

Atmospheric Concentrations and Air–Water Flux of Organochlorine Pesticides along the Western Antarctic Peninsula

REBECCA M. DICKHUT,^{*,†}
ALESSANDRA CINCINELLI,[‡]
MICHELE COCHRAN,[†] AND
HUGH W. DUCKLOW[†]

School of Marine Science, College of William and Mary, Gloucester Point, Virginia 23062, and Department of Chemistry, University of Florence, Via della Lastruccia, 3-50019 Sesto Fiorentino, Florence, Italy

Air, seawater, sea ice, and snow were collected during the austral winter (September–October 2001) and summer (January–February 2002) along the Western Antarctic Peninsula. Hexachlorobenzene (HCB) > heptachlor > α - and γ -hexachlorocyclohexane (HCH) and heptachlor epoxide, were the most frequently detected organochlorine pesticides in air. HCB and HCH levels declined over the past 20 years, with a half-life of 3 years for Σ HCH in Antarctic air. However, heptachlor epoxide levels have not declined in Antarctic air over the past decade, possibly due to continued use of heptachlor in the southern hemisphere. Peak heptachlor concentrations in air were measured coincident with air masses moving into the region from lower latitudes. Levels of lindane were 1.2–200 times higher in annual sea ice and snow compared to α -HCH, likely due to greater atmospheric input of γ -HCH. The ratio of α/γ -HCH in Antarctic air, sea ice and snow was <1, illustrative of a predominance of influx of lindane versus technical HCH to the regional environment. However, α/γ -HCH in seawater was >1, likely due to more rapid microbial degradation of γ - versus α -HCH. Water/air fugacity ratios for HCHs demonstrate continued atmospheric influx of HCHs to coastal Antarctic seas, particularly during late summer.

Introduction

Persistent organic pollutants (POPs) have become ubiquitous in the environment and have been detected in air, seawater, and biota from remote regions such as the Arctic and Antarctic (1–4). The presence of POPs in areas remote from known sources is thought to be the consequence of long-range atmospheric transport and deposition (5–9). It has also been hypothesized that at temperate and tropical temperatures, where the majority of POPs are used, POPs with sufficiently high vapor pressures volatilize and then move through the atmosphere and subsequently condense at colder, higher latitudes onto vegetation, soil, and bodies of water (8, 9). The cycle of volatilization and deposition may be repeated many times, resulting in POP accumulation in an area far removed

* Corresponding author phone: (804)684-7247; fax: (804)684-7786; e-mail: rdickhut@vims.edu.

[†] College of William and Mary.

[‡] University of Florence.

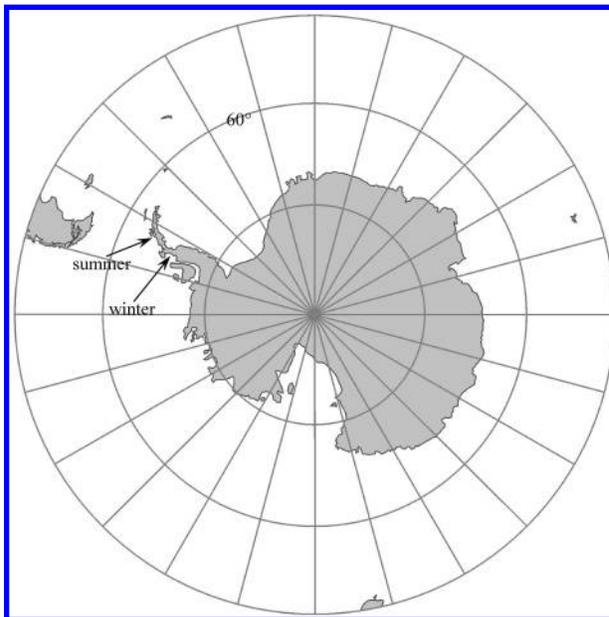


FIGURE 1. Map of Antarctica and the Southern Ocean showing summer and winter sampling locations.

from the area where the compounds were originally used or emitted (8–10).

Chlorinated pesticides were first discovered in wildlife from the Antarctic in the 1960s (11, 12). Recent studies continue to demonstrate the presence of organochlorine pesticides in the Antarctic marine food web (13–18), despite bans or restrictions on use of many of these compounds. Likewise, organochlorine pesticides are still found in Antarctic air, with levels of some compounds similar to those found in Arctic air (4, 19).

