

The Air–Sea Equilibrium and Time Trend of Hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica

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Hexachlorocyclohexanes (HCHs) were determined simultaneously in air and seawater during two cruises across the Atlantic Ocean between the Arctic Ocean (Ny-Ålesund/ Svalbard, 79°N; 12°E) and the Antarctic Continent (Neumayer Station/ Ekstroem Ice Shelf, 70°S; 8.2°W) in 1999/2000. The concentrations of α -HCH and γ -HCH in air and surface waters of the Arctic exceeded those in Antarctica by 1–2 orders of magnitude. The gaseous concentrations of γ -HCH were highest above the North Sea and between 20°N and 30°S. Fugacity fractions were used to estimate the direction of the air–sea gas exchange. These showed for α -HCH that the measured concentrations in both phases were close to equilibrium in the North Atlantic (78°N–40°N), slightly undersaturated between 30°N and 10°S and again close to equilibrium between 20°S and 50°S. γ -HCH has reached phase equilibrium in the North Atlantic as α -HCH, but the surface waters of the tropical and southern Atlantic were strongly undersaturated with γ -HCH, especially between 30°N and 20°S. These findings are significantly different from two earlier estimates around 1990 as a result of global emission changes within the past decade. Therefore, we investigated the time trend of the HCHs in the surface waters of the Atlantic between 50°N and 60°S on the basis of archived samples taken in 1987–1997 and those from 1999. A decrease of α -HCH by a factor of approximately 4 is observed at all sampling locations. No decrease of γ -HCH occurred between 30°N and 30°S, but there was a decrease in the North Atlantic, North Sea, and in the South Atlantic south of 40°S. The constant level of γ -HCH in the tropical Atlantic confirms the conclusion that the tropical Atlantic acts as a sink for γ -HCH at present time. The measured α -HCH seawater concentrations were compared with results from a global multimedia fate and transport model. Whereas the time trend over 13 years and the latitudinal gradient were well reproduced by the model, the absolute levels were too

high by a factor of 4.5. This may be explained by the zonal averaging employed in the model as well as uncertain emissions and degradation rates.

Introduction

Semivolatile organic compounds (SOCs), such as hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), and polychlorinated biphenyls (PCBs) are transported globally from the areas where they have once been released into the environment to very remote places including Antarctica (1–4). This redistribution occurs by long-range transport in both atmosphere and oceans.

HCHs have been used as insecticides since 1943, mainly in the northern hemisphere. In the past decades different technical-grade products, which contained 55–80% α -HCH, 5–14% β -HCH, and 8–15% γ -HCH (5), have been used in large quantities. The insecticidal component is γ -HCH, lindane, which is only a byproduct of the technical synthesis. At present, lindane is still used in some areas of the world. In 1990 the main consumers were India, France, Italy, Nigeria, Canada, Honduras, U.S.A., and China (6). The chronology of the change from technical products to lindane, the global usage reduction, and its impact on the Arctic has been described in ref 7. A strong decline of the atmospheric α -HCH concentrations in the Arctic was observed when China stopped using technical HCH in 1983, and a second drop of the gaseous concentrations occurred after India and the former Soviet Union (SU) banned technical HCH in 1990. As a result, a reversal of the air–sea exchange of α -HCH from net depositional to outgassing was observed in the Bering and Chuckchi Seas between 1988 and 1993 (8).

Whereas we have a detailed knowledge about the response of the Arctic environment to the emission changes, it is not known how the ban of technical HCH usage in India and the SU has influenced the concentrations in air and seawater as well as the air–sea gas exchange of HCHs in the tropical and southern Atlantic. The situation around 1990 is documented as a result of two Atlantic cruises. Iwata et al. (9) took samples along a west–east transect at 30°N and Schreitmüller and Ballschmiter (10) along a north–south transect between 50°N and 50°S. The former study reported net depositional fluxes of both HCHs at 30°N using the two-film model and measured gaseous and seawater concentrations. The latter study confirmed these results with respect to the North Atlantic, but reported air–seawater equilibrium for both HCHs in the South Atlantic, based mainly on the temperature dependency of the measured gas-phase concentrations.

The main goal of the present study was to determine the state of equilibrium that has been reached by the HCHs within the past decade, after the ban of technical HCH in India. The two earlier estimates may have lost their currency due to the change of the global usage pattern. We also hoped to establish the time trend of HCH levels in the surface waters of the Atlantic Ocean. Seawater concentrations are more indicative of long-term changes than atmospheric concentrations, because the oceans are a major storage compartment for HCHs (11) and are much less affected by short-term events such as regional emissions.

A second objective was to provide a consistent data set for use in the evaluation of presently available global models. There is a growing interest in modeling the fate of SOC. Specifically, three different models (12–14) have recently been used to estimate the global distribution of α -HCH. Wania et al. (12) state that the number of measurements in

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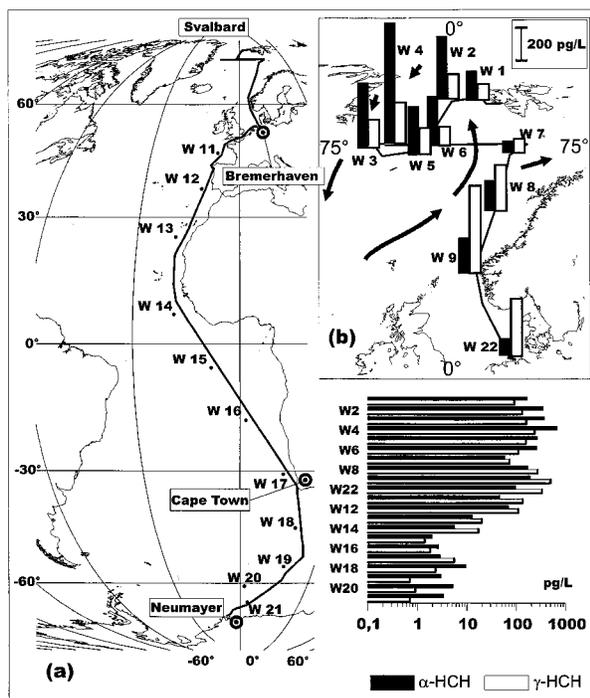


