· Article · **Advances in Polar Science**
doi: 10.13679/j.advps.2015.3.00239 September 2015 Vol. 26 No. 3: 239-248

Atmospheric polychlorinated biphenyls measured during the 2008 Chinese National Arctic Research Expedition

WU Xiaoguo[1,2,3], James C W Lam[3], XIA Chonghuan[1,2,3], KANG Hui[1],
XIE Zhouqing[1,2]* & Paul K S Lam[2,3]

[1] Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China;
[2] Advanced Lab for Environmental Research and Technology (ALERT), University of Science and Technology of China−City University of Hong Kong (USTC−CityU) Joint Advanced Research Center, Dushu Lake Higher Education Town, SIP, Suzhou 215123, China;
[3] State Key Laboratory in Marine Pollution; and Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Hong Kong, China

Received 16 June 2015; accepted 6 September 2015

Abstract From July to September 2008, air samples were collected aboard the R/V *XUE LONG* icebreaker (Snow Dragon) as part of the 2008 Chinese National Arctic Research Expedition program. $\sum_{20}$PCBs in the atmosphere ranged from 6.20 to 365 pg·m^{-3} with average concentration 117±107 pg·m^{-3}. Congener profiles in all samples showed a prevalence of tri- and tetra-chlorobiphenyls, dominated by PCB-18, PCB-28, PCB-44 and PCB-52. Along the cruise, the highest concentration was observed over the Sea of Japan and the lowest over the high-latitude Arctic Ocean. Air mass backward trajectories indicated that samples with relatively high levels of PCBs might have been influenced by atmospheric transport of these chemicals from primary and/or secondary sources. PCB-18 displayed a significant correlation between vapor pressure and ambient temperature along the cruise, but there was no such correlation between gas-phase concentration and latitude. This suggests that atmospheric PCB-18 was related to volatilization from the earth surface during summer 2008, during which temperatures were relatively high. PCB-52 presented a significant correlation between gas-phase concentration and latitude, but no such correlation was found between vapor pressure and ambient temperature, indicating that atmospheric PCB-52 detected during the cruise might be attributed directly to atmospheric transport from source regions. In the Arctic, levels of PCB-52 in the floating sea ice region were higher than those measured in the open sea area and pack ice region. Intense ice retreat during summer 2008 might have enhanced the volatilization of previously accumulated PCBs from sea ice, especially those with heavier molecular weight and lower vapor pressure such as PCB-52.

Keywords **PCBs, North Pacific Ocean, Arctic Ocean, air, sea ice**

Citation: Wu X G, Lam J C W, Xia C H, et al. Atmospheric polychlorinated biphenyls measured during the 2008 Chinese National Arctic Research Expedition. Adv Polar Sci, 2015, 26: 239-248, doi: 10.13679/j.advps.2015.3.00239

1 Introduction

Polychlorinated biphenyls (PCBs) are classified and regulated as persistent organic pollutants (POPs) under the Stockholm Convention. Following their introduction in 1929, PCBs were used in industrial and consumer applications worldwide, especially in electrical equipment[1]. Total production of PCBs was estimated to be as much as 1.3 million tons from 1930 to 1993[2-3]. About 50% of PCBs were made in the United States of America (USA), whereas European and Russian outputs contributed 27.2% and 13.2% of global manufacturing[2]. Approximately 97% of PCBs

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* Corresponding author (email: zqxie@ustc.edu.cn)

manufactured were used in the Northern Hemisphere, mostly between 30°N and 60°N[4]. Although open use of PCBs was ultimately banned in the late 1970s/early 1980s in Europe and the USA[5], large amounts remain in use in closed electrical systems such as transformers, electric capacitors, and fluorescent light ballast[6]. Vaporization and uncontrolled burning of these products are currently the principal sources of atmospheric PCBs[4].

Once released to the environment, PCBs can be transported in different environmental media and undergo long-range transport through atmospheric circulation and/or ocean currents to remote regions[7–11]. The atmosphere has been regarded as the most important and rapid means of PCB transport from low to high latitudes[12-13]. As mixtures of semivolatile compounds, PCBs may also be subjected to global fractionation[14-15]. The atmospheric fate of PCBs at continental scale has been studied extensively[6,8,16-22]. However, in open sea areas, the collection of atmospheric data of PCB concentration is challenging, and reports in the literature are sparse[5,23]. Long-term monitoring since the early 1990s under the Arctic Monitoring and Assessment Programme (AMAP) did not find any evidence to support declining PCB concentrations in the Arctic region[24]. As ice coverage in the Arctic Ocean decreases in response to rising temperatures in the Arctic, PCBs deposited in sinks such as sea ice are expected to revolatilize into the atmosphere, and there is evidence that this process may have already begun[23-25].

From July through September 2008, shipboard air samples were collected during the Chinese National Arctic Research Expedition (CHINARE2008) program from the Bohai Sea to high-latitude Arctic. Detailed information about this expedition has been given elsewhere[26-27]. The purposes of the current study were to: (1) update data of atmospheric levels of PCBs and assess spatial variations and congener profiles of PCBs over the North Pacific and adjacent Arctic; (2) identify sources of PCBs and their environmental fates; (3) investigate the potential influence of sea ice retreat on atmospheric levels of PCBs in the Arctic Ocean.

