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Published in:

Atmospheric Pollution Research

Published: 01/07/2014

Document Version:

Final Published version, also known as Publisher's PDF, Publisher's Final version or Version of Record

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Publication record in CityU Scholars:

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Published version (DOI):

[10.5094/APR.2014.056](https://doi.org/10.5094/APR.2014.056)

Publication details:

Wu, X., Lam, J. C. W., Xia, C., Kang, H., Xie, Z., & Lam, P. K. S. (2014). Atmospheric hexachlorobenzene determined during the third china arctic research expedition: Sources and environmental fate. *Atmospheric Pollution Research*, 5(3), 477-483. <https://doi.org/10.5094/APR.2014.056>

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Atmospheric hexachlorobenzene determined during the third China arctic research expedition: Sources and environmental fate

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ABSTRACT

In July to September 2008, air samples were collected aboard a research expedition icebreaker, Xuelong (Snow Dragon), under the support of the 2008 Chinese Arctic Research Expedition Program. All the air samples were analyzed for determination of the concentrations of Hexachlorobenzene (HCB). The levels of HCB ranged from 24 to 180 pg m⁻³, with an average concentration of 88 pg m⁻³. Generally, HCB were more uniform than other organochlorine pollutants in the North Pacific Ocean and the Arctic Ocean. Geographically, the average concentrations of HCB from high to low were in the following order: the Central Arctic Ocean (110±57 pg m⁻³), the Chukchi and Beaufort Seas (93±29 pg m⁻³), the East Asia (75±49 pg m⁻³) and the North Pacific Ocean (69±38 pg m⁻³). In the East Asia Sea and the North Pacific Ocean, both primary and secondary emissions of HCB from the nearby continents and/or oceans might contribute to the atmospheric HCB. In the Arctic, intense sea–ice melting in the summer of 2008 might result in the remobilization of HCB and enhance its atmospheric levels in this region.

Keywords: POPs, spatial variations of HCB, atmospheric concentration, Arctic Ocean, sea–ice melting



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Article History:

Received: 13 September 2013

Revised: 23 February 2014

Accepted: 16 March 2014

doi: 10.5094/APR.2014.056

1. Introduction

Hexachlorobenzene (HCB) is a chlorinated monocyclic aromatic compound in which the benzene ring is fully substituted by chlorine. It was listed by the Stockholm Convention as one of twelve persistent organic pollutants (POPs) in 2004 (Stockholm Convention, 2008; Su et al., 2008). Historically, HCB had been used as pesticide/fungicide and an industrial chemical for carbon anode treatment, synthetic rubber additives, and wood preservatives (Emma, 2006). HCB is also produced as a by-product in the production of a large number of chlorinated compounds, particularly lower chlorinated benzenes, and in the production of several pesticides (Bailey, 2001).

Industrial production of HCB began in 1945 in the United States, and was subsequently formed in Canada, Europe, the former Union of Soviet Socialist Republics (USSR) and possibly elsewhere (IPCS, 1997). Global production exceeded 100 kt and primary emissions to atmosphere probably peaked in the 1970s (Barber et al., 2005). Restrictions on its use started in most countries in the 1970s and production of HCB subsequently declined steeply. The levels of HCB in the environment presented a consistent downward trend with the declining production and usage. Current emissions are estimated to be 70%–95% lower than that in 1970s (Barber et al., 2005; Wang et al., 2010). By the early 1990s there was no significant production of HCB in Europe and North American, but the production is believed to have continued

in India at least until the year 1997 (Basel Convention, 2006). In China, HCB was used as an intermediate or as a byproduct in chemical processes, but was not used for agricultural purposes (Kunisue et al., 2004; Zheng et al., 2010). The production of HCB in Tianjing, China occurred for years but ended in 2003 (Kunisue et al., 2004; Zheng et al., 2010).

