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Distribution and air–sea exchange of organochlorine pesticides in the North Pacific and the Arctic

Distribution and air–sea exchange of organochlorine pesticides in the North Pacific and the Arctic

Minghong Cai[a,b,*], Yuxin Ma[a,b], Zhiyong Xie[c,**], Guangcai Zhong[c], Axel Möller[c], Haizhen Yang[b], Renate Sturm[c], Jianfeng He[a], Ralf Ebinghaus[c], Xiang-Zhou Meng[b]

[a]SOA Key Laboratory for Polar Science, Polar Research Institute of China, Shanghai 200136, China

[b]State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

[c]Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research GmbH, Institute of Coastal Research, Max-Planck Street 1, D-21502 Geesthacht, Germany

[1] Surface seawater and boundary-layer air samples were collected on the icebreaker *Xuelong* (Snow Dragon) during the Fourth Chinese Arctic Research Expedition (CHINARE2010) cruise in the North Pacific and Arctic Oceans during 2010. Samples were analyzed for organochlorine pesticides (OCPs), including three isomers of hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), and two isomers of heptachlor epoxide. The gaseous total HCH (ΣHCHs) concentrations were approximately four times lower (average 12.0 pg m^{-3}) than those measured during CHINARE2008 (average 51.4 pg m^{-3}), but were comparable to those measured during CHINARE2003 (average 13.4 pg m^{-3}) in the same study area. These changes are consistent with the evident retreat of sea ice coverage from 2003 to 2008 and increase of sea ice coverage from 2008 to 2009 and 2010. Gaseous β-HCH concentrations in the atmosphere were typically below the method detection limit, consistent with the expectation that ocean currents provide the main transport pathway for β-HCH into the Arctic. The concentrations of all dissolved HCH isomers in seawater increase with increasing latitude, and levels of dissolved HCB also increase (from 5.7 to 7.1 pg L^{-1}) at high latitudes (above 73°N). These results illustrate the role of cold condensation processes in the transport of OCPs. The observed air–sea gas exchange gradients in the Arctic Ocean mainly favored net deposition of OCPs, with the exception of those for β-HCH, which favored volatilization.

1. Introduction

[2] Although the Arctic Ocean has been a semi-enclosed basin for 60–100 million years, it is no longer a pristine environment free of anthropogenic contaminants [*MacDonald et al.*, 2000]. Numerous studies have focused on the fates of persistent organic pollutants (POPs) in the Arctic Ocean. Organochlorine pesticides (OCPs), which have mainly been applied in temperate and tropical areas of the world, can be transported to the Arctic Ocean via atmospheric long-range transport (LRT), through ocean currents, and by runoff into the Arctic's large drainage basin [*Li et al.*, 2005]. The LRT potential of hexachlorocyclohexane isomers (α-HCH, γ-HCH) and hexachlorobenzene (HCB) is higher and their global dispersion is faster relative to those of other POPs [*Barber et al.*, 2005]. After the early 1990s, decreasing emissions of α-HCH into the atmosphere were superseded by the historical burden of α-HCH in upper ocean waters, accumulated over 40 years of technical HCH use. As a result, ocean currents have become a significant pathway to transport α-HCH into the Arctic Ocean [*MacDonald et al.*, 2000; *Li et al.*, 2004]. Moreover, Ocean current through the Bering Strait is believed to be an important pathway for β-HCH entering into the Arctic because of relatively low Henry's Law Constant (HLC) of β-HCH compare to other POPs [*Li et al.*, 2002].

[3] In the Pacific Ocean, a large clockwise gyre moves water from the western side of the North Pacific (Taiwan and Japan) across the Pacific Ocean to the west coast of North America. Then a complex mix of northward-flowing water masses enters Bering Sea through a variety of passages. This combination of currents supplies the water that flows into the Arctic Ocean across the 50-m-deep sill in the Bering Strait. Sea level in the North Pacific Ocean is approximately 0.5 m higher than that in the Arctic Ocean, so that the net flow is into the Arctic Ocean [*MacDonald et*

al., 2000]. Although the occurrence of atmospheric OCPs in the Arctic region has been extensively monitored [*Hung et al.*, 2010; *Su et al.*, 2006, 2008], the influence of the oceans on the distribution of OCPs is still uncertain. Moreover, the behavior and occurrence of POPs in different aquatic media is driven by dynamic oceanic biogeochemical cycles, especially the "biological pump". The biological pump acts to remove POPs from the atmosphere via air-to-water deposition, partitioning into organic matter, and removal via carbon export to the deeper oceans [*Dachs et al.*, 2002]. This process has also been insufficiently studied, especially against the backdrop of climate change.