FIGURE 1. (a) Concentrations of α -HCH and γ -HCH in surface water along the transects of the R/V *Polarstern* cruises ARK XVI (Bremerhaven – Svalbard) and ANT XVII (Bremerhaven-Neumayer Station). (b) Spatial variability in the North Atlantic and Greenland Sea. Sample W22 was collected in March 2001.

the southern hemisphere is too sparse to determine whether there is an increase in α -HCH concentration with southern latitude.

For investigating the air–sea exchange of the HCHs air and water samples were collected simultaneously during two R/V *Polarstern* cruises across the Atlantic Ocean. The first cruise (ANT XVII) led from Bremerhaven (53.5°N; 8.6°E) to Neumayer Station/Antarctica (70°S; 8.2°W) and back to Cape Town in the time period of December to March 1999/2000. The second cruise (ARK XVI) started in Bremerhaven and ended in Ny-Ålesund/Svalbard (79°N; 12°E) in July 2000. Two short cruises were made with the R/V *Heincke* and the R/V *Ade* to the North Sea in September 1999 and March 2001. For the determination of the time trend we analyzed archived water samples collected during five R/V *Polarstern* cruises between the North Sea and Antarctica in 1987–1997. These samples and those from 1999/2000 were used for a comparison with the global distribution model of Wania et al.

Experimental Section

Sample Collection. Air and water samples were collected simultaneously during the cruises and at Neumayer Station. The cruise tracks and sampling locations are shown in Figures 1 and 2 (based on data from Table S1, Supporting Information).

Air Samples. The air samplers (isap 2000, Schulze Automation & Engineering, Germany; flow rate: 18 m³/h) were operated on the top deck of R/V *Polarstern* at 20 m above sea level. The sampling device consisted of a metal frame holding a glass fiber filter (GF 8, 14 cm diameter, Schleicher & Schuell, Germany) and a glass cartridge with two polyurethane foam (PUF) plugs (10 cm × 7 cm). The cartridges could be connected directly to a modified Soxhlet extractor (15) for solvent extraction, minimizing the risk of contamination from indoor air (16) during sample workup. Contamination control during sampling was performed using a wind sensor. At Neumayer Station samples were collected

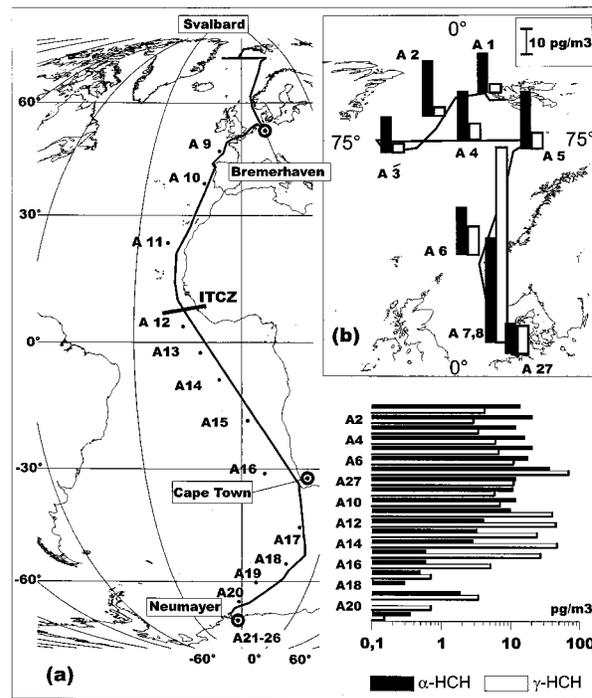


FIGURE 2. (a) Concentrations of α -HCH and γ -HCH in air along the transects of the R/V *Polarstern* cruises ARK XVI (Bremerhaven-Svalbard) and ANT XVII (Bremerhaven-Neumayer Station). (b) Spatial variability in the North Atlantic. Samples A7, 8 and A27 were collected in August 1999 and March 2001. Concentrations measured at Neumayer Station (A21–A26) are shown as mean.

in the clean air sector (17) 1.6 km southward of the main station. Air samples were collected within 1–3 days during the cruises, but weekly samples were taken at Neumayer Station (Sampling volumes ranged between 240 m³ in the North Sea and 1600 m³ in Antarctica, see Supporting Information).

Seawater Samples. These were taken out of 11 m depths, while the ship was moving. The inlet manifold for seawater was 0.6 m below the hull. To avoid contamination or losses due to adsorption at the pipe walls only stainless steel parts were used, and the seawater was pumped continuously through this system with a magnetically driven rotary pump at 10–30 m³/h depending on the ship's speed. Subsamples were taken from the pipeline at lower flow rates by use of a bypass. The samples on ARK XVI were collected using 1 g C-8 solid phase extraction (SPE) cartridges (Varian Mega Bond-Elute) as described by Jantunen and Bidleman (8). The sampling volumes lay between 1 and 3 L, which is sufficient due to high concentrations of both HCH isomers in Arctic waters. The samples on ANT XVII were collected with 150 mL XAD-2 (Supelco) columns, because the low aqueous concentrations in the South Atlantic required larger sampling volumes. Between 700 and 1000 L were collected at an average flow rate of 0.6 L/min. The comparability of both methods was checked by collecting parallel XAD-2 and SPE samples on ARK XVI, indicating that the efficiency of XAD-2 columns for HCHs was lower by approximately 30% (see quality assurance section, Supporting Information). The particulate fractions were collected on glass fiber filters (GF 52, Schleicher & Schuell, Germany).