2 Methodologies

2.1 Air sampling, extraction and analysis

Air samples were taken on the uppermost deck of the ship, about 20 m above sea level, using a high-volume air sampler (TH1000, fabricated by Wuhan Tianhong, Wuhan, China). To avoid potential sample contamination by the ship, the air sampler was controlled by a wind sensor to ensure that samples were collected only when there was wind over the ship's bow. Before deployed for sampling, polyurethane foam plugs (PUFs) were pre-cleaned by Soxhlet extraction for 24 h, using acetone and hexane (1∶1 v/v). A total of 19 gas-phase samples were taken using two 6.5-cm diameter × 6-cm height PUFs. Air volumes ranged from 567 to 2916 m^3 (at 0°C, 1 atm, and flow rate ~1.0 $m^3 \cdot min^{-1}$). In addition, three field/travel blanks were transported to the sampling sites and handled in the same way as the other samples in the high-volume sampling process.

2.2 Sample treatment and analytical procedures

PUFs were spiked with PCB-30 as a surrogate standard, and then put into pre-cleaned extraction cartridges and extracted with hexane and dichloromethane (1∶4 v/v) using accelerated solvent extraction (ASE 200, Thermo Fisher Scientific Inc.), operating in two static cycles with heating time 6 min at 110°C and 1500 psi). Extracts were evaporated to ~1 mL and then purified by elution with 80 mL of hexane and 80 mL of a hexane and dichloromethane mixture (1∶1 v/v) through a chromatographic column of activated silica gel and alumina. Elutes were spiked with 2,4,5,6-Tetrachloro-m-xylene (TCMX) and concentrated to 100 µL under a nitrogen stream. All extracts were then kept in sealed vials at −20°C prior to instrumental analysis.

Quantification of PCBs was performed using a GC (Agilent 7890A) equipped with a mass-selective detector (Agilent 5975c, Santa Clara, CA, USA) in the negative chemical ionization (NCI) mode, with methane used as the reactant gas. The GC column used for quantification was a DB-XLB fused silica capillary (J &W Scientific Inc., Folsom, CA, USA) with a 0.25 mm i.d. ×60 m ×0.25 µm film. PCB standards were measured and samples were analyzed separately in selective ion monitoring (SIM). The most abundant ions were selected for quantification and two reference ions were used for confirmation of each analyte in SIM mode. We monitored the following compounds: tri-PCBs 18 and 28; tetra-PCBs 44, 52, and 66; penta-PCBs 87, 101, 105, 114, 118, 123 and 126; hexa-PCBs 128, 138, 153, 154, 156 and 167; hepta-PCBs 180 and 187.

2.3 Quality control

Procedural blanks were analyzed simultaneously with every batch of five samples to check for interference or contamination from solvent and glassware. Three field blanks were analyzed to check for potential contamination during sampling, storage and travel. Samples were blank-corrected using the mean of the field blanks. Method detection limits (MDL) defined as a mean of a field blank plus three times the standard deviation were 0.01–1.2 $pg \cdot m^{-3}$ for PCB congeners, when calculated using an average sampling volume of 1732 m^3. To check potential breakthrough during the sampling, three samples with the largest air volume and highest temperature were selected, and separate upward PUFs and downward PUFs were analyzed. PCB breakthrough (<30%) was estimated to be low, especially for samples from high-latitude regions where the temperature was lower than that at midlatitude. Absolute PCB concentrations were not corrected using the breakthrough results. Surrogate recovery was 96±13% for PCB-30. Recoveries (n=3) of analytes from spiked PUF plugs were 79%–123% for different PCB congeners.

2.4 Air mass backward trajectories

Air mass backward trajectories (BTs) were calculated to determine the origin of the air masses sampled, using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion model from the NOAA Air Resources Laboratory. BTs were traced for 3 d with 6-h steps, at 100, 500, and 1000 m above sea level for mean locations of the start and end of a sampling period.

3 Result and discussion

3.1 Spatial distribution of PCBs

Atmospheric concentrations of $\sum_{20}$PCBs along the cruise were from 6.20 to 365 pg·m^{-3}, with average 117±107 pg·m^{-3}. Concentrations of $\sum_{ICES}$PCBs (PCB 28, 52, 101, 118, 138, 153 and 180, identified by the International Council for the Exploration of the Sea as markers of the degree of contamination) were 0.540–275 pg·m^{-3} with average 66.0±69.4 pg·m^{-3}, constituting 50.8%±22.6% of the $\sum_{20}$PCBs. Congener profiles in all samples showed prevalence of tri- and tetra-chlorobiphenyls. PCB-18, PCB-28, PCB-44 and PCB-52 were dominant in all samples, representing 74.0%–99.2% of $\sum_{20}$PCBs (Table 1). The spatial distribution of $\sum_{20}$PCBs is shown in Figure 1. The highest concentration was observed over the Sea of Japan (site 1), and the lowest at the highest latitude in the Arctic Ocean (site 19), which was covered by multiyear sea ice. Geographically, the average concentration of $\sum_{20}$PCBs from high to low was in the following order: East Asia (245±170 pg·m^{-3}), North Pacific Ocean (151±126 pg·m^{-3}), Chukchi and Beaufort Seas (81.5±52.8 pg·m^{-3}), and central Arctic Ocean (56.2±41.5 pg·m^{-3}) (Table 1). Generally, atmospheric concentrations of $\sum_{20}$PCBs had strong variations by region. In the North Pacific Ocean, high levels of PCBs were observed in samples near the east coast of Russia (site 24 with $\sum_{20}$PCBs at 263 pg·m^{-3}) and the Bering Strait (site 6 with $\sum_{20}$PCBs at 364 pg·m^{-3}). In the Arctic Ocean, relatively high levels of $\sum_{20}$PCBs were found over the Chukchi and Beaufort seas, whereas two samples at the highest latitude had the lowest concentrations (sites 17 and 19) (Table 1; Figure 1).

