

# Atmospheric Hexachlorocyclohexanes in the North Pacific Ocean and the Adjacent Arctic Region: Spatial Patterns, Chiral Signatures, and Sea–Air Exchanges

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During the 2003 Chinese Arctic Research Expedition (CHINARE2003) from the Bohai Sea to the high Arctic (37° N to 80° N) aboard the icebreaker Xuelong (Snow Dragon), air samples were collected for the analysis of hexachlorocyclohexanes (HCHs) in the North Pacific Ocean and adjacent Arctic region. The  $\Sigma$ HCHs ( $\alpha$ -HCH +  $\gamma$ -HCH) ranged from 2.3 to 95.1 pg/m<sup>3</sup> with the highest levels observed in Far East Asia (32.5 pg/m<sup>3</sup>), followed by the North Pacific Ocean (17.0 pg/m<sup>3</sup>) and the Arctic (7.3 pg/m<sup>3</sup>). Compared to previous studies in the same areas in 1990s, our measurements were approximately 1 order of magnitude lower. Because of disproportionate chemical reduction and physical fractionation during long-range transport, the ratios of  $\alpha$ -HCH to  $\gamma$ -HCH ( $\alpha/\gamma$ -HCH) showed a significant increasing trend from low to high latitudes, suggesting that the  $\alpha/\gamma$ -HCH range of 4–7 could not be used to identify sources of technical HCHs especially in remote areas. The ratios of (+)- $\alpha$ -HCH to the sum of (+)- $\alpha$ -HCH and (–)- $\alpha$ -HCH were on average much more biased from 0.5 compared to previous observations in mid-1990s, indicating the exchange of atmospheric  $\alpha$ -HCH with those in the oceans, where (+)- $\alpha$ -HCH was selectively depleted in biological degradation processes. Estimated fugacity ratios based on available data for both  $\alpha$ -HCH and  $\gamma$ -HCH further implied their net volatilization from seawater to air in the Arctic Ocean.

## Introduction

Hexachlorocyclohexanes (HCHs) have been used as insecticides since 1943. Technical HCHs containing 60–70%

$\alpha$ -HCH, 5–12%  $\beta$ -HCH, 10–15%  $\gamma$ -HCH, 6–10%  $\delta$ -HCH, and 3–4%  $\epsilon$ -HCH (1) have been used in large quantities in early years. Only  $\gamma$ -HCH known as lindane is insecticidally active. At present, technical HCHs have been banned for a long time, but lindane is still used in some areas of the world (2). As persistent organic pollutants (POPs), HCHs are subject to long range atmospheric transport (LRAT); they can be redistributed on a global scale after being emitted from source areas (3) and tend to move from warmer to colder areas, such as Arctic and Antarctica (4). Therefore long-range spatial surveys are necessary and effective to understand the global sources, distribution, and LRAT of HCHs. In the land, several studies have been done describing the atmospheric fate of POPs over a continental scale including Arctic (5), North America (6, 7), Asia (8), and Europe (9). In the open oceans, there are a few cruises for HCHs in the open oceans during the past two decades, focusing on spatial distribution (10, 11), air–sea gas exchange (12, 13), long-range transport (1), and temporal trend (14). Although LRAT of HCHs from Eurasia have been found to have profound influence on the Arctic atmosphere (15), only one cruise in 1989–1990 (1) is available regarding the LRAT of HCHs in the North Pacific Ocean and adjacent Arctic Ocean.

Although HCHs have been extensively studied for several decades, there are still issues incompletely understood even for HCHs in the atmosphere. Technical HCHs have been banned worldwide for a long time and have not been used since 2000 (2, 16). However, field studies still identified technical HCH sources in the environment, even in Arctic region in 2001–2003 (5) based on  $\alpha/\gamma$ -HCH ratios of 4–7, which represents a typical proportion of technical HCHs. This raises the question whether this ratio range is fit to identify technical HCH source in environment, especially in remote areas. On the other hand, as atmospheric levels of HCHs continue to decrease, air–water exchange direction of these pollutants in oceans may be changing from deposition to volatilization. This changing trend for  $\alpha$ -HCH was first observed in the Bering and Chukchi Seas (17) and in the Arctic Ocean (18) in 1993. Net deposition and near equilibrium of  $\gamma$ -HCH were also reported in the Arctic Ocean in 1990s (19, 20). The enantiomeric ratios of  $\alpha$ -HCH can be interpreted as a bioindicator showing whether the  $\alpha$ -HCH residues have encountered biota. In the Arctic Ocean, the similar chiral signatures were observed in surface water and in the atmosphere providing a direct evidence for ocean evaporation (20). About 10 years later, are there any changes in their atmospheric levels and sea–air exchange direction in case lindane is still used worldwide? How does the chiral signature evolve in the ocean atmosphere on a global scale? These questions need further examination for a better understanding of the sources and environmental fate of HCHs.

In July to September 2003, ship-board air samples were collected along a cruise from Bohai Sea to the North Pole Area (37° N to 80° N). Detailed information about this expedition has been described elsewhere (21). The purposes of the current study are (1) to update the data for atmospheric levels and compositional patterns of HCHs over the North Pacific Ocean and the adjacent Arctic Ocean, (2) to identify HCHs source areas and factors influencing the fate of HCHs during LRAT, and (3) to detect the chiral signature of  $\alpha$ -HCH in oceanic atmosphere, and along with fugacity calculation, provide information about their ocean evaporation.