Storage of Samples. All PUF, XAD-2, and SPE cartridges were stored before and after sampling in heat sealed, airtight polypropylene/aluminum/polyethylene bags (PP/AL/PE, Tesseraux, Germany) at low temperatures (water filled XAD-2 cartridges at 0 °C, all other samples at –25 °C). Cleaned filters were stored between aluminum foil in PP/AL/PE bags and used filters in fused test tubes at –25 °C.

Chemical Analysis. The solvents, *n*-hexane (Suprasolv, Merck, purified by adsorptive filtration and distillation), dichloromethane (DCM), and acetone (both: Picograde, Promochem), were routinely analyzed for blank values.

Air Samples. New PUF plugs were washed with distilled water, dried, and cleaned by three Soxhlet extractions lasting for 12 h (two times with acetone, finally with *n*-hexane). The PUFs were dried in a stream of purified nitrogen and stored until usage. Filters were cleaned by heating at 350 °C for 15 h. After sampling the PUF cartridges were Soxhlet extracted overnight with 550 mL of *n*-hexane after adding 1 ng of ϵ -HCH in 100 μ L of *n*-hexane as internal standard. The extracts were concentrated to 1 mL in a rotary evaporator and purified using glass columns filled with 2 g of Florisil (Carl Roth, cleaned and 1% deactivated) and 1 g of basic Al₂O₃ (ICN Biomedicals, cleaned and 10% deactivated). α -, γ -, and ϵ -HCH were eluted with 30 mL of DCM/*n*-hexane (1:5).

Seawater Samples. The pretreatment of the SPE cartridges and the elution after sampling was performed as described in ref 8. The XAD-2 columns used for seawater samples were cleaned by Soxhlet extraction with acetone for 36 h. The solvent was changed after 12 and 24 h. Each column was analyzed for blank values and—after passing this control step—filled with water and stored. After sampling the XAD-2 columns were eluted with 100 mL of DCM (including 0.5 ng of ϵ -HCH as internal standard) and then Soxhlet extracted for 15 h. For extraction the DCM regained from the elution step was used again after separating the water phase. The water was extracted three times with 20 mL of *n*-hexane that was later combined with the Soxhlet extract. The organic phases were purified like the air samples with 1 g of silica gel (Merck, cleaned and 1% deactivated) and 1 g of neutral Al₂O₃ (see above). Samples with strong interferences were further purified by a HPLC fractionation (18). The extracts were concentrated to volumes between 50 and 300 μ L prior to the measurements.

Archived Water Samples. During five R/V *Polarstern* cruises from Bremerhaven to the South Atlantic between 1987 and 1997 water samples had been collected for archiving purposes (see Table S2, Supporting Information). The samples had been taken over a distance of 300 km within 12 h using the same seawater system as in 1999/2000. The water had been extracted with *n*-hexane using centrifugal solvent extraction (5 L hexane for 6000 L seawater). Sampling locations were chosen in dependency of the main ocean currents and salinity/temperature profiles. The organic extracts had been concentrated to 1–5 mL and stored untreated in fused glass ampoules at –25 °C. Because the sampling technique has not been modified over the years, these samples provide a basis for determining the time trend of HCH concentrations in the Atlantic Ocean. Twenty percent fractions of the extracts (corresponding to 1200 L water) were analyzed after adding the internal standard and purification as described above (solvents, instruments, and procedures were identical with those used for the samples from 1999/2000). There could be small differences between the archived samples and those taken in 1999/2000 due to differences in the efficiencies of the two extraction techniques. However, the α - and γ -HCH concentrations for the archived samples were practically identical with those reported for the same time period and location (30°N) by Iwata et al. (9), who used XAD-2 columns.

Gas Chromatography–Mass Spectrometry. All samples and field blanks were analyzed using a Varian Saturn 2000 ion-trap mass spectrometer (MS) connected to a Varian 3800 gas chromatograph (GC). The MS was operated in the MS/MS mode (19). (GC: retention gap: IP-DEACT, 5 m \times 0.53 mm, Hewlett-Packard followed by capillary column: SIL 8, 60 m \times 0.25 mm, 0.25 μ m film, Chrompack; Injections: 3–5 μ L, temperature programmed on-column; carrier gas: he-

lium, constant flow, 1.3 mL/min.) The instrumental detection limits (IDL), applying MS/MS mode, were defined as the amount of standard that generates a peak with a signal/noise ratio of 10. For the quantification of HCHs the ions with $m/e = 145$ and 147 (parent ion $m/e = 183$) were used. The resulting detection limits under these conditions were 0.8 and 0.7 pg for α - and γ -HCH. Confirmations were performed using a high-resolution GC-MS (GC: HP-5890 II, column: HP-5-MS, 30 m \times 0.25 mm, 0.25 μ m film, Hewlett-Packard; MS: Auto Spec, Micromass).

Quality Assurance. The quality control included collection of parallel samples, breakthrough experiments for air and water samples during the cruises, storage experiments for air samples, the determination of field blanks, and detection limits for air and water samples. A detailed description of these experiments is given in the Supporting Information. No blank subtraction had to be made. The detection limits of HCHs, derived from the IDL, were approximately 25 fg/L in water and 25 fg/m³ in air. All concentrations were corrected for losses with the recovery rate of the internal standard, which ranged between 75% and 90%. Lower collection efficiencies of XAD-2 resin columns compared to SPE cartridges were corrected. For HCHs no breakthrough from the upper two PUFs was observed when using two back PUFs in a subsequent cartridge at temperatures between +26 °C and –18 °C. There was no indication that the composition of the samples may have changed during storage.