HCB is a highly persistent environmental pollutant due to its chemical stability and resistance to biodegradation (AMAP, 2004; Mackay et al., 2006). The Junge–Pankow adsorption model indicated that HCB in the atmosphere occur predominantly in the gas-phase at moderate temperatures (Bidleman, 1988). Furthermore, an early study on Canadian Arctic also indicated atmospheric HCB was almost exclusively in the gas-phase, with only less than 1% associated with particle-phase (Hung et al., 2002). Atmospheric half-life is about 700 d for HCB (AMAP, 2004; Mackay et al., 2006). These results hint that HCB can be transported great distances in the atmosphere before removal by deposition or degradation. In fact, HCB has been found in areas distant from source regions, including the Arctic and Antarctic (Su et al., 2006; Hung et al., 2010; Kang et al., 2012). For example, Kang et al. (2012) reported that HCB was frequently detected in the surface snow of East Antarctica. Most of the total quantity of HCB found in these remote regions is derived from distant sources in the tropical and/or subtropical regions (Wania and Mackay, 1996; Gouin et al., 2004; Montone et al., 2005; Su et al., 2006; Lohmann et al., 2009; Hung et al., 2010). Furthermore, the air concentrations of HCB in

non-source regions were remarkably uniform in space and time owing to the exceptionally long atmospheric residence time (Barber et al., 2005; Shen et al., 2005; Su et al., 2006; Liu et al., 2010). Among the individual POPs in Arctic air, HCB was found at the highest concentration (Hung et al., 2010). Compared with other POPs (like DDTs and PCBs), the octanol–water partition coefficient of HCB is relatively lower, and the volatility of HCB is relatively higher, which indicate it is apt to evaporate from water and soil to air and is more likely to undergo environmental recycling than for other POPs (Brubaker and Hites, 1998; Barber et al., 2005). Hence, it is hypothesized that HCB will reach a global equilibrium quickly than other POPs, and thus, it may be possible to use to predict the ultimate environmental fate of other POPs (Barber et al., 2005).

Ship-board air samples were collected during the Chinese Arctic Research Expedition 2008 (CHINARE2008) from the Bohai Sea to the high latitude Arctic Ocean from July to September 2008. The concentration of hexachlorocyclohexane (HCH), DDT and chlordane have been reported in previous publications (Wu et al., 2010; Wu et al., 2011). The purposes of the current study are (1) to update the data for atmospheric levels and distribution of HCB along the expedition, (2) to make a comparison with the previous monitoring data and reveal the temporal variations of HCB, and (3) to reveal the potential sources and environmental fate of HCB.

2. Methodologies

2.1. Sampling

Shipboard air samples were collected from July to September 2008 during a cruise from Shanghai, China to the high-latitude Arctic (33°N to 85°N). The information of sampling sites can be found in Table S1 (see the Supporting Material, SM). The preparation, collection, storage and transportation of samples were accomplished according to previously established methods with minor modifications (Ding et al., 2007a; Ding et al., 2007b). A high volume air sampler was placed on the upper-most deck of the ship. Air sampler (TH1000 made by Wuhan Tianhong, China) was controlled by a wind sensor to ensure that the samples were collected only when wind was blowing 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). Twenty-three gas-phase samples were collected using two separated PUFs (6.5 cm diameter × 6 cm height each). The downward PUFs were used to test any potential breakthrough. The air volumes ranged from 567 to 2 916 m³ (at 0 °C and 1 atm, flow rate of ~1.0 m³ min⁻¹). Field/travel blanks included three pre-cleaned PUFs, which were exposed to atmosphere over the sampling period.

2.2. Sample preparation and analytical procedure

PUFs spiked with PCB30 as surrogate standard were loaded into the pre-cleaned extraction cells (22 mL) and extracted by accelerated solvent extraction (ASE 200, DIONEX Inc.) using a mixture of hexane and dichloromethane (1:4, v/v) at 110 °C and 1 500 psi for two static cycles with a heating time of 6 min, static time of 3 min. Extracts were evaporated to about 1 mL and then purified by elution with 80 mL of hexane and 80 mL of hexane and dichloromethane mixture (1:1, v/v) through a chromatographic column of activated silica gel (60 Å average pore size) and deactivated alumina. The activated silica gel and alumina were heated at 450 °C for 4 h and maintained at 180 °C overnight. Elutes were spiked with 2,4,5,6-Tetrachloro-m-xylene (TCMX) as internal standard 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 HCB was performed using a GC (Agilent 7890A) equipped with a mass-selective detector (Agilent 5975c) 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) having 0.25 mm i.d. × 60 m × 0.25 µm film. Reference standard was determined and the samples were analyzed separately in selected ion monitoring (SIM).