[4] The decline in the global use of some OCPs, and hence the reduction in their primary sources, may further highlight the role of environmental processing and the influence of climatic variability on OCP levels in the Arctic region [*Becker et al.*, 2008]. As the atmospheric levels of α-HCH have continued decreasing, the net air–sea exchange has been observed to switch from net deposition to net outgassing [*Ding et al.*, 2007; *Wu et al.*, 2010; *Jantunen et al.*, 1995, 2008; *Bidleman et al.*, 1995]. Reductions in sea ice coverage because of global warming may contribute significantly to enhancements of HCH concentrations observed in the Chukchi and Beaufort Seas during 2008 [*Wu et al.*, 2010] and elevated atmospheric HCB concentrations observed at the Zeppelin station between 2003 and 2006 [*Hung et al.*, 2010]. This relationship is difficult to confirm, however, due to the co-variability of climate and different intrinsic physical-chemical properties of OCPs. Further monitoring is still needed.

[5] During the Fourth Chinese National Arctic Research Expedition (CHINARE2010), marine boundary layer air and surface seawater samples were collected from July to September 2010 between East Asia and the high Arctic (35°N to 82°N). The occurrences of OCPs, notably HCHs, HCB and heptachlor epoxide, were measured and analyzed. In addition to providing updates on

environmental OCP levels, these measurements provide additional information on whether the global warming and the associated rapid retreat of sea ice play an important role in determining the variability of OCPs and the direction of air–sea exchange.

2. Experimental Methods

2.1. Sampling Cruise

[6] Air and seawater samples were taken from the East China Sea to the high Arctic (33.23°N–84.5°N) during an Arctic expedition of the research ice-breaker *R/V Xuelong (Snow Dragon)* between July and September 2010. Air samples (~500 m^3 per sample, 17 samples) were taken via a high-volume air sampler placed at the front of the ship's upper deck (20 m). The sampler consisted of a glass fiber filter ([GFF], GF/F, pore size: 0.7 μm) to trap airborne particles, followed by a self-packed PUF/XAD-2 glass column to collect species in the gaseous phase. The air columns and filters were stored at –20°C between collection and analysis. Seawater samples (176–1120 L per sample, 18 samples) were taken using the ship's intake system through a sampler consisting of a GFF (GF/C, pore size: 1.2 μm) followed by a self-packed PAD-3 glass column. The filters were stored at –20°C and the columns at 4°C. The dates, positions, temperatures, and wind speeds of the samples are listed in Tables A1 and A2 in the Auxiliary Materials.

2.2. Chemicals

[7] All solvents (methanol, acetone, dichloromethane and n-hexane) were residue grade and were distilled further in an all-glass unit prior to use. Analytical standards of HCHs, HCB, heptachlor epoxide, and deuterated α-HCH (d_6-HCH) were purchased from Dr. Ehrenstorfer (Augsburg, Germany), and an analytical standard of ^{13}C-HCB was obtained from Cambridge Isotope Laboratories.

2.3. Extraction, Clean-up, and Analysis

[8] Extraction, clean-up, and analysis of the samples were performed according to the method described elsewhere [*Zhong et al. 2012; Xie et al., 2011*]. Briefly, each sample was spiked with the surrogate standard d_6-HCH prior to extraction, then extracted using dichloromethane with MX extractor and purified on a 10% water-deactivated silica gel column. The extracts were spiked with injection standard ^{13}C-HCB and concentrated down to 30 µL. Analysis was done using a gas chromatography/mass spectrometry (GC/MS) system (6890 GC/5975 MSD) in electron-capture negative chemical-ionization mode (ECNCI).GC-MS conditions for the determination of OCPs were listed in Table A3 in the Auxiliary Materials. Quantification and quality control are monitored using *m/z* values for selective ions of 255 and 71 for HCH, 255 and 284 for HCB, 310 and 306 for *cis-* and *trans*-heptachlor epoxide, 261 and 73 for d_6-HCH and 290 for ^{13}C-HCB.