The objective of this study was to measure the atmospheric concentrations of various organochlorine pesticides in Antarctica to determine seasonal and long-term temporal trends. Air/water exchange of hexachlorocyclohexanes (HCHs) was also evaluated to determine if atmospheric (gas) deposition of these chemicals is still occurring or if Antarctic coastal waters are currently a source of HCHs to the atmosphere.

Experimental Section

Air samples were collected during the austral late winter/early spring west of the Antarctic Peninsula and southwest of Adelaide Island, at ca. 69° W, 68° S on the 2001 Palmer–LTER Ice Cruise (September 7–October 26) aboard the R/V *Nathaniel B. Palmer* (Figure 1). Summer sampling took place between January 7 and March 14, 2002, in the vicinity of Palmer Station, Antarctica (64.7° S, 64.0° W), located southwest of Anvers Island (Figure 1). Air samples were collected by use of two high-volume air samplers (Model GS2310, ThermoAndersen, Smyrna, GA). The air was pulled through a preashed (4 h at 400 °C) and preweighed glass fiber filter (GFF, 8 in × 10 in, Gelman type A/E) followed by two polyurethane foam (PUF) plugs (7.8 cm diameter × 7.5 cm thick). PUF plugs were precleaned with acetone and petroleum ether each for 24 h in a Soxhlet extractor. Sample volumes averaged 1365 (±398) m³. After sampling, filters were individually wrapped in preashed aluminum foil and PUF plugs were packed in precleaned glass jars, and both were stored at –20 °C until analysis.

Sea ice and snow were also sampled during the winter. Snow (92.5–128.5 L water) was collected upwind of the ship,

TABLE 1. Atmospheric (Gas Phase) Concentrations of Organochlorine Pesticides along the Western Antarctic Peninsula^a

	HCB	α -HCH	γ -HCH	heptachlor	heptachlor epoxide
09/15–16/01	32.1(±3.2)	0.2(±0.2)	2.26(±1.04)	<1	2.54(±0.42)
09/16–18/01	19.5	0.49	2.08	5.14	<0.3
09/18–20/01	12.2(±10.3)	0.46(±0.58)	0.8(±1.1)	19.1(±10.7)	20.7(±8.25)
09/22–23/01	22.4	0.52	0.48	10.32	1.68
09/25–26/01	23.1(±2.80)	0.35(±0.04)	0.87(±0.38)	6.51(±0.95)	<0.3
09/29–10/1/01	12.6	0.38	0.29	4.77	<0.3
10/01–02/01	28.1(±0.12)	0.39(±0.17)	2.41(±3.38)	6.26(±4.01)	<0.3
10/06–07/01	24.0(±5.51)	0.16(±0.15)	0.24(±0.32)	9.31(±9.79)	<0.3
10/07–08/01	24.7	0.41	0.42	13.8	<0.3
10/11–13/01	15.3	0.26	1.18	4.75	<0.3
10/13–15/01	11.9	0.28	2.09	8.83	<0.3
10/15–16/01	<5	0.33(±0.07)	0.06(±0.05)	4.39(±1.53)	<0.3
10/16–18/01	21.2(±9.87)	0.37(±0.01)	0.28(±0.02)	7.74(±2.75)	<0.3
01/12–13/02	NQ	<0.05	0.91	12.9	0.40
01/15–17/02	NQ	0.39	0.45	8.80	<0.3
01/17–18/02	NQ	0.32	0.45	4.19	<0.3
01/18–20/02	NQ	0.24	2.98	4.41	1.05
01/20–21/02	NQ	0.34	0.31	4.66	0.97
01/21–23/02	NQ	0.19(±0.10)	<0.02	4.64(±0.23)	<0.3
01/23–24/02	NQ	0.10(±0.08)	0.45(±0.12)	1.90(±0.56)	<0.3
01/24–26/02	NQ	0.20(±0.04)	0.20(±0.26)	4.08(±3.93)	0.72(±0.6)
01/30–31/02	NQ	0.30	0.29	1.76	0.52
02/01–02/02	NQ	0.47	0.26	2.35	2.03
02/02–03/02	NQ	0.39	0.32	2.46	<0.3
02/04–05/02	NQ	0.35	0.47	3.25	0.60
02/06–07/02	NQ	0.18(±0.19)	0.20(±0.25)	2.08(±0.92)	0.46(±0.06)
02/08–09/02	NQ	0.31(±0.01)	<0.02	1.01(±0.02)	<0.3
02/13–14/02	NQ	0.24	0.41	<1	<0.3
02/15–16/02	NQ	0.25	<0.02	2.02	<0.3
02/18–19/02	NQ	0.34	0.43	1.94	<0.3
02/28–03/01/02	NQ	0.32	0.34	1.60	<0.3