2.3. Quality control

Three field blanks, six laboratory blanks were processed to check for laboratory and field contamination. There were no major differences in the trace amounts of HCB detected between field and laboratory blanks (see the SM, Table S2). Samples were therefore corrected using the mean of field blanks (SI). Method detection limits (MDL) of HCB defined as mean of field blank with 3 times the standard deviations were 0.22 pg m⁻³, when calculated with an average sampling volume of 1 732 m³. HCB is a relatively volatile substance and can be prone to breakthrough during high volume air sampling (Jaward et al., 2004a). In order to check the potential breakthrough during the sampling, three samples with the highest air volume and highest temperature were selected and the separate upward PUFs and downward PUFs were analyzed. Concentrations of HCB on the downward PUFs were less than 30% of the upward PUFs. Hence, HCB breakthrough is estimated to be low with the samples collected on the cruise, especially for the samples collected at high latitude region where the temperature was relatively lower than that of mid-latitude. Surrogate recovery ($n=32$, including field and laboratory blanks) was 96±13% for PCB 30. Analytical (method) recoveries were determined by spiking clean PUFs. The recovery ($n=3$) was 97±10%.

2.4. Air mass back trajectories

Air mass back trajectories (BTs) were calculated to determine the origin of the air masses sampled using the HYSPLIT transport and dispersion model from the NOAA Air Resources Laboratory (Draxler and Rolph, 2003). BTs were traced for 5 d with 6 h steps at 100, 500, and 1 000 m above sea level for the start and end of each sampling episodes. All the BTs can be found in the SM.

3. Results and Discussion

3.1. Geographical trends of HCB

The concentration of HCB was greater than the method detection limit (MDL) in all the samples and ranged from 24 to 180 pg m⁻³, with an average concentration of 88 pg m⁻³ (see the SM, Table S3). Figure 1 shows the spatial distribution of HCB along the expedition route. Both of the sites with the highest (site 20) and lowest concentrations (site 19) of HCB were found in the Central Arctic Ocean. Generally, levels of atmospheric HCB were relatively uniform in the North Pacific Ocean and the Arctic Ocean. HCB concentrations varied by a factor of 7.5, while other POPs, such HCHs and DDTs, varied by orders of magnitude over the expedition (Wu et al., 2010; Wu et al., 2011). This result was similarly with previous studies which also found the atmospheric levels of HCB in non-source regions were relatively uniform in space, varying by less than a order of magnitude at back ground sites, even on a hemispheric scale (Jaward et al., 2004b; Barber et al., 2005; Shen et al., 2005; Su et al., 2006; Liu et al., 2010; Wang et al., 2010; Cai et al., 2012). The uniform distribution reflected the exceptionally long atmospheric residence time of HCB. Moreover, Lohmann et al. (2009) reported that HCB is much closer to equilibrium between air and sea water in the Northern hemisphere than most other POPs, including HCHs, DDTs and chlordanes. The equilibrium might be also affected the uniformity of HCB in the open sea area where the re-emission from sea water is an important source of atmospheric HCB.