Results and Discussion

Latitudinal Profiles. The HCH concentrations obtained from 21 air and 22 water samples are summarized in Table 1 and Figures 1 and 2. All concentrations refer to the dissolved and gaseous fractions, because the HCH contents in the filters were negligible.

HCHs in Water (Figure 1a,b). The concentrations of both HCHs exhibited a strong latitudinal gradient, with higher levels in the northern hemisphere. Average concentrations between 75°N and 80°N (W1–W7, Figure 1b) were 315 \pm 184 pg/L α -HCH (range 59–689) and 137 \pm 49 pg/L γ -HCH (range 72–230). The lindane concentrations are close to concentrations reported by Jantunen and Bidleman (20) for 1994 and those reported by Harner et al. (21) for 1996 in the same area, whereas the α -HCH levels were higher in 1994 (20) as expected from the decreasing time trend. For α -HCH a west/east gradient was observed along the 75°N transect during ARK XVI. The analytical precision of 10–15% determined from parallel samples (W3, W5) indicates that the spatial variability at 75°N and the higher concentration level near Greenland (W2, W3, W4) are significant. Both, the East Greenland Current, that transports cold water-masses from the central Arctic southward, and the Norwegian Current transporting water-masses northward cause this gradient (see Figure 1b and ref 22 for Arctic currents). The decrease of the surface water temperature (23) indicated a front near 12°W at 75°N (close to W3, W4). In contrast to α -HCH, γ -HCH exhibited higher concentrations at stations W7–W9 (Norwegian Current) and in the North Sea, which may reflect the present use of lindane in Europe. In the North Sea at station 22 (Figure 1b and Supporting Information) we measured 330 pg/L γ -HCH and 98 pg/L α -HCH in March 2001. The predominance of lindane is typical for the North Sea, but much higher levels are observed in early summer near shore due to agricultural lindane applications (see ref 24 for monitoring data from the North Sea). On the transect from Bremerhaven to Antarctica (samples W11–W21 in Figure 1a) we observed a steep decline of the concentrations of both isomers after leaving the Canary Current (W11–W12) from a level above 100 pg/L to values below 10 pg/L on the remaining part of the cruise. A regional maximum was observed near Cape Town for γ -HCH (W17) and south of the Subtropical Front

TABLE 1. Concentrations of HCHs in Air and Surface Water (see also Supporting Information)

sample ^a	lat. ^b [°]	α-HCH		γ-HCH		α-γ-HCH	
		air [pg/m ³]	water ^c [pg/L]	air [pg/m ³]	water ^c [pg/L]	air	water
ARK XVI							
A1/W1	77.2	14	169	4.2	91	3.4	1.9
A2/W2	76	21	357	2.9	130	7.2	2.7
W3	74.1	n.a. ^d	380	n.a.	166		2.3
W3b	74.1	n.a.	385	n.a.	158		2.4
W4	75	n.a.	689	n.a.	230		3.0
A3/W5	74.9	12	279	3.4	165	3.5	1.7
W5b	74.9	n.a.	262	n.a.	145		1.8
A4/W6	74.9	14	263	7.1	108	2.0	2.4
A4b	74.9	18	n.a.	5	n.a.	3.6	-
A5/W7	74.6	21	59	6.7	72	3.1	0.8
W8	68.2	n.a.	172	n.a.	266		0.6
A6/W9	62.1	16	194	6.7	504	2.4	0.4
A6b	62.1	20	n.a.	15	n.a.	1.3	
S North Sea^e							
A7/A8	54	37	n.a.	69	n.a.	0.5	
A27/W22	54.3	12	98	11	332	1.1	0.3
ANT XVII							
A9/W11	46.9	11	46	5.8	133	1.9	0.3
A10/W12	36.7	12	69	7.0	107	1.7	0.6
A11/W13	41.5	10	13	40	20	0.3	0.7
A12/W14	7.6	4.1	5.7	45	17	0.1	0.3
A13	-2.6	3.3	n.a.	24	n.a.	0.1	
A14/W15	-8.7	2.9	2	47	1.4	0.1	1.4
A15/W16	-17.8	0.6	2.7	27	1.8	0.02	1.5
A16/W17	-30.2	0.6	2.9	5.1	5.5	0.1	0.5
A17/W18	-44.5	0.5	9.6	0.7	2.3	0.7	4.1
A18/W19	-56.3	0.3	3	0.1	0.7	3	4.6
A19/W20	-61.4	1.9	5.3	3.4	0.9	0.6	5.9
A20/W21	-66.2	n.a.	3.4	0.7	0.7		5.2
Neumayer Station							
A21-A26 ^f	-70.4	0.36	sea-ice	0.15	sea-ice	2.4	

^a A = air sample, W = water sample; samples A4b, A6b were collected using a different sampler (Digitel DH 80) and were analyzed independently by the Inst. for Baltic Sea Research/Warnemuende; W3b, W5b were duplicates taken from the CTD/Rosette; W22 average of triplicate sample. ^b Mean latitude of water sample; for A7/A8 and A13 mean latitude of air sample. ^c W1–W9 and W22 were SPE samples, W11–W21 were XAD-2 samples; the collection efficiency is approximately 30% lower in XAD-2 samples and the concentrations in W11–W21 are corrected for this. ^d n.a. not available, only water or air sample collected. ^e Samples were collected during two cruises in the southern North Sea. ^f Average of six weekly samples.

for α-HCH (W18). More southward toward the Antarctic continent the concentrations decreased (W19–W21). In conclusion, the distribution of HCHs in the surface waters of the Atlantic is very uneven, especially in the transition areas between the North Atlantic and Arctic Ocean or in the sea region of the southern fronts (50°S). The small-scale variability reflects more or less ocean currents, whereas the steep global north/south gradient is a result of the predominant release of HCHs in the industrialized northern hemisphere.