2.4. Quality Assurance and Control

[9] Aluminum foil was used to protect the air columns from ultraviolet light during sampling and avoid degradation of the target compounds in the column. All air columns were precleaned with solvents of different polarities and GFFs were baked at 450°C for 12 h prior to use. All used glassware was baked at 250°C for 10 h and rinsed with solvent, and silica gel columns were cleaned with dichloromethane for 12 h and baked at 450°C for 12 h prior to usage. The effectiveness of these sampling methods for the target analytes has been checked previously on board the German icebreaker *R/V Polarstern* [*Montone et al.*, 2002]. Three field blanks were run for each sample type. All blanks showed very low values, generally in the one- to two-digit absolute pg range. Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation (σ). For compounds showing no blanks, a peak area of 200 was

adopted to represent the background response. MDLs for air samples were 0.03 pg m^{-3} for α-HCH, 0.01 pg m^{-3} for γ- and β-HCH, 0.1 pg m^{-3} for HCB, and 0.01 pg m^{-3} for *cis-* and *trans*-heptachlor epoxide, respectively. MDLs for seawater samples ranged from 0.01 pg L^{-1} for *cis-* and *trans*-heptachlor epoxide to 3.0 pg L^{-1} for HCB. Recoveries of d$_6$-HCH were 81 ± 23% for water samples and 89 ± 35% for air samples. Concentrations of OCPs given in Table 1 are not corrected with recoveries and MDLs.

2.5. Air Mass Back Trajectories

[10] The air mass origins of individual air samples along the cruise were evaluated using back trajectories (BTs) calculated by the NOAA HYSPLIT model. BTs were used to trace the evolution of each air mass backward in time over the previous seven days at 6-hourly intervals. BTs were initialized using the sampling height as arrival height (individual BTs are shown in Figure A1 in the Auxiliary Materials).

3. Results and Discussion

3.1. Hexachlorocyclohexanes

[11] Among the OCPs measured in this study, only HCHs can be detected in some water particulate phase with concentrations just above the MDLs (particle proportion < 2%), therefore, we only discuss observations of OCPs in gaseous and dissolved phases in this work (Table 1). The spatial distribution of atmospheric HCH is shown in Figure 1. The sum of the three HCH isomers (ΣHCHs) ranged from 5.5 to 30.6 pg m^{-3} during the cruise, with a mean and standard deviation of 12.0 ± 5.8 pg m^{-3}. These results are comparable to other measurements taken over global oceans [*MacDonald et al.*, 2000; *Ding et al.*, 2007; *Wu et al.*, 2010; *Montone et al., 2002,* 2005; *Wurl et*

al., 2006; *Jaward et al.*, 2004; *Wong et al.*, 2011]. We observed an increase in ΣHCHs with increasing northern latitude. The observed mean concentrations of ΣHCHs were 10.2 pg m^{-3} in East Asia (38–48°N), 10.8 pg m^{-3} in the North Pacific Ocean (50–66°N), and 14.7 pg m^{-3} in the Arctic Ocean (>70°N). Significant differences analysis (ANOVA) results showed there were significant differences of the concentrations in East Asia, the North Pacific Ocean and the Arctic.

[12] In the atmosphere, the concentration of gaseous α-HCH ([α-HCH]$_{gas}$) ranged from 4.9 to 26.8 pg m^{-3}, with an average of 10.3 ± 5.1 pg m^{-3}. Levels in the boundary layer above the Arctic Ocean were particularly variable, ranging from 5.7 to 26.8 pg m^{-3}. For γ-HCH (lindane), [γ-HCH]$_{gas}$ ranged from less than 1 to 3.8 pg m^{-3}, with an average of 1.7 ± 0.8 pg m^{-3}. Unlike α-HCH, lindane has continued to be used in a number of countries as an insecticide until recently [*Baek et al.*, *2011*]. [γ-HCH]$_{gas}$ showed one very high value in East Asia (3.2 pg m^{-3} at site A17) in which the air masses mainly originated from Northeast China, Korea and Japan. The concentrations of both α- and γ-HCH at site A9 were the highest; however, observed concentrations of β-HCH in the atmosphere were generally very low (less than 0.02 pg m^{-3}), and were often below the MDL. [β-HCH]$_{gas}$ has been reported with relatively high concentrations in 2008 [*Wu et al., 2010*], which might be resulted from the sampling and material preparation procedure, thus it should take great care for comparison with the present data.