Geographically, the average concentration of HCB from high to low was in the following order: the Central Arctic Ocean (110±

57 pg m^{-3} , the Chukchi and Beaufort Seas ($93 \pm 29 \text{ pg m}^{-3}$), the East Asia ($75 \pm 49 \text{ pg m}^{-3}$) and the North Pacific Ocean ($69 \pm 38 \text{ pg m}^{-3}$). This geographical trend indicates that HCB was found at relatively higher concentrations in the Arctic Ocean than those in the North Pacific Ocean and the East Asia (Kruskall–Wallis test, $P < 0.05$). Sample of the highest latitude was excluded from the Kruskall–Wallis test due to the cease of air–sea exchange of the sampling region (see Section 3.3). Similar geographical trend was also found in the same track during CHINARE2010 (Cai et al., 2012). Historically, HCB was widely used in industry and agriculture in the countries with low latitudes, including Japan, India, and Mexico. However, the levels of HCB found in the current study were lower in the source regions (East Asia) than those in high latitude regions (Arctic Ocean). The prevalence of HCB detected in the high latitude Arctic region could be explained by the “global fractionation” hypothesis (Wania and Mackay, 1996). Briefly, as emissions of HCB from point sources in the tropical and/or subtropical regions have reduced, HCB is subject to long–range atmospheric transport and condense in the cold high latitude Arctic regions due to its high volatility and long atmospheric life (Mackay and Wania, 1995; Muir et al., 1995; Wania and Mackay, 1996; Barber et al., 2005).

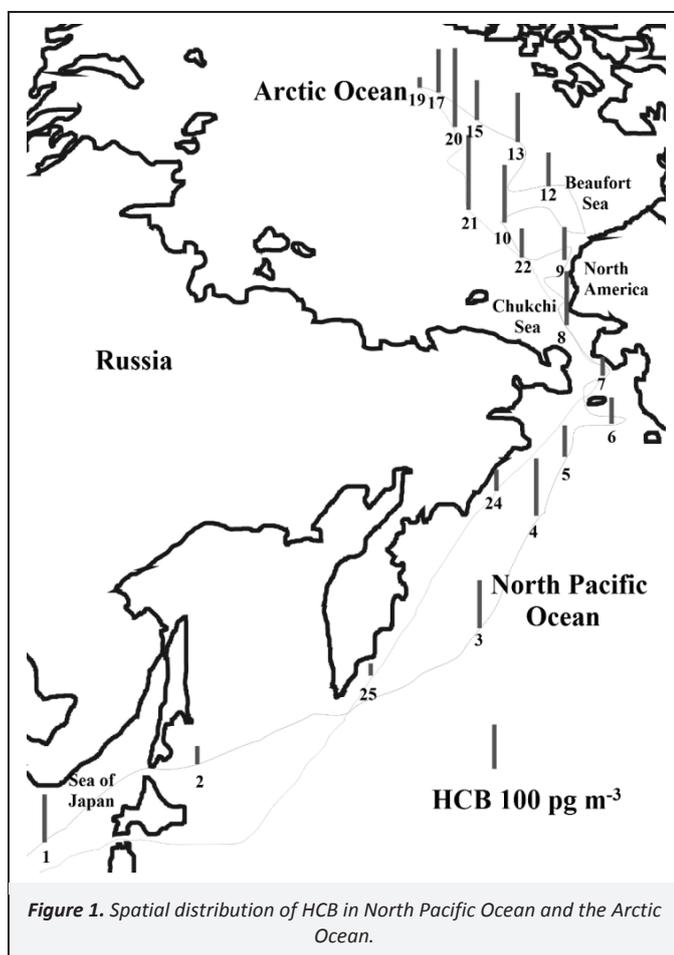


Figure 1. Spatial distribution of HCB in North Pacific Ocean and the Arctic Ocean.

3.2. Environmental fate and potential sources of HCB in the East Asia Sea and the North Pacific Ocean

In the current study, HCB concentrations in the East Asia Sea and the North Pacific Ocean ranged from 27 to 130 pg m^{-3} . As shown in Table 1, the concentrations of HCB in these two regions were similar to those found in other studies during 2000–2007: 25– 140 pg m^{-3} were found across South Korea in 2004 (Jaward et al., 2005); 14– 95 pg m^{-3} were found across Japan in 2004 (Jaward et al., 2005); 82– 103 pg m^{-3} were found at a coastal site of South Korea in 2007 (MOE, 2007); 73– 114 pg m^{-3} were found in Mongolia

