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# Transport and fate of hexachlorocyclohexanes in the oceanic air and surface seawater

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## Abstract

Hexachlorocyclohexanes (HCHs) are ubiquitous organic pollutants derived from pesticide application. They are subject to long-range transport, persistent in the environment, and capable of accumulation in biota. Shipboard measurements of HCH isomers ( $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH) in surface seawater and boundary layer atmospheric samples were conducted in the Atlantic and the Southern Ocean in October to December of 2008.  $\Sigma$ HCHs concentrations (the sum of  $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH) in the lower atmosphere ranged from 11.8 to 36.9  $\text{pg m}^{-3}$  (mean:  $26.6 \pm 11.0 \text{ pg m}^{-3}$ ) in the Northern Hemisphere (NH), and from 1.5 to 4.0  $\text{pg m}^{-3}$  (mean:  $2.8 \pm 1.1 \text{ pg m}^{-3}$ ) in the Southern Hemisphere (SH), respectively. Water concentrations were:  $\alpha$ -HCH 0.33–46.8  $\text{pg l}^{-1}$ ,  $\gamma$ -HCH 0.02–33.2  $\text{pg l}^{-1}$  and  $\beta$ -HCH 0.11–2  $\text{pg l}^{-1}$ . HCH concentrations decreased from the North Atlantic to the Southern Ocean, indicating historical use of HCHs in the NH. Spatial distribution showed increasing concentrations from the equator towards North and South latitudes illustrating the concept of cold condensation and less interhemispheric mixing process. In comparison to concentrations measured in 1987–1999/2000, gaseous HCHs were slightly lower, while dissolved HCHs decreased by factor of 2–3 orders of magnitude. Air-water exchange gradients suggested net deposition for  $\alpha$ -HCH (mean:  $3759 \text{ pg m}^{-2} \text{ day}^{-1}$ ) and  $\gamma$ -HCH (mean:  $1987 \text{ pg m}^{-2} \text{ day}^{-1}$ ), whereas  $\beta$ -HCH varied between equilibrium (volatilization:  $<0\text{--}12 \text{ pg m}^{-2} \text{ day}^{-1}$ ) and net deposition (range:  $6\text{--}687 \text{ pg m}^{-2} \text{ day}^{-1}$ ), indicating a multi-hopper transport behavior. Climate change may significantly accelerate the releasing process of “old” HCHs from continental storage (e.g. soil, vegetation and high mountains) and drive long-range transport from sources to deposition in the open oceans. Biological productivities may interfere with the air-water exchange process as well. Consequently, further investigation is necessary to elucidate the long term trends and the biogeochemical turnover of HCHs in the oceanic environment.

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## 1 Introduction

Hexachlorocyclohexanes (HCHs) are ubiquitous organic pollutants derived from pesticide application. They are subject to long-range transport, persistent in the environment, and capable of accumulation in biota (Nizzetto et al., 2010). HCHs can enter the coast, marine and oceanic environment by a number of processes, once introduced they are subject to biogeochemical cycling, sinks, and bioaccumulation processes. Apart from river discharge and continental runoff, the atmospheric deposition is considered to be the primary and most rapid pathway for persistent organic pollutants to the coast and the marine environment as a result of their hydrophobic and semi-volatile nature (Lohmann et al., 2007). Besides, it has been discussed that re-emission of HCHs from indirect sources such as soils, sediments, vegetation, phytoplankton and “old” concentrations in the deep ocean, which may interfere the air-water exchange process and governs their circulation and transport in the marine environment (Dachs et al., 2002; Fenner et al., 2004; Jaward et al., 2004; Lohmann et al., 2006).

As one of legend pesticides, hexachlorocyclohexanes (HCHs) have been extensively studied for their regional and long-range transport via atmosphere, ocean current and exchange among different media (Wu et al., 2010; Bidleman et al., 1992; Schreitmuller and Ballschmiter, 1995; Lakaschus et al., 2002; Jantunen et al., 2004; Shen et al., 2004; Ding et al., 2007; Brown and Wania, 2008; Lohmann et al., 2009). Briefly, HCHs have been used mainly in the Northern Hemisphere from 1940s to 2000 with technical mixtures containing 55–80 %  $\alpha$ -HCH, 5–14 %  $\beta$ -HCH and 8–15 %  $\gamma$ -HCH (Lakaschus et al., 2002).  $\gamma$ -HCH known as lindane has been used in Europe and North America until end of 2000 (Li and Macdonald, 2005; Weber et al., 2006). Previous studies showed increasing concentrations of  $\alpha$ -HCH with increasing latitude, indicating net deposition and cold condensation (Lakaschus et al., 2002; Lohmann et al., 2009). As a consequence of declining atmospheric concentrations, the air-water change of  $\alpha$ -HCH was expected changing from net deposition to volatilization, and the oceans will subsequently turn into sources (Jantunen and Bidleman, 1995). Along the Atlantic,

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in 1999/2000, air-sea exchange of  $\alpha$ - and  $\gamma$ -HCH reached an equilibrium in the North Atlantic, whereas the surface waters of the tropical and southern Atlantic were strongly undersaturated with  $\gamma$ -HCH (Lakaschus et al., 2002). Due to the variability of climate and different intrinsic physical-chemical properties of organo-chlorine pesticides, it is necessary to further investigate the state of HCHs in the oceanic environment.

In this study, we analyzed marine boundary layer air and surface water samples in the Atlantic transect and the southern Ocean for HCHs. The objectives of this study are (1) to update the levels of HCHs in the atmosphere and the surface seawater, (2) to estimate the air-sea gas exchange directions and fluxes of HCHs, and (3) to evaluate the temporal and latitudinal variability of dissolved HCHs.

