

Atmospheric HCH Concentrations over the Marine Boundary Layer from Shanghai, China to the Arctic Ocean: Role of Human Activity and Climate Change

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From July to September 2008, air samples were collected aboard the research expedition icebreaker XueLong (Snow Dragon) as part of the 2008 Chinese Arctic Research Expedition Program. Hexachlorocyclohexane (HCH) concentrations were analyzed in all of the samples. The average concentrations (\pm standard deviation) over the entire period were 33 ± 16 , 5.4 ± 3.0 , and 13 ± 7.5 pg m^{-3} for α -, β - and γ -HCH, respectively. Compared to previous studies in the same areas, total HCH (Σ HCH, the sum of α -, β -, and γ -HCH) levels declined by more than $10\times$ compared to those observed in the 1990s, but were approximately $4\times$ higher than those measured by the 2003 China Arctic Research Expedition, suggesting the increase of atmospheric Σ HCH recently. Because of the continuing use of lindane, ratios of α/γ -HCH showed an obvious decrease in North Pacific and Arctic region compared with those for 2003 Chinese Arctic Research Expedition. In Arctic, the level of α -HCH was found to be linked to sea ice distribution. Geographically, the average concentration of α -HCH in air samples from the Chukchi and Beaufort Seas, neither of which contain sea ice, was 23 ± 4.4 pg m^{-3} , while samples from the area covered by seasonal ice ($\sim 75^\circ\text{N}$ to $\sim 83^\circ\text{N}$), the so-called "floating sea ice region", contained the highest average levels of α -HCH at 48 ± 12 pg m^{-3} , likely due to emission from sea ice and strong air-sea exchange. The lowest concentrations of α -HCH were observed in the pack ice region in the high Arctic covered by multiyear sea ice ($\sim 83^\circ\text{N}$

to $\sim 86^\circ\text{N}$). This phenomenon implies that the re-emission of HCH trapped in ice sheets and Arctic Ocean may accelerate during the summer as ice coverage in the Arctic Ocean decreases in response to global climate change.

1. Introduction

Technical hexachlorocyclohexane (HCH), which is mainly composed of α -, β -, γ -isomers, has been used as insecticides since 1943 (1). Only γ -HCH known as lindane is insecticidally active (2). Usage of technical HCH was banned in most western countries and Japan in the 1970s but continued in China and Russia until 1983 and 1990. In 1990, India also banned technical HCH for agricultural use but kept it for public health uses (3). Technical HCH usage steadily declined and is now virtually out of use worldwide. However, there are indications that the use of stockpiles, limited use for public health purposes and/or illegal use cannot be excluded (4). Due to their high volatility, α -HCH and γ -HCH have spread globally via long-range atmospheric transport (LRAT) (5, 6). Once these compounds are released into the environment, they can migrate through the atmosphere as gases and condense in low-temperature regions such as the Arctic (7). Therefore, the Arctic Ocean has become one of the important global sinks of HCHs. Environmental modeling has suggested that about half of the global α -HCH inventory remains in the Arctic oceans (8). Due to the direct connection facilitated by atmospheric transport, α -HCH concentrations in Arctic air samples have shown a rapid response to changes in global emissions resulting from regulation of HCH usage: atmospheric α -HCH concentrations in the Arctic declined about 50% when China stopped using technical HCH in 1983, and declined more than 60% after India and the former Soviet Union banned technical HCH in 1990 (2). However, as atmospheric levels of HCHs continue to decrease, the direction of air–water exchange of these pollutants in oceans may change from deposition to volatilization (9). A reversal of the air–sea exchange of α -HCH from net deposition to outgassing was observed in the Bering Sea and Arctic Ocean, e.g., the Chukchi Sea, between the 1988 and 1993 (10). Consequently, the re-emission of α -HCH from the Arctic Ocean may become an important source now. During the ice retreat in Arctic, the evaporation of old storage of HCH from sea ice may become another important source (11, 12).