Table 1 Concentrations of PCBs in marine atmosphere from East Asia to Arctic Ocean (pg·m^{-3})

Site	Latitude^{a} /°N	Longitude^{b}	Temperature/°C	PCB-18	PCB-28	PCB-44	PCB-52	$\sum_{ICES}$PCBs	$\sum_{20}$PCBs
1	38.45^{b}	133.27^{b}	–	15.7	10.6	58.4	262	275	365
2	46.35	145.45	12.8	8.79	11.9	14.4	82.8	96.7	125
East Asia			12.8	12.2	11.3	36.4	172	186	245
25	54.45	163.63	14.8	43.1	15.9	27.0	88.2	107	184
3	56.3	174.26	10.7	12.0	4.30	2.52	ND	5.90	24.0
4	58.99	176.99	10.1	38.2	10.1	34.3	6.04	21.8	105
5	61.32	−173.27	9.5	14.8	9.16	5.35	2.44	14.3	42.9
24	61.86	177.6	13.5	112	14.1	24.9	103	120	263
6	63.14	−170	9.4	200	13.5	9.12	139	153	364
7	64.22	−168.32	9.5	13.9	11.8	26.3	5.69	21.5	70.1
North Pacific Ocean			11	62.0	11.3	18.5	49.2	63.4	150.6
8	66.91	−166.87	3.9	16.3	12.4	2.56	3.30	18.1	45.4
9	70.45	−166.05	4.2	16.7	8.48	10.7	129	139	170
22	70.96	−170.52	2.4	4.75	7.53	8.70	12.7	21.4	36.8
10	73.18	−165.53	5	24.3	8.21	11.7	27.5	37.9	77.0
12	73.56	−156.01	4	43.7	8.38	7.71	13.4	22.1	78.1
Chukchi and Beaufort seas			3.9	21.2	9.00	8.27	37.2	47.7	81.5
13	76.84	−151.85	3.3	12.7	11.3	4.77	58.5	70.8	91.4
15	80.7	−146.14	0.4	11.31	6.97	9.88	63.4	71.4	100
20	82.57	−152.58	0.1	4.23	9.37	12.2	29.2	41.8	61.7
17	84.46	−144.88	−0.9	4.16	2.14	1.14	13.3	16.1	21.4
19	85.1	−147.08	−0.3	4.60	0.540	0.940	ND	0.540	6.20
Central Arctic Ocean			0.5	7.40	6.06	5.79	32.9	40.1	56.2
Entire Cruise			5.9	31.6	9.30	14.3	54.7	66.0	117

Notes: [a] Latitude and longitude show mean locations of start and end of each sampling period. [b] Sample sites in longitude west and east are respectively denoted by “-” and “+”. [c] ND means that concentration was less than the MDL. 0 was assigned as the value of ND when calculating the sum of PCBs and average concentration.

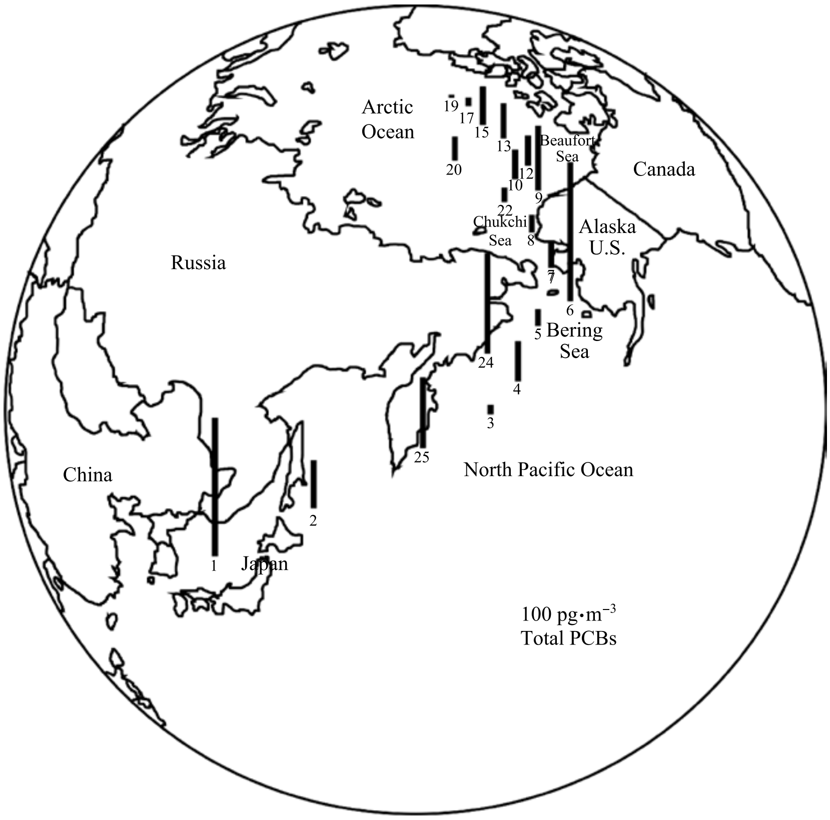

Figure 1 Spatial distribution of $\sum_{20}$PCBs in North Pacific and Arctic oceans. Concentrations are displayed at average sampling locations (bars).