^a Concentrations are given in picograms per cubic meter. Values in parentheses are standard deviations for the reported mean value of *n* = 2 samples. Method detection limits: HCB (5 pg/m³), α -HCH (0.05 pg/m³), γ -HCH (0.02 pg/m³), heptachlor (1 pg/m³), heptachlor epoxide (0.3 pg/m³). NQ, not quantifiable due to sample breakthrough; HCB, hexachlorobenzene; HCH, hexachlorocyclohexane.

placed into closed (air- and water-tight) 60-L, solvent-rinsed, stainless steel containers and transported back to the ship. After removal of the overlying snow, sea ice (95.5–132 L water) was collected with a 1 m (3-in. diameter) barrel corer. Ice cores were then cut into sections, placed into closed (air- and water-tight) 60-L, solvent-rinsed, stainless steel containers and transported back to the ship. Subsequently, the snow and ice samples were melted by placing the sealed containers in a warm water bath, and the thawed contents were filtered through precombusted (4 h at 400 °C) 142 mm diameter GFFs (Gelman Type A/E, nominal pore size 1 μ m). Dissolved-phase pesticides were then collected by passing the filtrate over Amberlite XAD-2 resin (Sulpeco, Bellefonte, PA) columns (35 cm \times 25 mm i.d.). Similarly, surface seawater samples were collected at 5 sites within 1 mi of Palmer Station coincident with the summer air sampling. The seawater samples (127–527 L) were collected by pumping seawater from a depth of 5 m into stainless steel holding tanks, and the dissolved and particulate phases were isolated as described above for the sea ice and snow samples.

The PUF plugs were Soxhlet-extracted for 24 h each with acetone followed by petroleum ether after addition of deuterated α -hexachlorocyclohexane (α -HCH-*d*₆) as a surrogate standard. Both extracts were combined, exchanged into hexane, and reduced in volume to 1 mL by rotary evaporation followed by blowdown under purified N₂. Extracts were then cleaned up by silica column chromatography (20) with the addition of anhydrous Na₂SO₄. Prior to analysis for POPs, the extracts were spiked with an internal standard (γ -HCH-*d*₆) and reduced in volume under a stream of purified N₂. Each sample was then analyzed for selected organochlorine pesticides on a Hewlett-Packard 6890 GC (gas chromatograph) and a 5973 MSD (mass-selective detector) operated in the negative chemical ionization mode

as described elsewhere (18). Surrogate standard recoveries (\pm standard deviation) averaged 68.8(±17.7)%.

The breakthrough of analytes from front to back PUF plugs was monitored by a separate analysis of each plug for 60% of the samples. Breakthrough was only evident for hexachlorobenzene (HCB) in the summer season samples, with HCB levels on the back plug exceeding 33% of quantities found on the front PUF in most samples. Thus, HCB was not quantified in the summer air samples. For HCB in the winter samples and for all other analytes, average levels measured on the back PUF plugs (i.e., field blanks) and the average air sample volume were used to determine the method detection limits (Table 1).

The XAD-2 resin (sea ice, snow, and seawater) samples were Soxhlet-extracted for 18–24 h each with acetone followed by hexane after addition of α -HCH-*d*₆ as a surrogate standard. The acetone fraction was then back-extracted with hexane and hexane-extracted water three times via agitation for 3 min. The hexane extracts were then combined and analyzed as described above. Surrogate standard recoveries (\pm standard deviation) for the XAD-2 samples averaged 76.8(±14.9)%. Average levels of the compounds measured in lab blanks and the median water sample volume, were used to determine the method detection limits (Tables 2 and 3).

