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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 to180 pg m^{-3}, with an average concentration of 88 pg m^{-3}. Generally, HCB were more uniform than other organchlorine 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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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 m^3 (at 0 °C and 1 atm, flow rate of ~1.0 m^3 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 m^3. 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±