## 2 Materials and methods

### 2.1 Sampling protocol

The sampling of air (Fig. 1a) and seawater (Fig. 1b) has been described in (Xie et al., 2011). Briefly, seawater and air samples were collected onboard the R/V *Polarstern* in the Atlantic and Southern Ocean (51° N–67° S) in October to December 2008. Sampling locations, dates and general sampling conditions were recorded aboard from PO-DAS (Polarstern Data System) and are summarized in Tables 1 and 2. Seawater samples were collected from the ship's intake system located in the keel (depth: 11 m) using a combination of PAD-2 resins (Polystyrene-DVB-copolymer resin, SERVA GmbH, Heidelberg, Germany) and glass fibre filters (GFF: pore size, 0.7  $\mu$ m). Air samples were collected using GFF filters combined with a glass column packed with PUF/PAD-2 at the upper deck (Altitude: 2 m). Water and air samples were stored at  $-4^{\circ}\text{C}$  and  $-20^{\circ}\text{C}$ , respectively.

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## 2.2 Chemicals

All solvents (methanol, acetone, dichloromethane and n-hexane) were residue analysis grade and additionally distilled in a full glass unit prior to use. Analytical standards of HCHs and deuterated  $\alpha$ -HCH (d6-HCH) were purchased from Ehrenstorfer (Augsburg, Germany), and  $^{13}\text{C}$ -HCB was obtained from Cambridge Isotope Laboratories.

## 2.3 Extraction, clean-up and analysis

Extraction, clean-up and analysis of the samples were done based on our previously published method (Xie et al., 2011). Briefly, samples were spiked with the surrogate standard d6-HCH prior to extraction, then Soxhlet extracted and purified on 10 % water deactivated silica column. Analysis was done by a GC/MS-system (6890 GC/5975 MSD) in electron capture negative chemical ionization mode (ECNCl). The  $m/z$  values monitored for quantification and quality control are selective ions of 255 and 71 for HCHs, 261 and 73 for d6-HCH and 290 for  $^{13}\text{C}$ -HCB.

## 2.4 QA/QC

Breakthrough of the target analytes of the sampling methods has been checked on board R/V *Polarstern* (Lakaschus et al., 2002), and further proved during this cruise. Three field blanks were run for each sample type while blank showed very low values which were generally in the  $10^{-1}$  to  $10^{-2}$  absolute pg range. Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation ( $\sigma$ ) (for compounds showing no blanks a peak area of 200 was adopted as background response). Atmospheric MDLs were  $0.03 \text{ pg m}^{-3}$  for  $\alpha$ -HCH,  $0.01 \text{ pg m}^{-3}$  for  $\gamma$ - and  $\beta$ -HCH, and seawater MDLs were 0.02, 0.06 and  $0.01 \text{ pg l}^{-1}$  for  $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH. Recoveries of internal standard d6-HCH were  $81 \pm 23 \%$  for water samples and  $89 \pm 35 \%$  for air samples, respectively.

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## 2.5 Air mass back trajectories

Air mass origins along the cruise segments of the individual air samples were calculated using NOAA's HYSPLIT model. Air mass back trajectories were calculated in 6 h steps tracing back the air masses for 7 day using the sampling height as arrival height (Fig. 2).

## 3 Results and discussion

Individual concentrations of HCHs in air and seawater are given in Tables 1 and 2. For aqueous samples, only dissolved concentrations were considered, since the proportion of particles on the filters was negligible.

### 3.1 HCHs in the atmosphere

The spatial distribution of the sum of gaseous  $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH ( $\Sigma$ HCHs, Fig. 1a) ranged from 11.8 to 36.9  $\text{pg m}^{-3}$  (mean:  $26.6 \pm 11.0 \text{ pg m}^{-3}$ ) in the Northern Hemisphere (NH), and from 1.5 to 4.0  $\text{pg m}^{-3}$  (mean:  $2.8 \pm 1.1 \text{ pg m}^{-3}$ ) in the Southern Hemisphere (SH). Our results were comparable to those of global oceans (Wong et al., 2011; Wu et al., 2010; Lakaschus et al., 2002; Dickhut et al., 2005; Ding et al., 2007). The highest concentration was present in the coast near Western Europe and north-western Africa (36.9  $\text{pg m}^{-3}$ ) and the lowest concentration was observed in southern Ocean (1.5  $\text{pg m}^{-3}$ ). HCH concentrations decreased significantly ( $R^2 = 0.555, 0.001$ ) from the North Atlantic to the Southern Ocean, reflecting the extensive utilization of HCHs in the NH in the 1980s.

In the NH, average concentrations of  $17.2 \pm 11.4 \text{ pg m}^{-3}$  (range: 4.8–30.7  $\text{pg m}^{-3}$ ),  $9.0 \pm 4.0 \text{ pg m}^{-3}$  (range 4.7–13.9  $\text{pg m}^{-3}$ ) and  $0.40 \pm 0.75 \text{ pg m}^{-3}$  (0.01–1.52  $\text{pg m}^{-3}$ ) were determined by  $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH. The gaseous concentrations of  $\alpha$ -HCH