Results and Discussion

Pesticide Levels in Air. The organochlorine pesticides that occurred most frequently in our Antarctic air samples were HCB, α -HCH, γ -HCH, heptachlor, and heptachlor epoxide, and levels of HCB were significantly higher (*p* < 0.001, *df* = 20 for winter data only) than for the other chlorinated pesticides. Concentrations of gaseous HCB ranged from <5 to 32.1 [19.4(±7.6); average (\pm standard deviation)] pg/m³

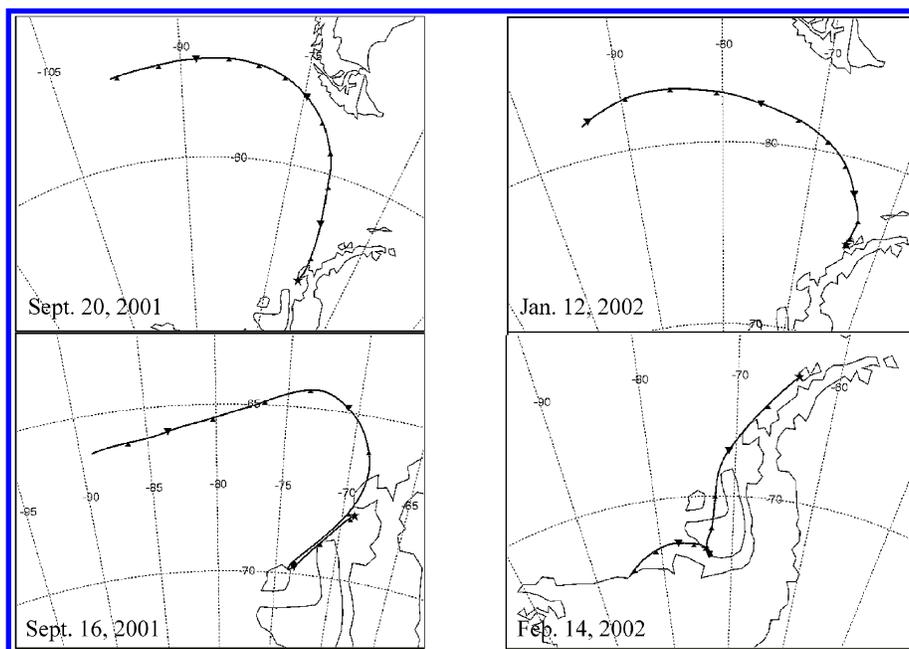


FIGURE 2. Three-day back trajectories (22, 23) for air masses sampled with maximum (winter, September 20, 2001; summer, January 12, 2002) and minimum (winter, September 16, 2001; summer, February 14, 2002) heptachlor concentrations.

during winter; however, summer HCB concentrations could not be quantified because of substantial (>33%) breakthrough. The atmospheric HCB levels measured in this study were significantly lower ($p < 0.001$, $df = 14$) than those reported by Bidleman et al. (1) [$62.7(\pm 20)$ pg/m^3] for air samples collected along a shipborne transect between New Zealand and the Ross Sea, during the austral summer (January–March) 1990. The significantly lower air concentrations of HCB measured in the present study may reflect a long-term temporal decline in atmospheric HCB levels in the Antarctic or may simply reflect seasonal or spatial differences in concentrations.

Heptachlor concentrations in air ranged from <1 to 19.1 [$7.84(\pm 4.66)$] pg/m^3 in winter and from <1 to 12.9 [$3.61(\pm 2.98)$] pg/m^3 in summer, and were significantly higher ($p < 0.005$, $df = 29$) in winter versus summer, potentially illustrating different seasonal sources or removal rates/processes. Although contamination of the winter samples by shipboard sources cannot be ruled out, it is unlikely since both winter and summer levels of heptachlor in air ranged from below the method detection limit (1 pg/m^3) to >10 pg/m^3 (Table 1). Rather, it is more likely that heptachlor levels in air are dependent upon the source of the air mass sampled, as described below.

Heptachlor was the second most abundant organochlorine pesticide measured in the Antarctic air samples and was significantly higher ($p < 0.001$, $df = 42$) than all other compounds measured except for HCB. In contrast to northern temperate regions, Karlsson et al. (21) found high levels of heptachlor (44 ± 66 pg/m^3 , $\text{max} = 283$ pg/m^3) along Lake Malawi, South Africa, and concluded that repeated regional use of heptachlor was the source of this compound. The average heptachlor epoxide/heptachlor ratio in our Antarctic air samples was higher (0.46) compared to the Lake Malawi air samples (0.02; 21), indicating that heptachlor is degraded during atmospheric transport to the Antarctic.