3.2 Comparison of atmospheric PCB concentrations with other datasets

Atmospheric PCB concentrations in the oceanic area of East Asia were higher than those reported for air samples over surrounding land[28], but lower than those at a coastal site in Qingdao, China (Table 2)[29]. Compared with measurements during 1989–1990 over the East China Sea[30], PCB levels remained relatively constant (Table 2). Levels of $\sum_{20}$PCBs over the North Pacific were in the same range as those reported from the same oceanic area during 1989–1990 (Table 2)[30]. Levels of $\sum_{\mathrm{ICES}}$PCBs over the North Pacific were comparable to those detected over the North Atlantic Ocean at the same latitudes (~55°N–65°N), in 2002 (87± 34 pg·m^{-3}) and 2005 (53±55 pg·m^{-3})[23], and in the same range as those in open sea areas of the North Pacific during December 2006 through January 2007 (28–108 pg·m^{-3}, with average 51 pg·m^{-3})[31]. In the Arctic region, PCBs have been routinely measured at land-based sites in the Canadian and European Arctic since the 1990s[8,16-17,24]. Air concentrations of $\sum_{\mathrm{ICES}}$PCBs in the Arctic in the current study were higher than measurements of $\sum_{\mathrm{AMAP}}$PCBs (PCB 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180, called the AMAP subset) at the Arctic stations Alert, Zeppelin and Barrow (Table 2)[24], but comparable with $\sum_{\mathrm{AMAP}}$PCBs at Arctic Valkarkai Station in Russia (Table 2)[24].

In the East China Sea and North Pacific Ocean, PCB levels did not show obviously declining trends from 1989 to 2008[30]. During the CHINARE2012, air samples were collected and analyzed for PCBs. Compared with the 2012 result, atmospheric concentrations of PCBs detected during summer 2008 in the East China Sea and North Pacific were about one order of magnitude higher (Table 2)[32]. It is difficult to explain such a large difference between these two expeditions, because samples were taken by different workers at different times and analyzed in different laboratories. However, congener profiles of PCBs during these expeditions were similar, and were dominated by low chlorinated congeners, including tri- and tetra-chlorobiphenyls[30,32]. Both PCB-28 and PCB-52 were the most abundant congeners during the expeditions[30,32].

In the Arctic Ocean, air samples were collected and analyzed for PCBs in 2004 and 2012[5,32]. PCB levels in the Arctic Ocean presented an increasing trend from 2004 to 2008[5]. However, there was a decreasing trend during the CHINARE2008 and CHINARE2012[32]. Similar to the congener profiles in the East China Sea and North Pacific, tri- and tetra-chlorobiphenyls were the dominant congeners in the Arctic Ocean[5,32].

Table 2 Comparison of PCB concentrations measured in the present study with previous data worldwide (average concentrations and ranges in pg·m^{-3})

Location	Sampling time	$\sum_{\mathrm{ICES}}$PCBs	$\sum$PCBs	Reference
North Pacific	Apr.1989–Aug.1990		130(12–390)^{a}	[30]
Northern North Pacific	Apr.1989–Aug.1990		83(15–580)^{a}	[30]
Bering Sea	Apr.1989–Aug.1990		93(18–260)^{a}	[30]
Chukchi Sea	Apr.1989–Aug.1990		85(60–110)^{a}	[30]
East China Sea	Apr.1989–Aug.1990		140(62–250)^{a}	[30]
China	Sep.–Nov.2004	62(7–117)	179(21–336)^{b}	[28]
Japan	Sep.–Nov.2004	39(1.6–76)	127(7–247)^{b}	[28]
South Korea	Sep.–Nov.2004	17(4.0–29)	48(12–84)^{b}	[28]
Qingdao, China	Jun.2003		360(166–551)^{c}	[29]
Gosan, Korea	Jun.2003		3(1.3–5.8)^{c}	[29]
North Atlantic	2001	31±28		[45]
North Atlantic	2002	87±34		[23]
North Atlantic	2005	53±55		[23]
Alert (82°30′N, 62°20′W)	1993–2005		4(1.1–6.1)^{d}	[24]
Zeppelin(78°55′N, 11°56′E)	1998–2000		24(14–34)^{d}	[24]
Zeppelin(78°55′N, 11°56′E)	2001–2006		7.7(5.7–9.9)^{d}	[24]
Barrow(71°18′N, 156°36′W)	Mar.2002–Apr.2003		17(8.6–47)^{d}	[24]
Valkarkai (70°05′N, 170°56′E)	Jul.–Sep.2002		58(31–120)^{d}	[24]
North Sea and Norwegian Sea	Jun.–Aug. 2004	30(6–100)	83(22–250)^{e}	[5]
Greenland Sea	Jun.–Aug. 2004	9(3.5–22)	30(10–85)^{e}	[5]
Arctic Ocean	Jun.–Aug. 2004	7(0.76–43)	21(3.3–130)^{e}	[5]
Alert (82°30′N, 62°20′W	Dec.2004–Mar.2005		55^{f}	[46]
Barrow(71°18′N, 156°36′W)	Dec.2004–Mar.2005		30^{f}	[46]
Zeppelin(78°55′N, 11°56′E)	Dec.2004–Mar.2005		58^{f}	[46]
Dalian, China	Dec.2004–Mar.2005		62^{f}	[46]
Dalian, China	Jan.–Jun.2005		61(61–62)^{f}	[47]
Alert (82°30′N, 62°20′W	Jan.–Mar.2005		50^{f}	[47]
Barrow(71°18′N, 156°36′W)	Jan–Dec.2005		31(8–45)^{f}	[47]
Zeppelin(78°55′N, 11°56′E)	Jan–Dec.2005		23(2–58)^{f}	[47]
North Pacific Ocean	Dec.2006–Jan.2007	51(28–103)	94(59–169)	[31]
East Asia	Jul.–Sep.2008	186(97–275)	245(125–365)^{g}	This study
North Pacific Ocean	Jul.–Sep.2008	63.4(5.9–150)	150(42.9–364)^{g}	This study
Chukchi and Beaufort Seas	Jul.–Sep.2008	47.7(18.1–139)	81.5(45.4–170)^{g}	This study
Central Arctic Ocean	Jul.–Sep.2008	40.1(0.5–71.4)	56.2(6.2–100)^{g}	This study
East Asia	Jul.–Sep.2012		35.3(16.5–67.7)^{h}	[32]
North Pacific Ocean	Jul.–Sep.2012		17.8(10.9–36.8)^{h}	[32]
Arctic Ocean	Jul.–Sep.2012		12.2(7.97–17.19)^{h}	[32]