in 2006 (MOE, 2007); 13– 305 pg m^{-3} were found in Hateruma Island of Japan in 2004–2007 (MOE, 2007); 13– 130 pg m^{-3} were found in Alaska of U.S. in 2002–2003 (Stockholm Convention, 2009); 50– 133 pg m^{-3} were found across the North America in 2000–2001 (Shen et al., 2005); and 42– 89 pg m^{-3} were found in the North Pacific Ocean in 2006–2007 (Zhang and Lohmann, 2010). However, the levels of HCB in the East Asia Sea and the North Pacific Ocean found in the current study was more than three times lower than those found across China in 2004 ($10\text{--}460 \text{ pg m}^{-3}$) (Jaward et al., 2005), and was more than two times higher than those reported by CHINARE2010 in the same region ($1\text{--}62 \text{ pg m}^{-3}$) (Cai et al., 2012).

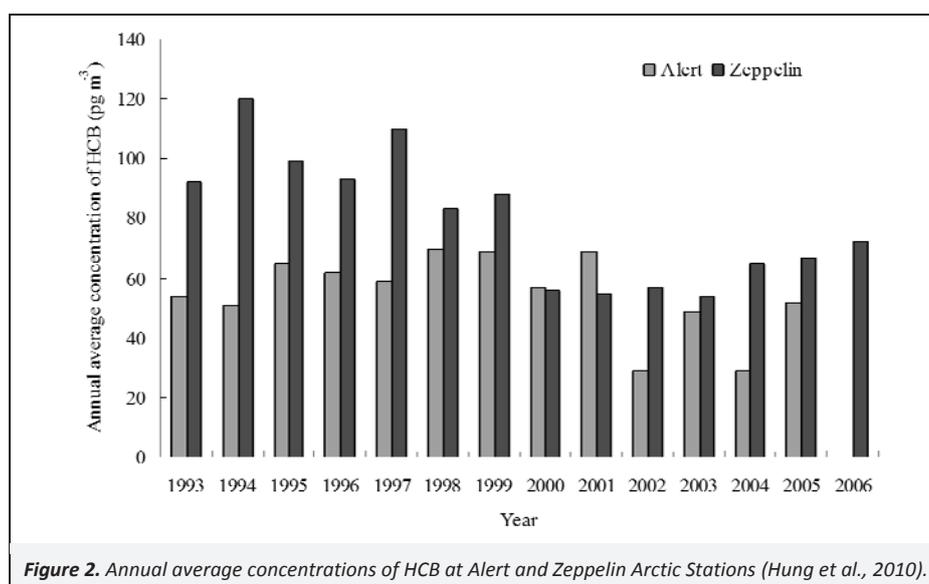
As mentioned above, the levels of HCB found in 2008 were similar to those found in the surrounding continent in 2000–2007 (Table 1). Multiyear monitoring of HCB in Japan also did not find any obvious decreasing trend during 2004–2007 (MOE, 2007). This temporal trend was attributed to both primary and secondary emissions of HCB in these regions. In the Asia, the direct usage of HCB as pesticide and fungicide is believed to have stopped after the year 2000 (Barber et al., 2005). However, the release of HCB as an impurity of other chemicals, e.g. pentachlorophenol which has been used widely for killing snails in areas of China where schistosomiasis is epidemic, cannot be excluded (Kunisue et al., 2004; Barber et al., 2005; Zheng et al., 2012). The total consumption of pentachlorophenol in China was about 1 310 t in 2002. This value increased to 4 330 t in 2009 (Zheng et al., 2012). The primary emission of HCB caused by the extensive usage of pentachlorophenol in China might be contributed to the high levels of HCB in the East Asia and adjacent regions during about 2000–2007 (Jaward et al., 2005; MOE, 2007). On the other hand, the secondary emission of HCB from soil, which might be hundreds to thousands of tons per year worldwide, cannot be ignored (Barber et al., 2005). However, the concentrations reported by Cai et al. (2012) in the same track during CHINARE2010 were much lower than the found of 2008. This phenomenon hinted that as the Stockholm Convention was entered into force on 2004, the usage and production of HCB was retreated gradually in China accompanied and the residue of HCB in the East Asia and adjacent regions had decreased in recent years.