The 2003 Chinese Arctic Research Expedition (CHINARE-2003) from the Bohai Sea to the Arctic onboard the icebreaker Xuelong collected air samples for the analysis of HCHs (9), and the spatial distribution, source identification, long-range transportation, and sea–air exchange of HCHs were investigated (9). In order to update this information for HCHs in respond to rapid changes in the Arctic environment, air samples were collected during the 2008 Chinese Arctic Research Expedition (CHINARE2008) and compared with the observations of CHINARE2003 to elucidate changes in HCH levels and distribution.

2. Methodologies

2.1. Sampling. During CHINARE2008, 38 particulate samples and 23 gas phase samples were collected from July to September between the Bohai and the Arctic (33°N to 85°N). A high volume air sampler controlled by a wind sensor was placed on the upper-most deck of the ship. The preparation, collection, storage, and transportation of samples were accomplished by use of previously established methods (9) with minor modifications. The details can be found in Supporting Information.

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2.2. Sample Treatment and Analytical Procedures. The Junge–Pankow adsorption model (13) and previous field studies (14, 15) have indicated that HCHs occur predominantly in the gas phase at moderate temperatures, thus gas phase samples were selected to analyze. Analysis of HCHs was accomplished by use of previously established methods with modifications (16, 17). Instrumental analysis of HCHs was performed using a GC (Agilent 7890A) equipped with a mass-selective detector (Agilent 5975c) in the negative chemical ionization (NCI) mode. Details of the extraction and chemical analysis can be found in Supporting Information.

2.3. Quality Control. Three field blanks, six laboratory blanks, and three downward PUFs were processed to check for laboratory and field contamination. Little or no HCH isomers were detected in the blanks and downward PUFs, indicating contamination during the analysis was negligible and no breakthrough occurred during the sampling. Samples were blank corrected using the mean of the field blanks. Method Detection limits (MDL) defined as mean of field blank with $3 \times$ the standard deviations were 0.26 pg m^{-3} , 0.39 pg m^{-3} , and 0.62 pg m^{-3} for α -HCH, β -HCH, and γ -HCH, respectively, when calculated with an average sampling volume of 1732 m^3 . Surrogate recovery ($n = 32$, including field and laboratory blanks) was $96 \pm 13\%$ for PCB 30. The recoveries ($n = 3$) of analytes from spiked PUF plugs were $81 \pm 7\%$, $102 \pm 7\%$, and $76 \pm 12\%$ for α -HCH, β -HCH, and γ -HCH, respectively.

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 (18). BTs were traced for 5 days with 6 h steps at 100, 500, and 1000 m above sea level for the mean location of the start and end of one sampling episode. Air mass origins were generally indicated in Figure S1 of the Supporting Information (SI).

3. Results and Discussion

3.1. Spatial Distribution of HCH Levels. To elucidate the spatial distribution of HCHs in the air samples, sampling sites were geographically separated into four groups: East Asia, North Pacific Ocean, Chukchi and Beaufort Seas and central Arctic Ocean (Table S1 of the SI). In the Arctic Ocean, the fate of HCHs was complex and may be influenced by the air-sea exchange and retreat of sea ice. This region was further divided into two subgroups: the Chukchi and Beaufort Seas characterized by open water, and the central Arctic Ocean covered by seasonal or multiyear sea ice. Σ HCHs (the sum of the three isomers) during the whole cruise ranged from 1.6 to 97 pg m^{-3} (Table S1 of the SI). The spatial distribution of Σ HCHs is shown in Figure 1. The highest concentration was observed near the east coastline of Russia (Site 4). Geographically, the average concentration of Σ HCHs from high to low was in the following order: North Pacific Ocean ($65 \pm 21 \text{ pg m}^{-3}$), central Arctic Ocean ($48 \pm 33 \text{ pg m}^{-3}$), East Asia ($41 \pm 1 \text{ pg m}^{-3}$) and the Chukchi and Beaufort Seas ($40 \pm 6 \text{ pg m}^{-3}$).

