Air-Sea Gas Exchange of Toxaphene in Arctic and Subarctic Waters

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1. Introduction

The mixture of chlorinated bornanes (CHBs) commonly known as toxaphene accounts for a large proportion of organochlorine pesticide residues in arctic biota[1-3]. CHBs and other organochlorines are atmospherically transported to the Arctic and enter oceans and lakes by wet and dry deposition and gas exchange across water surfaces[4]. The latter is a two-way process that may result in net deposition or volatilization, depending on the fugacity gradient between the atmosphere and ocean surface water. In response to declining atmospheric concentrations, the net flux direction of alpha-hexachlorocyclohexane (α-HCH) in the Bering and Chukchi seas during late summer has reversed, from deposition in 1988 to volatilization in 1993[5,6]. This investigation was done to determine the present-day concentrations and air-sea exchange direction of CHBs.

2. Methods

Air and water samples were collected in the Bering and Chukchi seas in the region bounded by 54-72°N, 175°E-162°W from August - September 1993[5]. Air was drawn through a glass fiber filter followed by two polyurethane foam plugs as described previously[5]. Water samples were obtained by suspending a submersible pump on a floating buoy ~1 m below the water surface and pumping the water onboard through Tygon tubing. The water was pumped through a continuous flow centrifuge to separate particles $\leq$0.5 µm and then into stainless steel cans. For determination of organochlorines in the dissolved phase, 70-100 L was spiked with the recovery surrogate compounds tribromobenzene and octachloronaphthalene and extracted on board ship with dichloromethane in a Goulden apparatus. Air sampling media and water extracts were frozen and returned to the laboratory for analysis.

Because of the low levels of CHBs anticipated in air, 2-4 individual samples were combined to represent 1100 - 3500 m^3 air. Only the polyurethane foam plugs were analyzed, since previous work indicated that quantities of CHBs on filters were negligible under summer arctic conditions[7]. Plugs were extracted with petroleum ether and the solvent was exchanged to isooctane. Cleanup was done using a 1-g column of neutral aluminum oxide, eluting the CHBs with 15 mL 20% dichloromethane in petroleum ether. After adding internal standard (mirex) the samples were blown down with nitrogen to ~100 µL for analysis.

Dichloromethane extracts of water samples were washed with saline water, exchanged into hexane, and cleaned up on silica gel. Volumes were adjusted to 1.0 mL and the samples were analyzed by capillary GC with electron capture detection on 30-m DB-1 and DB-5 columns to determine recoveries of the added surrogate compounds. They were then spiked with mirex internal standard, blown down to ~100 µL, and analyzed for CHBs.

CHBs were determined by capillary GC with detection by negative ion mass spectrometry, using instrument conditions and procedures previously described[8]. Ions monitored for samples and a toxaphene standard were 343*, 345, 377, 379*, 381, 413*, 415 for CHBs containing 7-9 chlorines and 404* for mirex (* indicates quantification ions).

3. Results and Discussion

The percent recovery of CHBs from four polyurethane foam plugs spiked on board ship was 74 ± 14. Backup foam plugs from two air samples contained 0.7 and 1.5 ng CHBs. The mean (1.1 ng) was used as the blank value for CHBs in air. By comparison, the uncorrected quantity of CHBs found on front plugs ranged from 6-29 ng (mean 15 ng). Front plug values were corrected for the blank and mean recovery, then divided by the air volume to obtain CHB concentrations. Water samples were not spiked with CHBs, but recoveries of tribromobenzene and octachloronaphthalene surrogates were 60-80%. The yield of CHBs from three experiments in which spiked solutions were blown down to ~100 µL was 70% ± 3%. Results for CHBs in water were corrected for 70% recovery.

Average concentrations of CHBs over the cruise track were 4.2 pg/m^3 in air and 21 pg/L in surface water. CHB levels decreased slightly from south to north (Table 1). By comparison,

CHBs averaged 6.9 pg/m^3 in air and 48 pg/L in water at Resolute Bay[8]. CHBs in air appear to have declined since 1986-88, when concentrations were 17-40 pg/m^3 in the Canadian Arctic[7,9] and 38 pg/m^3 in the Bering and Chukchi seas[10].

Chromatographic profiles of 7-9 chlorinated CHBs in air and water were similar to those shown for samples collected in 1992 from the Canadian Archipelago at Resolute Bay (74°N, 95°W)[8]. Two CHBs that are abundant in arctic biota were also found in air and water. These are 2-exo,3-endo,5-exo,6-endo,8,8,10,10-octachlorobornane (T2) and 2-exo,3-endo,5-exo,6-endo,8,8,9,10,10-nonachlorobornane (T12)[11].

The net direction of air-sea gas exchange of CHBs was assessed from the water/air fugacity ratio[8]

$$f_w/f_a = C_wH/C_aRT$$

where C_w and C_a are the dissolved and gaseous CHB concentrations in water and air (both ng/m^3), H is the Henry's law constant (Pa m^3/mol) at the water temperature, T is the air temperature and R = 8.31 Pa m^3/deg mol. Values of the fugacity ratio <1.0 and >1.0 imply net deposition and volatilization. The Henry's law constant of toxaphene in distilled water at 20°C is 0.67 Pa m^3/mol[12]. This value was extrapolated to the temperature of surface water in the Bering and Chukchi seas using a slope measured for polychlorobiphenyls[8,13,14]

$$\text{Log } H = 11.48 - 3416/T$$

We also assumed that Henry's law constants of CHBs were 20% higher in seawater than in fresh water[7]. Results (Table 1) show fugacity ratios of CHBs <1.0 in all locations, decreasing from 0.66-0.59 in the south and middle Bering Sea to 0.25 in the Chukchi Sea. The predicted net flux direction is thus air-to-sea (deposition). These calculations are intended to be only approximate, as they are limited by lack of Henry's law constants under environmentally relevant conditions. A more accurate assessment of CHB gas exchange requires Henry's law constants for individual CHB congeners as a function of temperature and salinity.

4. Acknowledgements

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5. References

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Table 1. Concentrations of CHBs in Air and Water (ng/m^3) and Fugacity Ratios (f_w/f_a)

	C_a Range and Mean	n	C_w Range and Mean	n	H Pa-m^3/mol	f_w/f_a
South Bering $T_w = 283$ $T_a = 284$	0.0035-0.0066 0.0050	4	17-33 25	3	0.31	0.66
Mid Bering $T_w = 280$ $T_a = 281$	0.0030-0.0039 0.0035	2	17-26 21	4	0.23	0.59
Chukchi $T_w = 275$ $T_a = 275$	0.0030-0.0035 0.0033	2	13-14 13.5	2	0.14	0.25