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Spatial and Seasonal Variations of Hexachlorocyclohexanes (HCHs) and Hexachlorobenzene (HCB) in the Arctic Atmosphere

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Weekly high-volume air samples were collected between 2000 and 2003 at six Arctic sites, i.e., Alert, Kinngait, and Little Fox Lake (LFL) in Canada, Point Barrow in Alaska, Valkarkai in Russia, and Zeppelin in Norway. Hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB) were quantified in all samples. Comparison showed that α -HCH and HCB were homogeneously distributed in the circumpolar atmosphere and uniform throughout the seasons. However, significantly higher atmospheric concentrations of α -HCH and HCB and stronger temperature dependence of α -HCH and γ -HCH were found at LFL in Yukon (YK), which is unique among the sites by virtue of its high altitude and low latitude, resulting in higher precipitation rates and summer temperatures. Strong temperature dependence of α - and γ -HCH at this location suggests that secondary emissions, i.e., re-evaporation from surfaces, were more important at this site than others. It is hypothesized that a higher precipitation rate at LFL facilitated the transfer of α -HCH from the atmosphere to surface media when technical HCH was still in use worldwide. On the other hand, higher temperature at LFL enhanced re-evaporation to the atmosphere after the global ban of technical HCH. In contrast to α -HCH and HCB, larger spatial and seasonal differences were seen for γ -HCH

(a currently used pesticide), which likely reflect the influence of different primary contaminant sources on different Arctic locations. Fugacity ratios suggest a net deposition potential of HCB from air to seawater, whereas seawater/air exchange direction of α -HCH varies in the circumpolar environment.

Introduction

Hexachlorocyclohexanes (HCHs) were applied globally as pest control for decades (1–3). Usage of HCHs included both technical HCH (major α -, β -, and γ -isomer) and lindane (purified γ -isomer) (1, 2). Technical HCH was banned from use in North America in the 1970s, but it was used in China until the 1980s and in India and the former Soviet Union until the 1990s (1). Lindane, the active insecticidal ingredient of the technical mixture, was still being used in the Canadian prairie region up to 2002 (3). Air concentrations of α -HCH in the Arctic adjusted to changing global emissions quickly (4). With declined primary emissions, gas exchange direction of α -HCH between seawater and air reversed in the Arctic from net deposition in the 1980s to net volatilization in the 1990s (5, 6). Modeling study further suggests that about half of the global α -HCH inventory was in the Arctic oceans (7). Hexachlorobenzene (HCB) was used for industrial and agricultural purposes historically, and its production and emissions peaked in the late 1970s and early 1980s. Current HCB is from both secondary emissions (e.g., re-emission from soils and sediments) and primary emissions (e.g., byproducts of chlorinated chemicals and incomplete combustion processes) (8). Air concentrations of HCB showed uniform behavior in continental and semi-hemisphere scales (8–10).

Compared to other organic contaminants, long-range transport (LRT) potential of α - and γ -HCH and HCB is higher (11), and they dispersed faster globally (8). Improved understanding of legacy α -HCH and HCB may facilitate prediction of environmental pathways and fate of other organic contaminants in the Arctic. In this study, a unique large set of HCH and HCB measurements in Arctic air was obtained from collaborative study between an air monitoring program under NCP (Northern Contaminants Program) and other Arctic monitoring programs, i.e., measurements in Point Barrow and Zeppelin (12–14). The overlapped sampling periods at the six sites in 2000–2003 allow the comparison of spatial and seasonal variations of these compounds in the Arctic atmosphere. These six sites cover a large area of the Arctic and data comparison could provide insight into potential contaminant sources (e.g., LRT or local secondary emissions) and environmental behavior in the entire circumpolar atmosphere. Air measurements conducted in this study, together with observations in seawater, may further shed light on seawater/air exchange potentials.