Concentrations of α -HCH varied between 1.1 and 59 pg m^{-3} , with an average \pm standard deviation of $33 \pm 16 \text{ pg m}^{-3}$ (Table S1 of the SI). These concentrations increased in the North Pacific Ocean and peaked near eastern Russia, then decreased in the Chukchi and Beaufort Seas. α -HCH levels in the high-latitude Arctic Ocean were highly variable, and both of the sites with the highest (site 21) and lowest (site 19) concentrations were found in this area.

Concentrations of γ -HCH ranged up to 36 pg m^{-3} , while the level in one sample was less than the MDL (Site 19). The highest concentration was observed near the eastern coast of Russia (Site 4). A decreasing trend of γ -HCH levels with increasing latitude was observed in the samples from the

North Pacific, Chukchi and Beaufort Seas, to the high-latitude Arctic, with average concentrations of 18 ± 8.5 , 11 ± 5.3 , and $8.9 \pm 6.2 \text{ pg m}^{-3}$, respectively (Table S1 of the SI). Both α -HCH and γ -HCH concentrations were relatively high near eastern Russia.

In addition to α -HCH and γ -HCH, β -HCH was also quantified, since it is more bioaccumulative and toxic than the other stereoisomers (19). Concentrations of β -HCH ranged from below MDL (Site 19) to 11 pg m^{-3} with an average of $5.4 \pm 3.0 \text{ pg m}^{-3}$. Lower concentrations were observed in the Japan Sea (Site 1) and in the high-latitude area covered by multiyear sea ice (Sites 17 and 19). Levels in most of the samples from the North Pacific and lower-latitude Arctic showed minor variation, ranging from approximately 5 to 8 pg m^{-3} .

3.2. Temporal Variations of HCH Levels. Globally, the levels of Σ HCHs in the marine boundary layer obtained since 2000 varied from below MDL to 100 pg m^{-3} (1, 20–22). The measurements obtained in the present study were in the range of these previous results. The average concentration of Σ HCHs over the entire cruise ($51 \pm 24 \text{ pg m}^{-3}$) was higher than that observed during the CHINARE2003 campaign by a factor of 3.8 (9), while Σ HCH levels were reported to have declined by more than $10 \times$ over the last 20 years in the open sea areas near east Asian Countries, North Pacific Ocean, and Arctic Ocean (23) (Table S2 of the SI).

Among areas in East Asia, α - and γ -HCH levels in the present work were comparable to monitoring data collected in the same oceanic area (9), but were lower than those for a coastal site of Qingdao and Dalian, China (24, 25), while β -HCH levels were lower than those reported in air samples collected over the surrounding land in 2003 (25). Compared with measurements made during 1989–1990 (23), the level of α -HCH declined by about $20 \times$ in the East Asian Ocean, but no obvious declining trend for γ -HCH was found. In the North Pacific Ocean, levels of α - and γ -HCH were higher by factors of about 2.8 and 6.5 than those reported by CHINARE2003 (9), but about 2.6–13 and 1.3–4.2 \times lower than levels measured in the 1990s (10, 23) (Table S2 of the SI).

In the Chukchi and Beaufort Seas and Central Arctic Ocean, α - and γ -HCH concentrations measured in the present study were lower than the measurements in the same area in 1990s (10, 14, 23), but higher than the measurements of CHINA2003 (9). Compared to these measurements carried in Arctic Stations after 2000, our data of α - and γ -HCH were in the same range (Table S2 of the SI) (6, 24, 26). It is notable that α - and γ -HCH levels during 2000–about 2004 were lower than previous studies in the 1990s (Table S2 of the SI), indicating a general decrease of α - and γ -HCH in the Arctic, especially in the high-latitude region (e.g., ALERT) during the 1990s and 2000–about 2004. However, a comparison of α - and γ -HCH levels during 2000–about 2004 to those reported here as well as in previous studies showed a slight increase in levels of α - and γ -HCH in the Arctic Ocean since 2005 (e.g., levels of α - and γ -HCH in ALERT after 2004 were about $2 \times$ higher than those during 2000–about 2004, and were comparable to those in 1990s. Table S2 of the SI). Levels of β -HCH measured in the present study were higher than previous measurements (6, 14).