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( $[\alpha\text{-HCH}]_{\text{gas}}$ ) in the NH were  $\sim 2$  times higher than those ( $4.1\text{--}12\text{ pg m}^{-3}$ ) found in December 1999 (Lakaschus et al., 2002), and comparable to the Canadian Arctic during 2007–2008 ( $7.5\text{--}48\text{ pg m}^{-3}$ ) (Wong et al., 2011), 2000–2003 ( $23 \pm 10\text{ pg m}^{-3}$ ) (Su et al., 2006), and European Arctic in July 2000 ( $17 \pm 4\text{ pg m}^{-3}$ ) (Lakaschus et al., 2002). Varying  $[\alpha\text{-HCH}]_{\text{gas}}$  has been also observed in the northern Pacific Ocean in summer of 2003 ( $9.9 \pm 8.3\text{ pg m}^{-3}$ ) and 2008 ( $33 \pm 16\text{ pg m}^{-3}$ ), respectively.  $[\gamma\text{-HCH}]_{\text{gas}}$  ( $4.7\text{--}13.9\text{ pg m}^{-3}$ ) decreased in comparison to concentrations measured in December of 1999 ( $0.1\text{--}45\text{ pg m}^{-3}$ ) (Lakaschus et al., 2002) and were also lower than those values presented for the North Pacific in 2003 ( $0.2\text{--}49.4\text{ pg m}^{-3}$ ) (Ding et al., 2007), and comparable to those in the Arctic in 2008 (Wu et al., 2010; Ding et al., 2007).  $[\gamma\text{-HCH}]_{\text{gas}}$  was slightly higher than concentrations reported from International Polar Year expeditions in the Canadian Arctic in 2008 ( $2.1\text{--}7.7\text{ pg m}^{-3}$ ) (Wong et al., 2011). This implies that atmospheric HCHs are homogeneously distributed across the NH (Weber et al., 2006) as suggested previously by (Li and Macdonald, 2005) Concentrations of  $\beta\text{-HCH}$  were 1–2 orders of magnitude lower than those measured in the North Pacific and adjacent Arctic (Wu et al., 2010), indicating geographic application of  $\beta\text{-HCH}$  in the world. Generally, the elevated concentrations of HCHs measured in air samples near the European and northwest African coast (A4, A7 and A9; Fig. 2) revealed volatilization of “old” HCHs from the continents or deep Ocean with past contamination along with undefined sources (Nizzetto et al., 2010; Jaward et al., 2004; Lohmann et al., 2009).

In the SH, the means of  $[\alpha\text{-HCH}]_{\text{gas}}$ ,  $[\gamma\text{-HCH}]_{\text{gas}}$  and  $[\beta\text{-HCH}]_{\text{gas}}$  were  $1.6 \pm 0.84\text{ pg m}^{-3}$ ,  $1.1 \pm 0.52\text{ pg m}^{-3}$  and  $0.14 \pm 0.14\text{ pg m}^{-3}$ , respectively, which are  $\sim 10\text{--}30\%$  of those in the NH, indicating slow interhemispheric mixing and lower previously usage in the Southern Hemisphere. From the Equator to Cape Town,  $[\alpha\text{-HCH}]_{\text{gas}}$  were similar to those measured in 1999, whereas  $[\gamma\text{-HCH}]_{\text{gas}}$  decreased by factor of 10, which likely results from the global reduction of lindane usage in the late 1990s (Lakaschus et al., 2002). From Cape Town ( $32^\circ\text{ S}$ ) to Neumayer Station ( $70.4^\circ\text{ S}$ )

(A14–A17) concentrations of  $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH were relatively constant and comparable to those measured in 1999 (Lakaschus et al., 2002), and along the Western Antarctic peninsula (Dickhut et al., 2005), illustrating background levels of HCHs in the Southern Ocean.

### 3.2 HCHs in seawater

Dissolved  $\alpha$ ,  $\beta$  and  $\gamma$ -HCH concentrations in seawater displayed a wide range of concentrations from 50.9°N to 67.3°S (Fig. 1b).  $[\alpha\text{-HCH}]_{\text{diss}}$  ranged from 0.33 to 46.8  $\text{pg l}^{-1}$ , with an average of  $16.7 \pm 14.2 \text{ pg l}^{-1}$  in the NH and  $1.46 \pm 1.74 \text{ pg l}^{-1}$  in the SH.  $[\gamma\text{-HCH}]_{\text{diss}}$  were generally lower than  $[\alpha\text{-HCH}]_{\text{diss}}$ , ranging from 0.02 to 33.2  $\text{pg l}^{-1}$  across Atlantic transect with an average of  $5.68 \pm 9.93 \text{ pg l}^{-1}$  in the NH and  $0.14 \pm 0.10 \text{ pg l}^{-1}$  in the SH. Except the sample W1 (50.923°N, 1.311°E) from the North Sea,  $[\beta\text{-HCH}]_{\text{diss}}$  showed similar level as  $\gamma$ -HCH with a mean of  $2.26 \pm 2.76 \text{ pg l}^{-1}$  in the NH and  $0.34 \pm 0.28 \text{ pg l}^{-1}$  in the SH. The highest concentrations were observed in the North Sea for  $\alpha$ - and  $\gamma$ -HCH, while  $\beta$ -HCH dominated near the southern European coast. As  $\beta$ -HCH has 10 times lower Henry's law constant (HLC) than  $\alpha$ - and  $\gamma$ -HCH (Sahsuvar et al., 2003) and can more efficiently be transported through ocean current (Li et al., 2002), this peak may indicate intensive river input to the Atlantic Ocean from aquaculture region in southern Europe (Breivik et al., 1999).  $\alpha$ - and  $\gamma$ -HCH also showed elevated concentrations in this area. In general, both  $\alpha$ - and  $\gamma$ -HCH showed clearly increasing concentrations with increasing latitude north and south of the Equator, further illustrating the concept of cold condensation (14) and less interhemispheric mixing. Correlation analyses also revealed that both  $[\alpha\text{-HCH}]_{\text{diss}}$  ( $R^2 = 0.792$ ) and  $[\gamma\text{-HCH}]_{\text{diss}}$  ( $R^2 = 0.0329$ ) were significantly positively correlated to latitude in the NH and inversely correlated to  $T_{\text{water}}$  ( $\alpha$ -HCH,  $R^2 = 0.690$ ;  $\gamma$ -HCH,  $R^2 = 0.244$ ). Similar trends were observed in the SH as well, with positive correlation with latitudes ( $\alpha$ -HCH,  $R^2 = 0.558$ ;  $\gamma$ -HCH,  $R^2 = 0.379$ ) and negative correlation with temperatures  $T_{\text{water}}$  for

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$\alpha$ -HCH ( $R^2 = 0.674$ ), respectively. However, no clear latitudinal and temperature trends were observed for  $\beta$ -HCH ( $R^2 = 0.108 - 0.134$ ).

