

# Fate of Chiral and Achiral Organochlorine Pesticides in the North Atlantic Bloom Experiment

Lin Zhang,<sup>†</sup> Terry Bidleman,<sup>‡,§</sup> Mary Jane Perry,<sup>§</sup> and Rainer Lohmann<sup>†,\*</sup>

<sup>†</sup>Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882-1197, United States

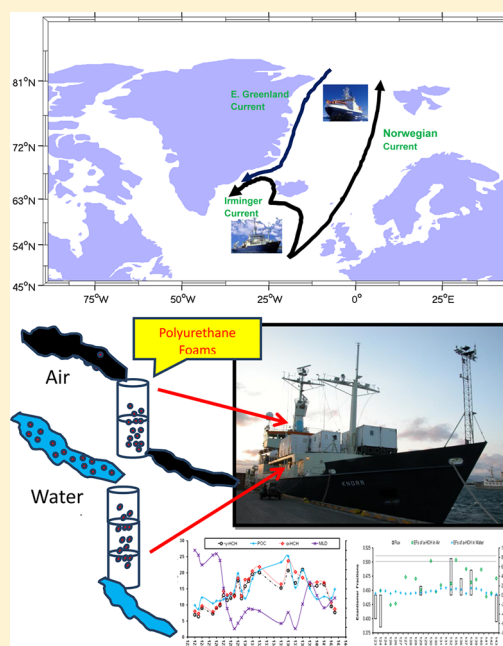
<sup>‡</sup>Chemistry Department, Umeå University, Umeå, SE-901 87 Sweden

<sup>§</sup>Centre for Atmospheric Research Experiments, Environment Canada, Egbert, Ontario L0L 1N0, Canada

<sup>§</sup>Ira C. Darling Marine Center, University of Maine, Walpole, Maine 04573, United States

## S Supporting Information

**ABSTRACT:** Organochlorine pesticides (OCPs) were measured in the surface seawater and lower atmosphere during the North Atlantic Bloom Experiment in the spring 2008 from samples collected on the R/V *Knorr*. The gaseous concentration profiles resulted from both long-range transport (LRT) from the Arctic by polar easterlies and local biogeochemical processes. Relatively constant  $\alpha/\gamma$ -hexachlorocyclohexane (HCH) ratios and enantiomer fractions of  $\alpha$ -HCH indicated that a single water mass was sampled throughout the cruise. Changes in dissolved phase concentrations were dominated by bloom processes (air–water exchange, partitioning to organic particles, and subsequent sinking) rather than LRT.  $\alpha$ -HCH and dissolved phase trans-chlordanes showed depletion of (+) enantiomer, whereas depletion of the (–) enantiomer was observed for heptachlor *exo*-epoxide (HEPX) and cis-chlordanes. Fugacity ratio calculations suggest that hexachlorobenzene (HCB) and  $\gamma$ -HCH were depositing from air to water whereas heavier OCPs (chlordanes, HEPX) were evaporating. Dissolved phase concentrations did not decrease with time during the three-week bloom period; neither were lipophilic OCPs drawn down from air to water as previous studies hypothesized. Comparison with Arctic measurements suggested that the Arctic returned higher concentrations of  $\alpha$ -HCH and HCB through both the atmospheric (polar easterlies) as well as oceanic transport (East Greenland Current) to the lower latitudes.



## INTRODUCTION

Persistent organic pollutants (POPs) have been banned globally over the past four decades. However, POPs can still be detected in the atmosphere and seawater in the remote oceans, such as the Atlantic,<sup>1,2</sup> Pacific,<sup>3</sup> and Arctic.<sup>4</sup> Certain POPs such as several organochlorine pesticides (OCPs) were found at higher concentrations in the Arctic than in temperate and tropical areas.<sup>5</sup>

Some regions in the Arctic Ocean (i.e., Canadian Basin) could be the last refuge for OCPs such as  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH).<sup>6</sup> A mass balance model has been constructed for the historical  $\alpha$ -HCH budget in the Arctic Ocean up to 2000; it predicted that  $\alpha$ -HCH will be removed from the Arctic Ocean by 2020.<sup>7,8</sup> However, climate change may complicate this mass balance prediction. A recent study suggested that despite the overall declining trend of atmospheric levels of POPs in the Arctic, rising temperature and declining sea ice coverage are remobilizing POPs from the snowpack and surface ocean, which buffers the reductions in the atmosphere.<sup>9</sup> We

were interested if the released POPs from the retreating sea ice could increase the residence time of POPs and eventually increase human and biological exposure in the Arctic and if these POPs are “coming in from the cold” and exported to sub-Arctic ecosystems.<sup>10</sup>

In the past, concentrations of these POPs were correlated with global emissions (primary sources).<sup>11–13</sup> Eventually, primary sources will be eliminated because the Stockholm Convention requires its signatory countries to phase out the production and usage of POPs.<sup>14,15</sup> POPs continue to be released from the previously polluted reservoirs (“secondary sources”) such as large water bodies,<sup>3</sup> soil,<sup>16,17</sup> and glaciers.<sup>18,19</sup> With the weakening and disappearing of primary sources, the biogeochemical processes happening within the secondary

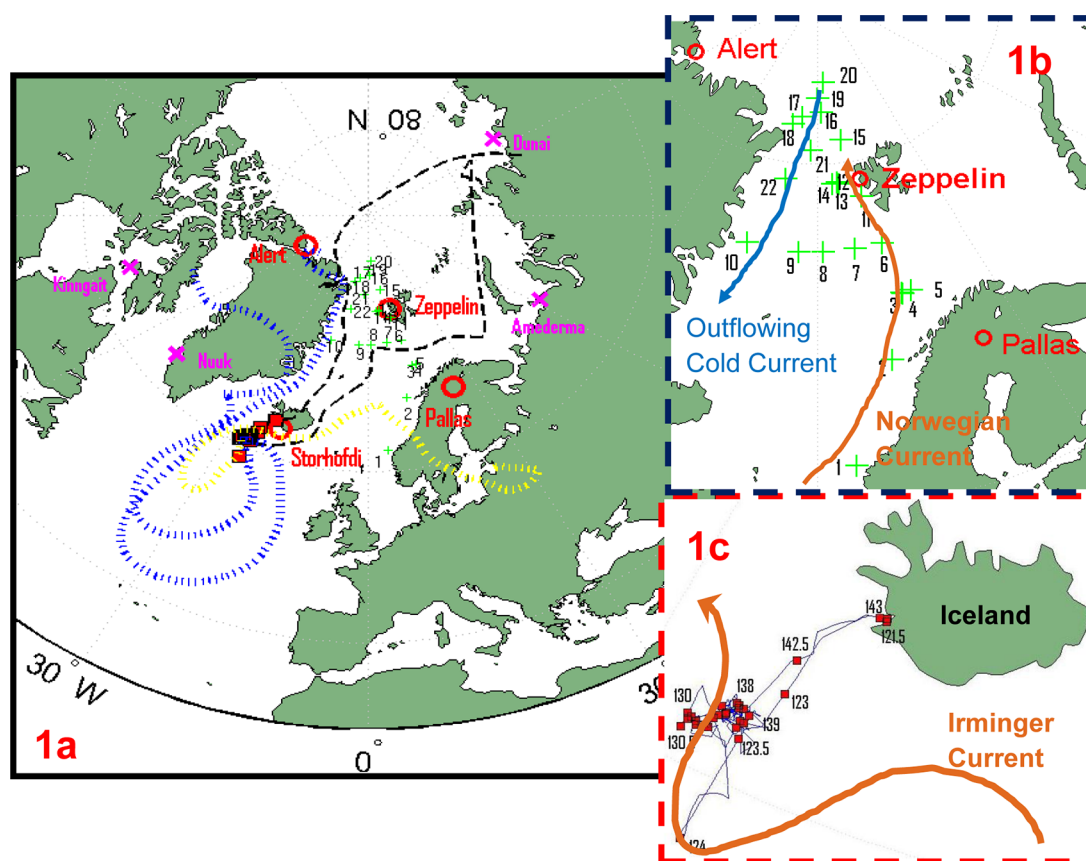
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**Figure 1.** In part a, the red circles indicate the location of long-term monitoring station under AMAP. Purple crossings are satellite stations. A total of 28 back trajectories were computed using NOAA's Hysplit model; 11 of them indicate the air masses were from Russian Arctic (black dashlines), seven of them were from Canadian Arctic/Greenland (blue dashlines), two were from western Europe (yellow dashlines), and the rest were originated in the oceans close to Iceland. In part b, green plus signs are the sampling locations of research cruise ARKXX.<sup>33</sup> Norwegian Current is a warm, northward flowing current. The blue line indicates outflowing cold current from the Arctic. In part c, the blue line indicates the cruise track of R/V *Knorr* during NABE. Red squares denote the locations of air and water sampling. The numbers are the year-day of 2008. The Irminger Current is flowing westward.

sources and at their interfaces are playing an ever more important role in controlling the environmental fate of the POPs.<sup>20</sup> Dachs et al. proposed that biogeochemical activities associated with phytoplankton in the water column would lead to the coupling of air–plankton systems to draw down the lipophilic POPs from the overlying atmosphere,<sup>21</sup> similar to the biological pump uptaking CO<sub>2</sub> from the atmosphere during the phytoplankton blooms.<sup>22</sup> This process has rarely been investigated in the ocean,<sup>23</sup> and so far no study has been conducted taking air and water samples simultaneously during a phytoplankton bloom.