Notes: ^{a} Sum of 32 PCBs. ^{b} Sum of 29 PCBs. ^{c} Sum of 5 PCBs. ^{d} Sum of 10 PCBs. ^{e} Sum of 29 PCBs. ^{f} Sum of 48 PCBs. ^{g} Sum of 35 PCBs. ^{h} Sum of 26 PCBs.

3.3 Discussion of potential pathway and source regions of PCBs

In the East Asian Sea, samples from the Sea of Japan (site 1) had the highest concentrations of $\sum_{\mathrm{ICES}}$PCBs and $\sum_{20}$PCBs, whereas those levels at site 2 were much lower (Table 1; Figure 1). As presented in Figure 2, the episode on 14 July 2008 (Figure 2a, site 1) was characterized by air masses originating from northeastern China and/or passing over the East China Sea and Korea, whereas the episode on 16 July (Figure 2b, site 2) was characterized by air masses originating predominantly from open sea areas of the North Pacific. In Japan, multiyear observations indicated that PCB concentrations declined after the ban on PCB use in 1974[33]. But in Hong Kong, annual average atmospheric PCBs did not obviously decline after about 2000[33]. High levels of PCBs (mean concentration of total PCBs was 414800 pg·m^{-3}) were found in the atmosphere at a major electronic waste recycling center of China (Guiyu, Guangdong Province) in 2006, indicating that PCBs derived from open burning of circuit and cable wires could be an important source of PCB pollution globally[34]. Currently, electronic waste recycling plants are concentrated in South China[34]. However, North China, especially the northeast, is traditionally an industrial base, so large amounts of PCBs may still be in use within closed electrical systems. There, vaporization and uncontrolled burning of these products containing PCBs cannot be ignored. High levels of PCBs have been found in North China, suggesting that it is a source region of atmospheric PCBs[29]. Hence, the relatively high levels of PCBs found at site 1 may be attributed to the influence of polluted air masses originating over the source regions of China.