### 3.3 Temporal and latitudinal trends of HCHs in surface seawater

Comparison of HCH in 1999/2000 with those obtained between 1987 and 1997 have been performed in (Lakaschus et al., 2002), and exhibited a strong decline for  $\alpha$ -HCH between 50° N and 60° S, and no clear trend for  $\gamma$ -HCH. To evaluate updated temporal variation in the Atlantic, the new data set from this study and the historical data were merged into Fig. 3a and b for a close comparison.

Similar latitudinal trends in the NH have been observed in all cruises from 1987 to 2008. Slightly increasing tendency from the Equator to the Southern Ocean also appeared in the SH. From 50° N to 30° S, concentrations of  $\alpha$ -HCH in the present work were lower by factor of 10–50 than those measured in 1987–1997 and just slightly lower than those in 1999/2000. The concentrations of  $\gamma$ -HCH obviously decreased in comparison to those reported in 1987–2000, especially showed clearly declining trend from 2000–2008. The different trends for  $\alpha$ - and  $\gamma$ -HCH suggest (i) the influence of international regulation on technical HCHs and lindane; and (ii) variable environmental behavior and fate for  $\alpha$ - and  $\gamma$ -HCH. There was a rather high variability presented in the tropic region for both  $\alpha$ - and  $\gamma$ -HCH. Unlike explanation by Lakaschus et al. (2002) for  $\gamma$ -HCH in 1999, the high precipitation rate of approximately 2000 mm/year in the Intertropical Convergence Zone could cause significantly dilution rather than addition due to the intensive wet deposition. Another important factor is intensive biomass blooming in the tropical region, which has been observed during this cruise as well. The Equator trade wind brings massive Sahara dust containing nutrients and elements into the tropic ocean (Jullien et al., 2007; Cole et al., 2009; Pohl et al., 2011), which accelerates phytoplankton and zooplankton blooming in surface water of the Atlantic (Fernandez et al. 2010; Guieu et al., 2010; Neogi et al., 2011; Taylor et al., 2011). The adsorption of  $\alpha$ - and  $\gamma$ -HCH to biomass and particles and further removal by sedimentation and degradation may reduce the dissolved HCHs in the tropic region.

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The concentrations of  $\alpha$ -HCH in the Southern Ocean are quite variable, which can be addressed to the complex frontal system. It has been pointed out that elevated [ $\alpha$ -HCH]<sub>diss</sub> was present between 40° S and 50° S from 1993 to 2000 (Lakaschus et al., 2002), this phenomenon was also found in this present study. The sampling data of W27, W29 and W31 showed a salinity decrease from 35.5 to 33.9 and 34.0, and temperature decreased from 22.3 °C down to 4.6 and -1.6 °C as well. This is caused by an influx of fresh melting sea ice and snow water from the Antarctic shelf and results in a transfer the “old” contamination back to the Southern Ocean (Dickhut et al., 2005). Moreover, the Southern African current may transport HCHs from Indian Ocean to the Atlantic and moves them northward by the path of thermohaline circulation. This input may significantly contribute to the elevated HCHs in the Southern Ocean.

### 3.4 $\alpha/\gamma$ -HCH and $\alpha/\beta$ -HCH ratios in surface water

Variations of  $\alpha/\gamma$ -HCH and  $\alpha/\beta$ -HCH ratios in space and time are highly influenced by the historical usage of technical HCH and lindane, and the environmental behaviors of different isomers. As show in Fig. 4, obviously high  $\alpha/\gamma$ -HCH values were present in 2008 in comparison to 1987–2000, and mostly above the range of 5–7 of the  $\alpha/\gamma$ -HCH ratio in technical mixture (Iwata et al., 1993). In contrast to the present results,  $\alpha/\gamma$ -HCH ratios in the NH were mostly less than 4.5, and reached 0.1–2 in 1991 and 1999, indicating intensive application of lindane after a ban for technical  $\gamma$ -HCH during long range transport (Oehme et al., 1996). The highest  $\alpha/\gamma$ -HCH ratio 33 was found in the Southern Ocean; again indicates high persistence of  $\alpha$ -HCH in remote region.

So far,  $\alpha/\beta$ -HCH ratios were only insufficiently studied. In this study,  $\alpha/\beta$ -HCH ratios varied from 0.5 to 52, highlighted different environmental behavior of  $\alpha$ - and  $\beta$ -HCH isomers. Generally,  $\beta$ -HCH is one of the five stable isomer of technical HCH, and accounts for 5–14 % of the technical formation. Unlike  $\alpha$ - and  $\gamma$ -HCH,  $\beta$ -HCH has a higher affinity to water than air, reflected in its lower Henry’s law constant and higher water solubility. Low  $\alpha/\beta$ -HCH ratios (<4) may suggest fresh input sources of HCHs from adjacent landmasses and rivers. In the Southern Ocean as atmospheric transport

and deposition is the major pathway, high  $\alpha/\beta$ -HCH ratios were present in this region (31 for W27 and 17 for W31).

### 3.5 Air-water gas exchange

The direction (or equilibrium status) of the gas exchange was estimated based on the fugacity ratio  $f_A/f_W$ , and the exchange fluxes were calculated using the two-film model which have been applied in (Xie et al., 2011; Lohmann et al., 2009). Briefly, the fugacity ratio was calculated using Eq. (1).

$$\frac{f_A}{f_W} = \frac{C_A RT_A}{C_W H} \quad (1)$$

where  $f_W$  and  $f_A$  are the fugacities in water and air,  $C_W$  and  $C_A$  are the dissolved and gaseous concentrations in water and air ( $\text{pg m}^{-3}$ ),  $H$  is the Henry's Law constant ( $\text{Pa m}^{-3} \text{mol}^{-1}$ ) at the given water temperature and corrected by the salinity according to ref (Schwarzenbach et al., 2003),  $R$  is the gas constant ( $8.31 \text{ Pa m}^{-3} \text{K}^{-1} \text{mol}^{-1}$ ) and  $T_A$  is the air temperature (K). The Henry's Law constant of HCH and its temperature dependence was taken from (Sahsuvar et al., 2003; Cetin and Odabasi, 2005). Generally, a fugacity ratio  $f_A/f_W = 1$  means a system at equilibrium, whereas  $f_A/f_W > 1$  and  $f_A/f_W < 1$  indicates deposition and volatilization, respectively (14). Due to uncertainties of knowing air-water transfer coefficient, a significant deviation from equilibrium cannot be assessed within a factor of 3 around a fugacity ratio of 1 (Bruhn et al., 2003; Lohmann et al., 2009).