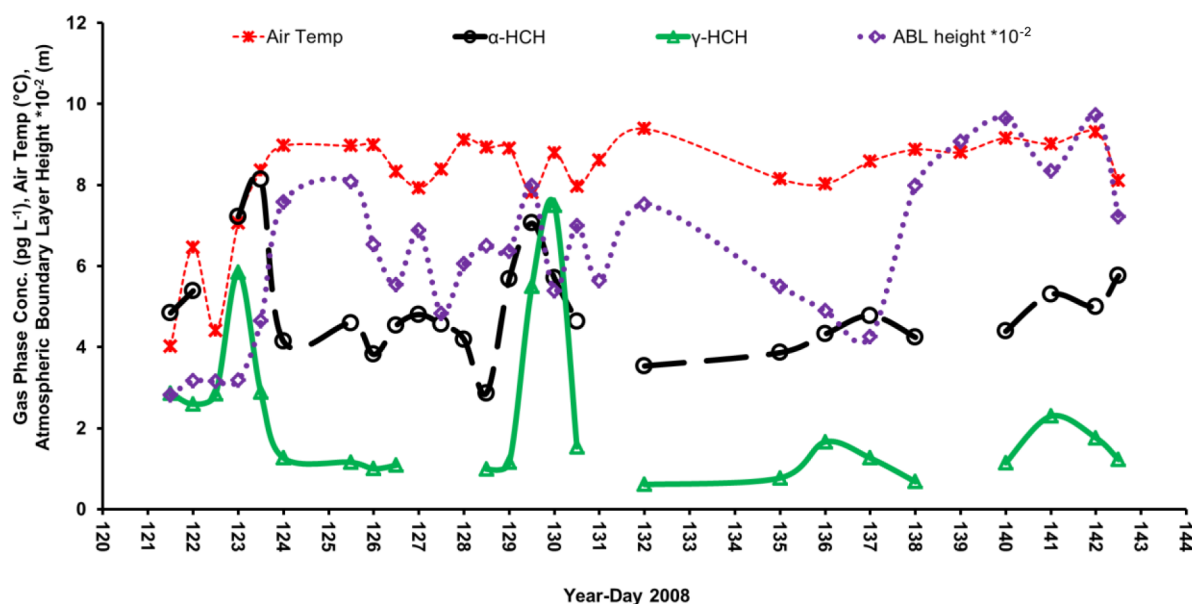
The North Atlantic Bloom Experiment (NABE) 2008 provided a unique opportunity to investigate the fate of POPs during the North Atlantic spring bloom,<sup>24</sup> which has been well-known for its sequestration of CO<sub>2</sub> and subsequent vertical export to deeper waters.<sup>25</sup> The study area (61° N, 26° W) was just south of the Arctic circle (66.5° N) (Figure 1a,c), which gave us the opportunity to conduct baseline studies of POPs in the sub-Arctic atmosphere and seawater. This is of critical importance for future observations and modeling assessments of how climate change will affect the fate of POPs in the Arctic and sub-Arctic ecosystems. During the experiment the NABE 2008 study area received air masses from the Arctic through polar easterlies via the Icelandic low pressure cell (Figure 1a). Although this location is not directly connected by any outflowing current from the Arctic Ocean,

it receives water from the Irminger Current which passes south of Iceland. The Irminger Current is one of two branches fed by the North Atlantic Current; the other one is the Norwegian Current which transports heat and pollutants into the Arctic Ocean (Figures 1 and SI-4, Supporting Information). We were wondering if the Irminger and Norwegian Currents would retain certain characterizations of POPs from the North Atlantic Current.

In this study, the marine boundary layer air and surface seawater were collected simultaneously on the R/V *Knorr* in May 2008 in the N. Atlantic south of Iceland during the NABE. These samples were analyzed for different OCPs and PCBs (reported separately) to study their concentration variations and air–water exchange directions as the bloom evolved.

## MATERIALS AND METHODS

**Survey Cruise Track.** The goal of the North Atlantic Bloom Experiment 2008 was to study the entire evolution of the spring bloom within a single phytoplankton bloom patch using instrumented autonomous platforms.<sup>24</sup> A Lagrangian float designed to mimic the motion of plankton in the mixed layer was deployed from April 4 to May 25, which collected temperature, salinity, dissolved nitrate, oxygen, and optical measurements of particulate organic carbon (POC) concentrations using physical, chemical and bio-optical sensors.<sup>26</sup> R/V



**Figure 2.** Gas phase concentrations of  $\alpha$ ,  $\gamma$ -HCH, air temperature, and atmospheric boundary layer height as a function of YD 2008 along the cruise track during NABE.

Knorr joined the survey (Cruise KN193-03) for Yearday (YD) 123–142 (May 2 to May 21) in the North Atlantic south of Iceland around  $61^{\circ}$  N,  $26^{\circ}$  W. In situ casts of conductivity–temperature–depth (CTD) were made typically within 1 km of the positions of the float. Chlorophyll, POC, oxygen, nitrate, and silicate were measured from CTD cast water samples to calibrate float sensor measurements.<sup>26</sup> Water temperature was always a little higher than the corresponding air temperature (Table SI-1, Supporting Information) throughout the cruise. Both temperatures showed small variations during the cruise (air,  $8$ – $9^{\circ}$  C; water,  $9$ – $10^{\circ}$  C) except a few air samples taken in the Reykjavik Harbor with lower air temperatures ( $4$ – $7^{\circ}$  C).

**Air and Water Sample Collection, Extraction, and Analysis.** A total of 28 air samples (sample nos. 120a–142.5a) and 25 water samples (sample nos. 123w–142.5w) were collected every 12 or 24 h. Sampling details (date, time, volume, temperature, coordinates, and wind speed) are presented in Table SI-1, Supporting Information. Between Year-Days 125 and 142 of 2008, the ship essentially cruised around a small region (Figure 1c). The samples collected in those days were treated as time series samples from the same location.

Detailed sampling scheme, extraction, and analysis methods have been described elsewhere.<sup>3</sup> In brief, two polyurethane foams (PUFs) were used to retain OCPs in the gaseous phase and Whatman glass fiber filters (GFF, QMA,  $0.3\ \mu\text{m}$  retention) to collect particle-bound OCPs using a high-volume air sampler placed on the flying bridge of R/V Knorr. Three PUFs were used on the water side for collecting OCPs in the dissolved phase. GFFs (Whatman GF/F,  $0.7\ \mu\text{m}$  retention) were used to filter particles and replaced whenever the flow rate was below 1 L/min.