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## Experimental Section

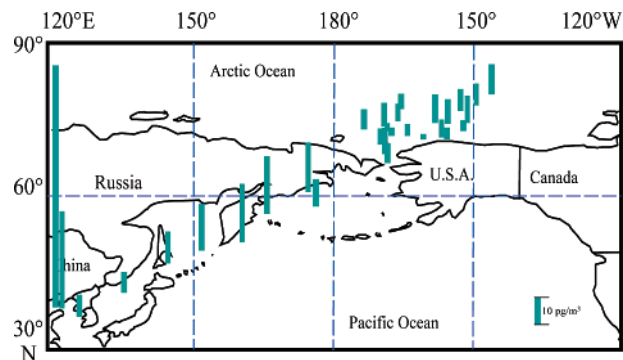
**Field Sampling.** During the cruise, a total of 49 particle samples were taken from July 11 to September 21, 2003, between Bohai Sea (37.78° N, 123.12° E) and the Arctic (80.22° N, 146.75° W) (Figure S1, Supporting Information (SI)), among which 30 vapor samples were collected simultaneously. A high volume air sampler was placed windward on the uppermost deck of the ship. The air volumes were ranged from 1215 to 3030 m<sup>3</sup> (at 0 °C and 1 atm). At a flow rate of ~1.0 m<sup>3</sup>/min, air was aspirated through a quartz fiber filter (QFF) (Whatman QM-A, 20.3 × 25.4 cm) to remove particles from the air stream, and the gas-phase compounds were trapped on a polyurethane foam plug (PUF, 6.5 cm diameter × 8 cm height) contained in an aluminum cylinder. To remove possible organic impurities, before field use, the QFFs were heated at 450 °C for 4 h, and the PUFs were Soxhlet extracted for 24 h with methanol and dichloromethane (DCM) subsequently. Exposed QFFs and PUFs were wrapped in aluminum foil, zipped in Teflon bags, and stored in freezers at -20 °C until analysis. Besides, three clean QFFs and PUFs were exposed to the atmosphere during the sampling period and processed as field blanks. The detailed information about sampling was described elsewhere (22).

**Sample Extraction.** Sample extraction was conducted based on an analytical procedure published elsewhere (23). Briefly, prior to 72 h Soxhlet extraction with DCM, PCB15 was added to all samples as a surrogate. The extracts were concentrated and solvent-exchanged to hexane and then purified using a 1:2 alumina/silica gel column. The first fraction, containing aliphatic hydrocarbons, was eluted with 30 mL of hexane. The second fraction, containing HCHs, was collected by eluting 70 mL of DCM/hexane (3:7 v/v). Then the latter was concentrated to a final volume of 50  $\mu$ L under a gentle stream of nitrogen. 2,4,5,6-Tetrachloro-*m*-xylene (TCmX) was added to the samples as internal standard before instrumental analysis.

**Instrumental Analysis and Parameters.** All samples were analyzed by an Agilent 6890 series gas chromatograph (GC) /5973 mass spectrometric detector (MSD) in electron impacting (EI) mode and selective ion monitoring (SIM) mode with a 30 m HP-5 MS capillary column (i.d. 0.25 mm, 0.17  $\mu$ m film thickness). HCHs were quantified using an internal calibration method with *m/e* = 217 and 219. Splitless injection of 1  $\mu$ L sample was performed with a 5-min solvent delay. The oven temperature was initiated at 80 °C (held for 2 min) and increased to 290 °C at 4 °C/min (held for 10 min). The method detection limits (MDLs) were 0.20, 0.15 pg/m<sup>3</sup> for  $\alpha$ -HCH,  $\gamma$ -HCH, respectively, when calculated with an average sampling volume of 2051 m<sup>3</sup>.

**Chiral Analysis for  $\alpha$ -HCH.** Determination of the enantiomeric composition of  $\alpha$ -HCH was performed with an Agilent 6890 series GC coupled with 5973 MSD in EI mode. Separation was carried out using a CP-Chirasil-Dex-CB column (25 m, 0.25 mm i.d., 0.25  $\mu$ m film thickness; Varian, Inc.). Selected ions 217 and 219 were monitored with a 2  $\mu$ L sample injection. As described by Zhao et al. (24), the (+)- $\alpha$ -HCH elutes first on this column. The elution order was also confirmed by injecting standard solutions of (+)- $\alpha$ -HCH and (-)- $\alpha$ -HCH (Ehrenstorfer Laboratories, Germany), respectively. The GC temperature program was: 80 °C held for 2 min, 4 °C/min to 190 °C, and held for 30 min. Chiral signatures are expressed using enantiomer fractions (EFs), calculated as the ratios of the peak areas of (+)- $\alpha$ -HCH to the sum of (+)- and (-)- $\alpha$ -HCH. The EFs of seven successive injection of racemic standard were 0.497 ± 0.001.

**QC/QA.** Three field blanks and six laboratory blanks were processed. These samples were extracted and analyzed in the same way as field samples. There were no target compounds detected in the laboratory and field blanks.



**FIGURE 1.** Spatial distribution of HCHs in the North Pacific Ocean and the Arctic Ocean ( $n = 30$ ). Concentrations are displayed at the average sampling locations (bars).

Surrogate recovery ( $n = 97$ , including field and laboratory control samples) was  $90.2 \pm 10.5\%$  for PCB15. Recoveries for HCH isomers in six spiked blank samples (HCH congeners spiked into solvent with clean QFFs and PUFs) were  $87 \pm 8\%$  for  $\alpha$ -HCH and  $91 \pm 11\%$  for  $\gamma$ -HCH. Recoveries for HCH isomers in six matrix spiked samples (HCH congeners spiked into pre-extracted QFFs and PUFs) were  $85 \pm 12\%$  and  $81 \pm 9\%$  for  $\alpha$ -HCH and  $\gamma$ -HCH, respectively. The reported results in the present study were not recovery adjusted. Before the field campaign, breakthrough was tested by sampling ambient air for 48 h in Guangzhou with 1.5 PUFs instead of one PUF installed in the high-volume sampler. HCHs were below the detection limits in the backup half PUF, so for the relatively lower HCHs over the oceans, breakthrough was not a problem in this study.

**Back Trajectories.** Air mass origins were determined for the cruise samples using HYSPLIT transport and dispersion model from the NOAA Air Resources Laboratory (25). Two back trajectories (BTs) were performed, for the start and end of each sampling episode. BTs were traced for 5 days with 6 h steps at 100, 500, and 1000 m above sea level. Air mass origins were also generally indicated in Figure 1S in SI.

## Results and Discussion

In the present study, the concentrations of HCHs in the particulate phase were less than MDLs. Predictions based on the Junge–Pankow adsorption model indicate that HCHs are predominantly gaseous at moderate temperatures (26). Ambient measurement also confirmed that over 95% of  $\alpha$ -HCH and  $\gamma$ -HCH in air is in the gas phase (27). Therefore, only gaseous data are used in this study (Table 1S in SI).