3.3. Environmental fate and potential source of HCB in the Arctic Ocean

In the Arctic Ocean (including Chukchi Sea, Beaufort Sea, and the high latitude Arctic Ocean), atmospheric concentrations of HCB ranged from 24 to 180 pg m^{-3} , which were lower than those reported at the end of the 1980s (Hinckley et al., 1991), but relatively higher than the monitoring data of the Arctic stations under the AMAP (Hung et al., 2010). Higher concentrations detected in the Arctic area may be due to our sampling period (July 2008–September 2008). Previous study indicated that the HCB levels in the Arctic showed a bimodal seasonal distribution, with maxima in February–May and July–August (Hargrave et al., 1997). High temperatures during the summer (July–August) might enhance the volatilization of HCB from environmental medias of the Arctic (seawater of the Arctic Ocean and/or soils of the nearby land masses), and resulted in the high HCB concentrations found in the current study. It is notable that an increasing trend of HCB was found at the Zeppelin station and Alert station in the Arctic after 2003 (Figure 2) (Hung et al., 2010). Especially the levels of HCB found at the Alert station in 2005 were about two times higher than those found in 2004, which hinted that huge year–to–year fluctuations of atmospheric HCB could occur in the Arctic region (Hung et al., 2010). Compared to the levels of HCB found during the CHINARE2010, those found of CHINARE2008 study were also much higher. The huge year–to–year fluctuations of HCB might be attributed to the different emission intensities (secondary emission) of HCB in the Arctic region. The details will be discussed later.

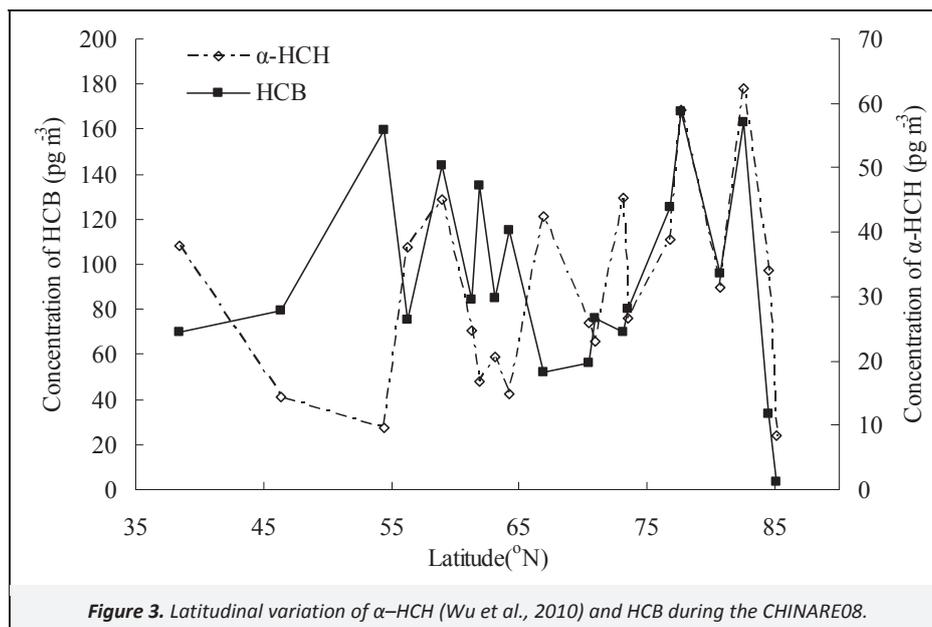
Table 1. Comparison of HCB concentrations in the present study with previous data (average concentrations and ranges in pg m^{-3})