Materials and Methods

Field Sampling. Samples were collected in the Canadian (i.e., Little Fox Lake [LFL] and Kinngait [KNG]), American (i.e., Point Barrow [PTB]), and Russian (i.e., Valkarkai [VKK]) Arctic between 2000 and 2003. During this period of time, long-term air monitoring programs were also in operation at Alert, Canada (ALT, started in 1992) and Zeppelin, Norway (ZPN, started in 1993). The available monitoring data at these two sites were included to expand spatial coverage in this study. The site map is shown in Figure 1. Detailed site information and sampling periods can be found in Table S1

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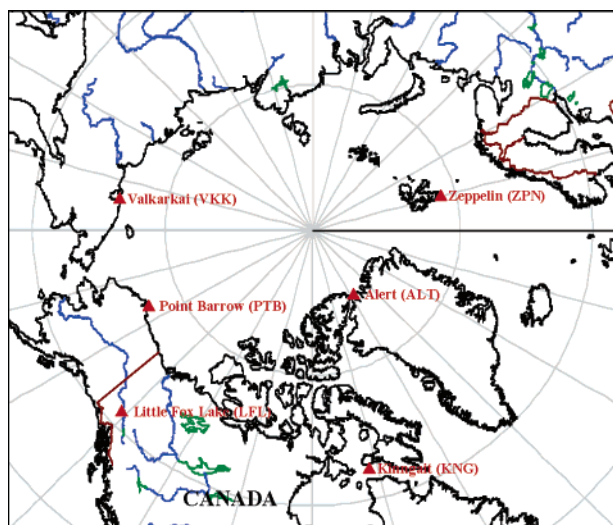


FIGURE 1. Sampling site map.

of the Supporting Information. LFL is quite unique among the six sites: (i) higher altitude—higher precipitation rates; (ii) lower latitude—higher temperatures; (iii) the only inland site—stronger diurnal temperature variations.

Weekly HiVol air samples of $\sim 13\,000\text{ m}^3$ of air were taken over 7 days at all sites, except for ZPN, where a 48-hr sample was collected weekly ($\sim 1000\text{ m}^3$). Each sample set was composed of one glass fiber filter (GFF) and two polyurethane foam (PUF) plugs. Samples were prepared and extracted by AirZone One for ALT, KNG, LFL, and PTB, whereas VKK samples were extracted by Typhoon Laboratory in Russia. Extracts of all five sites were analyzed by Freshwater Institute, Canada. Sampling and analytical methods can be found elsewhere (12, 15). The samples at ZPN were collected, extracted, and analyzed by the Norwegian Institute for Air Research (NILU) (14). A detailed description of field sampling and sample treatment is listed in the Supporting Information.

Quality Assurance/Quality Control (QA/QC). Strict QA/QC procedures were followed as published previously (12, 15, 16). GFF and PUF blanks were taken once every four weeks at all sites. Mean blank (B) and standard deviation (SD) were calculated for PUF (i.e., B_{PUF} and SD_{PUF}) and GFF (i.e., B_{GFF} and SD_{GFF}) individually at each site over the entire sampling period. Method detection limit (MDL) was defined as the mean B plus $3SD$. Since total air concentration (i.e., AC composite) was composed of one GFF and two PUFs, MDL of AC was calculated from B_{GFF} , B_{PUF} , SD_{GFF} , and SD_{PUF} as follows:

$$MDL_{\text{AC}} = (B_{\text{GFF}} + 2B_{\text{PUF}}) + (SD_{\text{GFF}}^2 + 2SD_{\text{PUF}}^2)^{0.5} \quad (1)$$

Mean blanks (B_{AC} or $B_{\text{GFF}} + 2B_{\text{PUF}}$) and derived MDL s of AC samples (MDL_{AC}) are summarized in Table S2 of the Supporting Information. Compounds below instrument detection limits (IDL s) were substituted with $2/3$ IDL s. Data reported here were not blank-corrected, and they are available in Excel format upon request. Total sample number (n) and sample number above MDL s (n') at each site are summarized in Table S2.

Results and Discussion

Gaseous and particle-bound concentrations were combined for individual HCHs and HCB in the current data analysis, since particle-bound phase accounts for only a minor fraction ($<5\%$) of the total concentrations of HCHs and HCB in the Arctic, e.g., at Alert (17).

Spatial and Seasonal Variations of Air Measurements. To illustrate differences in seasonality of HCH and HCB air

concentrations, monthly averages were calculated by averaging all samples collected in the same month, not necessarily from the same year at each site. The monthly average concentrations were further normalized by the total yearly concentrations (i.e., sum of 12 monthly concentrations) to enhance the seasonal profiles. Spatial variations were illustrated by comparing overall and monthly mean concentrations of all HCHs and HCB at the six sites, whereas seasonality was compared by the normalized seasonal profiles among these sites. Note that sampling at VKK only occurred during the warm period of July to September; therefore, seasonal variability analysis does not include this site.