**Concentrations and Spatial Patterns.** Figure 1 shows the spatial distribution of  $\Sigma$ HCHs ( $\alpha$ -HCH +  $\gamma$ -HCH) during the expedition.  $\Sigma$ HCHs ranged from 2.3 to 95.1 pg/m<sup>3</sup>, with an average of  $13.4 \pm 17.1$  pg/m<sup>3</sup>. Our results were comparable to those of global oceans (1, 10, 13, 14, 28). Highest levels occurred near the Liaodong peninsula (95.1 pg/m<sup>3</sup>, both  $\alpha$ -HCH and  $\gamma$ -HCH > 40 pg/m<sup>3</sup>, site 1), and the lowest concentration was observed in the Arctic (2.3 pg/m<sup>3</sup>, site 31). A decreasing spatial distribution was observed where mean concentrations of  $\Sigma$ HCHs in Far East Asia (34–48 °N), North Pacific Ocean (48–66 °N), and the Arctic (>66.7 °N) were 32.5, 17.0, and 7.3 pg/m<sup>3</sup>, respectively.

**$\alpha$ -HCH.** As shown in Figure 2,  $\alpha$ -HCH varied between 2.1 and 45.6 pg/m<sup>3</sup> with an average of  $9.9 \pm 8.3$  pg/m<sup>3</sup>. The highest concentration observed near the Liaodong peninsula, 45.6 pg/m<sup>3</sup>, was 1 order of magnitude lower than that of East China Sea in 1989–1990 (520 pg/m<sup>3</sup>) (1). After a wane in the Bohai Sea, the air concentrations rose in the North Pacific Ocean and peaked near the east coastal areas of Russia. Several factors may explain high levels of  $\alpha$ -HCH observed in this region, including LRAT from Russia source areas, re-

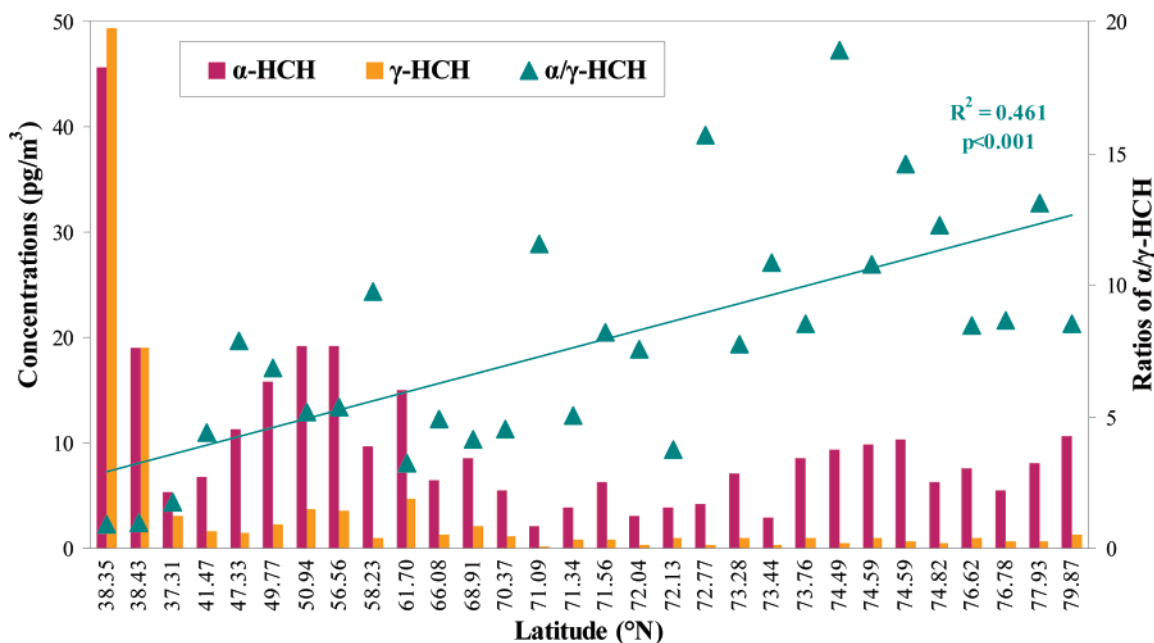


FIGURE 2. Spatial distribution of  $\alpha$ -HCH,  $\gamma$ -HCH, and  $\alpha/\gamma$ -HCH.

emission from seawater and transformation from other isomers to  $\alpha$ -HCH during LRAT. BTs clearly showed that oceanic atmosphere in this region were influenced deeply by eastern Russia (sites 12–17). But considering the fact that technical HCHs had been banned by many countries for a long time, such as China in the early 1980s and the former Soviet Union in the beginning of 1990s (2), input from fresh technical HCHs should be impossible. The global distribution model displayed that both in the atmosphere and seawater  $\alpha$ -HCH had peak concentrations in the area about 60°N (29). The model also indicated that sea–air exchange direction in this area changed from deposition in 1980s to volatilization in 1990s (29). The photoisomerization of  $\gamma$ -HCH to  $\alpha$ -HCH has been reported both under high-energy UV light (30) and direct sunlight (31). However, it is still a hypothesis due to the lack of evidence both in laboratory chamber study and in ambient atmosphere. If the phototransformation does exist in the ambient atmosphere, the process may contribute a great amount of  $\alpha$ -HCH in atmosphere as lindane is still used worldwide (2). In the Arctic,  $\alpha$ -HCH showed a slight variation,  $6.5 \pm 2.7$  pg/m<sup>3</sup>. Unstable air circulation and sufficient atmospheric mixing in the Arctic region might effectively compromise spatial differences in the concentration of air pollutants (21). In other studies,  $\alpha$ -HCH in the high Arctic was  $23 \pm 10$  pg/m<sup>3</sup> during 2000–2003 (5) and  $17 \pm 4$  pg/m<sup>3</sup> in July 2000 in the Arctic Ocean between 75 and 80°N (13). Since technical HCHs were phased out worldwide, the lower air concentrations determined in the current study is consistent with the reducing temporal trend of  $\alpha$ -HCH on a global scale (32, 33).