Location	Year	HCB (pg m^{-3})	Reference
South Korea	Sep–Nov 2004	81 (26–140)	(Jaward et al., 2005)
China	Sep–Nov 2004	236 (10–460)	(Jaward et al., 2005)
Japan	Sep–Nov 2004	55 (14–95)	(Jaward et al., 2005)
Hateruma Island, Japan	Apr–Dec 2004	70 (42–115)	(MOE, 2007)
Hateruma Island, Japan	Jan–Dec 2005	86 (39–305)	(MOE, 2007)
Hateruma Island, Japan	Mar–Dec 2006	49 (13–94)	(MOE, 2007)
Hateruma Island, Japan	Feb–Jul 2007	92 (64–125)	(MOE, 2007)
Terelj, Mongolia	Sep 2006	94 (73–114)	(MOE, 2007)
South Korea	Spring 2007	93 (82–103)	(MOE, 2007)
Alaska of U.S.	2002–2003	69 (13–130)	(Stockholm Convention, 2009)
Bering Sea and Chukchi Sea	1988	210 (144–324)	(Hinckley et al., 1991)
Alert (82°30'N, 62°20'W)	1993–1999	61 (51–70)	(Hung et al., 2010)
Zeppelin (78°55'N, 11°56'E)	1993–1999	98 (83–120)	(Hung et al., 2010)
Alert (82°30'N, 62°20'W)	2000–2005	48 (29–69)	(Hung et al., 2010)
Zeppelin (78°55'N, 11°56'E)	2000–2006	61 (54–72)	(Hung et al., 2010)
Barrow (71°18'N, 156°36'W)	2002–2003	47 (13–130)	(Hung et al., 2010)
Valkarkai (70°05'N, 170°56'E)	2002	76 (27–100)	(Hung et al., 2010)
North Pacific Ocean	Dec 2006–Jan 2007	61 (42–89)	(Zhang and Lohmann, 2010)
North American	2000–2001	89 (50–133)	(Shen et al., 2005)
North Atlantic and Arctic Ocean	2004	47 (23–87)	(Lohmann et al., 2009)
Greenland Sea	2007	53 (36–77)	(Galban–Malagon et al., 2013)
Arctic Ocean	2007	42 (10–61)	(Galban–Malagon et al., 2013)
East Asia	2008	75 (41–110)	This study
North Pacific Ocean	2008	69 (27–130)	This study
Chukchi and Beaufort Seas	2008	93 (66–130)	This study
High Latitude Arctic Ocean	2008	110 (24–180)	This study
East Asia	2010	29 (16–56)	(Cai et al., 2012)
North Pacific Ocean	2010	31 (1–62)	(Cai et al., 2012)
Arctic Ocean	2010	36 (6.9–64)	(Cai et al., 2012)



For the air samples collected during the CHINARE2008, concentrations of HCH were also determined and reported (Wu et al., 2010). The spatial distribution of HCB in the Arctic Ocean was remarkably similar to that of α -HCH (Figure 3), indicating that these two chemicals might be influenced by secondary sources in the Arctic Ocean rather than advective inputs from external sources. Change in ice cover and seasonality are especially impor-

tant for POPs like HCB and α -HCH where air–sea exchange is a significant component of regional budgets (MacDonald et al., 2000; Ma et al., 2011). As the ice breaks up and the area of open water increased during the summer, direct exchange between air and the previously obscured surface water recommenced. Hence, the levels of HCB and α -HCH in the marginal ice zone were relatively higher than those in the North Pacific Ocean.