OCPs were analyzed using a Quattro micro GC-MS/MS (Waters Corporation, Milford, MA, US) with a DB-SMS capillary column (Agilent). A total of 21 OCPs including  $\alpha$ ,  $\beta$ ,  $\gamma$ -hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), *cis*, *trans*-chlordanes (CC, TC), heptachlor *exo*-epoxide (HEPX), dichlorodiphenyltrichloroethane (DDT), and its degradation products (DDD and DDE) were quantified using

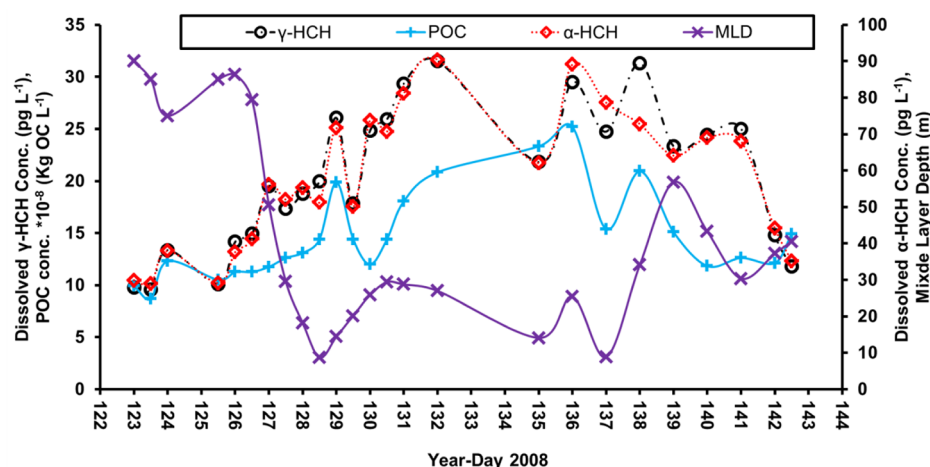
an internal standard method. More details about sample processing, analysis, and QA/QC can be found in Supporting Information. Breakthrough of OCPs trapped on second/third PUF in series was detected for HCBs in both the gas and the dissolved phase and  $\alpha$ ,  $\gamma$ -HCH in the dissolved phase only, which was corrected based on equilibrium partitioning (see Supporting Information for more details).

## RESULTS AND DISCUSSION

**HCHs. Gas Phase Concentrations.**  $\alpha$ - and  $\gamma$ -HCH were the most abundant HCH isomers detected in the atmosphere. The gaseous  $\alpha$ -HCH concentration ( $[\alpha\text{-HCH}]_{\text{gas}}$ ) was  $4.9 \pm 1.2\ \text{pg m}^{-3}$  with little variation during the sampling campaign (Figure 2). The two highest concentrations were found on YD123 and 123.5. Back trajectories indicated that both air masses were from the same location in the East Arctic Ocean (Figure 1,  $50^{\circ}$  W,  $180^{\circ}$  E).  $[\gamma\text{-HCH}]_{\text{gas}}$  ranged from  $0.6$  to  $7.5\ \text{pg m}^{-3}$  with the highest concentration found in YD130. Its air mass origin was from the Atlantic Ocean south of Iceland, having moved over the United Kingdom back to the Iceland area. The  $\alpha/\gamma$ -HCH ratios varied from 0.8 to 6.3 with an average of 3.3, which is lower than the ratio in the technical HCH mixture ( $4$ – $7$ ),<sup>27,28</sup> probably suggesting that lindane ( $>99\%$   $\gamma$ -HCH) was cotransported with technical HCH mixtures.<sup>29</sup> Technical HCH mixtures were banned in most countries by the 1990s and replaced by lindane, which were used in Canada and Germany until 2004.<sup>11–13</sup>

These results agree with previous data from the North Atlantic.  $\alpha$ ,  $\gamma$ -HCHs and their ratios were  $2.7 \pm 1.4\ \text{pg m}^{-3}$ ,  $2.2 \pm 2.3\ \text{pg m}^{-3}$ , and  $2.7 \pm 2.3$ , respectively, in the ARKXX cruise (Figure 1b, Table SI-7a, Supporting Information). Xie et al. reported  $[\alpha, \gamma\text{-HCHs}]_{\text{gas}}$  of  $4.8$  and  $7.0\ \text{pg m}^{-3}$  in the N. Atlantic ( $50.1^{\circ}$  N,  $2.2^{\circ}$  W).<sup>30</sup> This shows little spatial variations of HCHs in the N. Atlantic marine boundary layer. As back trajectories indicated that air masses were either from East Arctic Ocean or North American Arctic Ocean (Figure 1,  $50^{\circ}$  W– $180^{\circ}$  W), we also compared their concentrations to measurements from the Arctic atmosphere (Figure SI-3, Supporting Information).  $[\alpha\text{-HCHs}]_{\text{gas}}$  of  $13 \pm 5.7\ \text{pg m}^{-3}$





**Figure 3.** Dissolved phase concentrations of  $\alpha$ ,  $\gamma$ -HCH, particulate organic carbon (POC) conc. in the mixed layer, and mixed layer depth (MLD) as a function of YD 2008 along the cruise track during NABE.

was reported with a range of  $5.2\text{--}33\text{ pg m}^{-3}$  at Alert in 2005 and  $11 \pm 3.3$  ( $6.6\text{--}19$ )  $\text{pg m}^{-3}$  at Zeppelin in 2006 for  $\alpha$ -HCH (Figures 1 and SI-3, Table SI-7a, Supporting Information).<sup>31</sup>  $[\gamma\text{-HCH}]_{\text{gas}}$  was  $1.7 \pm 0.68\text{ pg m}^{-3}$  at Alert and  $1.9 \pm 0.65\text{ pg m}^{-3}$  at Zeppelin, very similar to what we observed in this study. Global Atmospheric Passive Sampling (GAPS) studies reported even higher average values for  $\alpha$ -HCH at Alert ( $36\text{ pg m}^{-3}$ ) and Ny-Alesund (same coordinates with Zeppelin,  $16\text{ pg m}^{-3}$ ), but values for  $\gamma$ -HCH were similar ( $5$  and  $6\text{ pg m}^{-3}$ ) at these two locations.<sup>32</sup> Wong et al. reported  $[\alpha, \gamma\text{-HCHs}]_{\text{gas}}$  of  $26 \pm 8.8$  and  $2.3 \pm 0.4\text{ pg m}^{-3}$ , respectively.<sup>4</sup> These results suggest there is a concentration gradient for  $\alpha$ ,  $\gamma$ -HCHs between the Arctic and sub-Arctic atmospheres, with higher concentrations in the Arctic, declining toward the Atlantic Ocean.

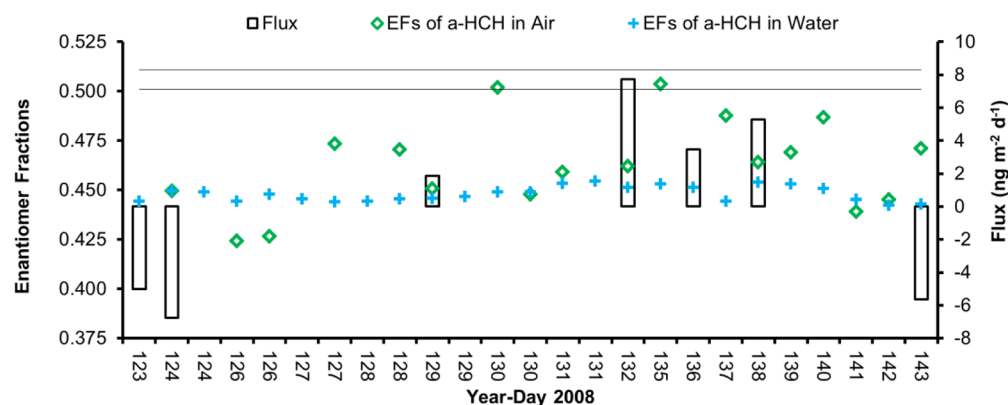
**Dissolved Phase Concentrations.** Three HCH isomers ( $\alpha$ ,  $\beta$ , and  $\gamma$ -HCH) were found in all water samples collected. The concentration of dissolved  $\alpha$ -HCH ( $[\alpha\text{-HCH}]_{\text{dissolved}}$ ) was  $57.6 \pm 28.9\text{ pg L}^{-1}$ .  $\gamma$ -HCH was the second most abundant HCH in the dissolved phase with an average concentration of  $20.4 \pm 9.6\text{ pg L}^{-1}$ . Both  $\alpha$  and  $\gamma$ -HCH displayed a similar temporal trend, with lowest concentrations at the beginning of the cruise, increasing to highest values at YD136 and then decreasing again (Figure 3). Therefore, the  $\alpha/\gamma$ -HCH ratios did not vary much in the water samples ( $3.6 \pm 0.23$ ).  $\beta$ -HCH had the lowest concentration among the three isomers ( $1.2\text{--}3.4\text{ pg L}^{-1}$ ) and did not show a clear trend with time ( $2.5 \pm 0.7\text{ pg L}^{-1}$ , Figure SI-2a, Supporting Information).