[13] The concentrations of dissolved α-, β-, and γ-HCH in seawater ranged widely during the cruise (Figure 2). [α-HCH]$_{diss}$ ranged from 7.6 to 536 pg L^{-1}, with an average of 167 ± 158 pg L^{-1}. [γ-HCH]$_{diss}$ was generally lower than [α-HCH]$_{diss}$, ranging from 1.1 to 134 pg L^{-1} with an average of 34.9 ± 38.3 pg L^{-1}. The highest concentrations for both α- and γ-HCH were observed in the Arctic Ocean, and the lowest concentrations for both species were observed in the sea near East

Asia. The concentrations of both α- and γ-HCH increased slightly with increasing latitude. This result further illustrates the importance of cold condensation [*Wania et al.*, 1993]. Correlation analysis reveals that both [α-HCH]$_{diss}$ and [γ-HCH]$_{diss}$ were significantly positively correlated with latitude and inversely correlated with air temperature (T_{air}) and water temperature (T_{water}) (Figure A2, Table A4 in the Auxiliary Materials).

[14] β-HCH is more bioaccumulative and toxic than the other HCH stereoisomers [Wu *et al.*, 2010; Willett *et al.*, 1998], has a HLC that is 20 times lower than that of α-HCH, and is more efficiently deposited into the North Pacific through solvent-switching [*Li et al.*, 2005; *Xiao et al.*, 2004; *Sahsuvar et al.*, 2003]. Therefore, although observed concentrations of β-HCH in the atmospheric boundary layer were consistently low, observed concentrations of β-HCH in surface seawater ranged from 0.4 to 90 pg L^{-1}, with an average of 39.3 ± 24.5 pg L^{-1}. With the exception of one extremely high level 90 pg L^{-1} observed at site W1 in East Asia, the concentration of β-HCH also increased with increasing latitude, much like the concentrations of α- and γ-HCH. Although the use of technical HCH has been banned in East Asia and Russia, some stockpiles of technical HCH are believed to still exist and usage may continue in some locations [*Primbs et al.*, 2007; *Zheng et al.*, 2010]. The re-emission into the atmosphere and subsequent deposition of 'old' HCH from adjacent contaminated soils may also contribute to the remarkably high concentration observed at site W1 [*Li et al.*, 2005]. Oceanic flow through the Bering Strait might be a more important pathway for β-HCH transport into the Arctic than atmospheric LRT [*Li et al.*, 2002]. The relatively high concentrations observed in the Chukchi Sea confirm elevated concentrations of β-HCH in the Bering Sea. The Bering and Chukchi Seas are known to be the most vulnerable locations for β-HCH loading [*Li et al.*, 2005].

[15] [HCH]$_{diss}$ in this study were significantly lower than those observed in the same areas before 2000 [*Li et al.,* 2002]. No seawater concentration data for these water bodies are available for recent years, however, so we cannot evaluate the recent variability of HCH concentrations in the North Pacific and Arctic Oceans. In agreement with previous studies, HCH concentrations observed in the North Pacific and North American Arctic Oceans (NAAO) were higher than those observed in the North Atlantic and Eurasian Arctic Oceans (EAO) [*Montone et al.*, 2002; *Jantunen et al.*, 1995; *Lohmann et al.*, 2009].

3.2. Hexachlorobenzene

[16] Observations of [HCB]$_{gas}$ ranged from 1.0 to 63.8 pg m^{-3}, with an average of 32.0 ± 19.3 pg m^{-3}. These results are similar to those reported by previous studies [*Lohmann et al.,* 2009]. Concentrations of gaseous HCB showed spatial variability in the study area (Figure A3 in the Auxiliary Materials). This variability may be explained by a combination of differences in proximity to suspected key source regions and differences in atmospheric LRT potential [*Hung et al.*, 2010]. Values of [HCB]$_{gas}$ were relatively high in regions adjacent to the suspected key sources (Japan, Russian and USA; sites A17, A16, and A11). These high values indicate possible secondary emissions (e.g., re-emission from soils and sediments), as well as continuing primary emissions (e.g., byproducts of chlorinated chemicals and incomplete combustion processes) [*Barber et al.*, 2005]. During 2003–2006, the atmospheric concentrations of HCB at the Zeppelin station (Svalbard, Norway) increased continuously, with an increase in the mean value from 54 pg m^{-3} in 2003 to 72 pg m^{-3} in 2006, and a similar increase was observed at Alert (Canada) during 2002–2005 [*Hung et al.*, 2010]. *Hung et al.* [2010] attributed this enhancement to reductions in sea ice coverage, which may result in increasing volatilization of chemicals previously deposited in the

ocean, as well as continuing use of pesticides containing HCB. Our observations of HCB in the Arctic Ocean atmosphere (average of 36.2 pg m^{-3}) are obviously lower than those reported by *Hung et al.* [2010].