HCHs in Air (Figure 2a,b). Between 75°N–80°N (A1–A5) average concentrations of 16.3 ± 3.5 pg/m³ (range 12–21) and 5.2 ± 1.7 pg/m³ (range 3–7) were measured for α-HCH and γ-HCH, respectively. These are lower by a factor of 4.8 (α-HCH) and 2.6 (γ-HCH) than the concentrations determined during a year-round measurement campaign at Svalbard in 1993 (25) (annual mean values of 77 pg/m³ α-HCH (range 6.8–203) and 14 pg/m³ γ-HCH (range 3.3–38)). α-HCH concentrations reported by Harner et al. (21) for July 1996 were closer to our measurements. The declining trend of α-HCH air concentrations during the 1990s mirrors the decreasing time trend of technical HCH usage (6, 21). Above the North Sea (A7,8 and A27) the concentrations ranged between 10 and 40 pg/m³ α-HCH and 10–69 pg/m³ γ-HCH

in March 2001 and August 1999, which is close to the present level in the southern Baltic Sea at the same latitude (26). Toward the tropical climate zones α-HCH decreased in air, but γ-HCH showed a maximum between 30°N and 30°S (range 24–47 pg/m³ A11–A15). The α/γ-HCH-ratio was significantly lower in this region (<0.1) indicating recent lindane usage. Karlsson et al. (27) observed episodes with very high gaseous lindane concentrations at Senga Bay (Lake Malawi, southern Africa, 10°S) in 1997/1998. The average reported concentrations of α- and γ-HCH were 9 ± 9 pg/m³ and 25 ± 42 pg/m³, very close to our measurements. However, 5 day back trajectories (German Weather Service, Offenbach) did not show a clear emitter-receptor relationship between Africa and the ship's position for all samples with high lindane concentrations, but their use may be questionable due to the long sampling intervals and a fast zonal mixing of air masses. Between Cape Town and Neumayer Station (A17–A20) the average gaseous concentrations of α-HCH and γ-HCH were 1.1 pg/m³ and 1.4 pg/m³ and decreased further to 0.36 ± 0.03 pg/m³ and 0.15 ± 0.04 pg/m³ on the Ekstroem Ice Shelf (6-weekly average at Neumayer Station A21–A26). Kallenborn et al. (28) reported α- and γ-HCH concentrations of 2.8 pg/m³ and 22 pg/m³, measured at Signy Island (60°S) during December 1994–March 1995. The α-HCH concentrations are comparable to the ones we observed, but the γ-HCH concentrations were 100 times higher at Signy Island. This may be explained by several long-range transport episodes from South America, that resulted in elevated concentrations of γ-HCH and PCBs (28). Neumayer Station is influenced to a minor extent by such long-range transport episodes, because the station is located in the inner part of the polar vortex.

HCH Time Trends in Surface Waters of the Atlantic. The results obtained from the five transect cruises undertaken between 1987 and 1997 are shown together with those from 1999/2000 in Figure 3a,b. The eastern cruises (Bremerhaven – South Africa – Weddell Sea) were selected only, to allow for a better comparability with the data from 1999/2000 (for a complete list of HCH concentrations and sampling locations from R/V *Polarstern* cruises ANT V, ANT VII, ANT X, ANT XI, and ANT XV see Table S2, Supporting Information).

A comparison between our results and HCH seawater concentrations reported by Iwata et al. (9), Schreitmüller and Ballschmiter (10), and Harner et al. (21) is shown in Figures Sa and Sb (Supporting Information). The α-HCH concentrations were in a good accordance with our results. Also lindane concentrations from the Arctic (21) and North Atlantic (9, 10) agreed with ours, whereas the four South Atlantic lindane concentrations from May 1991 (10) had surprisingly high levels (range 21–45 pg/L) when compared with all South Atlantic samples from ANT V–ANT XVII between 1987 and 1999.

α-HCH. During the past decade α-HCH exhibited a strong decline at all sampling locations between 50°N and 60°S. In the southern North Sea (Table S2 in Supporting Information and Figure 3a, at 50°N) the decline was strongest between 1989 and 1991, from 500 pg/L to 120 pg/L, and levels remained rather constant thereafter. The same trend was observed in the North Atlantic and Canary Currents. In the Benguela Current (15–30°S) the level was approximately 20 pg/L in March 1989, 8 pg/L in November 1993, and between 1 and 2 pg/L in December 1999. Further to the South, between 30°S and 60°S, our measurements are limited to the period 1993–1999. The concentrations in this region are spatially quite variable due to the complex frontal system, but they decreased by a rather constant factor of 4 and may have decreased less in the Weddell Sea. A slight maximum for α-HCH was measured during all cruises between 40°S and 50°S where temperature exhibits a steep gradient.