Potential sources of heptachlor to the Antarctic Peninsula were evaluated by examining 3-day back trajectories (22, 23) for air masses sampled with both maximum and minimum heptachlor concentrations in both the austral winter and summer (Figure 2). Air samples with the highest heptachlor levels (12.9 – 19.1 pg/m^3 , Table 1) originated north of 60° S latitude and passed by the southern coast of South America

(Figure 2, top). In contrast, air masses containing low heptachlor levels (<1 pg/m^3 , Table 1) traveled south of 60° S latitude and along the Antarctic coast prior to sampling (Figure 2, bottom). Although a specific source region for heptachlor was not identified by the 3-day back-trajectory analysis, it is clear that high levels of heptachlor in our Antarctic air samples are coincident with air masses travelling into the region from lower latitudes.

Heptachlor epoxide concentrations in air ranged from <0.3 to 20.7 [$2.14(\pm 5.6)$] pg/m^3 in winter and from <0.3 to 2.03 [$0.54(\pm 0.44)$] pg/m^3 in summer but were not significantly different ($p > 0.05$). Moreover, the average concentration of heptachlor epoxide in our summer air samples is comparable to that measured by Bidleman et al. (1) [$0.55(\pm 0.17)$ pg/m^3], indicating little spatial or temporal variability in atmospheric heptachlor epoxide levels in the Antarctic over the past decade.

Air concentrations of α -HCH ranged from 0.16 to 0.52 [$0.35(\pm 0.11)$] pg/m^3 in winter and from <0.05 to 0.47 [$0.28(\pm 0.11)$] pg/m^3 in summer. Levels of γ -HCH ranged from 0.06 to 2.41 [$1.04(\pm 0.87)$] pg/m^3 in winter and from <0.02 to 2.98 [$0.47(\pm 0.66)$] pg/m^3 in summer. No significant differences ($p > 0.05$) in atmospheric HCH concentrations in summer versus winter were found. However, concentrations of α -HCH in Antarctic air measured in this study were significantly lower ($p < 0.001$) than those previously measured in 1997–1998 [$1.05(\pm 0.30)$ pg/m^3] (24), 1990 [$3.23(\pm 0.38)$ pg/m^3] (1), and 1987 [$55.8(\pm 35.4)$ pg/m^3] (25). As with Arctic air concentrations of α -HCH, the temporal decline in atmospheric α -HCH in Antarctic air reflects the global decline in use of technical HCH (26), which is composed primarily of α -HCH. Similarly, concentrations of γ -HCH (lindane) in Antarctic air measured in this study were significantly lower ($p < 0.001$) than those previously measured in 1990 [$2.43(\pm 2.13)$ pg/m^3] (1), 1987 [$23.2(\pm 31.0)$ pg/m^3] (25), and 1988–1989 [$38.6(\pm 31.8)$ pg/m^3] (27). Overall, ΣHCH in air has significantly declined over the last 20 years, with a half-life of 3 years in the Antarctic atmosphere (Figure 3). However, continued use of HCHs in some developing countries in the southern hemisphere (29) may interfere with this rate of decline.

Lindane was also significantly higher in our Antarctic air samples compared to α -HCH (paired t -test, $p = 0.009$, $df =$

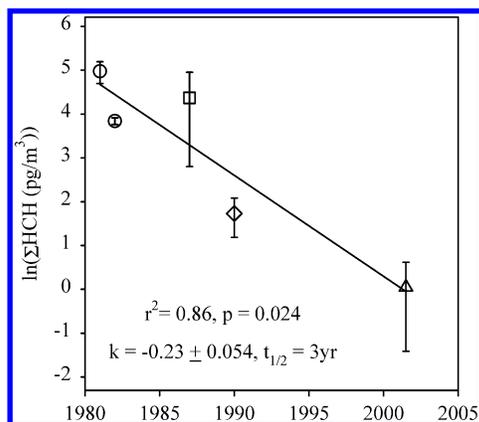


FIGURE 3. Decline in ΣHCH ($\alpha + \gamma\text{-HCH}$) in Antarctic air over the past 20 years (k = first-order rate constant, $t_{1/2}$ = half-life): (○) Tanabe et al. (28); (□) Weber and Montone (25); (◇) Bidleman et al. (1); (△) this study.