3.3. Potential Sources of HCHs. **3.3.1. Potential Sources and Pathways of HCHs.** The spatial distribution and temporal variations of HCHs discussed above were attributed to the different sources and pathways of HCH isomers. As the route for the East Asia and North Pacific Ocean locations was close to the coast of the Eurasian continent, air masses in this area were predominantly continental or partly continental and partly oceanic. In Chukchi and Beaufort Seas and central Arctic Ocean, the air masses for some samples originated from the Arctic Ocean, while those of other samples originated



FIGURE 1. Spatial distribution of HCHs in the North Pacific Ocean and the Arctic Ocean. Concentrations are shown with the average values for different sampling sites.

from the adjacent land masses of Eurasia and North America (Figure S2 of the SI). Noteworthy, there is some uncertainty associated with the back trajectory due to the changing position of the ship and long sampling period.

In East Asia and North Pacific Ocean, similar to those in 2003 (9), relatively higher levels of α- and γ-HCH were observed near eastern Russia. For α-HCH, there are two potential reasons for this pattern. The first is the role of LRAT from Russia revealed by air mass BTs (Figure S1 of the SI). The former Soviet Union was one of the major consumers of technical HCH (2), and previous measurement of HCH in major north-flowing rivers in Russia in 1990s also suggested that Russia was an important source area of HCH (3). Hence, α-HCH may be released from contaminated soils through revolatilization and transported to the adjacent North Pacific and Arctic (2). Measurements carried out at Arctic stations around Arctic Ocean also found higher α-HCH concentrations at Valkarka (more than 3× higher than at Alert and Zeppelin) (6) (Table S2 of the SI). Combined with the relatively higher α-HCH levels found during CHINARE2008

than CHINARE2003 (9) (Table S2 of the SI), the usage of technical HCH may still exist in Russia these years. In fact, a local source of α-HCH was the usage of technical HCH in the Russian North against nuisance insects on domesticated reindeer by indigenous human populations (4). The second reason may be attributed to re-emission of α-HCH from seawater near the east of Russia. A global distribution model found that peak concentrations of α-HCH in both the atmosphere and seawater occurred in the area of 60° N (27). The model results indicated that the direction of sea-air exchange changed from net deposition in the 1980s to net volatilization in the 1990s in this region (27). Although no significant uses of technical HCH have been reported after 2000, currently lindane is still used in some area (28, 29). Higher levels of γ-HCH detected near the eastern coast of Russia in the present study suggest potential continuing usage of lindane in Russia and adjacent areas. The ratios of α/γ-HCH also showed the same result, details will be discussed next. It is worth to notice that the manufacture of lindane in Eurasia has also resulted in huge amount of HCH residuals (4). The

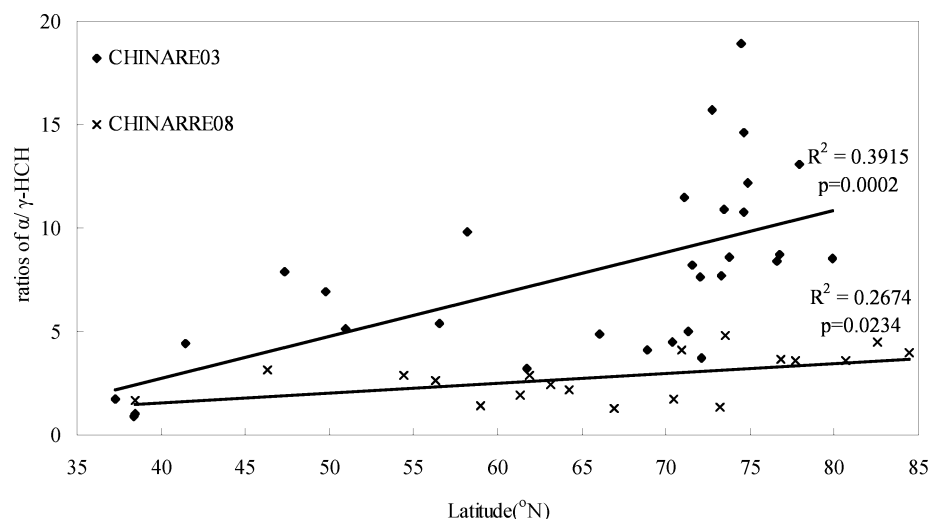


FIGURE 2. Latitudinal variation of α/γ -HCH ratios during the CHINARE03 (10) and CHINARE08 sampling expeditions.

management of these hazardous waste and stockpiles of HCH residuals may increase the potential of emission of α - and β -HCH these years.

