN 19 and 24) were the dominant congeners at most sampling sites, which accounted for 12.8–78.8% of the ΣPCNs in the atmosphere, followed by tetra-CNs (PCN 33/34/37, 47, 36/45, 28/43, 27/30, 38/40, and 46) and penta-CNs (PCN 52/

60, 61, 50, 57, and 49), with 15.7–45.0% and 5.47–51.8%, respectively. This phenomenon was also found in air samples of some regions, like Venice Lagoon (Manodori et al., 2006), Lake Ontario (Helm et al., 2003) and East Asia (Hogarh et al., 2012). A widely accepted explanation is that the preferential volatilization of the lower molecular weight congeners made them more prone to atmospheric transport or that there were differences in the source signature.

Although there have been numerous investigations on PCNs in a variety of environmental media in the world, only a few studies

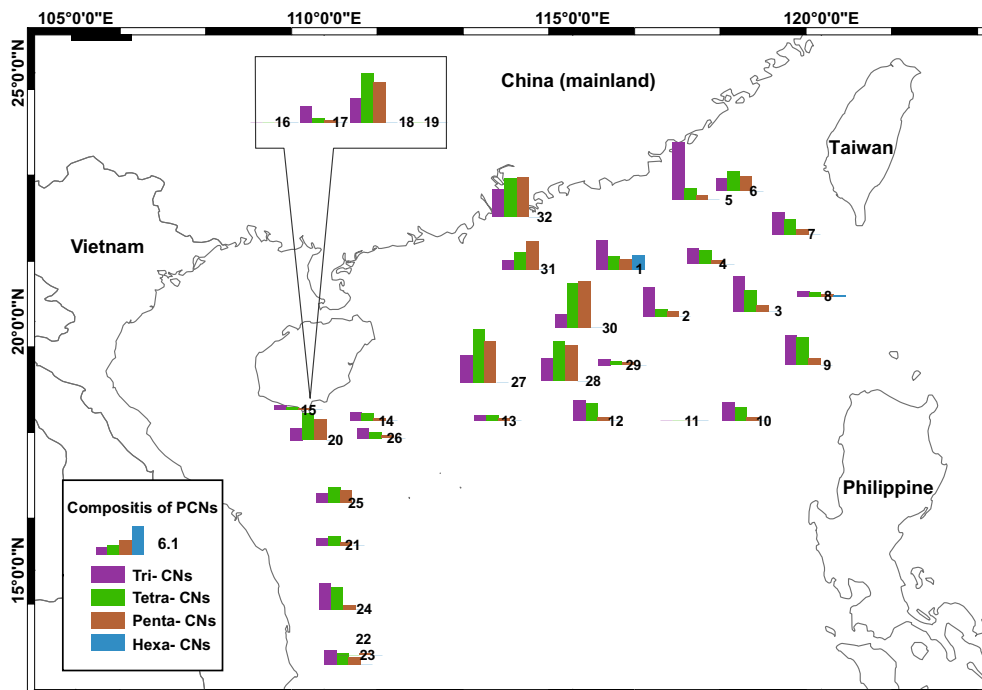


Fig. 2. Concentrations of each composition PCN (pg m^{-3}) in the atmosphere (gas phase) over the SCS.

have focused on PCNs in the air over oceans. To our knowledge, this study is the first report on PCN concentrations over the SCS. Compared with the previous studies of PCNs in other remote areas (Table S4), the concentration levels were relatively higher than those in the Venice Lagoon (Manodori et al., 2006), but they were at the same levels observed over the Atlantic (Jaward et al., 2004b) and the Lake Ontario (Helm et al., 2003). The results indicate that levels of PCNs in the gas phase from the SCS were in the middle range.

3.3. Correlation analysis and potential sources

Correlations between the concentrations of the contaminants may suggest common sources and a similar environmental fate. The results of the correlation analysis of PCBs and PCNs are illustrated in Table S2. PCB 28, 52, 70 and 101 were significantly correlated (generally $r > 0.5$, $p < 0.05$), but the other PCBs were not significantly correlated with each other. This is not in agreement with a previous study, which had a high correlation among each of the PCB congeners (ter Schure et al., 2004). This result possibly suggests that the above four congeners and the other PCBs were from different sources. In contrast, most of the PCN congeners have a relatively strong correlation ($p < 0.01$), with the strongest correlations found between the tetra- and penta-CN congeners (generally $r > 0.9$, $p < 0.001$) but the poorest correlations with the lighter PCNs (PCN 19 and 24). The results indicate that tetra- and penta-CN may share similar sources, but the tri-CN congeners were possibly influenced by different sources. Harner and Bidleman (1997) have proposed that PCNs could be by-products of technical PCB synthesis. Additionally, both volatilization from historical residues and unintentional production through combustion are contemporary emission sources of PCBs and PCNs (Masunaga et al., 2009). Surprisingly, in the present research, there were no significant correlations between the major concentrations of PCN and PCB congeners, except that PCBs 28, 70, 101 and 153 were correlated with PCNs ($r > 0.5$, $p < 0.05$). The implication of this observation is that major PCB homologues may be irrelevant to the sources of PCNs, yet these four PCB congeners possibly have similar sources to those of the PCNs.