$\gamma$ -HCH.  $\gamma$ -HCH ranged from 0.2 to 49.4 pg/m<sup>3</sup>, with the highest level near Liaodong peninsula and the lowest level in the Arctic (Figure 2). Unlike  $\alpha$ -HCH, lindane is still in use as an insecticide in many countries (2). Therefore the highest level observed in the Bohai Sea (site 1 and 2) suggested continuing usage of lindane in the adjacent continents. In Far East Asia, mean  $\gamma$ -HCH concentration ( $14.9 \pm 20.7$  pg/m<sup>3</sup>) was about 1 order of magnitude lower compared to an early measurement (120 pg/m<sup>3</sup>) in East China Sea in 1989–1990 (1). Relatively higher concentrations were also observed near the east coastal areas of Russia. The average  $\gamma$ -HCH level of  $2.8 \pm 1.4$  pg/m<sup>3</sup> in the North Pacific Ocean was much lower than those in the same area in 1990 (76 pg/m<sup>3</sup>) (1) or Bering and Chukchi Seas in 1990 (35 pg/m<sup>3</sup>) (1) and in 1993

(23 pg/m<sup>3</sup>) (17). The air concentrations in the Arctic were low but relatively constant,  $0.8 \pm 0.4$  pg/m<sup>3</sup>, also about 1 order of magnitude lower than that in the Arctic atmosphere in 2000–2003 (5.1 pg/m<sup>3</sup>) (5). Until 2003 lindane was still widely used as a treatment on crop seed in Canada (34), which could be regarded as a possible source area for the Arctic (35).

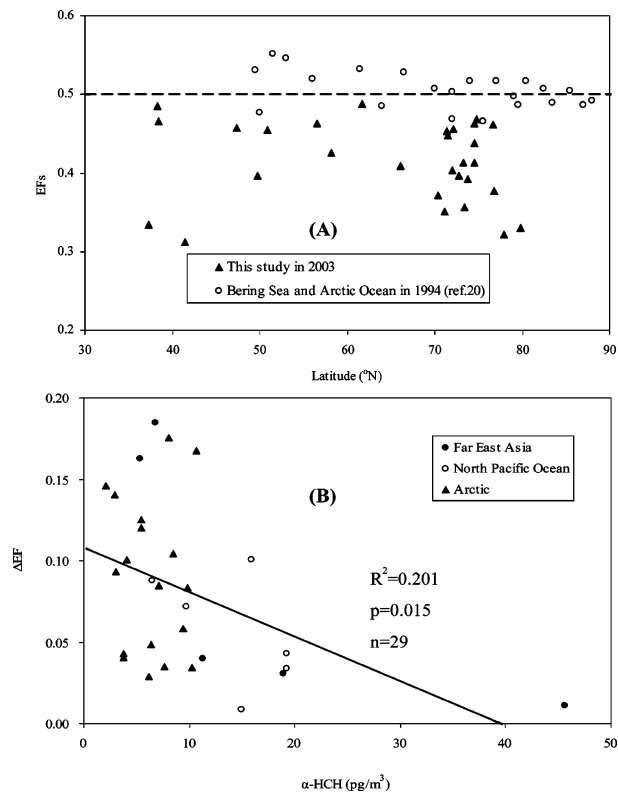
$\alpha/\gamma$ -HCH. The ratio of  $\alpha/\gamma$ -HCH is around 4–7 in technical HCHs (1, 36) and near or less than unity in lindane. Thus it used to be an indicator of sources of HCHs. In the Bohai Sea (site 1–3), ratios were close to 1.0 ( $1.2 \pm 0.4$ ). A study in Qingdao, China, and over the Yellow Sea during June 2003 also reported ratios of  $\alpha/\gamma$ -HCH from 0.6 to 2.0 with a mean of 1.5 (37). All these indicated fresh emission of lindane in the adjacent continents. As shown in Figure 2,  $\alpha/\gamma$ -HCH exhibited a significant increasing trend along the cruise with the increasing of latitudes ( $R^2 = 0.461$ ,  $p < 0.001$ ,  $n = 30$ ). The reason is that during long-range transport, different physical and chemical properties between  $\alpha$ -HCH and  $\gamma$ -HCH may contribute to the disproportionate reduction and fractioning of the isomers. In the troposphere the hydroxyl radical (OH) is the major oxidizing chemical responsible for the destruction of almost all hydrogen-containing gases (38), including HCHs. Estimated OH reaction rate constants and atmospheric lifetimes (39) using the average global OH concentration of  $9.7 \times 10^5$  cm<sup>-3</sup> (40), and Henry's Law constants (41) of HCHs in the different regions, were presented in Table S2 in SI. Compared to  $\alpha$ -HCH,  $\gamma$ -HCH has higher reaction rate with hydroxyl radical and lower Henry's Law constant, indicating that  $\gamma$ -HCH has a shorter lifetime in the atmosphere and is more susceptible to be removed either through direct partitioning into seawater or through washout by precipitation during LRAT (42). Thus  $\alpha/\gamma$ -HCH would increase while photochemically aging during LRAT to the remote areas. Moreover, photochemical transformation of  $\gamma$ -HCH to  $\alpha$ -HCH is also another possible explanation (43). If the photoisomerization of  $\gamma$ -HCH to  $\alpha$ -HCH (30, 31) exists in the atmosphere, this increase of  $\alpha/\gamma$ -HCH would be further enhanced. As discussed below, sea to air evaporation contributes to the atmospheric HCHs, since  $\alpha$ -HCH has a much higher Henry's Law constant than  $\gamma$ -HCH (Table S2 in SI), evaporated HCHs would have a higher  $\alpha/\gamma$ -HCH in comparison with HCHs in ocean surface waters. All these can explain the elevated ratios of  $\alpha/\gamma$ -HCH in the

remote atmosphere (44, 45). In the Arctic region the highest ratios during the cruise,  $9.6 \pm 4.1$ , were observed. They were similar to results observed in Alert (15). The North Pacific Ocean had a medium ratio of  $5.9 \pm 2.2$ . It seemed that the technical HCHs were still being used in Russia, since the ratio fell between the typical range of technical HCHs and the air masses did originate from eastern Russia. However, as mentioned above, the fact is that there has been no usage of technical HCHs worldwide since 2000 (16). As discussed above, the  $\alpha/\gamma$ -HCH ratios, though lower in areas where lindane is still used after the long-time ban of technical HCHs worldwide, may elevate during the migration of HCHs to the background regions, and possibly fall between 4 and 7, the typical range of technical HCHs. Therefore it is worthy noting that the  $\alpha/\gamma$ -HCH ratio range of 4–7 should be carefully used as a diagnostic tool to identify the source of technical HCHs in the environment, especially in the atmosphere of remote areas, such as ocean, polar regions and background lands.