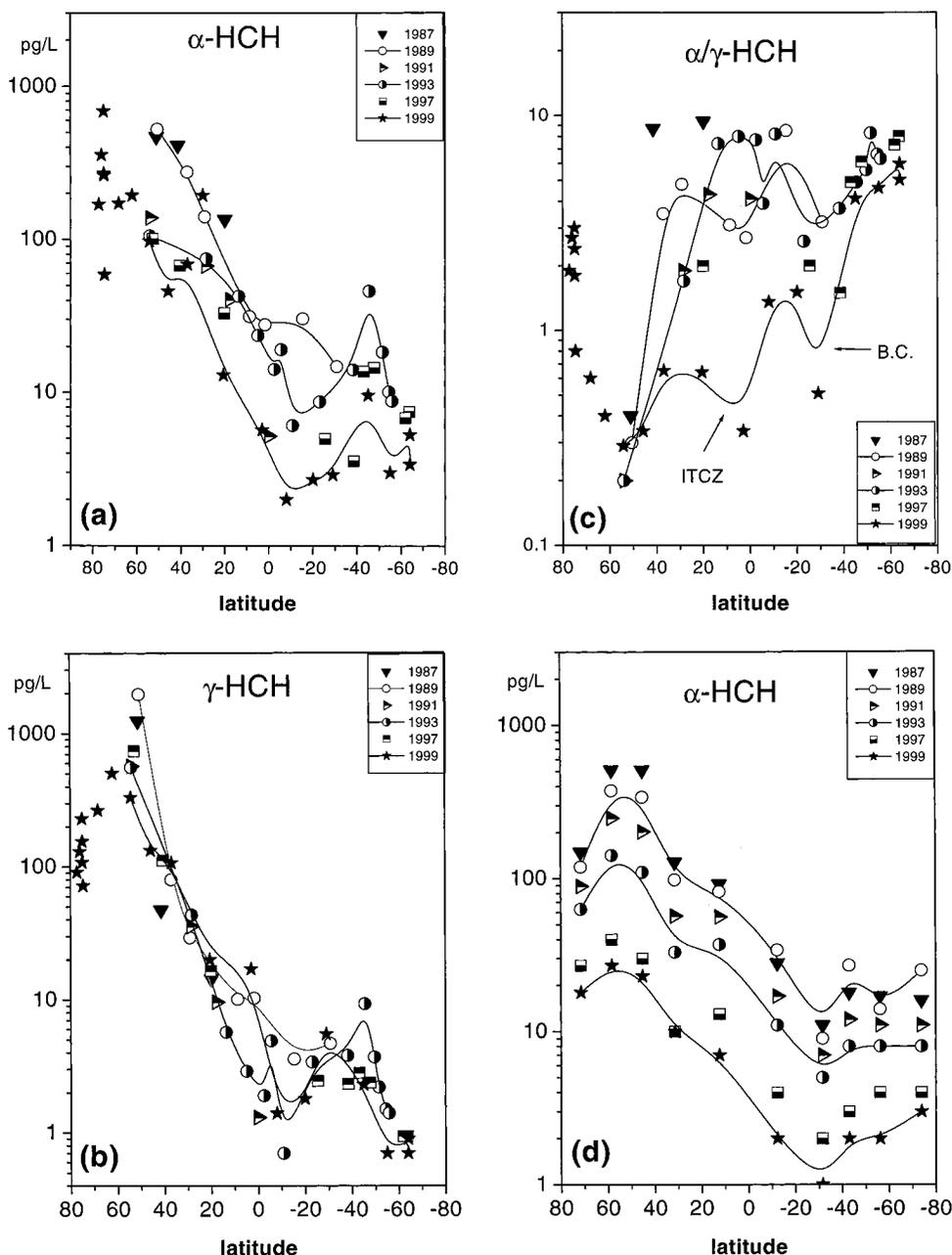


FIGURE 3. (a) Seawater concentrations of α -HCH and (b) γ -HCH in the Atlantic Ocean 1987–1999; samples from 1999 were collected using XAD-2 columns and between 1987 and 1997 using centrifugal extraction. (c) α/γ -HCH ratios 1987–1999; B.C. and ITCZ refer to Benguela Current and Intertropical Convergence Zone. (d) Calculated concentrations of α -HCH in ocean water for the 10 climate zones of the model. Emission data were divided by 4.5 to obtain the best accordance with the measurements between 50°N and 60°S, see text.

γ -HCH. In the southern North Sea a decline from 2000 pg/L to 300–400 pg/L between 1987 and 2001 was observed (see also Table S2 in Supporting Information). In contrast to α -HCH there was no significant change between 30°N and 30°S (Figure 3b), but a rather high variability is observed in this region. The losses of lindane due to degradation reactions and sedimentation seem to be balanced by atmospheric and freshwater inputs. The high precipitation rate of approximately 2000 mm/year in the Intertropical Convergence Zone (ITCZ) could cause a significant wet deposition of lindane. Further, the elevated gaseous concentrations (A11–A15) suggest that HCHs are transported to this region via the atmosphere. Interestingly, the concentrations measured during the six cruises were very similar near 30°N and 30°S. We assume meteorological factors to be responsible for this phenomenon. South of 40°S a decrease by a factor of approximately three is observed between 1993 and 1999.

α/γ -HCH Ratios in Surface Waters. This ratio and its variability in space and time are strongly influenced by the relative usage of technical HCH (ratio 4–7 (20) and lindane (ratio < 0.1). It is also influenced by variable partitioning and persistence of the two HCH isomers. We use the HCH-ratios (Figure 3c), calculated from the corresponding seawater concentrations (Figure 3a,b), to explore the time trend, because relative concentrations are less affected by methodological differences. The most striking observation is the strong decline of the ratio between 40°N and 40°S, whereas it decreased only slightly in the Antarctic waters and remained almost constant in the southern North Sea. The change of the ratio in the tropical waters may be explained by the strong decrease of α -HCH during 13 years and a more or less constant level of γ -HCH. There may be a minimum around the ITCZ due to atmospheric deposition of lindane (see 1989, 1993, and 1999 at 5–10°N in Figure 3c) and a second

minimum in the Benguela Current (see B.C.). The rather high ratio in Antarctica of 4–5, which decreases only slowly between 1993 and 1999, may reflect the same processes as in the Arctic around 1990 (7, 8). However, changes in the southern hemisphere are more moderate and occur on a lower level. We still observed a comparable high ratio of 2–3 in Arctic waters during ARK XVI in July 2000. The relative low and almost constant ratio of approximately 0.3 in the southern North Sea mirrors the ban of technical HCH in Europe that caused a strong decline of α -HCH around 1983. Both isomers declined thereafter more or less simultaneously in the period from 1987 to 1999.