[17] [HCB]$_{diss}$ ranged from below the MDL to 9.5 pg L^{-1}, with an average of 4.8 ± 2.3 pg L^{-1}. Our results are comparable to previous measurements in the North Atlantic and Arctic Oceans [*Lohmann et al.,* 2009]. Seven samples of dissolved HCB in seawater were below the MDL. Most of these samples were taken in East Asia; however, the sample with the highest concentration was also taken in East Asia (site W1 in the Japan Sea). The concentrations were also quite high (5.7 to 7.1 pg L^{-1}) at high latitudes (above 73°N), further illustrating the importance of cold condensation. Correlation analysis did not show significant correlations between concentrations of either gaseous or dissolved HCB with either latitude or temperature (Table A4 in the Auxiliary Materials).

3.3. Heptachlor Epoxides

[18] Relatively few studies of heptachlor epoxide concentrations have been performed in the region covered by CHINARE2010, especially since 2000. In the atmosphere, *cis*-heptachlor epoxide (*cis*-Hept.) was more abundant than *trans*-heptachlor epoxide (*trans*-Hept.): [*cis*-Hept.]$_{gas}$ ranged from 0.6 to 54.2 pg m^{-3} with an average of 7.9 ± 14.6 pg m^{-3}, while [*trans*-Hept.]$_{gas}$ ranged from 0.3 to 13.4 pg m^{-3} with an average of 2.6 ± 3.7 pg m^{-3}. Remarkably high concentrations of heptachlor epoxides were observed at two sampling sites A1 and A16 in East Asia. The concentrations of both isomers decreased slightly with increasing latitude and declining temperature (Figure A3 and Figure A4 in the Auxiliary Materials). Correlation analysis shows that both gaseous *cis*- and *trans*-Hept. were negatively correlated with latitude and positively correlated with average T_{air} (Table A4 in the Auxiliary Materials). In seawater, [*cis*-Hept.]$_{diss}$ ranged from 0.1

to 2.2 pg L^{-1} with an average of 0.5 ± 0.66 pg L^{-1}, whereas [*trans*-Hept.]$_{diss}$ ranged from 0.05 to

0.90 pg L^{-1} with an average of 0.3 ± 0.28 pg L^{-1}. Similar to the atmosphere, the highest

concentrations of both isomers in seawater were observed in East Asia. The nearby sources in East

Asia might lead to that spatial trend (Figure A5 in the Auxiliary Materials).

3.4. Influence of Sea Ice

[19] Air samples of HCH were also collected in these regions during the CHINARE2003 and

CHINARE2008 cruises, as well as during the 1990s [*Iwata et al.*, 1993; *Ding et al.*, 2007; *Wu et

al.*, 2010]. The measurements of ΣHCH taken during 2003 (average 13.4 pg m^{-3}) were

approximately one order of magnitude lower than those taken during the 1990s [*Ding et al.*, 2007],

while the measurements of ΣHCH taken during 2008 (average 51.4 pg m^{-3}) were approximately

four times higher than those taken during 2003 [*Wu et al.*, 2010]. The measurements taken during

2010 indicate an average ΣHCH of 12.0 pg m^{-3}, comparable to the measurements taken during

2003. Concentrations of α- and γ-HCH in the Arctic Ocean also increased from 2003 to 2008; the

concentrations reported by the present study fall in the middle of those measured in 2003 and those

measured in 2008. The concentrations of β-HCH observed in the atmospheric boundary layer

declined dramatically from 2008 to 2010 (Table A5 in the Auxiliary Materials).