**Enantiomers of  $\alpha$ -HCH.** Technical HCHs contain the (+)- and (–)- $\alpha$ -HCH enantiomers in a racemic proportion. Abiotic processes such as hydrolysis and photolysis do not favor either enantiomer. Only biological processes such as microbial degradation, a key elimination pathway of HCHs in oceans, show enantioselectivity and alter EFs (46). Extreme low EFs had been reported in deep seawater, like a minimum of 0.074 in Bering and Chukchi Seas (20) and 0.099 in eastern Arctic Ocean (47). The appearance of nonracemic  $\alpha$ -HCH in oceanic air can be explained by evaporation of partially biodegraded  $\alpha$ -HCH from seawater. Jantunen and Bidleman observed that (+)- $\alpha$ -HCH was depleted in the Canada Basin and Greenland Sea in the summer of 1994 (20). Harner et al. reported that (+)- $\alpha$ -HCH was preferentially lost in the eastern Arctic Ocean with mean EFs of  $0.462 \pm 0.057$  in seawater and  $0.487 \pm 0.009$  in air during July–September 1996 (47).

During our cruise in July–September 2003, the EFs of  $\alpha$ -HCH ranged 0.312–0.488 with a mean of  $0.414 \pm 0.052$ . The disproportionate degradation of the two enantiomers in seawater should bring about lower EFs in the Arctic Ocean as compared to those in mid 1990s, and thus lower EFs in the atmosphere due to the sea–air exchange. A recent study found that EFs of  $\alpha$ -HCH were a little biased from 0.5 (0.471–0.519) in North America continental atmosphere even though technical HCHs had been banned for several decades (6). During our cruise, sites 1 and 16 had EFs close to 0.5, indicating  $\alpha$ -HCH had less biodegradation than other sites and was much more impacted by the adjacent continents. For other sites, all the EFs were lower than 0.47, implying more impact from the sea–air exchange.  $EF > 0.5$  was reported in Bering and Chukchi Seas in 1994 (20), while our measurement ( $EF < 0.5$ ) showed a reversal of the enantiomer depletion in the same areas (Figure 3A). Microbial activity in seawater might be the main factor impacting the EF values. The half-lives for (+)- $\alpha$ -HCH and (–)- $\alpha$ -HCH in the Arctic Ocean were estimated as 5.4 and 16.9 years, respectively, considering both hydrolysis and microbial degradation (46, 47). The different EFs observed between 1994 and 2003 might also reflect further depletion of (+)- $\alpha$ -HCH in seawaters due to its faster degradation rate. The EFs in the North Pacific Ocean ranged from 0.396 to 0.488 with an average of  $0.439 \pm 0.035$ . This selectively enriched (–)- $\alpha$ -HCH also confirmed our above conclusion that there was no fresh  $\alpha$ -HCH emission, although  $\alpha/\gamma$ -HCH ratios in this region were typical of technical HCHs, which, however, have racemic enantiomers.

As done for global background soil (48), correlation is also tested between  $\Delta EF$  (defined as the absolute value of EF subtracted from 0.5) and the concentration of  $\alpha$ -HCH. A significant negative correlation is observed in the oceanic atmosphere ( $R^2 = 0.201$ ,  $p = 0.015$ ,  $n = 29$ , Figure 3B)



**FIGURE 3.** Latitudinal variation of EFs during the expedition (A) and correlation between  $\Delta EF$  (the absolute value of  $0.5 - EF$ ) and  $\alpha$ -HCH in different regions (B).

suggesting that sea–air exchange might play an important role when the air concentration is extreme low. It should be stressed that a nonracemic EF value does not indicate that sea–air exchange direction is net volatilization. Because of higher burdens of  $\alpha$ -HCH in seawater than in air, the EF of  $\alpha$ -HCH in air will change toward the seawater value regardless of whether sea–air exchange is approached from the deposition or volatilization side. To predict the direction of sea–air exchange, the fugacity ratio of a chemical between water and gas phase should be calculated, as discussed below.

**Sea–Air Exchange in the Arctic.** Because of the extensive use of HCH products (technical mixture in past and lindane at present), oceans, lakes, soil, and vegetation can all serve as sinks for HCHs. Oceans may play an important role influencing the fates of HCHs (1, 36), because oceans occupy about 71% of the earth surface. Since the phase-out of technical HCHs in the 1970s, atmospheric concentrations of HCHs have declined gradually, especially for  $\alpha$ -HCH (18, 49). Because of longer lifetimes of HCHs in oceans than in atmosphere, it is possible that HCHs accumulated in the oceans can be re-released into the atmosphere by the sea–air exchange. In 1990s a few studies showed the evidence of sea-to-air movement of HCHs in the Arctic region by comparing the fugacity of HCHs both in seawater and air (17, 18, 20). The sea–air exchange direction can be predicted by calculating the fugacity ratio of a chemical in both phases, which is defined as:

$$f_W/f_A = C_W \times H / (C_A \times R \times T_A) \quad (1)$$

where  $f_W$  and  $f_A$  are fugacity in water and air, respectively,  $C_W$  and  $C_A$  are concentrations in water and air, respectively,  $H$  is Henry's Law constant,  $R$  is the gas constant, and  $T_A$  is the air temperature. Values of  $f_W/f_A > 1$ ,  $= 1$  and  $< 1$  indicate net volatilization, equilibrium, and net deposition, respectively. Since surface seawater temperature was unavailable

in the current study, average air temperature in the Arctic was used instead to adjust the Henry's Law constant using the experimental temperature-dependent equations of Sahuvar et al. (50) (Table S2 in SI).