α -HCH. Monthly concentrations of α -HCH are shown in Figure S1A for the six sites. Box-and-whisker plots in Figure 2A summarize all α -HCH air measurements at the six sites. Figure 2A indicates that mean or median air concentrations of α -HCH were comparable in the circumpolar environment (i.e., ALT, KNG, PTB, and ZPN) (Table S3). Slightly higher α -HCH mean or median concentrations at VKK were probably due to summer sampling only (i.e., July–September), since summertime peaks were seen at the other stations as well (Figures S1A and 2B). However, a Student's t -test shows significantly higher air concentrations of α -HCH measured at LFL compared to the other four sites ($p < 0.0001$). To illustrate seasonal variations, monthly concentrations were normalized to percentages (%) by total yearly concentrations, as shown in Figure 2B for α -HCH. In general, seasonal profiles of α -HCH were fairly comparable among the four high Arctic sites (without VKK and LFL), but slightly different seasonality was found at the low Arctic site of LFL. The monthly normalized concentrations varied less than a factor of 3 and ranged from 4.7% to 14% between seasons at these four sites, i.e., higher concentrations in late summer and lower concentrations in winter. Relatively uniform distribution of α -HCH with less seasonal variation in the high Arctic atmosphere is consistent with the fact that the use of technical HCH was phased out worldwide, which is also supported by the nearly normal distribution of α -HCH air concentration at the four high Arctic sites (Figure 2C, $n = 387$). The arithmetic mean of α -HCH among the four high Arctic site was $23 \pm 10\text{ pg}\cdot\text{m}^{-3}$ ($n = 387$). In other studies, air concentrations of α -HCH were reported as $\sim 40\text{ pg}\cdot\text{m}^{-3}$ between July and August 1999 in Canadian Archipelago (18), and from 12 to $21\text{ pg}\cdot\text{m}^{-3}$ in July 2000 in the Atlantic Ocean between 75° N and 80° N (19).

Using the Clausius–Clapeyron equation, the relative contribution of re-evaporative emissions from local surfaces (e.g., soils, water, vegetation, etc.) versus advective LRT inputs can be assessed at a given sampling site (15, 20–22). Regression results of the natural logarithm of partial pressure (P , Pa) against reciprocal temperature (T , K) for α -HCH are summarized in Table S4 for all five sites except VKK, where only five samples were taken. All regressions of α -HCH were found statistically significant at a 95% confidence level (i.e., $p < 0.05$, Table S4). A higher correlation coefficient R^2 (0.50) and steeper slope m (-2200 ± 430) were found at LFL compared to the other four high Arctic sites. This suggests that 50% of the variation in atmospheric α -HCH concentrations can be explained by seasonal temperature changes. Also, the steeper slope m at LFL indicates greater dependence of atmospheric α -HCH on ambient temperature and stronger secondary emissions of α -HCH from surrounding surfaces. LFL is very close to Tagish ($\sim 160\text{ km}$ southeast of LFL) of Yukon (YK) where HiVol air sampling took place between 1992 and 1995 (15, 22). The slope m of α -HCH from this study was comparable to that found at Tagish previously ($m_{\text{Tagish}, \alpha\text{-HCH}} = -2395 \pm 525$) (15), although air concentrations reduced approximately by a factor of 1.5, suggesting that secondary emissions of α -HCH remained important in YK region. This is likely due to elimination of α -HCH primary