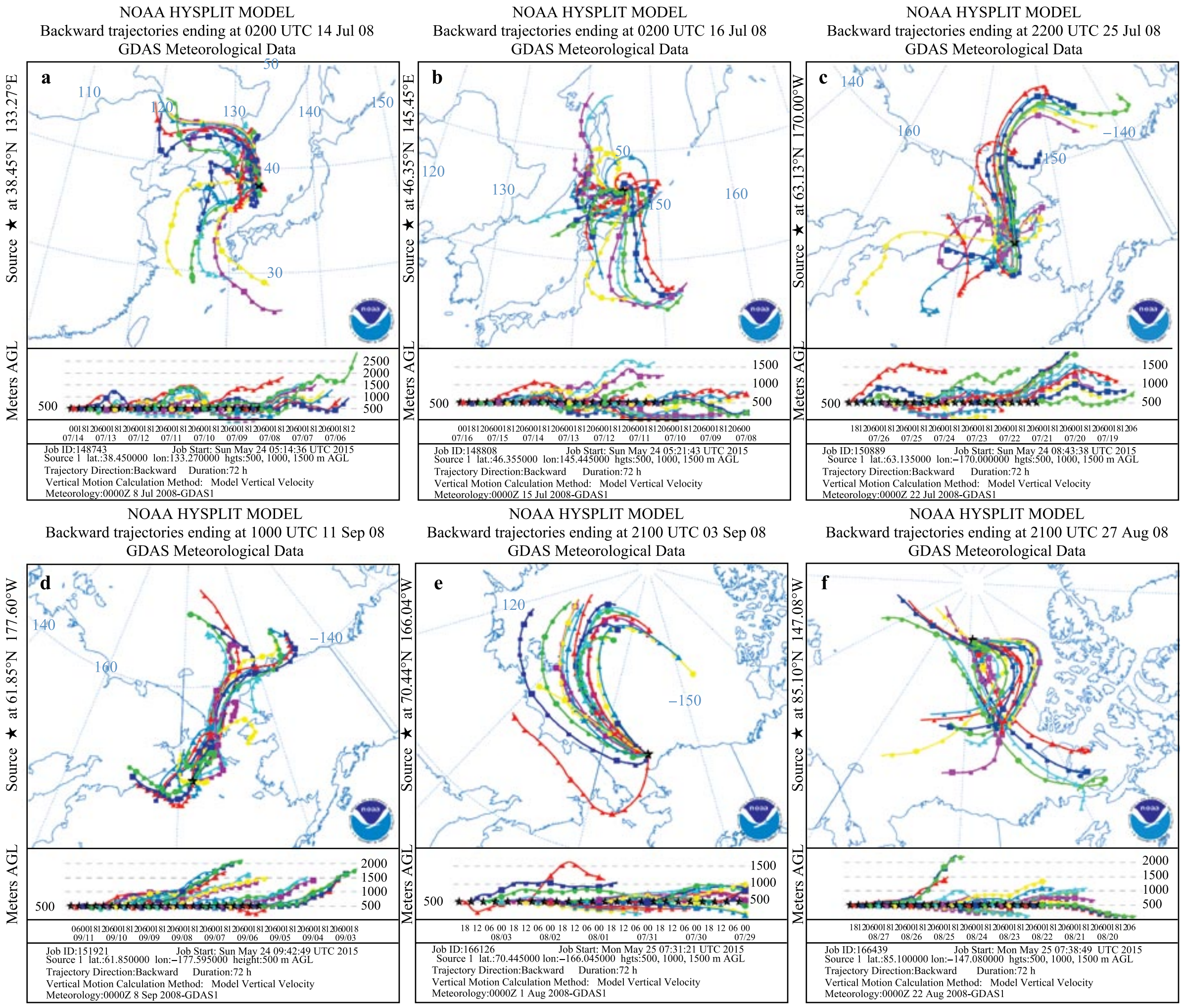

Figure 2 72-h backward trajectory for site 1 (**a**), site 2 (**b**), site 6 (**c**), site 24 (**d**), site 9 (**e**), and site 19 (**f**).

In the North Pacific, high levels of PCBs were found at sites 6 and 24, with $\sum_{20}$PCBs at 263 and 364 pg·m^3, respectively, and the lowest concentration at site 3 (24.0 pg·m^3). Concentrations at these sites of PCB-18 and PCB-52, the major congeners in commercial PCB mixtures[35], were also much higher than those at the other sampling sites in the North Pacific. Although the sampling period at site 6 (25–27 July) and site 24 (9–12 September) was more than 1 month, both were around the Bering Strait. BTs indicated that predominant air mass origins of these two samples were similar, from the Bering Strait and adjacent landmasses (Figures 2c and 2d). In this region, increasing human activities owing to the retreat of sea ice during summer (such as increasing vessel traffic, scientific and mineral exploration, coal mining, and port operation) might enhance PCB emissions.

In the Arctic, PCB levels were high compared with land-based measurements [24]. It is noteworthy that atmospheric concentrations of PCBs at Arctic Valkarkai Station were comparable with the current study, and were much higher than those found at other stations (Table 2)[24]. The measurements at Valkarkai and of the present study were both made during summer. As ice coverage in the Arctic Ocean decreases in response to rising temperatures in summer, PCBs deposited in sinks such as sea ice are expected to revolatilize into the atmosphere, so atmospheric levels of PCBs were relatively high during that season. However, atmospheric PCBs had high concentrations when air masses originated from and/or traversed the sea area adjacent to Russia (Figure 2e, site 9; $\sum_{20}$PCBs were at 129.3 pg·m^{-3}). When air masses originated from the Canadian Arctic (Figure 2f, site 19; $\sum_{20}$PCBs at 6.2 pg·m^{-3}), PCB concentrations were low. This phenomenon indicated that PCB emissions from local sources cannot be ignored. Russia may be an important source region of PCBs over the Arctic Ocean.

3.4 Congener profiles, latitudinal trends and temperature dependence of PCBs

PCBs are ideal chemicals for investigating global fractionation, because of their tremendous variability in air-surface exchange properties within the relevant temperature range[36-37]. The relative composition of PCB congeners can augment understanding of the long-range atmospheric transport of these chemicals[6]. Congener profiles in all samples showed the prevalence of tri- and tetra-chlorobiphenyls, respectively contributing 40.5%±21.2% and 55.0%±22.7% to the $\sum_{20}$PCBs in all samples. PCB-18, PCB-28, PCB-44 and PCB-52 were dominant in all samples, contributing 28.7%±20.0%, 11.8%±6.55%, 13.9%±9.20% and 36.3%±26.6% to the $\sum_{20}$PCBs in those samples (Table 1). This phenomenon is similar to that of other studies in which total PCBs were dominated by lower chlorinated congeners in the atmosphere of remote regions[23,38]. Such congeners should be more easily mobilized and transported over longer distances than congeners with high molecular mass, which would mobilize slowly and be deposited at low latitudes, with only a small fraction reaching remote regions[11].

Linear relationships were observed between latitude and concentrations of PCB-18, PCB-28, PCB-44 and PCB-52 (Figure 3). For PCB-28 and PCB-52, although r^2 values were small (0.2967 and 0.2905), the correlations were considered statistically significant (p<0.05), indicating that some of the variability could be explained by varying latitude. Atmospheric concentrations of PCB-44, on the other hand, tended to be much more correlated with latitude (r^2=0.4558, p<0.05). There was no significant correlation between atmospheric concentration of PCB-18 and latitude, with r^2=0.0319 (p=0.46). For PCB-18, as discussed above, primary and secondary emissions around the Bering Strait might have obscured the latitude trend. Moreover, with the strong volatility of PCB-18, enhanced air-surface exchange during summer complicated the environmental fate of PCB-18.