[20] The prominent reductions in the emission of technical HCH that occurred in 1982–1983

(China abandoning technical HCH use) and 1990–1992 (bans of technical HCH use in the former

USSR and in India for agricultural purposes) may contribute considerably to the significant

decrease of HCHs in 2003 relative to the 1990s [*Li et al.*, 2005]. Global warming processes,

especially the retreat of sea ice, may also significantly affect the global fates of some POPs. The

time series of anomalies in sea ice extent in September (the annual minimum value) is shown in

Figure A6 (Auxiliary Materials) for the period 1979–2010, calculated relative to the 1979–2000

average sea ice extent [*Perovich et al.*, 2010]. Sea ice coverage declines substantially from 2003 to

2008, with the lowest sea ice extent occurring in September 2007 and the second lowest in

September 2008. Exceptionally high values of HCHs have been observed under pack ice in the

Canada Basin of the Arctic Ocean [*Macdonald et al.,* 1997]. *Lohmann et al.* [2009] reported that

average concentrations of α- and γ-HCH were twice as high under ice as in water samples

collected in ice-free regions. The retreat of sea ice would enhance the re-emission of HCHs trapped

in the ice sheets. Several consecutive years of low sea ice extent might result in high

concentrations of gaseous HCHs in the atmospheric boundary layer over the Arctic Ocean, such as

those observed during CHINARE2008 [*Wu et al.*, 2010].

[21] The HLC decreases as temperature declines from summer to winter in the Arctic. This

seasonal change in the HLC could promote the re-deposition of gaseous HCHs, increasing the

storage of HCHs under sea ice again [*MacDonald et al.*, 2000; *Sahsuvar et al.*, 2003]. Precipitation

in the form of snow is also known to result in the accumulation of HCH in seasonal snowpack and

sea ice [*Halsall et al.*, 2004]. Sea ice coverage was greater during 2009 and 2010 than during 2008

(Figure A6 in the Auxiliary Materials). This increase in sea ice extent could prevent a portion of

the HCHs trapped under sea ice by seasonal changes from volatilizing to the atmosphere during

2009 and 2010, and result in the relatively low concentrations of HCHs in the Arctic boundary

layer, such as those observed during 2010 relative to 2008. Shifts toward net deposition and

enhancements in settling fluxes also occurred in 2010 relative to 2008. These changes are

discussed in detail in Section 3.5.

[22] The recent variability of HCB in the atmosphere is similar to that of HCHs: concentrations

continuously increased between 2003 and 2006 at the Zeppelin station [*Hung et al.*, 2010], and the concentrations observed during CHINARE2010 are significantly lower than those observed at the Zeppelin Station between 2003 and 2006. That variability may also be explained in part by re-emission of HCB that was previously trapped under sea ice, followed by re-deposition through scavenging by precipitation and air–sea deposition by gas exchange.

3.5. Air–sea Gas Exchange

[23] We have estimated the direction (or equilibrium status) of the air–sea gas exchange at the CHINARE2010 sampling locations based on the fugacity ratio f_{air}/f_{water}, and have calculated the exchange fluxes using a two-film model (details of the calculation are provided in the Auxiliary Materials) [*Wong et al.*, 2011; *Möller et al.*, 2011]. Much like variability in the concentration of α-HCH, changes in the net direction of air–sea exchange of gaseous α-HCH after 2000 are likely to be controlled more by global warming and rapid changes in sea ice coverages than by changes in global emissions of α-HCH. The net direction of gas exchange of α-HCH between seawater and air reversed in the western Arctic with declining primary emissions, from net deposition in the 1980s to net volatilization in the 1990s [*Ding et al.*, 2007; *Jantunen et al.*, 1995; *Bidleman et al.*, 1995; *Jantunen et al.*, 2008]. The retreat of sea ice extent accelerated this process [*Wu et al.*, 2010]; however, our results show that f_{air}/f_{water} ranged from 0.4 to 2.7 in the North Pacific and Arctic Oceans, indicating near-equilibrium states or net deposition of α-HCH. Volatilization potential is only observed at three sites in East Asia and at site 9, where the dissolved concentrations of α-HCH in seawater are very high (Table A6 in the Auxiliary Materials). The deposition fluxes of α-HCH were quite high throughout the cruise, with a median of 5475 pg m^{-2} day^{-1} (Figure 3). Continuous increases in atmospheric levels of α-HCH during recent years may have led to a

change in the direction of air–sea gas exchange and high deposition fluxes. Among the categories of flyers, multi-hoppers, single-hoppers and swimmers, HCHs have typically been placed in the 'swimmers' category [Wania et al., 2003]; however, from a temporal point of view, α-HCH manifests as a multi-hopper in a manner that has been described as the 'grasshopper effect' [Wania et al., 1996]. Due to reductions in primary emissions and climate change, α-HCH undergoes an iterative process consisting of deposition, remobilization into the atmosphere, and re-deposition.