The air-seawater gas exchange was calculated based on following Eq. (2) (Liss and Slater, 1974; Bidleman and McConnell, 1995)

$$F_{AW} = K_{OL} \left( C_W - \frac{C_A}{H'_{\text{salt},T}} \right) \quad (2)$$

where  $H'_{\text{salt},T}$  is the dimensionless temperature and salinity corrected Henry's Law constant defined as  $H' = H/RT$  ( $R = \text{gas constant}$ ,  $T = \text{Temperature}$ ).  $K_{OL}$  ( $\text{m h}^{-1}$ ) is the gas

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phase overall mass transfer coefficient compromising the resistances to mass transfer in both water ( $K_W$ ,  $\text{m h}^{-1}$ ) and air ( $K_A$ ,  $\text{m h}^{-1}$ ). The uncertainty of the flux can be estimated by propagation of the uncertainties in  $C_W$  (23%),  $C_A$  (35%),  $K_{OL}$  (40%) and  $H$  (20%, ref. Sahsuvar et al., 2003), which is 61%.

$f_A/f_W$  of  $\alpha$ -HCH ranged from 0.8 to 27 with most values  $>3$ , indicated air to water deposition dominating air-seawater gas exchange directions (Fig. 5). Two values (0.8 for W1 and 1.9 for W3) were within 0.3 to 3, which showed a dynamic equilibrium reached near the western European coast ( $51^\circ\text{N}$ – $45^\circ\text{N}$ ). For the  $\gamma$ -isomer,  $f_A/f_W$  indicated net deposition in all samples ( $774 > f_A/f_W > 3.8$ ,  $n = 17$ ). Although  $\beta$ -HCH has relatively low levels in the atmosphere, because it's lower  $H$  value,  $f_A/f_W$  varied between equilibrium (volatilization) and net deposition, indicating a multi-hopper transport behavior for  $\beta$ -HCH.

Lakaschus et al. (2002) found that in the North Atlantic air-water exchange status of  $\alpha$ -HCH changed from net deposition in 1990 to equilibrium in 1999, and a new equilibrium was being established on a lower concentration level than 1990 (Lakaschus et al., 2002). Obviously, the results from this work showed that a new equilibrium has established for  $\alpha$ -HCH on a lower level than 1999, while equilibrium status in the Atlantic and the Southern Ocean from  $45^\circ\text{N}$  to  $67^\circ\text{S}$  has been broken up and changed to net deposition again. This variability was also observed in the north Atlantic and the Arctic Ocean (Harner et al., 1999; Lohmann et al., 2009). Gas exchange directions of  $\alpha$ -HCH between seawater and air reversed in the western Arctic from net deposition in the 1980s to net volatilization in the 1990s with declined primary emissions (Bidleman et al., 1995; Jantunen and Bidleman, 1995; Jantunen et al., 2008). While air-water exchange direction for  $\gamma$ -HCH have been dominated by net deposition in most studies (Harner et al., 1999; Jantunen et al., 2008; Lohmann et al., 2009), with volatilization occasionally reported in the western Arctic.

The air-water deposition fluxes were quite high for  $\alpha$ -HCH with a median of  $3759 \text{ pg m}^{-2} \text{ day}^{-1}$  through the cruise (Fig. 5), except W1 for a volatilization of  $818 \text{ pg m}^{-2} \text{ day}^{-1}$ . Elevated net deposition occurred in the European and northwest

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African coast ranging from 3759 to 11488  $\text{pg m}^{-2} \text{day}^{-1}$ , and was just slightly lower than those measured in mid-Atlantic region in 2000/2001 (Gioia et al., 2005). In the SH, net deposition of  $\alpha$ -HCH ranged from 574 to 4692  $\text{pg m}^{-2} \text{day}^{-1}$ , which are  $\sim 10$  times lower than those in the NH. Relatively constant levels in atmosphere and decreasing water concentrations of  $\alpha$ -HCH in recent years may contribute to the changing direction of the air-seawater gas exchange and high deposition fluxes. A recent study in the Canadian Arctic (2007–2008) (Wong et al., 2011) showed net volatilization for  $\alpha$ -HCH with a mean of  $6800 \pm 3200 \text{ pg m}^{-2} \text{day}^{-1}$  where the air concentrations were similar to this present work; but the water concentrations were 2–3 orders of magnitude higher than our results. Nevertheless,  $\alpha$ -HCH undergoes the iterative process of deposition and adsorption onto soil and vegetation, reemission into the atmosphere and re-deposition because of reduction in primary emissions and climate change.

The  $\gamma$ -HCH was undergoing net deposition to surface waters with deposition fluxes ranging 395–5615  $\text{pg m}^{-2} \text{day}^{-1}$  (mean: 1987  $\text{pg m}^{-2} \text{day}^{-1}$ ) (Fig. 6), indicating continually loading into the Atlantic and the Southern Ocean since several decades. In comparison to the other two HCH species,  $\beta$ -HCH showed relatively low exchange fluxes (6–687  $\text{pg m}^{-2} \text{day}^{-1}$  for net deposition and  $<12 \text{ pg m}^{-2} \text{day}^{-1}$  for net volatilization). Atmospheric deposition might be less important than Ocean current transport for  $\beta$ -HCH.