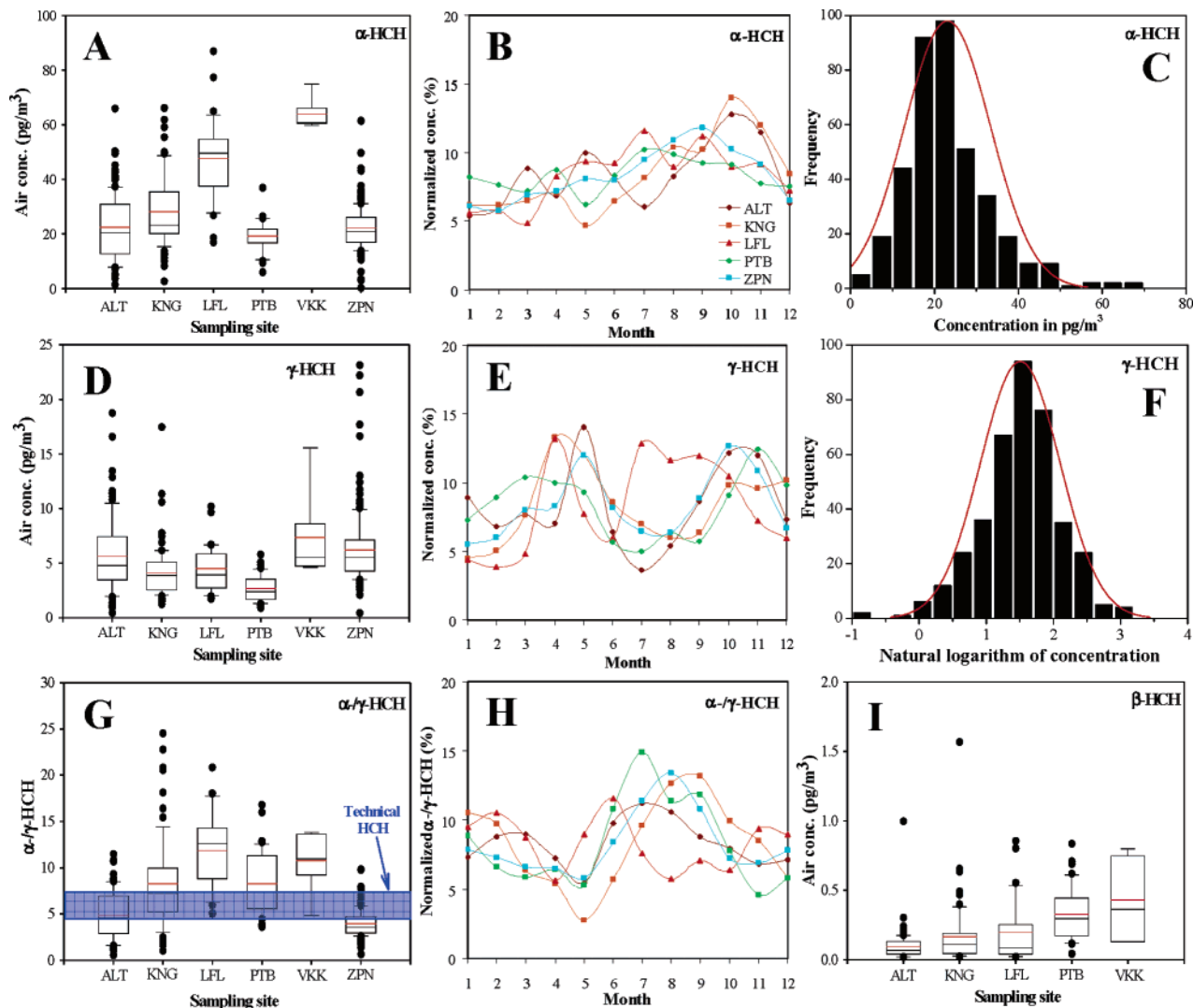


FIGURE 2. Box-and-whisker plots for α -HCH (A), γ -HCH (D), α/γ -HCH ratio (G), and β -HCH (I); normalized monthly concentrations (i.e., monthly concentrations divided by yearly total concentrations) for α -HCH (B), γ -HCH (E), and α/γ -HCH ratio (H); histograms for concentrations of α -HCH (C, $n = 387$) and natural log concentrations of γ -HCH (F, $n = 386$) in circumpolar air (i.e., ALT, KNG, PTB, and ZPN). In the box-and-whisker plots, the center box is bounded by the 25th and 75th percentiles, and whiskers indicate the 10th and 90th percentiles. Dots are outliers of the 10th and 90th percentiles. The black and red horizontal lines represent the median and arithmetical mean, respectively.

emission sources and consequent declined air concentrations in the Arctic (1, 4). Since no concurrent soil measurements were available at the sampling sites, re-evaporation potentials from soils cannot be evaluated directly. However, water/air exchange potential will be discussed later.