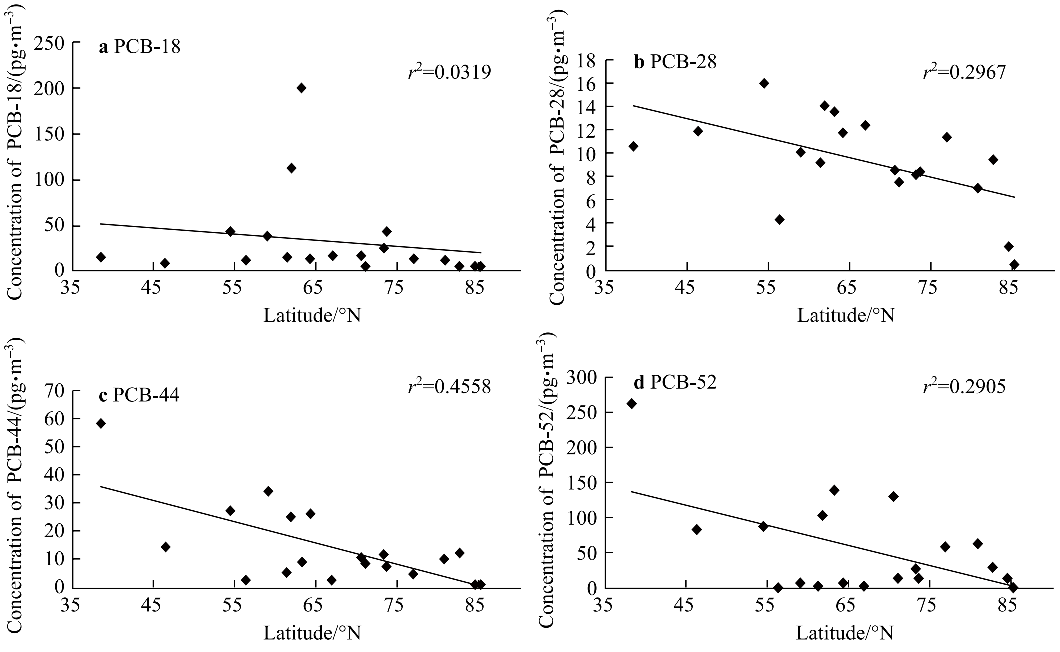

Figure 3 Latitude variation of PCB-18, PCB-28, PCB-44 and PCB-52 during CHINARE2008.

Atmospheric concentrations of PCBs are believed to be strongly controlled by volatilization from the surface of the earth, rather than from direct inputs. If there were no additional binding of PCBs, the vapor pressure (P, in Pa) would dominate the volatilization as temperature increases. The Clausius-Clapeyron equation was used to describe the relationship between ambient temperature (T) and P of PCBs. Details of the equation are in the literature[39-40]. Figure 4 shows a ln$P$ versus 1/T plot for PCB-18, PCB-28, PCB-44 and PCB-52. For PCB-18, PCB-28 and PCB-44, correlation coefficients were relatively low (r^2<0.4), but correlations were considered statistically significant (p<0.05), indicating that some of the variability of P could be explained by temperature fluctuations. However, PCB-52 displayed no significant correlation between P and 1/T (r^2=0.0236, p=0.54). It is notable that PCB-18 displayed no significant correlation between gas-phase concentration and latitude, whereas PCB-52 had significant correlation between the two. This suggests that atmospheric PCB-18 was related to volatilization from the earth surface during summer 2008, during which temperature was relatively high, whereas PCB-52 may have been related to direct atmospheric transport from source regions.

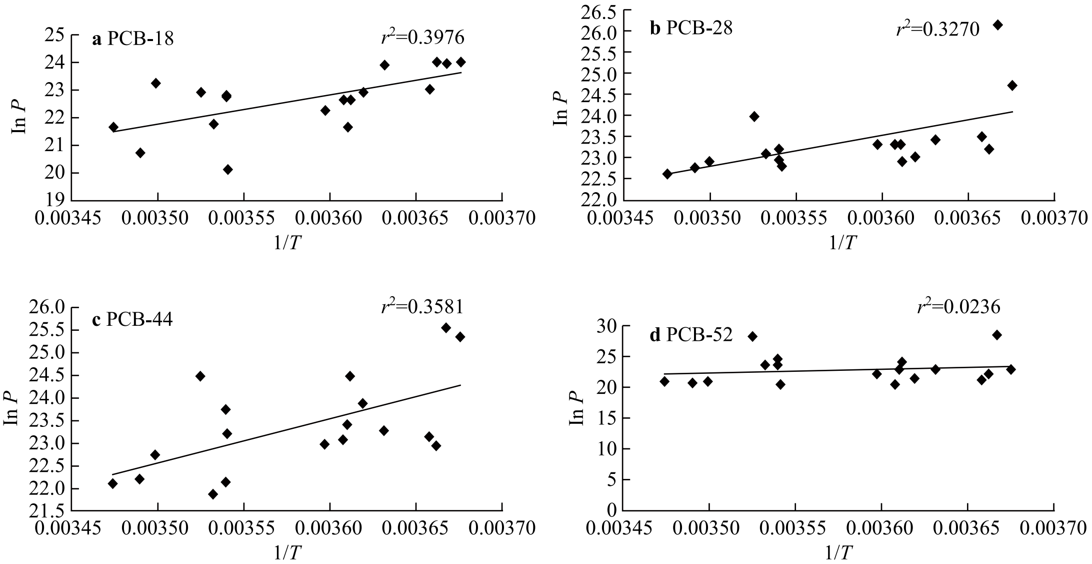

Figure 4 ln$P$ versus 1/T plot for selected PCB congeners in the atmosphere.