## 4 Conclusions

$\alpha$ -,  $\gamma$ -, and  $\beta$ -HCH have been simultaneously measured in air and seawater of the Atlantic and the Southern Ocean in 2008. There was a marked difference between contaminant trends in atmosphere and surface waters highlighting the different time-scales affecting compounds in either compartment, reemission from the continental soil, vegetation and forest fire are considered sources for atmospheric HCHs. Climate change may significantly accelerate the releasing process and drive long-range transport from sources to deposition in the open oceans. In the tropic ocean higher

biological productivities may increase metabolism, adsorption and settling fluxes and lead to lower concentrations of HCHs in the surface water, and thus control the air-water exchange process. Consequently, further investigation is necessary to elucidate the long term trends and the biogeochemistry process of HCHs in the oceanic environment.

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**Table 1.** Individual concentrations of HCHs in the atmosphere ( $\text{pg m}^{-3}$ ) in the Atlantic and the Southern Ocean.

Sample	Date	Latitude (° N)	Longitude (° E)	Volume ( $\text{m}^3$ )	Temp. (°C)	$\alpha$ -HCH ( $\text{pg m}^{-3}$ )	$\gamma$ -HCH ( $\text{pg m}^{-3}$ )	$\beta$ -HCH ( $\text{pg m}^{-3}$ )
A1	2–4 Nov 2008	50.120	–2.184	687	11.5	4.8	7.0	0.01
A4	7–9 Nov 2008	40.008	–12.511	640	16.5	30.7	4.7	1.52
A7	12–15 Nov 2008	22.500	–20.499	1101	21.3	22.0	10.5	0.02
A9	16–20 Nov 2008	8.503	–19.452	968	28.6	11.3	13.9	0.05
Mean + SD in NH						17.2 ± 11.4	9.0 ± 4.0	0.40 ± 0.75
A10	20–23 Nov 2008	–1.624	–10.699	877	25.5	3.0	1.0	0.09
A12	27–29 Nov 2008	–20.506	5.607	522	18.9	1.5	1.3	0.08
A14	6–8 Dec 2008	–41.492	9.476	602	19.3	1.6	2.0	0.09
A15	8–10 Dec 2008	–49.011	2.834	516	11.2	1.8	0.9	0.42
A16	10–12 Dec 2008	–58.910	0.131	573	3.6	0.9	0.5	0.12
A17	12–15 Dec 2008	–67.354	–2.064	934	–2.5	0.6	0.9	0.04
Mean + SD in SH						1.6 ± 0.84	1.1 ± 0.52	0.14 ± 0.14

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**Table 2.** Individual concentrations of HCHs in surface seawater ( $\mu\text{g l}^{-1}$ ) in the Atlantic and the Southern Ocean.

Sample	Date	Latitude (° N)	Longitude (° E)	Volume (l)	Temp. (°C)	Salinity (PSU)	$\alpha$ -HCH ( $\mu\text{g l}^{-1}$ )	$\gamma$ -HCH ( $\mu\text{g l}^{-1}$ )	$\beta$ -HCH ( $\mu\text{g l}^{-1}$ )
W1	2 Nov 2008	50.923	1.311	409	13.8	35.1	46.8	33.2	2.73
W3	4 Nov 2008	47.723	-6.758	1000	12.4	35.4	21.7	2.87	1.41
W5	6 Nov 2008	43.854	-10.516	1073	15.4	35.7	25.5	3.96	0.78
W6	7 Nov 2008	41.855	-11.946	1088	15.9	35.9	26.2	7.18	9.46
W7	8 Nov 2008	38.438	-12.979	835	15.9	35.9	19.5	5.20	2.60
W9	9 Nov 2008	31.175	-14.866	1463	17.2	36.4	10.1	0.60	0.19
W11	12 Nov 2008	25.196	-17.858	1296	21.0	36.8	10.1	2.80	3.34
W13	14 Nov 2008	16.861	-20.861	950	22.5	36.8	4.57	0.49	0.61
W15	17 Nov 2008	9.608	-19.830	1041	28.6	35.2	1.36	0.42	1.32
W17	19 Nov 2008	4.109	-15.606	925	29.1	34.6	1.58	0.09	0.18
Mean in NH							16.7 ± 14.2	5.68 ± 9.93	2.26 ± 2.76
W19	21 Nov 2008	-1.613	-10.708	935	26.1	36.1	0.33	0.02	0.11
W21	23 Nov 2008	-7.106	-6.061	1000	25.5	36.2	0.35	0.03	0.31
W23	25 Nov 2008	-13.414	-0.651	1000	22.9	36.2	0.43	0.07	0.84
W25	29 Nov 2008	-24.301	9.070	1000	19.1	35.5	0.91	0.21	0.61
W27	7 Dec 2008	-37.836	13.198	311	22.3	35.5	0.70	0.30	0.23
W29	10 Dec 2008	-52.941	10.836	804	4.6	33.9	5.01	0.15	0.16
W31	14 Dec 2008	-67.275	-1.949	771	-1.6	34.0	2.47	0.17	0.14
Mean in SH							1.46 ± 1.74	0.14 ± 0.10	0.34 ± 0.28