γ -HCH. Monthly average air concentrations of γ -HCH are shown in Figure S1B. Larger spatial and seasonal variations were observed for γ -HCH compared to α -HCH (Figure S1A). Figure 2D lists all measurements of γ -HCH at the six sites. Relative to α -HCH, differences between mean and median values appeared greater for γ -HCH at each site (Table S3), indicating that its air concentrations were not normally distributed (see below). Mean concentration of γ -HCH ranged from 2.7 pg·m⁻³ at PTB to 7.4 pg·m⁻³ at VKK. The large variability in γ -HCH air concentrations was not surprising since lindane was still registered for use between 2000 and 2003 in some countries (2, 3, 23). Seasonal profiles were similar at the four sites in the high Arctic, showing bimodal seasonal behavior (Figure 2E). This was previously reported for both legacy and current-use pesticides at ALT and has been termed “Spring Maximum Event” (13). One plausible explanation is that the two elevated events of γ -HCH were caused by application during the springtime followed

by tilling of soils in the fall. However, the red line in Figure 2E indicates different seasonality of γ -HCH at LFL.

Regressions of $\ln P$ versus $1/T$ were statistically significant at LFL, KNG, and ZPN at the 95% confidence level (Table S4). Same as with α -HCH, a higher correlation coefficient R^2 (0.55) and steeper slope m (-2900 ± 530) were found for γ -HCH at LFL than at the other sites. Steeper slope m indicates secondary emissions of γ -HCH were more important at LFL than the other Arctic sites. The slope m for γ -HCH was also similar to what was observed at Tagish in the 1990s ($m_{\text{Tagish}, \gamma\text{-HCH}} = -2700 \pm 425$) (15), suggesting the importance of secondary sources in YK region. At LFL, temperatures were above 0 °C between May and September and peaked in July (14 °C, Figure S2A). However, elevated concentrations of γ -HCH were found in spring and July–October (Figure 2E), a 1-month lag compared to the air temperature profile. The higher concentrations of γ -HCH during the summer were consistent with temperature-driven secondary emissions at LFL. Slightly higher concentrations of γ -HCH during the spring and fall were likely influenced by application and tilling of soils, respectively, and its consequent LRT to this site, which was also observed at the other locations (Figure 2E). Figure 2F ($n = 386$) shows the histogram for natural logarithm

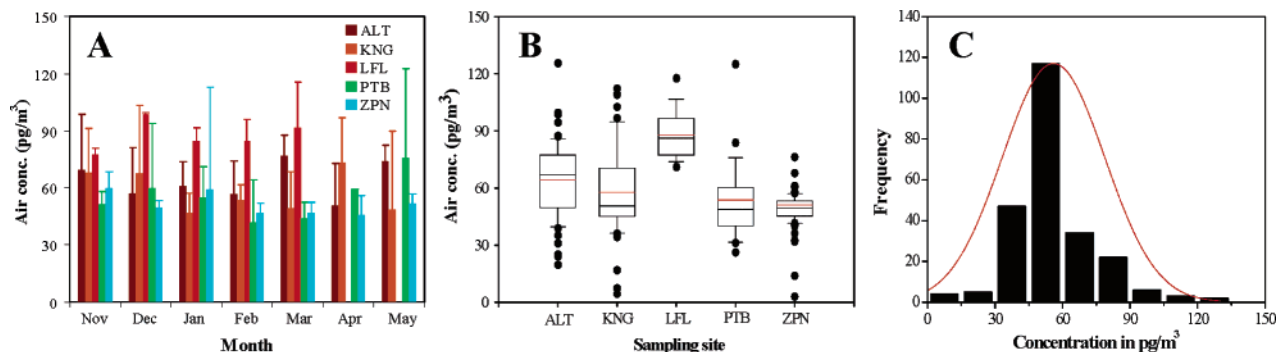


FIGURE 3. Monthly average air concentrations of HCB between November and May at five Arctic sites (A); box-and-whisker plots of HCB concentrations (B); histogram of HCB concentration ($n = 241$) among the four high Arctic sites (C), i.e., ALT, KNT, PTB, and ZPN (red line represents normal distribution).

of γ -HCH concentrations among the four high Arctic sites. Unlike α -HCH, γ -HCH is not normally distributed. Instead, a log-normal distribution describes the data better. This reflects seasonal and spatial variations of γ -HCH in global usage.