[24] The calculated ratios f_{air}/f_{water} for γ-HCH ranged from 0.7 to 18 (Table A6 in the Auxiliary Materials), suggesting that γ-HCH was also close to equilibrium or undergoing net deposition. This result is consistent with previous studies in the western and eastern Arctic Ocean [Jantunen et al., 2008; Sahsuvar et al., 2003; Lohmann et al., 2009]. γ-HCH was used in Europe and North America until very recently [Baek et al., 2011]. Our observations of net deposition to surface waters indicate continuing loading of γ-HCH into the marine system; however, the calculated exchange fluxes were quite low relative to those calculated for α-HCH (median deposition flux of 710 pg m^{-2} day^{-1}; Figure 3). This result indicates that air–sea transfer is relatively less important as an input flux of γ-HCH [MacDonald et al., 2000; Alexeeva et al., 2001].

[25] With the exception of one sample indicating equilibrium (site 14), all sampling sites indicated net volatilization of β-HCH, with an average f_{air}/f_{water} of 0.06 (Table A6 and Figure A7 in the Auxiliary Materials). This result is consistent with the very low and often undetectable concentrations of β-HCH in the atmosphere. The exchange fluxes of β-HCH are the lowest of any of the isomers, probably because the HLC is lowest for β-HCH.

[26] Previous studies have suggested that HCB is much closer to attaining air–sea equilibrium in the Northern hemisphere than most other POPs [Meijer et al., 2003]. Our results show a range of

f_{air}/f_{water} values from 0.8 to 6.6 in the North Pacific and Arctic Oceans (Figure A8 in the Auxiliary

Materials), indicating that HCB was either close to equilibrium or undergoing net deposition. Net

deposition was also observed in the Canadian Arctic during 2007–2008 [*Wong et al.*, 2011].

Complex air–sea gas exchange conditions were observed in East Asia: the sites with detectable

dissolved concentrations favored net volatilization, while in other sites, near-equilibrium

conditions or slight deposition dominated at other sites (Table A6 in the Auxiliary Materials). The

deposition fluxes obtained for HCB were the highest of any OCP observed during this experiment,

with a median of 10900 pg m^{-2} day^{-1} through the cruise (Figure 3). We suggest that the reason

underlying net deposition of HCB at the sampling locations is the same as that underlying net

deposition of α-HCH. Complicated air–sea exchange conditions for HCB in East Asia further

confirm the existence of secondary emissions of contaminant from soils on the nearby continent.

HCB is characterized as a multi-hopper, meaning that it is likely to adjust quickly to environmental

changes and achieve equilibrium.

[27] With the exception of one sample (site 2) indicating equilibrium, all of our observations

strongly favor net deposition of gaseous heptachlor epoxides (Table A6 in the Auxiliary Materials).

The average deposition fluxes during the cruise were 3200 pg m^{-2} day^{-1} for *cis*-Hept. and 950 pg

m^{-2} day^{-1} for *trans*-Hept. (Figure 3). Deposition was substantially higher in East Asia than in the

Arctic, as the concentrations of heptachlor epoxide isomers increased with decreasing latitude.

[28] Our data imply net deposition of all analyzed species except for β-HCH. This result holds

even for HCB, which is considered to be close to global equilibrium (Figures A7 and A8 in the

Auxiliary Materials). The variability of some OCPs in recent years may be explained by a

short-term release pulse resulting from reductions in sea ice coverage, followed by a change in the

direction of air–sea exchange and elevated settling fluxes. This latter response may enhance the rate at which concentrations of OCPs in the ocean establish equilibrium with those in boundary layer air; however, further monitoring is necessary as the ocean circulation and biological processes play complex roles in the fates of POPs.