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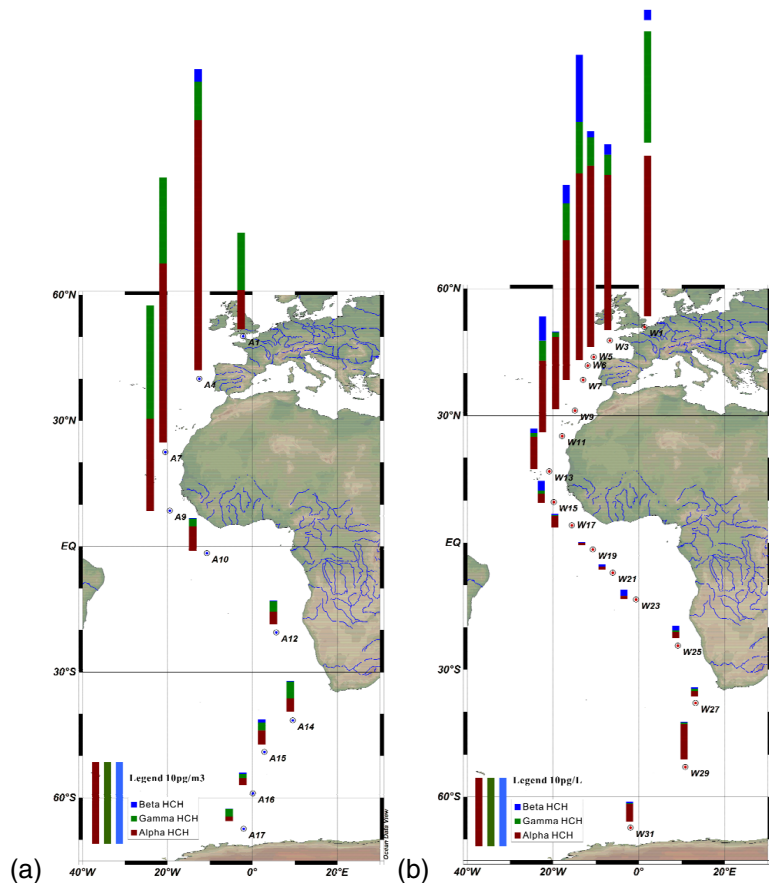
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**Fig. 1.** (a) gaseous ( $\text{pg m}^{-3}$ ) and (b) dissolved ( $\text{pg l}^{-1}$ ) concentrations of  $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH in the Atlantic and the southern Ocean. The bars are placed on the average position for each air and water sample.

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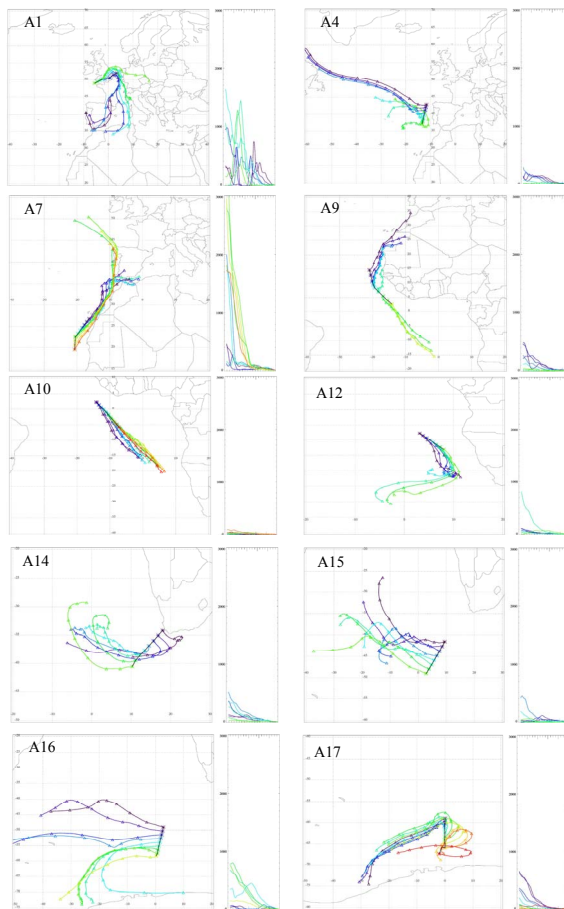
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**Fig. 2.** 96 h air mass back trajectories (6 h steps) and altitudinal profiles of the air mass parcels for the cruises ANT-XXV/1+2 (A1–A17). For samples longer than 72 h, only every second BT was plotted. The black line indicates the cruise leg.

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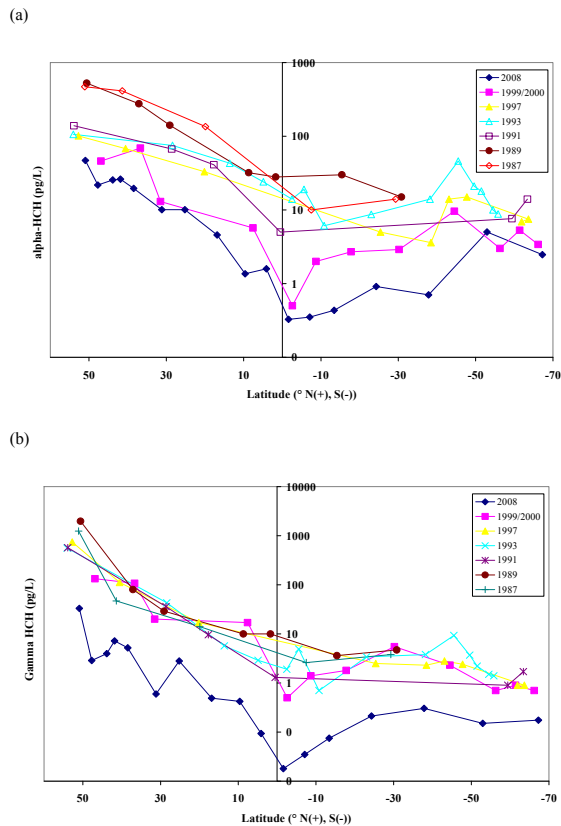
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**Fig. 3.** Temporal and latitudinal distribution of  $\alpha$ -HCH (a) and  $\gamma$ -HCH (b) in the Atlantic and the Southern Ocean measured during cruise ANT-V (1987), ANT-VII (1989), ANT-X (1991), ANT-XI (1993), ANT-XV (1997), ANT-XVII (1999/2000) and ANT-XXV (2008, this work).