Previous research shows that it is difficult to distinguish exact PCB sources because of the lack of an indicator congener of PCBs (Breivik et al., 2002b). By comparison with congener profiles of industrial products, it is difficult to define exactly commercial sources due to the diversity in homologue patterns (Fig. S3). As for PCNs, combustion-related PCN congeners exhibit subtly different composition profiles from other sources (Falandysz, 1998). Lee et al. (2005) have pinpointed that PCN 24 marked wood/coal burning.

Some studies have noted that penta-CN (PCN 52/60 and 50) dominate in fly ash from iron sintering and other industrial processes and are minor homologues in technical mixtures (Lee et al., 2007; Schneider et al., 1998). Although PCN 54 and 66/67 are the most popular and relatively abundant indicators for waste incineration (Falandysz, 1998; Meijer et al., 2001), they were not detected in present study. The congener patterns of typical samples in present study were quite different from Halowax series products (Falandysz et al., 2006) indicating that industrial usage was not necessarily the main source of PCNs over the SCS. Based on the correlation between each PCN congener and PCN compositions (Table S2), the results suggest that wood/coal burning and industrial processes might be two major combustion sources for PCNs.

3.4. Spatial variation and implication to source regions

The spatial distribution of the Σ PCBs in the 32 samples can be clearly seen in Fig. 3. The relatively high concentrations were mainly found in samples close to the continent. For example, samples 1, 2, 27 and 32 were close to mainland China, and sample 23 was collected over the vicinity of the seas of central and southern Vietnam. In terms of the composition pattern of PCBs (Fig. 1), samples with relatively high concentrations of tetra-CBs were generally found far from mainland China, such as sample 12, while samples with relatively high concentrations of tri-CBs were collected near the continent due to the relatively shorter half-lives in the atmosphere (Sinkkonen and Paasivirta, 2000).

Unlike the PCBs, the concentrations of the PCNs were obviously much higher in the samples close to the South China coastal region than the others (Fig. 4). For the composition pattern of PCNs (Fig. 3), relatively high levels of tri-CN (dominated by PCN 24) were concentrated in the area surrounded by the coasts of southeast China, Taiwan and the Philippines (sample 1–12), yet the proportions of tetra- and penta-CN (72.3–87.2%) are obviously higher than the tri-CN in the samples adjacent to the South China coastal region.

The spatial distributions of POPs in the marine atmosphere were influenced by the surrounding land sources and atmospheric transportation. Combined with the air mass trajectory, the characteristics of these pollutants in special samples could feature the outflows from different Asian source regions. At the beginning of the sampling (from site 1 to 12, see Fig. S2), back-trajectory analysis revealed that the air masses stemmed from southeast of China and Taiwan Island. At this time, relatively higher concentrations of PCBs and high proportion of tri-CN were observed both close to mainland China and over the open sea, especially in samples 1 and 2, of which the air masses flow from the northeast of the South

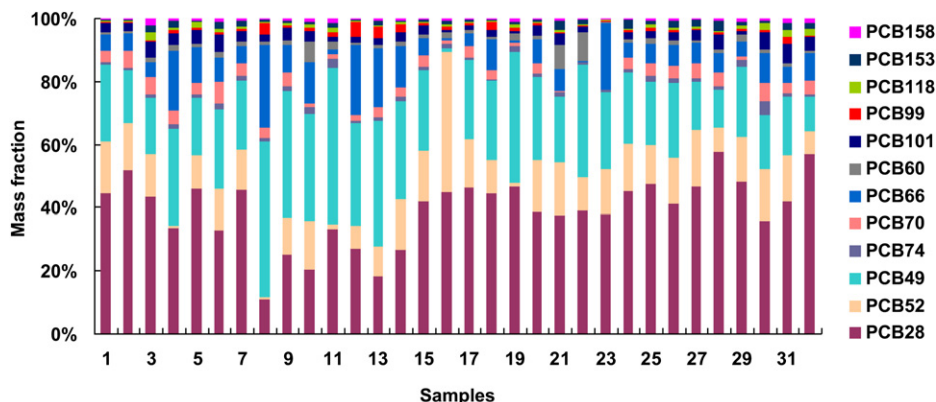


Fig. 3. Gaseous PCBs of each sample over the SCS.