TABLE 2. Surface Water (Dissolved Phase) Concentrations of HCHs in the Vicinity of Palmer Station, Antarctica^a

	$\alpha\text{-HCH}$	$\gamma\text{-HCH}$
01/13/02	1.65	1.05
01/16/02	4.28(±0.21)	10.4(±0.28)
01/18/02	2.91	0.91
01/21/02	4.54	10.5
01/22/02	4.29(±0.06)	10.3(±0.36)
01/27/02	4.25(±0.17)	9.31(±0.79)
02/04/02	3.43(±0.82)	5.09(±4.70)
02/05/02	4.22	8.36
02/08/02	2.88	1.23
02/12/02	2.63	1.03
02/13/02	2.61(±0.15)	1.07(±0.23)
02/18/02	2.53(±0.02)	1.22(±0.12)
02/19/02	2.81	1.05
02/21/02	2.73	1.21
02/26/02	2.77(±0.16)	1.34(±0.24)
02/28/02	2.81(±0.33)	1.56(±0.45)
03/04/02	2.45(±0.08)	1.60(±0.10)
03/07/02	3.06	1.20

^a Concentrations are given in picograms per liter. Values in parentheses are standard deviations for the reported mean value of $n = 2$ samples. Method detection limits: $\alpha\text{-HCH}$ (0.03 pg/L), $\gamma\text{-HCH}$ (0.34 pg/L).

42). The ratio of $\alpha/\gamma\text{-HCH}$ is reflective of a predominance of technical HCH sources ($\alpha/\gamma\text{-HCH} > 1$) or lindane ($\alpha/\gamma\text{-HCH} < 1$). The ratio of $\alpha/\gamma\text{-HCH}$ in our air samples averaged $0.81(\pm 0.61)$, calculated only for samples in which both compounds were above the method detection limit. On average, $\alpha/\gamma\text{-HCH}$ in our air samples was significantly lower ($p = 0.0004$, $df = 28$) than previously measured in the Antarctic peninsular region [$2.68(\pm 1.77)$; 25]. The lower average $\alpha/\gamma\text{-HCH}$ in our air samples probably reflects both the global decline in use of technical HCH (26), as noted above, as well as greater usage of lindane in the Southern Hemisphere (24).

Pesticide Levels in Seawater, Snow, and Sea Ice. The HCHs were the only organochlorine pesticides routinely detected in the Antarctic seawater (dissolved phase) samples. Concentrations of $\alpha\text{-HCH}$ ranged from 1.65 to 4.54 [$3.20(\pm 0.82)$] pg/L, and concentrations of $\gamma\text{-HCH}$ ranged 0.90 to 10.6 [$4.09(\pm 4.08)$] pg/L in seawater (Table 2). There was little spatial and temporal variability ($\pm 26\%$) in $\alpha\text{-HCH}$ levels in seawater, whereas concentrations of $\gamma\text{-HCH}$ varied more than 10-fold over the study period. Spikes in $\gamma\text{-HCH}$ concentrations in seawater occurred during the early part of summer (January–early February, Table 2), but simultaneous spikes of $\gamma\text{-HCH}$ in air were not detected. Consequently, the higher levels of $\gamma\text{-HCH}$ detected in surface water during the early

TABLE 3. Dissolved Phase Concentrations of Organochlorine Pesticides in Sea Ice and Snow along the Western Antarctic Peninsula^a

	$\alpha\text{-HCH}$	$\gamma\text{-HCH}$	heptachlor	heptachlor epoxide
Sea Ice				
09/17/01	2.18	4.38	5.66	2.21
09/25/01	1.77	3.60	<2.5	<0.63
09/26/01	<0.04	5.70	5.32	<0.63
10/08/01	1.57	4.72	<2.5	<0.63
10/12/01	0.81	4.43	<2.5	<0.63
10/17/01	2.06	5.40	5.80	2.22
Snow				
9/15/01	<0.04	8.91	5.06	<0.63
9/24/01	1.44	1.73	<2.5	<0.63
9/25/01	2.18	4.44	6.70	1.12
10/3/01	1.66	2.03	<2.5	<0.63

^a Concentrations are given in picograms per liter. Method detection limits: $\alpha\text{-HCH}$ (0.04 pg/L), $\gamma\text{-HCH}$ (0.49 pg/L), heptachlor (2.5 pg/L), heptachlor epoxide (0.63 pg/L).

part of summer may be due to influx from melting sea ice and snow. It is possible that lindane, a currently used pesticide, is preferentially accumulated in sea ice and snow during winter and released into surface waters when the sea ice recedes in spring and early summer. Indeed, we found $\gamma\text{-HCH}$ concentrations to be 1.2–200 times higher than $\alpha\text{-HCH}$ levels in sea ice and snow along the Western Antarctic Peninsula (paired t -test, $p = 0.0035$, $df = 9$; Table 3).