The concentrations of HCHs in seawater in 2000s are not available, so estimated values are used in this study. From a historical perspective and modeling, the degradation in the seawater was the most important factor determining the net burden of  $\alpha$ -HCH in the Arctic (51). Removal of HCHs from seawater is supposed to be governed by

$$C = C_0 \times e^{-k_d t} \quad (2)$$

where  $C$  is the concentration at time of  $t$ ,  $C_0$  is the original concentration, and  $k_d$  is the degradation rate. For  $\alpha$ -HCH, the concentration is the sum of two enantiomers as shown below,

$$C = EF \times C_0 \times e^{-k_{d+} t} + (1 - EF) \times C_0 \times e^{-k_{d-} t} \quad (3)$$

Since little is known about degradation rates of HCHs in the North Pacific Ocean, here we only focus on the discussion in the Arctic Ocean. Two sets of data were used to estimate the Arctic seawater concentrations in 2003. One is the mean concentrations (2900 and 470 pg/L for  $\alpha$ -HCH and  $\gamma$ -HCH, respectively) in the Arctic Ocean in 1990s (52) with 1990 as the start year ( $t = 13$  year). Another is from 1999 Chinese Arctic Research Expedition (CHINARE1999, 389 and 123 pg/L for  $\alpha$ -HCH and  $\gamma$ -HCH, respectively;  $t = 4$  year) with the similar route as our cruise (53). It is worthy noting that the levels in CHINARE1999 were much lower than those in the Canadian Archipelago (3.5 and 0.31 ng/L for  $\alpha$ -HCH and  $\gamma$ -HCH, respectively) during the same period (54). Using the EF value (0.462) and the degradation rate constants of (+)- $\alpha$ -HCH ( $k_{d+} = 0.127 \text{ year}^{-1}$ ) and (-)- $\alpha$ -HCH ( $k_{d-} = 0.041 \text{ year}^{-1}$ ) in the Arctic Ocean (46, 47), the concentrations of  $\alpha$ -HCH in the Arctic Ocean were estimated to be 1179 (starting from 1990) and 286 (starting from 1999) pg/L in 2003. Using these values with the average  $C_A$  of  $6.5 \text{ pg/m}^3$  in the Arctic and  $H$  of  $0.056 \text{ Pa m}^3 \text{ mol}^{-1}$ , the ratios  $f_w/f_A$  for  $\alpha$ -HCH would be 4.49 and 1.09, respectively. The ratios could be enhanced at most 21% if the salinity effect on  $H$  of  $\alpha$ -HCH was considered (50). These  $f_w/f_A$  values of more than 1.0 for  $\alpha$ -HCH suggested that net re-evaporation from sea to air was prevailing in the Arctic. This implication is consistent with previous studies (17, 18, 20) in the same region.

Considering both hydrolysis and microbial degradation, the half-life of  $\gamma$ -HCH in the Arctic Ocean is 16.1 years with a degradation rate constant of  $0.043 \text{ y}^{-1}$  (46, 47). Using this rate constant, the concentrations of  $\gamma$ -HCH in the Arctic Ocean were estimated to be 270 (starting from 1990) and 104 (starting from 1999) pg/L in 2003, and the fugacity ratios of  $\gamma$ -HCH in the Arctic were 3.43 and 1.32, correspondingly. This was different from studies in the Arctic Ocean in 1990s (19, 20) indicating net deposition and near equilibrium of  $\gamma$ -HCH. Our findings implied that the sea-air exchange direction was recently changed and net volatilization of  $\gamma$ -HCH was becoming an important secondary source in the Arctic.

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### Supporting Information Available

Tables of atmospheric concentrations and enantiomer fractions for HCHs at each site (Table S1), estimated rate constants, atmospheric lifetime and Henry's Law constants of HCHs in different regions during the cruise (Table S2), and a figure of sample route for the current cruise (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

### Literature Cited

- Iwata, H.; Tanabe, S.; Sakai, N.; Tatsukawa, R. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environ. Sci. Technol.* **1993**, *27*, 1080–1098.
- Li, Y. F.; McMillan, A.; Scholtz, M. T. Global HCH usage with  $1^\circ \times 1^\circ$  longitude/latitude resolution. *Environ. Sci. Technol.* **1996**, *30*, 3525–3533.
- Simonich, S. L.; Hites, R. A. Global distribution of persistent organochlorine compounds. *Science* **1995**, *269*, 1851–1854.
- Wania, F. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in Polar Regions. *Environ. Sci. Technol.* **2003**, *37*, 1344–1351.
- Su, Y.; Hung, H.; Blanchard, P.; Patton, G. W.; Kallenborn, R.; Konoplev, A.; Fellin, P.; Li, H.; Geen, C.; Stern, G.; Rosenberg, B.; Barrie, L. A. Spatial and seasonal variations of hexachloro-cyclohexanes (HCHs) and hexachlorobenzene (HCB) in the Arctic atmosphere. *Environ. Sci. Technol.* **2006**, *40*, 6601–6607.
- Shen, L.; Wania, F.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Bidleman, T. F. Hexachlorocyclohexanes in the North American atmosphere. *Environ. Sci. Technol.* **2004**, *38*, 965–975.
- Shen, L.; Wania, F.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Bidleman, T. F. Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America. *Environ. Sci. Technol.* **2005**, *39*, 409–420.
- Jaward, F. M.; Zhang, G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Jones, K. C. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environ. Sci. Technol.* **2005**, *39*, 8638–8645.
- Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ. Sci. Technol.* **2004**, *38*, 34–41.
- Montone, R. C.; Taniguchi, S.; Boian, C.; Weber, R. R. PCBs and chlorinated pesticides (DDTs, HCHs and HCB) in the atmosphere of the southwest Atlantic and Antarctic oceans. *Mar. Pollut. Bull.* **2005**, *50*, 778–782.
- Strachan, W. M. J.; Burniston, D. A.; Williamson, M.; Bohdanowicz, H. Spatial differences in persistent organochlorine pollutant concentrations between the Bering and Chukchi Seas (1993). *Mar. Pollut. Bull.* **2001**, *43*, 132–142.
- Jantunen, L. M.; Kylin, H.; Bidleman, T. F. Air-water gas exchange of  $\alpha$ -hexachlorocyclohexane enantiomers in the South Atlantic Ocean and Antarctica. *Deep-Sea Res. Part II-Top. Stud. Oceanogr.* **2004**, *51*, 2661–2672.
- Lakaschus, S.; Weber, K.; Wania, F.; Bruhn, R.; Schrems, O. The air-sea equilibrium and time trend of hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica. *Environ. Sci. Technol.* **2002**, *36*, 138–145.
- Wurl, O.; Potter, J. R.; Obbard, J. P.; Durville, C. Persistent organic pollutants in the equatorial atmosphere over the open Indian Ocean. *Environ. Sci. Technol.* **2006**, *40*, 1454–1461.
- Halsall, C. J.; Bailey, R.; Stern, G. A.; Barrie, L. A.; Fellin, P.; Muir, D. C. G.; Rosenberg, B.; Rovinsky, F. Y.; Kononov, E. Y.; Pastukhov, B. Multi-year observations of organohalogen pesticides in the Arctic atmosphere. *Environ. Pollut.* **1998**, *102*, 51–62.
- Li, Y. F.; Scholtz, M. T.; VanHeyst, B. J. Global gridded emission inventories of  $\beta$ -hexachlorocyclohexane. *Environ. Sci. Technol.* **2003**, *37*, 3493–3498.
- Jantunen, L. M.; Bidleman, T. F. Reversal of the air-water gas exchange direction of hexachlorocyclohexanes in the Bering and Chukchi Seas: 1993 versus 1988. *Environ. Sci. Technol.* **1995**, *29*, 1081–1089.