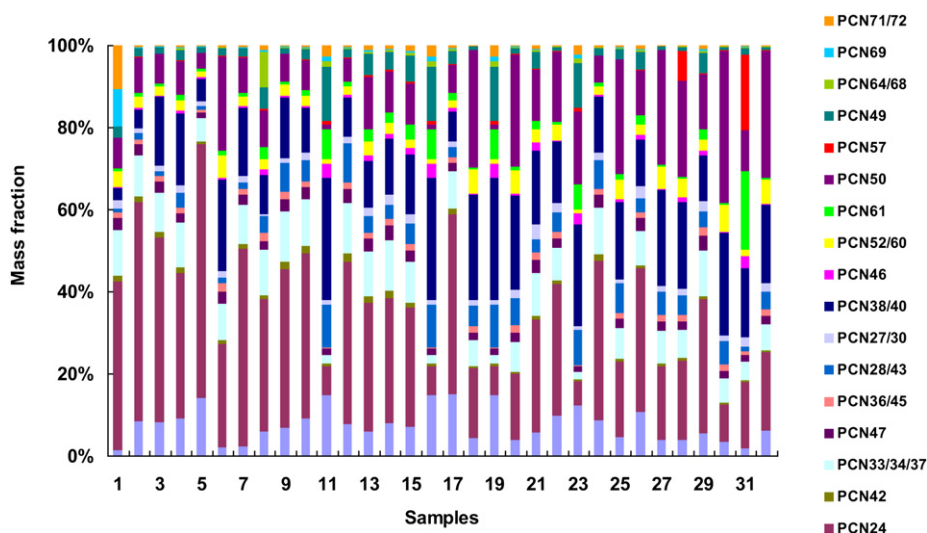


Fig. 4. Gaseous PCNs of each sample over the SCS.

China coastal region. There is an extensive historical usage (Xing et al., 2005) and e-waste recycling industry around this area (Bi et al., 2007). It was considered as “new” sources of PCBs in this region (Robinson, 2009). In addition, high levels of PCN 24, which probably mark wood and coal burning, were found in these samples, reflecting that these regions consume a large amount of coal-fired resources (Department of Industry and Transport Statistics and China, 2006). Additionally, wind direction changed due to several tropical cyclones and typhoons. During the period from September 13 to 21 of 2005, there were two types of air masses prevailing over the SCS. Relatively high PCB concentrations and relatively low PCN concentrations found in those samples, when the air parcels spent much of their 5-day history near some southeast Asian countries (TypeII). This result implies that some Southeast Asian countries might be the major sources of PCBs rather than PCNs over the SCS, due to emission of PCBs from ship-dismantling industry (Hess et al., 2001). In addition, the air samples collected at the harbor (samples 15, 17 and 18) displayed distinctly high concentrations of PCBs, possibly providing evidence of a strong local PCB source from the painted surfaces of buildings and vessels (Jartun et al., 2009; Jensen et al., 1972; Østberg and Schulze, 1998). At the end of the sampling (samples 30–32, see Fig. S2), the air masses had all traveled via the southern coast of China despite their different origins, giving rise to the discrepancy in the levels of PCBs and PCNs. Relatively high levels of PCBs and PCNs were observed in sample 32, whose air masses were from the northeast of the South China coastal region. Meanwhile, sample 30 and 31 possess relatively low levels of PCBs and relatively high levels of PCNs, whose air masses were from southwest of the South China coastal region. These results confirm that the region is the main source of PCNs once again. At the same time, tetra- and penta-CNns are typically the most abundant in these samples. As discussed above, PCN 52/60 and 50 are combustion markers of iron sintering and other industrial processes. Our observation implies that the South China coastal region was the potential source of PCNs, mainly from combustion. Moreover, the ratio of $\Sigma\text{PCN}/\Sigma\text{PCB}$ has been used to characterize polluted sources of PCNs. When a ratio from 0.2 to 0.25 denotes the background atmosphere, and a ratio > 0.25 indicates “non-diffuse” or “point sources” (Harner et al., 2000). In present study, the value of $\Sigma\text{PCN}/\Sigma\text{PCB}$ more than 0.25 was only found in sample 30 (Table S1), and is further evidence that the South China coastal region was an emission source of PCNs.

4. Conclusion

A comprehensive survey of 12 PCBs and 18 PCNs in the atmosphere of the northern SCS has been conducted. The results show that marine POP monitoring performs well in reflecting the background of regional atmospheric POPs. In this region, large amounts of e-waste recycling, ship dismantling and combustion in the South China and some Southeast Asian countries are suggested as being the major potential sources for atmospheric concentration of PCBs and PCNs, and some of the coastal samples were clearly affected by these sources. On the whole, the levels of atmospheric PCBs and PCNs over the northern SCS were in the same range as other seas or oceans in the world. Compared with previous studies, it was found that the concentrations of PCBs exhibit an obviously declining trend. The measured PCB and PCN concentrations in the atmosphere over the SCS were influenced by their proximity to source regions and air mass origins.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2012.03.074.

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