3.5 Arctic Ocean sea ice distribution as an influence

Since Open use of PCBs has been phased out in Europe and the United States[5] and PCB concentrations have declined in the atmosphere of source regions[24], PCB concentrations in the atmosphere of the Arctic are expected to decrease. Nevertheless, atmospheric PCBs there did not appear to decline after 2000. In particular, measurements of atmospheric PCBs at Zeppelin Station showed increasing trends of PCB congeners in 2005/2006[24]. This phenomenon may be ascribed to several factors: (1) Lower temperatures in the Arctic slow both biotic and abiotic degradation relative to temperate regions[41]; (2) Global fractionation may maintain air concentrations in the Arctic, while concentrations in temperate regions show apparent reductions[14-15]; (3) Volatilization of previously deposited PCB compounds from ice/snow, or from seawater due to decreasing sea ice coverage in the Arctic Ocean in response to rising Arctic temperatures[25].

During CHINARE2008, area fractions of open water and sea ice were investigated by aerial survey (helicopter flights)[42]. Figure 5 presents the distribution of PCB-18, PCB-28, PCB-44 and PCB-52 with sea ice variations in the Arctic Ocean. Concentrations of PCB-52 in at floating sea ice region in the Arctic were higher than those in the open sea and pack ice regions, except at site 9, which might be influenced by atmospheric transport from source regions (Figure 5 and Table 1). However, this trend was not observed for PCB-18, PCB-28 and PCB-44 (Figure 5 and Table 1). Vapor pressure P plays a role in deposition and volatilization of PCBs in the Arctic Ocean. Heavier PCB-52 accumulates more easily by dry deposition and snow scavenging because of lower P, and is therefore more likely to be retained within sea ice, whereas lighter PCB-18 and PCB-28 are likely to remain in the gas phase even at low temperatures during winter. Determination of PCBs in an ice core at Svalbard showed that PCB-52 was

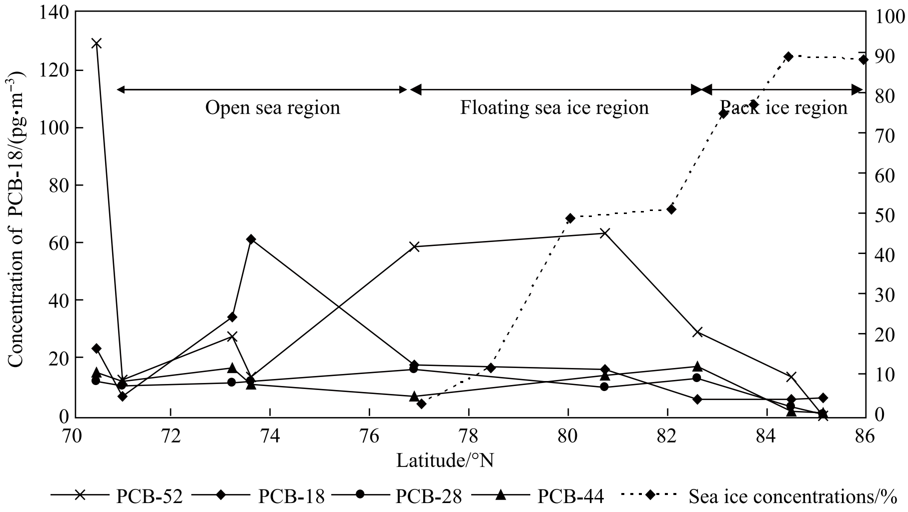

Figure 5 Distribution of PCBs with variation of sea ice in Arctic Ocean.

the most abundant of 209 PCB congeners[11]. The strong ice retreat during summer 2008 may have allowed for strong volatilization of previously accumulated PCBs in sea ice, especially those with heavier molecular weight and lower *P* such as PCB-52[43-44]. Therefore, levels of PCB-52 were relatively high near the marginal ice zone, where sea ice was melting intensively.

4 Conclusions

Atmospheric concentrations of 20 PCBs were measured from Shanghai, China to the Arctic Ocean during the CHINARE -2008. Congener profiles in all samples showed prevalence of tri- and tetra-chlorobiphenyls, dominated by PCB-18, PCB-28, PCB-44 and PCB-52. Along the cruise, the highest concentration was observed in the Sea of Japan and the lowest concentration over the high-latitude Arctic Ocean. Air mass backward trajectories indicated that samples with relatively high levels of PCBs might have been affected by atmospheric transport of these chemicals from primary and/or secondary sources. Atmospheric PCB-18 detected during the cruise may have been related to volatilization from the earth surface during summer 2008, whereas PCB-52 during the cruise may be attributable to direct atmospheric transport from source regions. In the Arctic, strong ice retreat during that summer may have enhanced the volatilization of previously accumulated PCBs from sea ice, especially those with heavier molecular weight and lower vapor pressure such as PCB-52.

Acknowledgments This study was supported by grants from the National Natural Science Foundation of China (Grant nos. 41025020, 40776001, and 41203075), Chinese Academy of Sciences (Grant no. KZCX2-YW-QN506) and the Fundamental Research Funds for the Central Universities. The work described in this paper was also funded by the Area of Excellence Scheme under the University Grants Committee of the Hong Kong Special Administrative Region, China (Grant no. AoE/P-04/2004), and a Hong Kong Research Grants Council (Grant no. CityU 160610). Field work was supported by the Chinese Arctic and Antarctic Administration and the 3rd Chinese National Arctic Research Expedition.

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