For comparison, there were fewer HCH measurements in North Atlantic seawater than in the atmosphere.  $[\alpha, \beta, \text{ and } \gamma\text{-HCH}]_{\text{dissolved}}$  were found to be  $47$ ,  $2.7$ , and  $33\text{ pg L}^{-1}$  at the beginning of the cruise ANT-XXV/1 + 2 ( $50.9^\circ\text{ N}$ ,  $1.3^\circ\text{ E}$ ) very similar to this study.<sup>30</sup> Lohmann et al. reported lower average concentrations for  $\alpha$  ( $13 \pm 16.3\text{ pg L}^{-1}$ ) and  $\gamma$ -HCH ( $4.7 \pm 5.6\text{ pg L}^{-1}$ ) but with greater concentration ranges ( $1.1\text{--}65\text{ pg L}^{-1}$ ) and ( $0.4\text{--}21\text{ pg L}^{-1}$ ) because the cruise ARKXX covered a large area in the Arctic and collected water samples from different ocean currents (Table SI-7b, Supporting Information).<sup>33</sup> Much higher concentrations were found in the Labrador Sea ( $\alpha$ -HCH,  $465 \pm 118\text{ pg L}^{-1}$ ;  $\gamma$ -HCH,  $150 \pm 59\text{ pg L}^{-1}$ ) and Hudson Bay ( $\alpha$ -HCH,  $628 \pm 108\text{ pg L}^{-1}$ ;  $\gamma$ -HCH,  $178 \pm 35\text{ pg L}^{-1}$ ) (Table SI-7b, Supporting Information).<sup>4</sup>

**Air–Water Gas Exchange.** The three HCH isomers all have high water solubility and  $K_{\text{aw}} < 10^{-3}$  (Table SI-5, Supporting

Information), such that the air–water exchange limiting step is on the atmospheric side.<sup>34</sup> The lowest  $K_{\text{aw}}$  is probably the reason that  $\beta$ -HCH was only detected in a few air samples. Fugacity ratios (FRs = fugacity in the air/fugacity in the water, see Supporting Information for more details), air–water exchange velocities, and fluxes were calculated (Table SI-4, Supporting Information).  $\alpha$ -HCH was found to undergo net deposition at the beginning of the cruise but was at equilibrium for most of the sampling (Table SI-4, Supporting Information). In contrast, most of the FRs of  $\gamma$ -HCH indicated deposition from air to water (Table SI-4, Supporting Information). The average air–water exchange velocities for both HCHs were very small ( $\alpha$ -HCH  $0.14\text{ m d}^{-1}$ ;  $\gamma$ -HCH  $0.07\text{ m d}^{-1}$ ) compared to other OCPs (see below) due to the differences in their physicochemical properties (Table SI-5, Supporting Information). In part due to their low  $K_{\text{aw}}$ , it is not uncommon to observe these two HCH isomers depositing into the ocean. It was shown that both HCHs were undergoing deposition in recent cruises of ARKXX<sup>33</sup> and ANT-XXV/1 + 2.<sup>30</sup> Wong et al. recently reported equilibrium was established for air–water exchange of  $\alpha$ -HCH in Hudson Bay and Labrador Sea and volatilization in Beaufort Sea.<sup>4</sup> Volatilization or equilibrium has been reported for  $\alpha$ -HCH in the North American Arctic Ocean and deposition or near equilibrium in the East Arctic Ocean,<sup>29,35–40</sup> which is probably due to the higher  $[\alpha\text{-HCH}]_{\text{dissolved}}$  in the North American Arctic Ocean than in the East Arctic Ocean and quite uniform air concentrations in the Arctic atmosphere.<sup>7,8</sup> Most previous cruise studies reported net deposition for  $\gamma$ -HCH in the Atlantic and Arctic Ocean,<sup>4,29,30,33,39</sup> except in Hudson Bay where volatilization was reported<sup>4</sup> and occasionally in some areas in the Arctic.<sup>29,39</sup> This is probably because of the recent usage of lindane, which was only added to the Stockholm Convention in 2009.<sup>4</sup>

The net flux for  $\alpha$ -HCH in this study ranged from  $-6.8$  to  $7.7\text{ ng m}^{-2}\text{ d}^{-1}$  and  $-12$  to  $-1.3\text{ ng m}^{-2}\text{ d}^{-1}$  for  $\gamma$ -HCH. The net volatilization fluxes reported for  $\alpha$ -HCH in Canadian Archipelago were from  $4.3$  to  $38\text{ ng m}^{-2}\text{ d}^{-1}$ <sup>29</sup> and  $6.8 \pm 3.2\text{ ng m}^{-2}\text{ d}^{-1}$  in Beaufort Sea in 2008<sup>4</sup> and  $34 \pm 12\text{ ng m}^{-2}\text{ d}^{-1}$  in 1999.<sup>29</sup> Net deposition fluxes calculated for  $\gamma$ -HCH ranged from  $-0.12$  to  $-2.2\text{ ng m}^{-2}\text{ d}^{-1}$  in the Canadian Archipelago in 1999<sup>29</sup> and  $-7.2 \pm 5.1\text{ ng m}^{-2}\text{ d}^{-1}$  in the Beaufort Sea in 1999 but with a net volatilization flux of  $0.76 \pm 0.40\text{ ng m}^{-2}\text{ d}^{-1}$  in 2008.<sup>4</sup> Xie et al. reported net deposition for  $\alpha$ -HCH ( $3.8\text{ ng}$



**Figure 4.** Enantiomer fractions of  $\alpha$ -HCH in gas and dissolved phase and net air–water gas exchange flux (positive numbers denote net evaporation and negative values indicate net deposition; the two horizontal lines indicate the racemic window at 95% confidence). Vertical bars denote  $\alpha$ -HCH fluxes (right-hand scale). A bar from 0 upwards indicates net evaporation, a bar from 0 downwards net deposition.

$\text{m}^{-2} \text{d}^{-1}$ ) and  $\gamma$ -HCH ( $2.0 \text{ ng m}^{-2} \text{d}^{-1}$ ) during cruise ANT-XXV/1 + 2 from  $51^\circ \text{N}$  to  $67^\circ \text{S}$  in the Atlantic Ocean.<sup>30</sup>

**Enantiomer Fractions (EFs).** The EFs of  $\alpha$ -HCH found in the atmosphere were in general closer to racemic than those in the water samples (Figure 4). They ranged from 0.424 to 0.504 ( $0.463 \pm 0.023$ ) in the air and showed less variations in the dissolved phase (0.442–0.454). Lohmann et al. reported EFs of  $0.454 \pm 0.020$  for higher air temperature ( $5.8 \pm 2.9^\circ \text{C}$ , all collected east of the Prime Meridian) and  $0.467 \pm 0.009$  for low air temperatures ( $-0.37 \pm 1.1^\circ \text{C}$ , all collected in western longitudes except Sample No. ARK12–13) which probably indicated different air masses were collected.<sup>33</sup> The EFs reported in Labrador Sea and Beaufort Sea air were  $0.456 \pm 0.008$  and  $0.476 \pm 0.010$ , respectively.<sup>4</sup> It was also found that EFs in the air of the Beaufort Sea were racemic ( $0.504 \pm 0.008$ ) when the sea was covered by ice and lower EFs ( $0.476 \pm 0.010$ ) when there was open water.