HCH Ratios in Air. At 75°N α -HCH/ γ -HCH ranged between 2 and 7 (Table 1), which is explained by contributions from outgassing α -HCH in some regions of the Arctic and intrusions of lindane from agricultural applications in Europe. For comparison, in southern Norway ratios of approximately 2 (29) and in the high Arctic between 4 and 10 (30) have been determined around 1993/1994. We received during ARK XVI air masses from both regions. In Antarctic air we measured HCH-ratios of approximately three during summer 1999/2000. We assume that this may be caused by temporary outgassing α -HCH from Antarctic surface waters. However, the ratio in Antarctic air was below that in the surface waters, which indicates departure from equilibrium of one or both HCH isomers as discussed below. In air between 40°N and 50°S γ -HCH exhibited higher concentrations than α -HCH due to lindane emissions. However, the low ratio in this region cannot be explained by the differences of the Henry's law constants and atmospheric degradation rates of both isomers, because lindane reacts faster with the hydroxyl radical (see ref 31, average atmospheric lifetimes based on this reaction for α -HCH: 120 days and γ -HCH: 96 days) and is more water-soluble than α -HCH. Both factors would cause an increase of the α/γ -ratio due to wet deposition and degradation.

Model Results for α -HCH. The global multimedia fate and transport model of Wania et al. (12, 32, 33) and the global emission estimates of Li et al. (6) were used to calculate α -HCH seawater concentrations for the years 1987–1999 and the 10 climate zones of the model (see model parameters, Supporting Information). In general, the calculated concentrations were four to five times higher than the measured ones but showed the same time trend in both hemispheres and a very similar latitudinal gradient. The best accordance between model results and measurements (cruises Bremerhaven-Antarctica) was achieved by dividing the emissions by a factor of 4.5 (Figure 3d). The measured Arctic concentrations would be better reproduced by the model without this correction. The overestimate of concentrations in the South Atlantic is likely due to the zonally averaged nature of the model, which distributes the emissions homogeneously within each of the latitudinal boxes. Most of the emissions of technical-grade HCH during the 1990s however occurred in India. Consequently, HCH levels in the Atlantic Ocean are likely to be lower than in the Indian Ocean, whereas the model can only calculate a zonally averaged concentration. In the Arctic averaging is more appropriate, in particular as the predominant emission sources are at low latitudes, and the above-mentioned correction would result in an underestimate. Other potential reasons for the discrepancy are uncertain emission estimates and degradation rates. In general, measurements contain errors too, but we assume that these are much smaller than the observed difference. More importantly, the latitudinal profiles of the model and measurements were similar. In particular the model showed a minimum around 20°S to 30°S with an increase in concentrations toward Antarctica, superposed by a distinct maximum between 40°S and 50°S, independently from the year. As the model does not contain any detailed parametrization of ocean currents, we assume that the measured

local maximum at 50°S must be caused by the steep temperature gradient. SOCs such as HCHs may be temporarily trapped in this region, and the phenomenon may be a manifestation of the cold condensation effect.

The Air–Sea Equilibrium of α - and γ -HCH in 1999/2000. The ratio of the fugacities in water (f_w) and air (f_A) has often been employed to assess the state of equilibrium of SOCs between the air and water phases (e.g. ref 20).

$$f_w = \frac{C_w \cdot H}{M}$$

$$f_A = \frac{C_A \cdot R \cdot T}{M}$$

$$FF_w = \frac{f_w}{f_A + f_w}; FF_A = \frac{f_A}{f_A + f_w}$$

The fugacities can be calculated from the Henry's law constants (H [$\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$]), gaseous concentrations (C_A [$\text{mol} \cdot \text{m}^{-3}$]), aqueous concentrations (C_w [$\text{mol} \cdot \text{m}^{-3}$]), molecular masses (M [$\text{g} \cdot \text{mol}^{-1}$]), the gas constant ($R = 8.314$ [$\text{Pa} \cdot \text{m}^3 \cdot \text{K}^{-1}$]), and temperature (T [K]) (34). When using fugacity fractions (FF_w , FF_A) instead of ratios, deviations from equilibrium in either direction are depicted on the same scale. FF can assume values between 0 and 1. Equilibrium is indicated by a value of 0.5, volatilization by FF_w values greater than 0.5 and deposition by values below 0.5. For both HCH isomers the fugacity fractions FF_w are depicted in Figure 4a,b. The Henry's law constants were calculated as a function of surface water temperature using the experimentally derived relationships given by Kucklick et al. (35). Jantunen and Bidleman (36) recently reported Henry's law constants for HCHs and toxaphen using the same method. We decided to use those reported for seawater (35) that cover a larger temperature range (0.5–45 °C). Error margins in Figure 4a,b were calculated by varying the concentrations within $\pm 10\%$ and the Henry's law constants within $\pm 20\%$. For the values that depend on XAD-2 columns we considered a systematic error of 30% due to incomplete adsorption (see unfilled circles).