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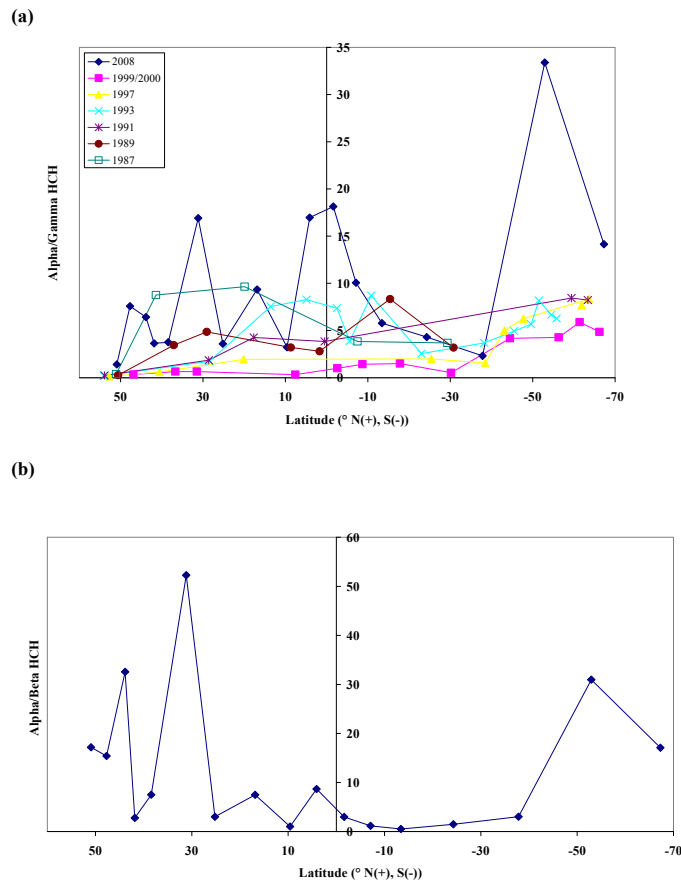
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**Fig. 4.** Temporal and latitudinal variation of  $\alpha$ - $\gamma$ -HCH ratio **(a)** in the Atlantic and the Southern Ocean measured during cruise ANT-V (1987), ANT-VII (1989), ANT-X (1991), ANT-XI (1993), ANT-XV (1997), ANT-XVII (1999/2000) and ANT-XXV (2008, this work), and the latitudinal variation of  $\alpha$ - $\beta$ -HCH ratio **(b)** obtained in this work (2008).

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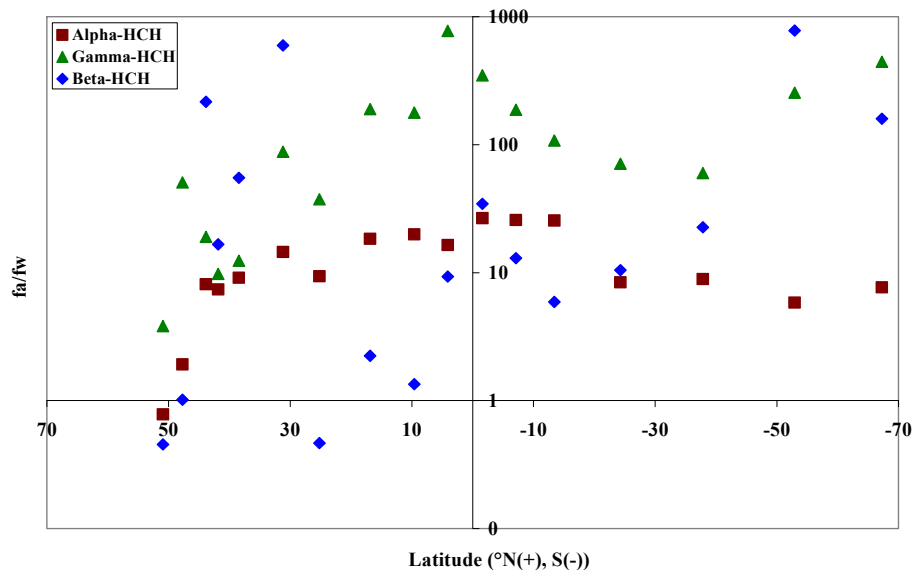


Fig. 5. Air-water fugacity ratio ( $f_A/f_W$ ) of  $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH in the Atlantic and Southern Ocean, a  $f_A/f_W$  within the range 0.3–3 means a system at equilibrium.

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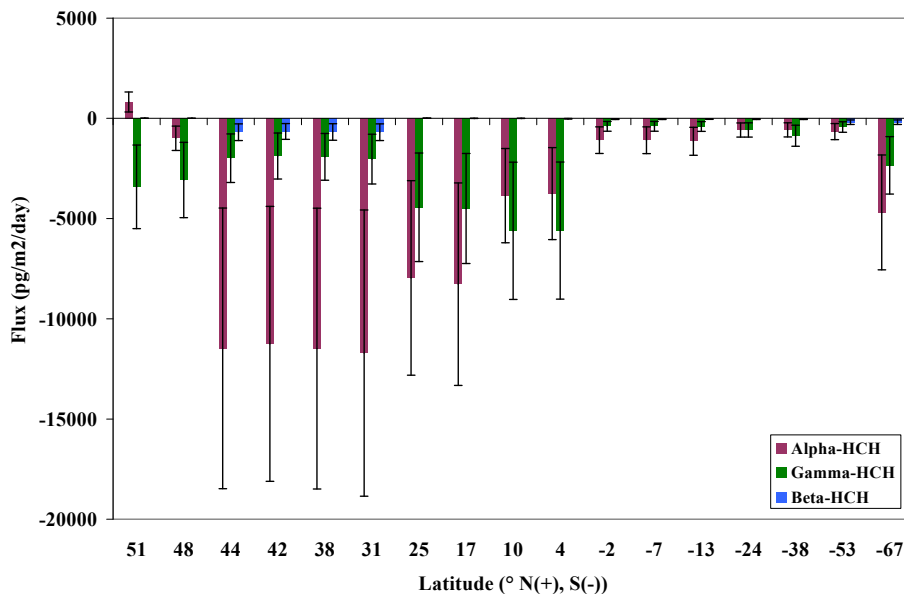
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**Fig. 6.** Air-water gas exchange fluxes ( $\text{pg m}^{-2} \text{day}^{-1}$ ) for  $\alpha$ -,  $\gamma$ - and  $\beta$ -HCH in the Atlantic and Southern Ocean, negative value means net deposition, and positive value means volatilization.

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