α -/ γ -HCH. The ratio of α -/ γ -HCH in air is used to follow emission sources and transport of technical HCH versus lindane (24). Ratios of α -/ γ -HCH were calculated for every sample at all sites and summarized in Figure 2G. The blue band represents an approximated ratio range in the technical mixture (i.e., 4–7) (5, 25). The mean ratios at KNG and PTB were close to the value of the technical mixture, indicating that HCHs were mostly affected by technical HCH at these sites. On the other hand, lower mean ratios of α -/ γ -HCH at ALT and ZPN suggested mixed influence of technical HCH and lindane usage. Higher ratios were observed at LFL and VKK. Technical HCH had been long banned in North America. Reaction rate of hydroxyl radicals with γ -HCH is higher than α -HCH in the atmosphere (26). Furthermore, γ -HCH has a lower Henry's Law Constant (H) than α -HCH. Thus γ -HCH preferentially partitions into seawater (27) and is more susceptible to washout by precipitation (28). All these factors lead to a lower residence time of γ -HCH in the atmosphere compared to that of α -HCH. Emitted technical HCH in mid-latitude source regions undergoes fractionation as it is transported globally and ultimately to the Arctic (29, 30). This may lead to high α -/ γ -HCH ratios at LFL and VKK. The seasonal α -/ γ -HCH ratios behaved similarly at the four Arctic sites, except for LFL (Figure 2H). The α -/ γ -HCH ratio was slightly enhanced during summer with a small decline in spring and fall, resulting from weak seasonality of α -HCH and elevated concentrations of γ -HCH in spring and fall (Figure 2B and 2E). The different seasonal profile of α -/ γ -HCH at LFL is mainly because of higher concentrations of γ -HCH observed during the fall.

β -HCH. In addition to α - and γ -HCH, measurements of β -HCH are often conducted since it is more bio-accumulative and toxic (25). Concentrations of β -HCH were low in Arctic air (17), and below MDL for greater than half the samples at ALT, KNG, and LFL (Table S2). However, β -HCH was above MDL in 36 of 38 samples at PTB, and 3 of 5 samples at VKK. Monthly concentrations of β -HCH are detailed in Figure S1C. Box-and-whisker plots in Figure 2I suggest that higher mean and median concentrations of β -HCH were found at PTB and VKK. At 0 °C, the water solubility of β -HCH is 6.2 and 11 times higher than α - and γ -HCH, and H of β -HCH is 30 and 12 times lower than α - and γ -HCH, respectively (31, 32). Oceanic flow through the Bering Strait is an important environmental pathway for transporting β -HCH to the Arctic environment (33). Both PTB and VKK are geographically closer to the Bering Strait than the other sites (Figure 1), where elevated seawater concentrations of β -HCH were observed (33). The high air concentrations suggest that

outgassing of β -HCH from seawater was likely an important source at PTB and VKK, as discussed later.

HCB. To avoid bias as a result of breakthrough, data comparison of HCB was done using measurements only when ambient temperature was below -5 °C (see Supporting Information). This includes measurements in November–March at LFL and in November–May at the other 4 sites (without VKK).

Monthly concentrations of HCB are shown in Figure 3A for November–March at LFL and November–May at the other four sites. Error bars here represent variations of HCB among different sampling events in a month. Monthly variations of HCB were less than a factor of 2 during the selected periods at all sites, although temperature varied up to 20 °C (Figure S2A), suggesting that variations of ambient temperature did not greatly affect HCB concentrations in the Arctic air. Differences of monthly average HCB concentrations were not large from site to site except LFL (Figure 3A). Individual site measurements are summarized in the box-and-whisker plots of Figure 3B. Comparable mean and median concentrations of HCB were observed at ALT, KNG, PTB, and ZPN (Table S4). Relatively uniform distribution of HCB concentration in the circumpolar air is supported by the nearly normal distribution among the four sites (without LFL or VKK), as indicated by a red line in Figure 3C. The homogeneity of HCB in the circumpolar air could be the result of fairly slow removal processes (e.g., degradations and dry/wet depositions) from the atmosphere and less influence of primary emissions on the atmosphere (8, 10). Mean concentration at these four high Arctic sites was 56 ± 23 $\text{pg}\cdot\text{m}^{-3}$ ($n = 241$) between November and May in 2000–2003. The mean value is similar to that measured in the spring of 2002 at Cheeka Peak Observatory, Washington State (35 – 57 $\text{pg}\cdot\text{m}^{-3}$) (34). Comparable concentrations of HCB were previously also reported in the northern hemisphere (55 $\text{pg}\cdot\text{m}^{-3}$) (8).