The EFs of  $\alpha$ -HCH in combination with dissolved phase concentrations have been used to characterize different water masses.<sup>5</sup> Microbial degradation half-lives have been estimated as 5.9 years for (+)  $\alpha$ -HCH and 23.1 years for (–)  $\alpha$ -HCH in the Eastern Arctic Ocean,<sup>39,41</sup> which suggests that the EFs of  $\alpha$ -HCH may potentially be used as a tracer to study fast-moving water currents. The EFs of  $\alpha$ -HCH in the Irminger Current were  $0.448 \pm 0.004$  (this study), but they were  $0.465 \pm 0.014$  in the Norwegian Current (Sample No. 1–6, 11–14 from cruise ARKXX, Figure 1b, Table SI-7b, Supporting Information). Since both the Irminger and Norwegian Current originate from the North Atlantic Current, additional sources or processes (air–water exchange and/or water current mixing) are needed to explain these differences. In the East Greenland Current flowing out of the Arctic, EFs were  $0.467 \pm 0.005$  (Sample No. 10, 16–22 from cruise ARKXX) and extremely low values ( $0.340$ ,  $n = 2$ ) in the middle of East Greenland Sea representing very old water mass (Sample No. 8,9).<sup>33</sup> Wong et al. reported values of  $0.425 \pm 0.010$  in Labrador Sea and  $0.447 \pm 0.005$  in Hudson Bay.<sup>4</sup>

Although most of the samples were at equilibrium for air–water exchange,  $\alpha$ -HCHs must have experienced extensive exchange between the two reservoirs. Thus the EFs of  $\alpha$ -HCHs in the air ( $\text{EF}_{\text{air}}$ ) should reflect both the signatures of air masses from long-range transport (background air  $\text{EF}_{\text{BKGD}}$ ) and local water masses ( $\text{EF}_{\text{seawater}}$ ).<sup>42</sup> The contribution of local seawater signature can be estimated according to  $(\text{EF}_{\text{air}} - \text{EF}_{\text{BKGD}})/(\text{EF}_{\text{seawater}} - \text{EF}_{\text{BKGD}})$ .<sup>29,43</sup> The EF of the background air

(0.479) was taken as the average of the EF in the Canadian Arctic over ice cover (racemic, 0.500) and the Norwegian-Greenland Sea (0.458), since air was equilibrated with the nonracemic  $\alpha$ -HCH in the water of the latter region.<sup>33</sup> The fraction contributed from air–water exchange is 52% when average EF at the NABE site ( $\text{EF}_{\text{air}} = 0.463$ ,  $\text{EF}_{\text{seawater}} = 0.448$ ) with  $\text{EF}_{\text{BKGD}}$ .

**HCB.** Detailed results of HCB are discussed in the Supporting Information (page SI-9). Gaseous HCB concentrations ( $[\text{HCB}]_{\text{gas}}$ ) averaged  $14.1 \pm 3.7 \text{ pg m}^{-3}$ . Similar  $[\text{HCB}]_{\text{gas}}$  ( $\sim 18 \text{ pg m}^{-3}$ ) were reported at  $51^\circ \text{N}$ ,  $1^\circ \text{E}$  and consistently low  $[\text{HCB}]_{\text{gas}}$  (i.e.,  $2.0 \pm 0.7 \text{ pg m}^{-3}$  in 2005) were reported in Storhofdi, Iceland.<sup>31</sup> Dissolved HCB concentrations ( $[\text{HCB}]_{\text{dissolved}}$ ) range from 0.1 to  $0.8 \text{ pg L}^{-1}$ , lower than those reported for the warm Norwegian Current ( $2.4 \pm 1.0 \text{ pg L}^{-1}$ ) and the cold East Greenland Current ( $7.4 \pm 1.6 \text{ pg L}^{-1}$ ).<sup>33</sup>

Air–water exchange directions of HCB were found to be mostly (92%) deposition from air to water (Table SI-4, Supporting Information). It has been reported that HCB was undergoing deposition in the Labrador Sea, Hudson Bay, Beaufort Sea,<sup>4</sup> and Arctic Ocean.<sup>33,35</sup>

**Heptachlor exo-epoxide (HEPX).** Details of this section are reported in Supporting Information (page SI-11).  $[\text{HEPX}]_{\text{gaseous}}$  averaged  $0.5 \pm 0.2 \text{ pg m}^{-3}$ , which agrees well with the annual average  $[\text{HEPX}]_{\text{gaseous}}$  at Alert ( $0.65$ – $0.84 \text{ pg m}^{-3}$ ) between 2003 and 2006.<sup>31</sup> The  $[\text{HEPX}]_{\text{dissolved}}$  was  $1.4 \pm 0.3 \text{ pg L}^{-1}$ . HEPX was generally at equilibrium between air and water (Table SI-4, Supporting Information). EFs of HEPX in the dissolved samples averaged  $0.596 \pm 0.023$  (Table SI-6, Supporting Information), which were in line with previous studies in the Arctic Ocean ( $0.632 \pm 0.019$ <sup>33</sup> and  $0.609$ – $0.638$ <sup>44</sup>).

**Chlordanes.** CC was more frequently detected in the air than TC. The average CC gas phase concentration ( $[\text{CC}]_{\text{gaseous}}$ ) was  $0.7 \pm 0.3 \text{ pg m}^{-3}$ , in line with the ARKXX cruise findings ( $0.4 \pm 0.3 \text{ pg m}^{-3}$ )<sup>33</sup> and measurements from Alert ( $0.64 \pm 0.21 \text{ pg m}^{-3}$ ) and Zeppelin ( $0.61 \pm 0.15 \text{ pg m}^{-3}$ )<sup>31</sup> (Table SI-7a, Supporting Information). This suggests that there was no concentration gradient for chlordanes between the Arctic Ocean and N. Atlantic. TC was more frequently detected in the dissolved phase than CC. The concentrations were comparable (TC  $0.7 \pm 0.4 \text{ pg L}^{-1}$  and CC  $0.7 \pm 0.1 \text{ pg L}^{-1}$ ) (Table SI-2b, Supporting Information) and were lower than the values in the Arctic in 1994 (TC,  $1.4 \pm 0.5 \text{ pg L}^{-1}$ ; CC,  $1.2 \pm 0.4 \text{ pg L}^{-1}$ ).<sup>44</sup> Lohmann et al. reported lower

Table 1. Concentrations and Enantiomer Fractions (EF) of OCPs in Air and Water

		$\alpha$ -HCH	HCB	$\beta$ -HCH	$\gamma$ -HCH	HEPX	TC	CC	p,p'-DDE	$\alpha/\gamma$ -HCH	EFs $\alpha$ -HCH	EFs HEPX	EFs TC	EFs CC
air (pg m <sup>-3</sup> )	min	2.9	4.1	2.1	0.6	0.3	0.6	0.4	0.3	0.8	0.424	0.491	0.490	0.495
	max	8.1	20.5	2.4	7.5	1.0	1.1	1.6	1.1	6.3	0.504	0.656	0.530	0.539
	mean	4.9	14.1	2.9	2.2	0.5	0.8	0.7	0.6	3.3	0.463	0.601	0.505	0.513
	median	4.6	14.1	<DL	2.1	0.4	<DL	0.4	0.3	3.1	N/A	N/A	N/A	N/A
	S.D.	1.2	3.7	1.2	1.8	0.2	0.2	0.3	0.3	1.5	0.023	0.078	0.024	0.011
	DL	0.2	0.8	0.2	0.2	0.2	0.5	0.6	0.4	N/A	N/A	N/A	N/A	N/A
	>DL (%)	89%	93%	11%	82%	71%	18%	57%	54%	79%	64%	14%	18%	46%
water (pg L <sup>-1</sup> )	min	28.9	0.1	1.2	9.6	0.3	0.2	0.3	0.2	2.3	0.442	0.549	0.396	0.437
	max	90.4	0.8	3.4	31.5	2.4	1.5	0.9	1.0	3.2	0.454	0.625	0.530	0.571
	mean	57.6	0.2	2.5	20.4	1.4	0.7	0.7	0.5	2.8	0.448	0.596	0.469	0.516
	median	56.1	0.2	2.5	20.0	1.4	0.6	0.5	0.3	2.8	N/A	N/A	N/A	N/A
	S.D.	28.9	0.1	1.2	9.6	0.3	0.2	0.3	0.2	2.3	0.004	0.023	0.036	0.033
	DL	0.2	0.7	0.1	0.1	0.1	0.4	0.5	0.4	N/A	N/A	N/A	N/A	N/A
	>DL (%)	100%	100%	100%	100%	88%	72%	56%	76%	100%	89%	64%	43%	46%

concentrations in both the Norwegian Current and East Greenland Current, and there is no difference in TC or CC concentrations between these two currents ( $p > 0.05$  Table SI-7b, Supporting Information),<sup>33</sup> which means there is no concentration gradient between the input and output of chlordanes by ocean currents in the East Arctic Ocean.

Air–water exchange of chlordanes was mostly from water to air (Table SI-4, Supporting Information). The air–water exchange velocities were higher than for HCHs and HEPX at the same wind speed due to their higher  $K_{aw}$  (Table SI-5, Supporting Information). The fluxes ranged from 0.21 to 1.3 ng m<sup>-2</sup> d<sup>-1</sup> for CC and −0.63 to 5.2 ng m<sup>-2</sup> d<sup>-1</sup> for TC.