4. Conclusion

[29] We have studied the concentrations of OCPs, including three isomers of HCH, HCB, and two isomers of heptachlor epoxide in marine boundary layer air and surface seawater between East Asia and the high Arctic (35°N to 82°N). Levels of ΣHCHs (the sum of α-, β-, and γ-HCH) increase with increasing northern latitude along the cruise track; however, no similar spatial gradients were identified for HCB or heptachlor epoxide. In addition to net volatilization of β-HCH, our data suggest that air–sea gas exchange is dominated by net deposition of all other analyzed species in the study area. These results represent a significant contribution to ongoing exploration of the global distribution of OCPs, particularly in the context of global warming and the associated rapid retreat of sea ice.

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Table 1. Individual concentrations of HCH isomers, HCB, and *cis*- and *trans*-heptachlor epoxide in the atmosphere (pg m^{-3}) and in seawater (pg L^{-1}) at sampling sites from East Asia to the Arctic

Site	α-HCH	β-HCH	Γ-HCH	HCB	Cis-Hept.	Trans-Hept.
East Asia						
A17	8.9	0.005	3.2	55.6	5.1	1.5
A1	7.1	n.d.	1.0	41.0	54.2	10.3
A16	7.2	n.d.	1.6	24.0	36.0	13.4
A15	6.6	n.d.	1.4	13.7	9.2	3.5
A2	12.6	n.d.	1.7	16.1	5.9	3.2
A14	8.8	n.d.	1.1	22.9	5.1	2.6
Mean	8.5	0.005	1.7	28.9	19.3	5.8
North Pacific						
A3	7.1	n.d.	1.0	1.0	1.5	0.7
A4	9.6	0.004	1.2	33.5	3.1	2.1
A5	4.9	0.005	0.7	14.0	0.7	0.3
A6	15.0	0.015	2.3	62.1	0.8	0.4
A7	10.6	0.005	1.7	42.6	0.7	0.3
Mean	9.4	0.007	1.4	30.6	1.4	0.8
Arctic Ocean						
A9	26.8	0.010	3.8	6.9	3.3	1.2
A8	5.7	0.003	1.0	17.4	2.0	1.0
A10	12.5	0.012	2.1	43.7	1.0	0.5
A11	13.4	0.018	2.5	63.8	2.9	1.4
A12	6.9	0.015	1.3	36.6	2.4	1.2
A13	10.7	0.014	1.6	49.0	0.6	0.3
Mean	12.6	0.012	2.0	36.2	2.0	1.0
Mean of the cruise	10.3	0.008	1.7	32.0	7.9	2.6
East Asia						
W1	33.7	90.0	11.7	9.5	2.2	0.8
W18	7.6	28.6	2.4	n.d.	1.0	0.5
W17	73.6	33.8	20.1	n.d.	0.2	0.1
W15	93.9	25.6	16.9	n.d.	0.3	0.2
W16	24.8	29.6	7.8	n.d.	0.4	0.2
W14	180.3	0.4	1.1	3.5	1.2	0.9
W13	57.3	23.4	14.3	n.d.	0.1	0.05
Mean	67.3	33.1	10.6	3.0	0.8	0.4
North Pacific						
W12	136.8	44.3	30.3	3.3	0.1	0.1
W2	102.5	33.6	16.8	3.6	2.1	0.8
W3	65.4	5.3	6.7	n.d.	0.1	0.1
Mean	101.6	27.7	17.9	2.8	0.8	0.4
Arctic Ocean						

W5	106.9	31.5	19.3	2.6	0.1	0.1
W7	223.0	47.0	51.3	2.3	0.2	0.2
W8	310.2	47.6	61.7	4.1	0.1	0.1
W6	67.2	23.7	16.0	n.d.	0.2	0.1
W9	536.0	88.7	134.2	7.1	0.3	0.3
W10	444.9	51.6	86.4	5.7	0.1	0.2
W11	377.8	64.2	96.8	6.2	0.4	0.6
Mean	295.1	50.6	66.5	4.2	0.2	0.2
Mean of the cruise	167.2	39.3	34.9	3.5	0.5	0.3

The site symbol of A indicates atmosphere sample sites, while the symbol of W represents seawater sampling sites.

Figure 1. Concentrations of α- and γ-HCH in the atmosphere along the sampling cruise.

Figure 2. Concentrations of α-, β-, and γ-HCH in sea water along the sampling cruise

Figure 3. Air–sea gas exchange fluxes of HCH isomers, HCB and *cis*- and *trans*-heptachlor epoxide as a function of latitude along the sampling transect. Negative (-) flux indicates deposition into the water column.