In the Arctic, the sources of atmospheric α -HCH are complex. Since technical HCH has been phased out worldwide since 2000 (29), concentrations of α -HCH in the atmosphere are expected to decrease. However, higher levels of α -HCH were observed in this study and others carried out after 2005 (Table S2 of the SI). This phenomenon may be ascribed to several factors, including LRAT from Eurasia (30, 31) and re-emission of α -HCH due to ice loss (32, 33). The decline in the global use of α -HCH and hence the reduction in primary sources, may make the role of environmental processing (e.g., air surface exchange) and influence of climatic variability on the levels in Arctic region more evident (26). The detail will be discussed in the next section. Canada, where lindane was widely used as a treatment on crop seeds until 2003 (34), could be a possible source region of γ -HCH (35).

Unlike the case for α -HCH and γ -HCH, the far lower Henry's law constant and higher water solubility of β -HCH (36, 37) does not favor direct atmospheric transfer of this isomer to the cold aquatic reservoir of the Arctic Ocean (38). Oceanic flow through the Bering Strait may be an important pathway for β -HCH transportation to the Arctic (38). However, fairly high concentrations and proportions of β -HCH are found in the air of source regions and coastal area of East Asia (25), suggesting that atmospheric transport of β -HCH can occur (38). For relatively high concentrations of β -HCH found in the present study, especially in North Pacific Ocean and relatively lower-latitude Arctic region, there are two potential explains. The first is outgassing of β -HCH from seawater, especially in summer. Because the Bering-Chukchi region was the important pathway and reservoir of β -HCH, seawater levels of β -HCH in this area were relatively higher (4, 38). During summer time, water solubility of β -HCH decrease with increasing temperature (4), yielding an increasing gradient of outgassing, especially in Bering-Chukchi region. Previous measurement carried out at the Arctic station Valkarkai (Bering-Chukchi region) during summer of 2002 also found relatively high air levels of β -HCH (Table S2 of the SI), suggesting the outgassing of β -HCH from seawater may happen in Chukchi Sea (6). Another factor which may contribute to the high levels of β -HCH is advective inputs from adjacent landmasses. As discussed above, although technical HCH has been banned in East Asian countries and Russian, some stockpiles and usage of technical HCH are believed to still exist (4, 31, 39). Air masses collected in North Pacific Ocean and relatively lower-latitude Arctic region were

primarily originated from adjacent land masses of Eurasia (Figure S1 of the SI). Hence, the advective input of β -HCH from Eurasia was a potential important source for β -HCH.