In addition to HCHs, heptachlor and heptachlor epoxide were also detected in 30–50% of the sea ice and snow samples (Table 3). The lower frequency of detection of these pesticides in snow and sea ice may be related to the higher air/water partition coefficients of these compounds (30). Nonetheless, the presence of heptachlor and heptachlor epoxide in annual sea ice and snow is indicative of current atmospheric deposition of these pesticides to the Antarctic, which is consistent with the observation that atmospheric heptachlor epoxide levels in the Antarctic have not declined over the past decade.

Finally, the ratio of $\alpha/\gamma\text{-HCH}$ in our Antarctic seawater samples averaged $1.59(\pm 0.92)$ and was significantly higher than in either air [$0.81(\pm 0.61)$, $p = 0.0005$, $df = 52$] or sea ice/snow [$0.50(\pm 0.22)$, $p = 0.002$, $df = 33$]. The $\alpha/\gamma\text{-HCH}$ ratio in both Antarctic air and sea ice/snow is illustrative of a predominance of influx of lindane versus technical HCH to the regional environment. However, this is not reflected in the $\alpha/\gamma\text{-HCH}$ ratio in seawater. The higher $\alpha/\gamma\text{-HCH}$ ratio observed in Antarctic coastal waters is likely due to more rapid microbial degradation of γ - versus $\alpha\text{-HCH}$ (31). Moreover, biodegradation is likely responsible for the shorter half-life for HCHs in Antarctic seawater (2 years; 18) compared to air (3 years).

Air/Water Exchange of HCHs. The measured HCH concentrations in seawater were also examined relative to concentrations in air by calculating the water/air fugacity ratios (f_w/f_a) as follows (32, 33):

$$f_w/f_a = C_w H / C_a R T \quad (1)$$

where C_w and C_a are the water and air concentrations (picograms per cubic meter) of each compound, respectively, H is the Henry's law constant [(pascal·cubic meters)/mole], R is the gas constant (8.314 Pa m³/deg mol), and T is temperature (kelvins). For these calculations an average temperature of 274 K based on the average seawater temperature (0.98 ± 0.6 °C, $n = 30$) was used, along with temperature-corrected H values for γ - and $\alpha\text{-HCH}$ in seawater (33). Uncertainty ($\pm 45\%$) in the calculated f_w/f_a values was determined on the basis of propagation of error in the

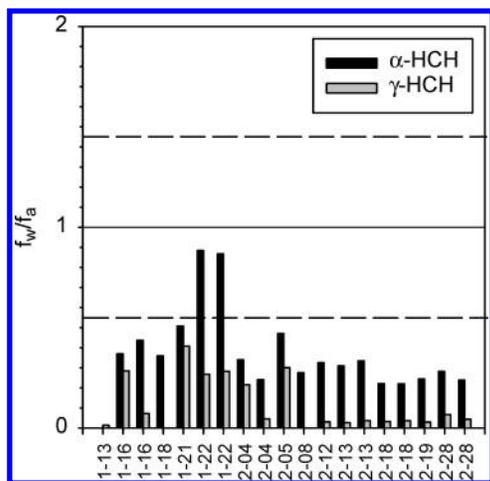


FIGURE 4. Water/air fugacity ratios (f_w/f_a) for α - and γ -HCH in coastal waters along the Western Antarctic Peninsula during January–February 2002. Ratios > 1 indicate transfer from water to air; ratios < 1 indicate transfer from air to water. Dashed lines illustrate the uncertainty for $f_w/f_a = 1$.

measured C_w , C_a , and H values. The water/air fugacity ratios for HCHs in coastal Antarctic seas demonstrate that the air/water flux of α -HCH is near equilibrium during the early summer (January) and from air to water during later summer, whereas gas deposition of γ -HCH is expected throughout the summer (Figure 4). This is similar to the Arctic, where α -HCH was found to be near equilibrium and γ -HCH demonstrated a potential for air to water exchange (i.e., deposition) (33). The air-to-water flux of HCHs observed in this study demonstrates continued deposition of these pesticides to coastal Antarctic seas and is consistent with a shorter half-life of HCHs in surface waters compared to air, which may in part help to establish the flux gradient.

Acknowledgments

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