EFs for TC in the dissolved phase averaged  $0.469 \pm 0.036$  (Table SI-6, Supporting Information), whereas CC in both gas ( $0.513 \pm 0.011$ ) and dissolved phase ( $0.516 \pm 0.033$ ) were depleted in (−) enantiomers (EFs > 0.500). There were only a few samples detected with TC in the gas phase with very low concentrations as well as EFs (Table SI-6, Supporting Information). The (+) enantiomer of TC in the Arctic air were found to be less abundant than the (−) one resulting in EFs lower than 0.500, and it is the opposite for CC, thus the EFs of CC were higher than 0.500.<sup>45</sup> The same pattern was also observed in the soil<sup>46</sup> and overlying air<sup>47</sup> and Great Lake region atmosphere.<sup>47,48</sup> In contrast, TC and CC were found to be racemic in the Arctic surface water under the ice cover in 1994, which represent unaltered fresh chlordanes loadings to the Arctic Ocean.<sup>44</sup> The nonracemic signals found in Arctic air and the subarctic seawater samples in this study suggest long-range transport of nonracemic chlordanes from the lower latitude continental sources.

**p,p'-DDE.** A detailed report can be found in Supporting Information. The  $[p,p'\text{-DDE}]_{\text{gaseous}}$  was  $0.5 \pm 0.3$  pg m<sup>-3</sup>. The  $[p,p'\text{-DDE}]_{\text{dissolved}}$  was  $0.5 \pm 0.2$  (0.2–1.0) pg L<sup>-1</sup>. The air–water exchange direction of p,p'-DDE was deposition before the bloom and evaporation during the bloom (YD 127–135). The flux ranged from −0.37 to 0.37 ng m<sup>-2</sup> d<sup>-1</sup>.

**Influence of Long Range Transport.** *Atmospheric Transport.* A total of 28 back trajectories were computed using NOAA's Hysplit model (Figure 1a), of which 11 indicated air masses were from East Arctic Ocean, seven from North America Arctic Ocean, while the rest originated above the Atlantic Ocean close to Iceland. The Arctic is dynamically exchanging OCPs with the sub-Arctic ecosystem through air and water currents. As discussed above, gas phase concen-

trations for low molecular weight OCPs ( $\alpha$ -HCH, HCB) in the Arctic were higher than those measured in this study and at lower latitudes in general, while heavier OCPs (HEPX, chlordanes, and p,p'-DDE) were lower or similar to what were found in this study. In other words, volatile OCPs that had previously reached the Arctic Ocean by both atmospheric and oceanic transport displayed higher concentrations there than at lower latitudes. This concentration gradient is probably augmented by the release from melting snow packs<sup>9</sup> and the Arctic Ocean.<sup>9,29</sup> Polar easterlies brought higher concentrations of low molecular weight OCPs to the Icelandic low pressure area which we sampled during this cruise and probably caused the observed net deposition of these OCPs. In contrast, the exchange of heavier OCPs between the Arctic and sub-Arctic atmosphere seemed at steady state.

*Ocean Currents.* The constant  $\alpha/\gamma$ -HCH ratios (Figure 3, Table 1, and Table SI-2b, Supporting Information) and EFs (Figure 4, Table 1, and Table SI-6, Supporting Information) of dissolved HCHs suggested that all dissolved phase samples were collected from the same water mass, in our case the Irminger Current. Although water temperature and density data at depth suggested there was cold water current intrusion below the mixed layer depth after YD130,<sup>24</sup> we sampled the upper mixed layer. OCP concentration profiles were characteristic of the Irminger Current combined with the influence of local biogeochemical processes with no or little influence from other water currents. Irminger and Norwegian Current both originate from the N. Atlantic Current (Figure 1c), but  $[OCPs]_{\text{dissolved}}$  were much higher in the Irminger Current (this study) than in the Norwegian Current (Figure SI-4, Table SI-7b, Supporting Information),<sup>33</sup> which demands future investigation. We propose to collaborate with oceanographers to measure POPs in major currents in the Arctic (i.e., Labrador Current, Norwegian Current, East Greenland Current) using passive samplers attached to Lagrangian Floats in the future to study the input/output of POPs to the Arctic Ocean by current transport. Lagrangian Floats have been shown to work well to stay within the same water mass.<sup>22,24</sup> The float attached passive samplers thus can retrieve the characterizations of POPs in that water mass.

The deposited low molecular weight OCPs in the N. Atlantic near Iceland are then flowing west and south with the Irminger Current, which loses its heat through air–water heat exchange and finally meets with the Labrador Current to form dense



overflows leading to North Atlantic Deep Water (Figure SI-4, Supporting Information).<sup>49,50</sup>

**Biogeochemical Processes during the Bloom.** The bloom periods were divided according to Alkire et al.<sup>22</sup> into prebloom (YD 123–127), main bloom (YD 127–134), termination (YD 134–135), and postbloom (YD 141–143).  $\alpha$ ,  $\gamma$ -HCH gas phase concentrations were significantly correlated with each other ( $r = 0.65$ ,  $P < 0.01$ , Figure 2). As  $\alpha$ ,  $\gamma$ -HCH have similar physicochemical properties and are thus affected by the same biogeochemical processes, they should correlate well with each other (see dissolved phase  $\alpha$ ,  $\gamma$ -HCHs) if the technical mixture of HCHs was their only source. The deviation of the correlation coefficient from 1 indicated there was an additional source of  $\gamma$ -HCH, probably due to the more recent usage of lindane (>99%  $\gamma$ -HCH) rather than of the technical HCH mixture. Although the air–water exchange directions for  $\gamma$ -HCH and HCB were always deposition throughout the cruise, the gas phase concentrations did not decrease over time, which indicates compensation by continuous advection/turbulent diffusion input from long-range atmospheric transport. The observed difference between EFs measured in water and atmosphere support the idea that long-range transport was important for gas phase concentrations. The Arctic was most likely the source due to the higher levels of these contaminants observed there (Figure SI-3, Supporting Information). HEPX and  $\alpha$ -HCH in the gas phase have a correlation coefficient of 0.84 ( $P < 0.01$ ). It is unclear if this indicated that they have the same source and long-range transport dominated over other processes such as air–water exchange or just a coincidence, which deserves further investigation. There was not any significant difference for any OCP gas phase concentrations among prebloom, main bloom plus termination, and postbloom period (see more discussions on biogeochemical processes in page SI-13, Supporting Information).

Changes in dissolved phase concentration trends should be governed by the biogeochemical processes happening within the bloom area as no mixing of other water masses occurred (see above).  $\alpha$ ,  $\gamma$ -HCH dissolved phase concentrations showed an even better correlation ( $r = 0.97$ ,  $P < 0.01$ , Figure 3) than in the gas phase. Thus the  $\alpha/\gamma$ -HCH ratios were relatively constant in the dissolved phase.  $[\alpha, \gamma\text{-HCH}]_{\text{dissolved}}$  was increasing as the bloom evolved and decreasing during the postbloom period (Figure 3), and the  $[\alpha, \gamma\text{-HCH}]_{\text{dissolved}}$  during the prebloom phase was significantly lower than those during the main bloom and termination period ( $P < 0.05$ ). The dissolved concentrations of  $\alpha$ ,  $\gamma$ -HCH were also positively correlated with the average POC concentrations ( $[\text{POC}]$ ) in the mixed layer ( $r = 0.71$ ,  $P < 0.01$ ) and negatively correlated with the mixed layer depth (MLD) ( $r = -0.70$ ,  $P < 0.01$ ).  $[\text{POC}]$ 's variations were caused by the phytoplankton bloom; thus, the  $[\text{POC}]$  profile was independent from the MLD.<sup>22</sup>  $\beta$ -HCH did show a weaker correlation with MLD ( $r = -0.40$ ,  $P < 0.05$ ). And  $[\beta\text{-HCH}]_{\text{dissolved}}$  during the prebloom was lower than during the main bloom and postbloom periods ( $P < 0.05$ ). Among heavier OCPs, only HEPX demonstrated a strong inverse correlation with MLD ( $r = -0.52$ ,  $P < 0.01$ ). Similar to the HCHs,  $[\text{HEPX}]_{\text{dissolved}}$  during the prebloom was lower than during the main bloom and postbloom periods as well ( $P < 0.05$ ). Interestingly, HEPX and  $\alpha$ -HCH also correlated with each other in the dissolved phase ( $r = 0.54$ ,  $P < 0.01$ ). The concentration profiles of more hydrophobic and lipophilic OCPs were also altered by the net evaporation and removal by sorption to sinking particles besides the MLD in contrast to low

molecular weight OCPs. Compared to HCHs and HEPX, the dissolved phase concentrations of heavier OCPs (i.e., p,p'-DDE, TC, CC) did not increase over time. HCB did not have any significant correlations with MLD or POC and not even with water temperature as observed in the Arctic.<sup>33</sup>