- (18) Bidleman, T. F.; Jantunen, L. M.; Falconer, R. L.; Barrie, L. A.; Fellin, P. Decline of hexachlorocyclohexane in the arctic atmosphere and reversal of air-sea gas exchange. *Geophys. Res. Lett.* **1995**, *22*, 219–222.
- (19) Weber, J.; Halsall, C. J.; Muir, D. C. G.; Teixeira, C.; Burniston, D. A.; Strachan, W. M. J.; Hung, H.; Mackay, N.; Arnold, D.; Kylin, H. Endosulfan and  $\gamma$ -HCH in the Arctic: An assessment of surface seawater concentrations and air-sea exchange. *Environ. Sci. Technol.* **2006**, *40*, 7570–7576.
- (20) Jantunen, L. M.; Bidleman, T. Air-water gas exchange of hexachlorocyclohexanes (HCHs) and the enantiomers of  $\alpha$ -HCH in arctic regions. *J. Geophys. Res.* **1996**, *101*(D22), 28837–28846.
- (21) Wang, X. M.; Ding, X.; Mai, B. X.; Xie, Z. Q.; Xiang, C. H.; Sun, L. G.; Sheng, G. Y.; Fu, J. M.; Zeng, E. Y. Polybrominated diphenyl ethers in airborne particulates collected during a research expedition from the Bohai Sea to the Arctic. *Environ. Sci. Technol.* **2005**, *39*, 7803–7809.
- (22) Ding, X.; Wang, X.; Xie, Z.; Xiang, C.; Mai, B.; Sun, L.; Zheng, M.; Sheng, G.; Fu, J.; Pöschl, U. Atmospheric polycyclic aromatic hydrocarbons observed over the North Pacific Ocean and the Arctic area: Spatial distribution and source identification. *Atmos. Environ.* **2007**, *41*, 2061–2072.
- (23) Chen, S. J.; Luo, X. J.; Mai, B. X.; Sheng, G. Y.; Fu, J. M.; Zeng, E. Y. Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River estuary and the Northern South China Sea. *Environ. Sci. Technol.* **2006**, *40*, 709–714.
- (24) Zhao, R.; Chu, S.; Zhao, R.; Xu, X.; Liu, X. Ultrasonic extraction followed by sulfuric acid silica gel cleanup for the determination of  $\alpha$ -hexachlorocyclohexane enantiomers in biota samples. *Anal. Bioanal. Chem.* **2005**, *381*, 1248–1252.
- (25) Draxler, R. R.; Rolph, G. D. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website. NOAA Air Resources Laboratory, Silver Spring, MD, 2003. <http://www.arl.noaa.gov/ready/hysplit4.html>.
- (26) Bidleman, T. F. Atmospheric processes. *Environ. Sci. Technol.* **1988**, *22*, 361–367.
- (27) Lane, D. A.; Johnson, N. D.; Hanley, M. J. J.; Schroeder, W. H.; Ord, D. T. Gas- and particle-phase concentrations of  $\alpha$ -hexachlorocyclohexane,  $\gamma$ -hexachlorocyclohexane, and hexachlorobenzene in Ontario air. *Environ. Sci. Technol.* **1992**, *26*, 126–133.
- (28) Jaward, F. M.; Barber, J. L.; Booi, K.; Dachs, J.; Lohmann, R.; Jones, K. C. Evidence for dynamic air-water coupling and cycling of persistent organic pollutants over the open Atlantic Ocean. *Environ. Sci. Technol.* **2004**, *38*, 2617–2625.
- (29) Wania, F.; Mackay, D.; Li, Y. F.; Bidleman, T. F.; Strand, A. Global chemical fate of  $\alpha$ -hexachlorocyclohexane. 1. Evaluation of a global distribution model. *Environ. Toxicol. Chem.* **1999**, *18*, 1390–1399.
- (30) Steinwandter, H. Beiträge zur umwandlung der HCH - isomere durch einwirkung von UV - strahlen: I. Isomerisierung des lindane in  $\alpha$ -HCH. *Chemosphere* **1976**, *5*, 245–248.
- (31) Malaiyandi, M.; Shah, S. M. Evidence of photoisomerization of hexachlorocyclohexane isomers in the ecosphere. *J. Environ. Sci. Health* **1984**, *A19*, 887–910.
- (32) Haugen, J. E.; Wania, F.; Ritter, N.; Schlabach, M. Hexachlorocyclohexanes in air in southern Norway. Temporal variation, source allocation, and temperature dependence. *Environ. Sci. Technol.* **1998**, *32*, 217–224.
- (33) Li, Y. F.; Bidleman, T. F.; Barrie, L. A.; McConnell, L. L. Global hexachlorocyclohexane use trends and their impact on the arctic atmospheric environment. *Geophys. Res. Lett.* **1998**, *25*, 39–42.
- (34) Tuduri, L.; Harner, T.; Blanchard, P.; Li, Y.-F.; Poissant, L.; Waite, D. T.; Murphy, C.; Belzer, W. A review of currently used pesticides (CUPs) in Canadian air and precipitation: Part 1: Lindane and endosulfans. *Atmos. Environ.* **2006**, *40*, 1563–1578.
- (35) Waite, D. T.; Hunter, F. G.; Wiens, B. J. Atmospheric transport of lindane ( $\gamma$ -hexachlorocyclohexane) from the Canadian prairies—a possible source for the Canadian Great Lakes, Arctic and Rocky mountains. *Atmos. Environ.* **2005**, *39*, 275–282.