3.3.2. Sources of HCH Identified by α/γ -HCH. Beside the residue concentrations, the composition of HCH related isomers could be used as complementary and available tools to understand the origin and the pathway of air mass in the LRAT of these contaminants. Technical HCH consists of 60–70% α -HCH, 5–12% β -HCH, and 10–15% γ -HCH and other minor isomers (23), while lindane consists of more than 99% of γ -HCH (23, 40). Due to the selective depletion of the less stable and more water-soluble γ -HCH, relatively higher ratios have been found in old air masses (41). However, continuing use of lindane may reduce the α/γ -HCH in remote regions through LRAT of γ -HCH from source regions, as there has been no usage of technical HCHs worldwide since 2000 (29). In the present study, α/γ -HCH ratios in East Asia, North Pacific Ocean and Chukchi and Beaufort Seas were in the range of 1.3–4.8 and with the average about 2.5. These ratios were much lower than these measurements in East China Sea, North Pacific Ocean and Chukchi Sea in 1990s (10, 23), and were about a half of those reported by CHINARE2003 (9) (Table S2 of the SI). Lower α/γ -HCH ratios found in the present study may suggest the influence of lindane usage in the adjacent terrestrial regions recently. In the Arctic, α/γ -HCH ratios were ranged from 3.6–4.5 (Table S2 of the SI) and were close to the value of technical HCH, but lower than those reported by CHINARE2003 (9.6 ± 4.1) (9). Compared with these measurements in Arctic Stations, the α/γ -HCH ratios in the present study were lower than those for Alert, but comparable with those for Zeppelin (26) (Table S1 of the SI). As mentioned above, the decrease of α/γ -HCH ratios during 2003 to 2008 in the Arctic Ocean (Figure 2) may be due to the continuing use of lindane after the phase out of technical HCH. Along the cruise, α/γ -HCH ratios showed an increasing trend from low latitudes to high latitudes (Figure 2), likely because of the different physical and chemical properties of the isomers. As γ -HCH has a lower Henry's Law Constant (H) than α -HCH, γ -HCH preferentially partitions into seawater (42) and is more susceptible to washout by precipitation (43). Chamber experiments also showed that α -HCH has a long atmospheric lifetime (120 days) compared to γ -HCH (96 days) based on $-\text{OH}$ reactions (44). All of these properties lead to a lower residence time of γ -HCH in the atmosphere compared to that of α -HCH, resulting in increased α/γ -HCH ratios.

3.4. Role of Sea Ice Distribution in the Arctic Ocean. In this study, levels of α -HCH in the Arctic Ocean showed high variation. Both the highest (Site 21) and lowest (Site 19)

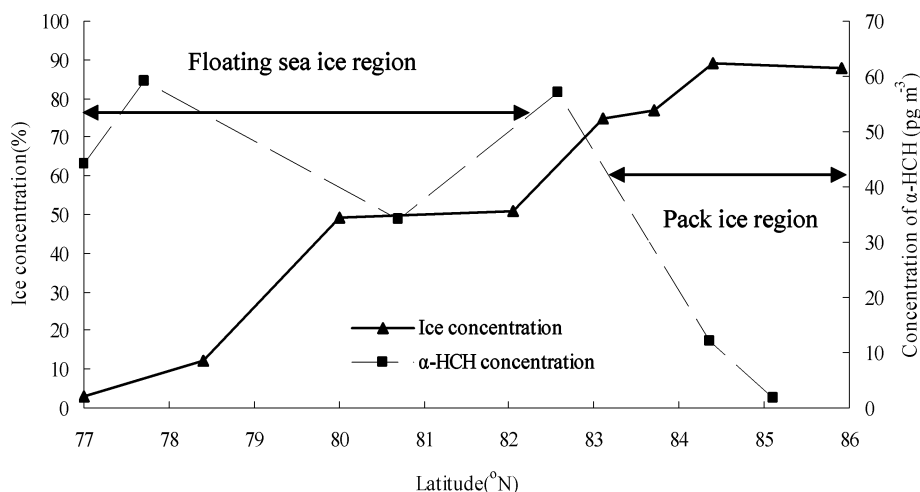


FIGURE 3. Sea ice distribution (derived from aerial surveys by helicopter flights during the CHINARE08) ⁴⁵ and air concentrations of α -HCH in Central Arctic Ocean.

concentrations were found in this region. In the Chukchi and Beaufort Seas (from $\sim 70^\circ\text{N}$ to $\sim 75^\circ\text{N}$) with open water during the cruise (45), the average concentration of α -HCH was $23 \pm 4.4 \text{ pg m}^{-3}$. The levels of α -HCH in this region showed little variation. However, concentrations of α -HCH showed an abrupt increase with increasing latitude. In the area of $\sim 75^\circ\text{N}$ to $\sim 83^\circ\text{N}$ (Sites 13, 15, 20, and 21), the so-called “floating sea ice region” covered by the seasonal ice (45), the average concentration was $48 \pm 12 \text{ pg m}^{-3}$ and was about $2\times$ higher than that in the Chukchi and Beaufort Seas. At even higher latitudes where the ocean was covered with multiyear sea ice, the so-called “pack ice region” (45), an abrupt decrease of α -HCH concentrations was observed from $\sim 83^\circ\text{N}$ to $\sim 86^\circ\text{N}$ (Sites 17 and 19) (Figure 3). This pattern implied that the fate of α -HCH is strongly affected by air-sea exchange and the distribution of sea ice in the Arctic Ocean.