In general, the bloom generated sinking POC did not play a dominant role in controlling the fate of these selected OCPs in the seawater as suggested by previous studies.<sup>51</sup> It was hypothesized that uptaking of POPs by phytoplankton and subsequent export of POPs with settling particles under eutrophic conditions would lead to depletion of dissolved phase concentrations and subsequent net deposition of POPs from air to water. The hypothesis also assumes steady-state conditions: air–water exchange flux of POPs equals the flux between water–plankton and in turn equals air–deep water flux and that POPs sequestered into deep water are considered not to be available for exchange anymore. As discussed in Dachs et al.,<sup>21</sup> this model is designed to study the effects of eutrophication on air–water exchange of POPs at mid- and long-term. Short-term variations (daily, weekly) in mixed layer depth and atmospheric boundary layer height would complicate the average effects of biological uptake on air–water gas exchange process. In addition, there was a rapid shift of phytoplankton community composition during the bloom. It was diatom dominated before the significant export of POC on YD134 and was picoeukaryotic phytoplankton thereafter.<sup>24</sup> The former sink faster (estimated 50–100 m d<sup>-1</sup>) than the latter.<sup>26</sup> Different species probably have different lipids which likely have different affinities to POPs.<sup>52</sup> All these short-term variances contributed to the observed dissolved phase concentration profiles. Thus, the Dachs model may not be applicable to the three-week NABE study. During the same NABE cruise, Bagniewski et al.<sup>24</sup> found that the POC flux at 600 m was much less than at 100 m, suggesting sinking POC was remineralized quickly below the mixed layer. This remineralization process would release POPs back to the water column in the dissolved phase. Vertical convective mixing in the NABE area can lead to deepening of mixed layer depth<sup>53</sup> and retrap these released POPs back to the mixed layer, which are then available for air–water exchange. For this NABE study, a box model is needed to evaluate the short-term variations in OCP concentrations observed.

**Role of Arctic.** OCPs with high dissolved phase concentrations displayed net volatilization in the Arctic Ocean (i.e.,  $\alpha$ -HCH). These pollutants are carried out by polar easterlies and deposited in lower latitudes, such as our study region south of Iceland (see above). Although  $\gamma$ -HCH has physicochemical properties similar to those of  $\alpha$ -HCH, different emission scenarios caused net deposition of  $\gamma$ -HCH even in the Arctic. The Arctic not only loses high levels of pollutants through atmospheric transport but also through outflowing water currents. The incoming warmer Norwegian current (average water temperature 6.9 °C, sample nos. 1–6 and 11–14 from cruise ARKXX) carried much lower concentrations of  $\alpha$ ,  $\gamma$ -HCH ( $4.1 \pm 3.1$  and  $1.7 \pm 1.5$  pg/L) and HCB ( $2.4 \pm 1.0$  pg/L) than the outflowing colder water (−1.0 °C, Sample No. 10 and 16–22 from cruise ARKXX) with an average  $[\alpha, \gamma\text{-HCH}]_{\text{dissolved}}$  of  $30.4 \pm 18.7$ ,  $10.6 \pm 6.4$  pg/L, and  $[\text{HCB}]_{\text{dissolved}}$  of  $7.4 \pm 1.6$  (Table SI-7b, Supporting Information),<sup>33</sup> respectively. The reduction of pollutant levels observed in the Arctic is thus partially due to the outflowing currents with high levels of these pollutants as predicted in previous modeling studies.<sup>7,8</sup>

The warm northward North Atlantic Current brings not only heat but also pollutants to the Arctic (Figure SI-4, Supporting Information). The current loses heat and sinks at downwelling sites in the Arctic and returns south when the water reaches the deep ocean. This is part of the ocean conveyor belt that redistributes heat, salt, and pollutants globally. However, the freshwater discharge of melting ice in the Arctic and Greenland is speculated to stabilize the water column and halt the deep water formation, which is a critical component of the thermohaline circulation.<sup>54,55</sup> It is unclear how climate change is going to affect the pressure systems (i.e., Icelandic low pressure cell in this study), polar fronts, and thermohaline circulations. Any changes in these planetary-scale circulations are going to change the distribution and residence time of OCPs in the recycling pool and thus influence the human and biological exposures to the contaminants.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional information on Materials and Methods, Results, Tables with sampling details, and Figures with OCPs' concentrations and comparisons. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Tel: 001-401-874-6612. Fax: 001-401-874-6811. E-mail: [lohmanna@gso.uri.edu](mailto:lohmanna@gso.uri.edu).

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Jaward, F. M.; Barber, J. L.; Booij, 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.
- (2) Gioia, R.; Lohmann, R.; Dachs, J.; Temme, C.; Lakaschus, S.; Schulz-Bull, D.; Hand, I.; Jones, K. C. Polychlorinated biphenyls in air and water of the North Atlantic and Arctic Ocean. *J. Geophys. Res., [Atmos.]* **2008**, *113*, D19302.
- (3) Zhang, L.; Lohmann, R. Cycling of PCBs and HCB in the Surface Ocean-Lower Atmosphere of the Open Pacific. *Environ. Sci. Technol.* **2010**, *44*, 3832–3838.
- (4) Wong, F.; Jantunen, L. M.; Pućko, M.; Papakyriakou, T.; Staebler, R. M.; Stern, G. A.; Bidleman, T. F. Air–Water Exchange of Anthropogenic and Natural Organohalogenes on International Polar Year (IPY) Expeditions in the Canadian Arctic. *Environ. Sci. Technol.* **2010**, *45*, 876–881.
- (5) Bidleman, T.; Kylin, H.; Jantunen, L.; Helm, P.; Macdonald, R. 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.
- (6) Macdonald, R.; McLaughlin, F.; Adamson, L. The Arctic Ocean—The Last Refuge of Volatile Organochlorines. *Can. Chem. News* **1997**, *49*, 28–29.
- (7) Li, Y.; Macdonald, R.; Ma, J.; 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.
- (8) Pućko, M.; Stern, G. A.; Macdonald, R. W.; Barber, D. G.; Rosenberg, B.; Walkusz, W. When will  $\alpha$ -HCH disappear from the western Arctic Ocean? *J. Mar. Syst.* **2011**, in press.
- (9) Ma, J.; Hung, H.; Tian, C.; Kallenborn, R. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. *Nat. Clim. Change* **2011**, *1*, 255–260.
- (10) Dachs, J. Atmospheric science: Coming in from the cold. *Nat. Clim. Change* **2011**, *1*, 247–248.
- (11) Li, Y. F.; Macdonald, R. W. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. *Sci. Total Environ.* **2005**, *342*, 87–106.
- (12) 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.
- (13) Becker, S.; Halsall, C.; Tych, W.; Kallenborn, R.; Su, Y.; Hung, H. Long-term trends in atmospheric concentrations of [alpha]- and [gamma]-HCH in the Arctic provide insight into the effects of legislation and climatic fluctuations on contaminant levels. *Atmos. Environ.* **2008**, *42*, 8225–8233.
- (14) UNECE. *Protocol on Persistent Organic Pollutants under the 1979 Convention on Long-Range Transboundary Air Pollution*; United Nations Economic Commission for Europe: 1998; ECE/EB, Air/60.
- (15) UNEP. *Final act of the plenipotentiaries on the Stockholm Convention on persistent organic pollutants*; United Nations Environment Program Chemicals: 2001.
- (16) Růžicková, P.; Klánová, J.; Čupr, P.; Lammel, G.; Holoubek, I. An assessment of air–soil exchange of polychlorinated biphenyls and organochlorine pesticides across Central and Southern Europe. *Environ. Sci. Technol.* **2007**, *42*, 179–185.
- (17) Li, Y. F.; Harner, T.; Liu, L.; Zhang, Z.; Ren, N. Q.; Jia, H.; Ma, J.; Sverko, E. Polychlorinated Biphenyls in Global Air and Surface Soil: Distributions, Air–Soil Exchange, and Fractionation Effect†. *Environ. Sci. Technol.* **2009**, *44*, 2784–2790.
- (18) Bogdal, C.; Nikolic, D.; Lüthi, M. P.; Schenker, U.; Scheringer, M.; Hungerbühler, K. Release of legacy pollutants from melting glaciers: model evidence and conceptual understanding. *Environ. Sci. Technol.* **2010**, *44*, 4063–4069.
- (19) Geisz, H. N.; Dickhut, R. M.; Cochran, M. A.; Fraser, W. R.; Ducklow, H. W. Melting Glaciers: A Probable Source of DDT to the Antarctic Marine Ecosystem. *Environ. Sci. Technol.* **2008**, *42*, 3958–3962.
- (20) Nizzetto, L.; Macleod, M.; Borgå, K.; Cabrerizo, A.; Dachs, J.; Guardo, A. D.; Ghirardello, D.; Hansen, K. M.; Jarvis, A.; Lindroth, A. Past, Present, and Future Controls on Levels of Persistent Organic Pollutants in the Global Environment. *Environ. Sci. Technol.* **2010**, *314*–327.
- (21) Dachs, J.; Eisenreich, S. J.; Hoff, R. M. Influence of Eutrophication on Air–Water Exchange, Vertical Fluxes, and Phytoplankton Concentrations of Persistent Organic Pollutants. *Environ. Sci. Technol.* **2000**, *34*, 1095–1102.
- (22) Alkire, M. B.; D'Asaro, E.; Lee, C.; Perry, M. J.; Gray, A.; Cetinić, I.; Briggs, N.; Rehm, E.; Kallin, E.; Kaiser, J.; González-Posada, A. Estimates of net community production and export using high-resolution, Lagrangian measurements of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, and POC through the evolution of a spring diatom bloom in the North Atlantic. *Deep-Sea Res.*, in press.
- (23) Berrojalbiz, N.; Dachs, J.; Del Vento, S.; Ojeda, M. J.; Valle, M. C.; Castro-Jiménez, J.; Mariani, G.; Wollgast, J.; Hanke, G. Persistent Organic Pollutants in Mediterranean Seawater and Processes Affecting