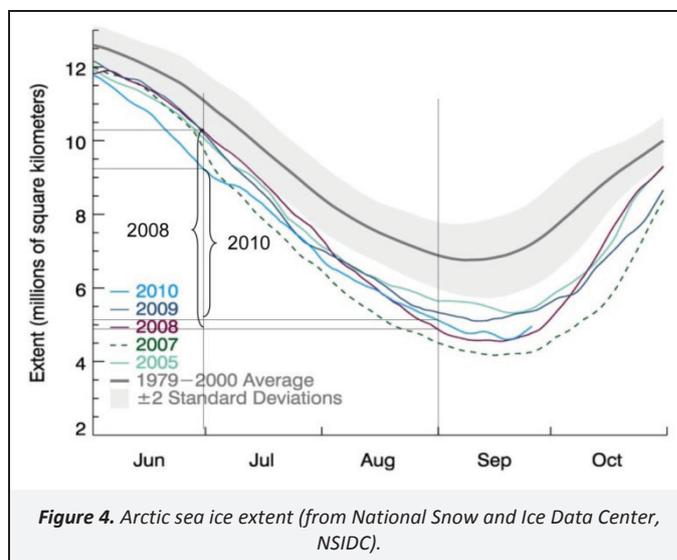


The other potential secondary source was the re-emission of HCB from melting sea-ice and/or snow. Measurements of HCB in snow of Polar Regions indicated that precipitation in the form of snow results in the accumulation of HCB in the snow pack and sea ice (Herbert et al., 2005; Kang et al., 2012). The lost sea ice/snow, especially the seasonal sea ice/snow in the Arctic Ocean, functions as a temporary storage reservoir that releases the HCB accumulated over the winter during a short melt period of summer, resulting in temporarily elevated concentrations in the atmosphere. The intensity of these emissions increased with the length of the snow accumulation period and the amount of the melting snow pack and sea ice during the summertime. The levels of HCB found during the CHINARE2008 and CHINARE2010 presented a similar spatial distribution, which HCB were higher in the Arctic regions than in low latitude regions. However, the levels of HCB found during CHINARE2008 were more than two times higher than those found during CHINARE2010. The huge fluctuation might be attributed to the different sea ice distributions of 2008 and 2010. Figure 4 presents the Arctic sea ice extent during the summer (data from National Snow and Ice Data Center, NSIDC). According to Figure 4, sea ice extent decreased by more than 50% during July and August 2008, and the decreasing trend remained strong in August 2008, while in a typical year, the retreat of ice would begin to slow as the Arctic began to cool at the end of August (NSIDC, 2008a; NSIDC, 2008b). Before July, sea ice extent of 2008 was higher than that in 2010. However, the sea ice extent of 2008 was lower than that in 2010 at the end of August. The sea ice lost during July to August of 2008 was about 1.5 millions of square kilometers more than that in 2010, indicating a much acutely melting of sea ice in 2008 than in 2010 (Figure 4). The intense ice retreat during the summer of 2008 may strongly volatilize previously accumulated HCB in seasonal and multiyear sea ice. Therefore, the levels of HCB were relatively higher in 2008 than in 2010. In the pack ice region where a large portion of the sea surface was covered by multiyear ice, it is reasonable to assume that the release of HCB from sea ice and sea water should be very weak. As a result, the levels of atmospheric HCB in this region were found to be the lowest during the expedition of 2008.

4. Conclusion

This study reports atmospheric concentrations of HCB determined from Shanghai, China to the Arctic Ocean during the Third China Arctic Research Expedition, 2008. The data were determined over a large area of North Pacific Ocean and adjacent

Arctic region, and thus provide updated information about spatial variations in these areas. Different spatial distributions indicated the fate of HCB was influenced by its emission pattern around the world. In the East Asia Sea and the North Pacific Ocean, both primary and secondary emissions of HCB from the nearby continents and/or oceans might contribute to the atmospheric HCB. In the Arctic, increase in sea-ice melting in the summer of 2008 might result in the remobilization of HCB and enhance its atmospheric levels in this region.



Acknowledgments

This study was supported by grants from the National Natural Science Foundation of China (Project Nos. 41025020, 41176170, 41203075), the Program of China Polar Environment Investigation and Assessment (Project No. CHINARE2011–2015) 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 (Project No. AoE/P-04/2004), and a Hong Kong Research Grants Council (CityU 160610). Field work was supported by China Arctic and Antarctic Administration and the third China Arctic Research Expedition.

Supporting Material Available

Information of sampling sites (Table S1), Amounts of HCB detected in field and laboratory blanks (Table S2), Concentrations of HCB in the marine atmosphere from East Asia to the Arctic Ocean (Table S3), Back trajectories for the start and end of each sampling episode (Figure S1). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

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