Although HCB was homogeneous during the winter months at the high Arctic sites, significantly higher concentrations of HCB (88 ± 14 $\text{pg}\cdot\text{m}^{-3}$, $n = 11$, $p < 0.0001$) were found at LFL between November and March, which were probably due to different LRT inputs at this site. Higher HCB concentrations were also observed at VKK (140 – 534 $\text{pg}\cdot\text{m}^{-3}$, $n = 5$) although breakthrough of HCB likely occurred at this site.

Effects of Emissions and Environmental Properties on α - and γ -HCH Air Concentrations at Different Sites. Data comparison shows that α - and γ -HCH behaved differently at different Arctic sites. Since all sampling sites were located in the remote Arctic far away from emission sources, HCHs observed in Arctic air are likely the result of LRT. Global usage of technical HCH peaked in the 1970s and declined in the 1980s and 1990s (1); therefore, primary sources of technical HCH are less important to the global environment.

However, historically when the technical mixture was widely used, these compounds could be transported via LRT and deposited in the Arctic surfaces. Technical HCH was used approximately 74% (6214 kt out of 8363 kt) of total technical HCH in China, India, and the former Soviet Union, and much longer in Asia than in North America (1). Strong trans-Pacific transport signals for some organic contaminants were identified previously (22, 34, 35). In particular, air concentrations of α - and γ -HCH observed at Tagish of YK positively correlated with residence time over eastern Asia before arriving at the sampling site (22). This finding suggested that HCHs in Tagish air were largely influenced by Asian emissions via LRT during the sampling period (December 1992–January 1995). When HCHs are atmospherically transported from the source regions, they can undergo rain and snow scavenging and deposition to surfaces. Thirty-year normal climate data indicate that the yearly precipitation rate at Whitehorse of YK (near LFL) was about 2.4 times higher than another western Arctic site, PTB (268 vs 112 mm, see details in Figure S2B). Higher precipitation rate at the elevated site of LFL may have led to enhanced deposition of HCHs compared to PTB when technical HCH was still in use, although the two sites could be subjected to different influence of emission sources (Figure 1). After primary emissions of HCHs ceased globally, it is believed that HCH transfer between the atmosphere and soil reversed from net deposition to net volatilization as air concentrations of HCHs declined in the Arctic (4). During the cold period, snow cover above soils was presumably less contaminated with HCHs than soils because current air concentration of HCHs was largely decreased (1) and scavenging of HCHs by snow is less efficient than that by rain (28). Therefore, snow cover could act as an effective barrier and further reduce secondary emissions of HCHs from soils in snow season (36), which is particularly important in the cold circumpolar regions. When the temperature rises above freezing, evaporation of HCHs from soils becomes significant. In general, the temperature at LFL is approximately 10 °C higher than that at other high Arctic sites (Figure S2A). Warmer climate would enhance secondary re-emissions of HCHs from soils to the atmosphere. The combined effect of elevated historical depositions and enhanced present re-evaporation may explain the higher air concentrations of α -HCH observed at LFL. Furthermore, stronger wind speed at this elevated site can accelerate chemical exchange process between air and surface environmental media because of increased mass transfer coefficient. In order to quantitatively investigate effects of environmental properties on HCHs' cycling in a transparent way at LFL, an evaluative multi-media fate model, for example, fugacity-based CoZMo-POP (37), is required to simulate their transport pathways and environmental fate. Moreover, simultaneous sampling of air, soil, and snow could provide direct evidence of chemical air/terrestrial interactions at locations such as LFL. Better understanding of chemical exchange processes between air and surface environmental media is particularly important at these Arctic locations, if snow/ice-covered periods and areas were reduced in the future as a result of climate change.

Seawater/Air Exchange. Gas exchange between seawater and air is one of the important inter-media transport pathways in the circumpolar environment since water accounts for a large part of earth's surface. Uniform concentrations of α -HCH and HCB in the circumpolar atmosphere allow assessing their seawater/air exchange directions. The gas exchange direction can be predicted using fugacity ratio, which is defined as

$$f_w/f_A = C_w \times H/(C_A \times R \times T_A) \quad (2)$$

where f_w and f_A are fugacity in seawater and air; C_w and C_A

are concentrations in seawater and air; H is Henry's Law Constant; R is the ideal gas constant; and T_A is the air temperature (5). Values of $f_w/f_A > 1$, $f_w/f_A = 1$, and $f_w/f_A < 1$ represent net volatilization, equilibrium, and net deposition, respectively. Fugacity ratio calculated below refers to air temperature at 0 °C.