Their Accumulation in Plankton. *Environ. Sci. Technol.* **2011**, *45*, 4315–4322.

(24) Bagniewski, W.; Fennel, K.; Perry, M. J.; D'Asaro, E. A. Optimizing models of the North Atlantic spring bloom using physical, chemical and bio-optical observations from a Lagrangian float. *Biogeosciences Discussions* **2010**, *7*, 8477–8520.

(25) Sieracki, M. E.; Verity, P. G.; Stoecker, D. K. Plankton community response to sequential silicate and nitrate depletion during the 1989 North Atlantic spring bloom. *Deep-Sea Res., Part II* **1993**, *40*, 213–225.

(26) Briggs, N.; Perry, M. J.; Cetinić, I.; Lee, C.; D'Asaro, E.; Gray, A. M.; Rehm, E. High-resolution observations of aggregate flux during a sub-polar North Atlantic spring bloom. *Deep-Sea Res., Part I* **2011**, *58*, 1031–1039.

(27) 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.

(28) Li, Y. Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *Sci. Total Environ.* **1999**, *232*, 121–158.

(29) Jantunen, L. M.; Helm, P. A.; Kylin, H.; Bidleman, T. F. Hexachlorocyclohexanes (HCHs) In the Canadian Archipelago. 2. Air–Water Gas Exchange of  $\alpha$ - and  $\gamma$ -HCH. *Environ. Sci. Technol.* **2007**, *42*, 465–470.

(30) Xie, Z.; Koch, B.; Möller, A.; Sturm, R.; Ebinghaus, R. Transport and fate of hexachlorocyclohexanes in the oceanic air and surface seawater. *Biogeosciences Discussions* **2011**, *8*, 5537–5562.

(31) Hung, H.; Kallenborn, R.; Breivik, K.; Su, Y.; Brorström-Lundén, E.; Olafsdottir, K.; Thorlacius, J. M.; Leppänen, S.; Bossi, R.; Skov, H. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Sci. Total Environ.* **2010**, *408*, 2854–2873.

(32) Pozo, K.; Harner, T.; Lee, S. C.; Wania, F.; Muir, D. C. G.; Jones, K. C. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. *Environ. Sci. Technol.* **2009**, *43*, 796–803.

(33) Lohmann, R.; Gioia, R.; Jones, K. C.; Nizzetto, L.; Temme, C.; Xie, Z.; Schulz-Bull, D.; Hand, I.; Morgan, E.; Jantunen, L. Organochlorine Pesticides and PAHs in the Surface Water and Atmosphere of the North Atlantic and Arctic Ocean. *Environ. Sci. Technol.* **2009**, *43*, 5633–5639.

(34) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental organic chemistry*; John Wiley: 2003.

(35) Su, Y.; Hung, H.; Blanchard, P.; Patton, G. W.; Kallenborn, R.; Konoplev, A.; Fellin, P.; Li, H.; Geen, C.; Stern, G. Spatial and seasonal variations of hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB) in the Arctic atmosphere. *Environ. Sci. Technol.* **2006**, *40*, 6601–6607.

(36) Ding, X.; Wang, X. M.; Xie, Z. Q.; Xiang, C. H.; Mai, B. X.; Sun, L. G.; Zheng, M.; Sheng, G. Y.; Fu, J. M.; 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.

(37) 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.

(38) Hargrave, B. T.; Barrie, L. A.; Bidleman, T. F.; Welch, H. E. Seasonality in exchange of organochlorines between Arctic air and seawater. *Environ. Sci. Technol.* **1997**, *31*, 3258–3266.

(39) 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.

(40) 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.

(41) 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.

(42) Shen, L.; Wania, F.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Bidlemans, T. F. Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America. *Environ. Sci. Technol.* **2005**, *39*, 409–420.

(43) Harner, T.; Wiberg, K.; Norstrom, R. Enantiomer fractions are preferred to enantiomer ratios for describing chiral signatures in environmental analysis. *Environ. Sci. Technol.* **2000**, *34*, 218–220.

(44) Jantunen, L.; Bidleman, T. Organochlorine pesticides and enantiomers of chiral pesticides in Arctic Ocean water. *Arch. Environ. Contam. Toxicol.* **1998**, *35*, 218–228.

(45) Bidleman, T. F.; Jantunen, L. M. M.; Helm, P. A.; Brorström-Lundén, E.; Juntto, S. Chlordane enantiomers and temporal trends of chlordane isomers in Arctic air. *Environ. Sci. Technol.* **2002**, *36*, 539–544.

(46) Leone, A. D.; Amato, S.; Falconer, R. L. Emission of chiral organochlorine pesticides from agricultural soils in the cornbelt region of the US. *Environ. Sci. Technol.* **2001**, *35*, 4592–4596.

(47) Bidleman, T.; Alegria, H.; Ngabe, B.; Green, C. Trends of chlordane and toxaphene in ambient air of Columbia, South Carolina. *Atmos. Environ.* **1998**, *32*, 1849–1856.

(48) Ulrich, E. M.; Hites, R. A. Enantiomeric ratios of chlordane-related compounds in air near the Great Lakes. *Environ. Sci. Technol.* **1998**, *32*, 1870–1874.

(49) Dong, L.; Colucci, S. J. The role of deformation and potential vorticity in Southern Hemisphere blocking onsets. *J. Atmos. Sci.* **2005**, *62*, 4043–4056.

(50) Lumpkin, R.; Speer, K. Global ocean meridional overturning. *J. Phys. Oceanography* **2007**, *37*, 2550–2562.

(51) Dachs, J.; Lohmann, R.; Ockenden, W. A.; Méjanelle, L.; Eisenreich, S. J.; Jones, K. C. Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36*, 4229–4237.

(52) Jonker, M. T. What is causing biomagnification of persistent hydrophobic organic chemicals in the aquatic environment? *Environ. Sci. Technol.* **2012**, *46*, 110–111.

(53) D'Asaro, E. A. Convection and the seeding of the North Atlantic bloom. *J. Mar. Syst.* **2008**, *69*, 233–237.

(54) Manabe, S.; Stouffer, R. J. Coupled ocean-atmosphere model response to freshwater input: Comparison to Younger Dryas event. *Paleoceanography* **1997**, *12*, 321–336.

(55) Broecker, W. S.; Peteet, D. M.; Rind, D. Does the ocean-atmosphere system have more than one stable mode of operation? *Nature* **1985**, *315*, 21–26.