- (36) Hinckley, D. A.; Bidleman, T. F.; Rice, C. P. Atmospheric organochlorine pollutants and air-sea exchange of hexachlorocyclohexane in the Bering and Chukchi seas. *J. Geophys. Res.* **1991**, *96*, 7201–7213.
- (37) Lammel, G.; Ghim, Y. S.; Grados, A.; Gao, H.; Hühnerfuss, H.; Lohmann, R. Levels of persistent organic pollutants in air in China and over the Yellow Sea. *Atmos. Environ.* **2007**, *41*, 452–464.
- (38) Lelieveld, J.; Dentener, F. J.; Peters, W.; Krol, M. C. On the role of hydroxyl radicals in the self-cleansing capacity of the troposphere. *Atmos. Chem. Phys.* **2004**, *4*, 2337–2344.
- (39) Brubaker, W. W.; Hites, R. A. OH reaction kinetics of gas-phase  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane and hexachlorobenzene. *Environ. Sci. Technol.* **1998**, *32*, 766–769.
- (40) Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang, J.; Aleya, F. N.; Cunnold, D. M.; Fraser, P. J.; Hartley, D. E.; Simmonds, P. G. Atmospheric trends and lifetime of  $\text{CH}_2\text{Cl}_2$  and global OH concentrations. *Science* **1995**, *269*, 187–192.
- (41) Kucklick, J. R.; Hinckley, D. A.; Bidleman, T. F. Determination of Henry's law constants for hexachlorocyclohexanes in distilled water and artificial seawater as a function of temperature. *Mar. Chem.* **1991**, *34*, 197–209.
- (42) Iwata, H.; Tanabe, S.; Tatsukawa, R. A new view on the divergence of HCH isomer compositions in oceanic air. *Mar. Pollut. Bull.* **1993**, *26*, 302–305.
- (43) Oehme, M. Dispersion and transport paths of toxic persistent organochlorines to the Arctic—levels and consequences. *Sci. Total Environ.* **1991**, *106*, 43–53.
- (44) Willett, K. L.; Ulrich, E. M.; Hites, R. A. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. *Environ. Sci. Technol.* **1998**, *32*, 2197–2207.
- (45) Walker, K.; Vallero, D. A.; Lewis, R. G. Factors influencing the distribution of lindane and other hexachlorocyclohexanes in the environment. *Environ. Sci. Technol.* **1999**, *33*, 4373–4378.
- (46) Harner, T.; Jantunen, L. M. M.; Bidleman, T. F.; Barrie, L. A.; Kylin, H.; Strachan, W. M. J.; Macdonald, R. W. Microbial degradation is a key elimination pathway of hexachlorocyclohexanes from the Arctic Ocean. *Geophys. Res. Lett.* **2000**, *27*, 1155–1158.
- (47) Harner, T.; Kylin, H.; Bidleman, T. F.; Strachan, W. M. J. Removal of  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane and enantiomers of  $\alpha$ -hexachlorocyclohexane in the Eastern Arctic Ocean. *Environ. Sci. Technol.* **1999**, *33*, 1157–1164.
- (48) Kurt-Karakus, P. B.; Bidleman, T. F.; Jones, K. C. Chiral organochlorine pesticide signatures in global background soils. *Environ. Sci. Technol.* **2005**, *39*, 8671–8677.
- (49) Hung, H.; Halsall, C. J.; Blanchard, P.; Li, H. H.; Fellin, P.; Stern, G.; Rosenberg, B. Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere. *Environ. Sci. Technol.* **2002**, *36*, 862–868.
- (50) Sahsuvar, L.; Helm, P. A.; Jantunen, L. M.; Bidleman, T. F. Henry's law constants for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hexachlorocyclohexanes (HCHs) as a function of temperature and revised estimates of gas exchange in Arctic regions. *Atmos. Environ.* **2003**, *37*, 983–992.
- (51) Li, Y. F.; Macdonald, R. W.; Ma, J. M.; Hung, H.; Venkatesh, S. Historical  $\alpha$ -HCH budget in the Arctic Ocean: the Arctic Mass Balance Box Model (AMBBM). *Sci. Total Environ.* **2004**, *324*, 115–139.
- (52) Li, Y.; Macdonald, R.; Jantunen, L.; Harner, T.; Bidleman, T.; Strachan, W. Transport and fate of hexachlorocyclohexanes in the North American Arctic Ocean. *Canadian Arctic Contaminants Assessment Report II*; Northern Contaminants Program: Hull, Quebec, 2003; pp 202–213.
- (53) Yao, Z.; Jiang, G.; Xu, H. Distribution of organochlorine pesticides in seawater of the Bering and Chukchi Sea. *Environ. Pollut.* **2002**, *116*, 49–56.
- (54) Bidleman, T. F.; Kylin, H.; Jantunen, L. M.; Helm, P. A.; Macdonald, R. W. Hexachlorocyclohexanes in the Canadian Archipelago. 1. spatial distribution and pathways of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCHs in surface water. *Environ. Sci. Technol.* **2007**, *41*, 2688–2695.

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