α -HCH. The fugacity fractions of α -HCH ranged between 0.4 and 0.6 along the 75° N transect, indicating conditions, close to equilibrium in this part of the Arctic. However, the variability is rather high (Figure 4a), caused mainly by the high inhomogeneity of the surface water in this region, and to a minor extent by the atmospheric variability (see Figures 1b and 2b). Fluctuations of the gaseous concentrations may have been obscured by the time integrated sampling over 1–3 days. The fugacity fractions further suggest net deposition of α -HCH in the tropical Atlantic between 30°N and 10°S, equilibrium conditions between 20°S and 40°S, and again net deposition south of 50°S. In comparison with the situation around 1990, assessed by both Iwata et al. (9) and Schreitmüller and Ballschmiter (10), we conclude that whereas the direction of α -HCH gas transfer in the North Atlantic has changed from net deposition to equilibrium, in the South Atlantic a new equilibrium has been established but on a lower concentration level than in 1990.

γ -HCH. The results obtained for γ -HCH are shown in Figure 4b. In the North Atlantic and Greenland Sea (samples W1–W9) the average FF_w value was 0.54 (range 0.37–0.84), which indicates a situation close to equilibrium. The sample pair A6/W9 ($FF_w = 0.84$) exhibited a strong oversaturation of the surface water at 60°N as a result of a high aqueous concentration of γ -HCH in this area. South of 40°N the phase equilibrium was changing to strongly net depositional. The maximum degree of undersaturation was observed between 20°N and 30°S caused by the enhanced level of γ -HCH in air. In the Antarctic Circumpolar Current (W18, W19) the FF_w

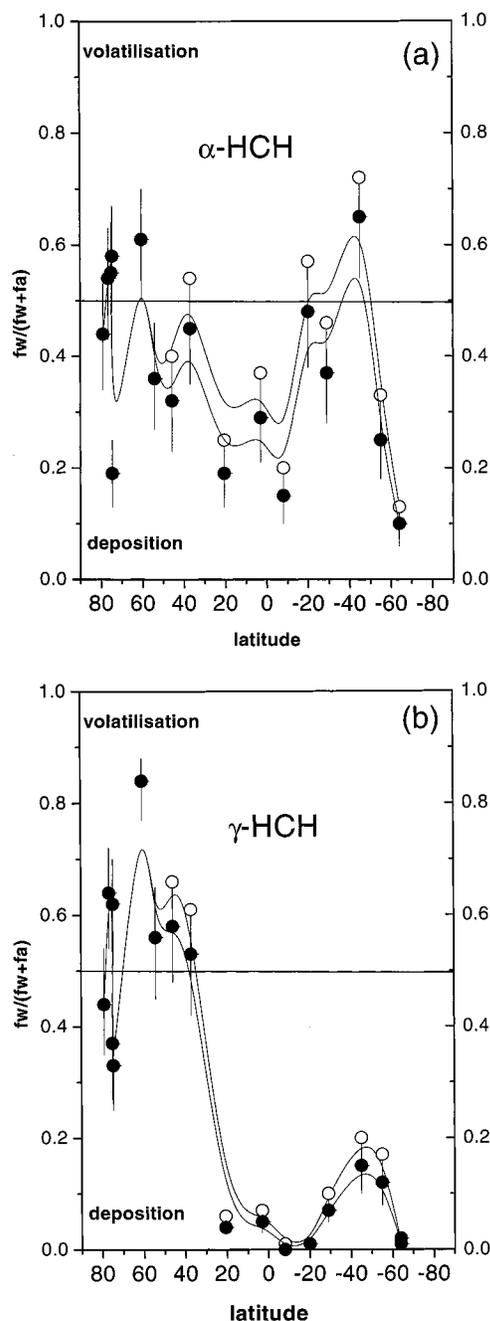


FIGURE 4. (a) Fugacity fractions of α -HCH and (b) γ -HCH versus latitude. The unfilled circles were calculated with 30% higher aqueous concentrations. The error bars indicate uncertainties of the measurements and Henry's law constants.

values were higher than in tropical waters but clearly remained depositional (below 0.5). A maximum of FF_w is reached at 50°S as the values decreased again toward the Antarctic continent. In general, FF -values are more sensitive to changes of the concentrations in water than in air, and therefore the local maximum of FF around 50°S, that was also observed for α -HCH, was mainly caused by the elevated aqueous concentrations in this region. In contrast to the earlier estimate for γ -HCH (10) our results suggest equilibrium in the North Atlantic and net deposition in the South Atlantic.

In conclusion, the state of the air-sea equilibrium of α -HCH and γ -HCH is very different. The sporadic occurrence of γ -HCH in air (e.g. refs 27 and 28) makes it difficult to obtain representative results from transect cruises, in particular the strong undersaturation of the surface waters in

Figure 4b could be weaker or stronger during a later cruise. However, long-term campaigns are restricted to a lower spatial resolution compared to transect cruises. But, there is no doubt that the sea areas of the tropical North Atlantic and the whole South Atlantic act as global sinks for γ -HCH at the present time. This result is confirmed by the constant level of γ -HCH in the surface waters between 30°N and 30°S, which can only be explained by equal inputs and losses. Without emissions the time trend of γ -HCH would be similar to that of α -HCH (Figure 3a) as a result of degradation reactions and export. We suggest that further measurements should be performed to estimate the extent of lindane usage in the tropical climate zones.

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Supporting Information Available

Sampling information for ARK XVI and ANT XVII in Table S1, HCH seawater concentrations from the five cruises between 1987 and 1997 in Table S2, model based α -HCH seawater concentrations (1987–1999) and model parameters in Table S3, and fugacity fractions, Henry's law constants, and ambient temperatures in Table S4. Further details about the quality assurance and two figures showing our results for HCH seawater concentrations in a comparison with literature data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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