According to Henry’s law, equilibrium with atmospheric α -HCH concentrations should produce an average surface water concentration of 0.87 ng L^{-1} (0°C) in the Chukchi and Beaufort Seas based upon an average concentration in air of 23 pg m^{-3} . Previous investigations reported that the seawater concentration of α -HCH in the Beaufort Sea was $4.5\text{--}7.1 \text{ ng L}^{-1}$ in 1986 to 1993, and $3.9\text{--}5.4 \text{ ng L}^{-1}$ in 1999 (46). Assuming that the average α -HCH concentration in seawater does not change significantly (change to $<0.94 \text{ ng L}^{-1}$), it should be supersaturating. This is in agreement with previous observations, which indicated that net re-evaporation from sea to air was prevailing in this region (9, 10, 32, 33). Due to technical HCH being banned for a long time, volatilization from seawater may currently be the significant source of α -HCH to the Arctic atmosphere.

The higher concentrations of α -HCH measured in air samples from the floating sea ice region ($\sim 75^\circ\text{N}$ to $\sim 83^\circ\text{N}$) compared to those from open sea areas may be ascribed to two potential reasons. One is the retreat of sea ice in response to climate warming during the cruise. It is known that precipitation in the form of snow results in the accumulation of α -HCH in the seasonal snowpack and sea ice (47). Measurements during the 1980s indicated that the concentrations of α -HCH in sea ice were $0.3\text{--}1.3 \text{ ng L}^{-1}$ (48). According to the data of National Snow and Ice Data Center (NSIDC), the monthly ice extent in August 2008 was the second-lowest recorded over the period of 1979 to 2008 (49). Modeling work has predicted that HCHs will evaporate into the atmosphere during ice or snow melts (11, 12). Therefore, when sea ice was widely lost in the summer of 2008, α -HCH stored in the multiyear ice and seasonal ice may have been emitted into the atmosphere (45, 49). The other reason can be ascribed to enhanced air-sea exchange. As technical HCH

has been banned by most countries, the air concentration of α -HCH decreased in the Arctic, declining by 14-fold during 1980–1996. Alternatively, α -HCH levels in inflowing water from the Bering Strait decreased by only 33% during 1980–1995 (11). Therefore, the inventory accumulated by ocean inflow during the previous decades may become source of atmospheric HCHs. In fact, net re-evaporation of α -HCH from sea to air has been found to be prevailing in the Arctic recently (9, 10, 32, 33). Notably, a previous study indicated that the residence time of water in the Chukchi Sea is less than one year with rapid replacement from the Pacific inflow, while in the central Arctic Ocean the residence time of surface water is ten years (50). This will spatially result in different concentrations in surface water of HCHs, which increase northward from Chukchi Sea to the central Arctic Ocean (11). Measurements of α -HCH in Arctic seawater have indicated that levels in the central Arctic Ocean were higher than those in marginal seas (seas adjacent to the land’s edge or coast) (3), yielding a larger fugacity gradient in the Arctic Ocean. Once the sea ice coverage above the water is lost, the storage of α -HCH in seawater will then re-evaporate from sea to air. The increasing area of open water due to the retreat of sea ice may thus accelerate α -HCH volatilization in this region. In the region with pack sea ice ($\sim 83^\circ\text{N}$ to $\sim 86^\circ\text{N}$), it is reasonable to assume that air-sea exchange should be very low, and the concentrations of α -HCH in ambient air in this region were found to be the lowest measured.

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Supporting Information Available

Details on field sampling, sample treatment and analytical procedures; tables containing concentrations of HCHs measured in the present study and previous studies world-

wide; and a figure showing origins of air masses sampled during the cruise. This material is available free of charge via the internet at <http://pubs.acs.org>.

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