Seawater concentration of α -HCH varies spatially in the circumpolar environment (18, 38, 39), although a comparable concentration of α -HCH was observed in the atmosphere. Higher concentrations of α -HCH were found in the central/western Canadian Archipelago (~ 2700 – 4700 pg·L⁻¹) and Bering/Chukchi/Beaufort seas (1500 – 2400 pg·L⁻¹), whereas lower concentrations were found in the northern Barents Sea and Greenland Sea (~ 400 pg·L⁻¹) (38, 39). The Tundra Northwest 1999 expedition showed an increase in α -HCH concentrations in seawater from the eastern to western Canadian Archipelago (averages 1800 – 4500 pg·L⁻¹) (18). Overall, seawater concentration of α -HCH varied by an order of magnitude in the Arctic (i.e., ~ 400 – 4700 pg·L⁻¹). Due to the high residence time of seawater in the Arctic and slow reaction rates in the cold water (40), it is assumed that α -HCH concentration in seawater did not change significantly within a few years. The extremes of the water concentrations are selected (400 and 4700 pg·L⁻¹) for deriving fugacity ratio. C_A of α -HCH is the average of the circumpolar air (23 pg·m⁻³) in this study and H is 0.061 Pa·m³·mol⁻¹ at 0 °C (32). Based on data selected here, fugacity ratios f_w/f_A of α -HCH are 0.47 and 5.5 for low and high water concentrations, respectively. The H of α -HCH can be enhanced 21% by the salting-out effect at 25 °C (32), and it becomes 0.074 Pa·m³·mol⁻¹ at 0 °C if salinity effect on H was the same at 25 °C. By considering the salting-out effect, fugacity ratios f_w/f_A for α -HCH are adjusted to 0.57 and 6.7 for low and high water concentrations, respectively. This suggests that α -HCH was close to equilibrium in the eastern Arctic, whereas it was over-saturated at most of other locations, such as the central and western Canadian Archipelago. Although large fugacity gradients exist in the Arctic, ice coverage inhibits volatilization of α -HCH during most of the year because most regions have little open water even in summertime, especially in the higher Arctic. It is notable that α -HCH volatilization from the Arctic Ocean could be accelerated as the Arctic becomes warmer and less ice-covered with climate change (18, 41).

Similar to air observations (i.e., average of 56 pg·m⁻³), relatively uniform distribution of HCB was also reported in Arctic surface seawater, averaging 5.5 pg·L⁻¹ (5 – 6 pg·L⁻¹) (38). H of HCB is 3.7 Pa·m³·mol⁻¹ at 0 °C (42). Salting-out effect increases H of HCB by 30% at 25 °C (43). Hence, H of HCB is adjusted to 4.8 Pa·m³·mol⁻¹ at 0 °C if salinity effect on H at 25 °C was applicable to 0 °C. Calculated fugacity ratio f_w/f_A of HCB is 0.21 , suggesting that HCB was undergoing net deposition from air to seawater in the Arctic.

Seawater concentration of β -HCH was ~ 250 pg·L⁻¹ in Chukchi Sea (32, 33). Median air concentrations of β -HCH (Table S3) were employed to evaluate seawater/air exchange potential at PTB and VKK. H for β -HCH is 0.0033 Pa·m³·mol⁻¹ at 0 °C (32). Calculated fugacity ratios (f_w/f_A) of β -HCH are 1.4 and 0.50 at PTB and VKK, respectively, assuming 21% enhancement as a result of salting-out. Therefore, elevated concentration of β -HCH at PTB could be partly explained by re-evaporative emissions from seawater. However, advective inputs from external sources other than outgassing from seawater likely also contributed to high β -HCH in VKK air.

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Supporting Information Available

Detailed description of field sampling and sample treatment; site information; discussion on potential breakthrough of HCB; MDLs; mean, median, and range of concentrations at each site; regression results of temperature dependence; monthly HCH concentrations at each site; and meteorological data. This material is free of charge via the Internet at <http://pubs.acs.org>.

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