High-volume Collection of Atmospheric Polychlorinated Biphenyls

by

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The atmosphere has been suggested as a major transport route of chlorinated pesticides and polychlorinated biphenyls (PCB) to the oceans (RISEBROUGH et al. 1968, WOODWELL et al. 1971, SEBA and PROSPERO 1971, NISBET and SAROFIM 1972), but only a few measurements of organochlorines in the marine atmosphere have actually been made. A barrier to obtaining this much-needed information has been the lack of suitable collection methods. The common approaches to sampling airborne pesticides are columns packed with solid adsorbents, impingers, and gas bubblers (YULE et al. 1971, MILES et al. 1970, STANLEY et al. 1971, THOMPSON 1971). Many of these methods were developed for use in agricultural areas or to monitor insecticide drift during forest spraying operations where concentrations of insecticide in the atmosphere are apt to be high and the volume of air required for a sample relatively small, on the order of 5 - 50 cubic meters. The lower levels of chlorinated hydrocarbons expected in the marine atmosphere require that hundreds or even thousands of cubic meters of air be sampled, necessitating high volume collection equipment. One approach to DDT collection over the ocean has been to hang nylon screens coated with an organic liquid in the wind to trap particulate matter (RISEBROUGH et al. 1968, SEBA and PROSPERO 1971). Several million cubic meters of air were sampled, but the collection efficiency of these screens for gaseous organochlorines is unknown and it has been suggested that PCB are likely to exist in the atmosphere as vapors rather than adsorbed on particles.

This paper reports an efficient collection system for PCB vapors that allows hundreds of cubic meters of air to be sampled per day. The trap is a plug of porous polyurethane foam, a substance that has been used to extract PCB from seawater (GESSER et al. 1971). The foam offers little resistance to air passage and therefore is compatible with high-volume sampling apparatus.

Experimental

The PCB isomers 3,4,2'-trichlorobiphenyl (tri), 2,5,2',5'-tetrachlorobiphenyl (tetra), and 2,4,5,2',5'-pentachlorobiphenyl (penta) were obtained from Analabs Inc., North Haven, Conn. 06473.

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Aroclor 1248 and 1254 analytical standards were supplied by the Pesticides Repository of the Perrine Primate Research Branch, Environmental Protection Agency (EPA), Perrine, Fla. 33157. Solvents were Mallinckrodt Nanograde petroleum ether and dichloromethane, B & A ACS reagent grade acetone, and Eastman ethylene glycol. Adsorbents for column chromatography were Woelm neutral alumina and Mallinckrodt 100-mesh silicic acid. Gelman glass fiber A (GFA) filters were wrapped in aluminum foil and baked at 450°C for 4 hours to remove organic matter. High-volume air samples were collected with a Gelman Hurricane Air Sampler, Model 16003. A small 1/6-hp air pump was used to draw air through the impinger for low-volume sampling.

Circular plugs 4 inches in diameter were cut from 2-inch polyurethane foam (density 0.021 g/cm^3). New plugs were washed by squeezing under running tap water and rinsed with acetone. The plugs were then extracted for 12 hours with acetone followed by 12 hours with petroleum ether in soxhlet extractors large enough to hold 6 plugs. One batch of the solvents was used to clean 18 - 24 plugs. The extracted plugs were rinsed with a small volume of fresh petroleum ether, squeezed as dry as possible, and the residual solvent was removed by gentle heating. A large vacuum desiccator heated to 40°C with heating tape and connected to a water aspirator was convenient for drying the plugs with a minimum of atmospheric contamination. Air was readmitted to the desiccator through a column packed with clean foam. Plugs for sample collection were squeezed dry after extraction of the sample, rinsed with petroleum ether, dried as above, and reused for subsequent sampling. Clean plugs and samples were stored in wide-mouth mason jars with aluminum foil between the jar and cap.

For high-volume air sampling two foam plugs were inserted into a 3-1/2-inch diameter aluminum cylinder, taking care to avoid empty spaces between the plugs and cylinder wall. The cylinder was attached to the rear of a stainless steel filter holder containing an 8" x 10" GFA filter and the filtering apparatus was connected to the Hurricane pump through 10 feet or more of flexible hose. Collections were also made with a Greenburg-Smith impinger charged with 100 ml ethylene glycol and backed up by a column packed with polyurethane foam. A small GFA filter placed over the entrance to the impinger ensured that only vapors were sampled. Glass beads coated with the compounds of interest served as known sources of atmospheric PCB. The beads were placed a few inches to several feet from the collection device, thus regulating the levels in the air being sampled.

After sampling had been completed, the GFA filters were cut into strips and refluxed for 2 hours with 150 ml petroleum ether and the foam plugs were extracted for 2 hours (30 cycles) in soxhlet extractors with 175 ml petroleum ether. The extracts were concentrated to a small volume by evaporation under reduced pressure or in a Kuderna-Danish apparatus and cleaned up by alumina or silicic acid column chromatography. In the former

procedure, 4 g activity grade III alumina (prepared by adding 6% water to activity grade I alumina) was slurried with petroleum ether and packed into a 1-cm diameter column. The sample was transferred to the column and eluted with petroleum ether. The first 3 ml of eluate was discarded; the next 8 ml containing the PCB was collected and adjusted to a suitable volume. The silicic acid procedure used was a modification of that reported by ARMOUR and BURKE (1970), and was carried out with a 3-g column of deactivated (3.3% water) silicic acid, using 50 ml petroleum ether and 10 ml dichloromethane to elute the PCB and DDT fractions respectively.

Extracts were analyzed with a Tracor Microtek 220 gas chromatograph equipped with two columns, two ^{63}Ni electron capture detectors, and a dual-channel recorder. Columns were 1.5% OV-17/1.95% QF-1 on 100/120-mesh Supelcoport (column A) and 4% SE-30/6% QF-1 on 80/100-mesh Supelcoport (column B). Instrumental conditions: nitrogen carrier gas, column temp. 200°C, detector temp. 350°C, flow rates 74 ml/min (column A) and 100 ml/min (column B). Peak heights of sample chromatograms were compared to those of standards. Quantitation of Aroclors in the atmospheric samples from Bermuda was based on the sum of the heights of the peaks in the sample that matched Aroclor 1248 or 1254 standards.

Results and Discussion

Extracts of polyurethane foam showed two major GC peaks (Fig. 1). These were obtained even after the plugs had been extracted several times and were assumed to come from the foam itself. Alumina chromatography removed the compounds responsible for these two peaks. Alternatively, if the sample was separated into PCB and DDT fractions on silicic acid these peaks were found in the DDT fraction and thus did not interfere with the PCB determination. The blank range for 7 plugs was 7 - 27 ng (mean, 15 ng) as Aroclor 1248.

Collection studies with PCB isomers on GFA filters and polyurethane foam plugs were conducted outdoors with sampling periods varying from 12 - 34 hours and the temperature range approximately 5 - 20°C. Table 1 shows the excellent collection efficiency of the foam plugs for tri-, tetra-, and pentachlorobiphenyl isomers. Comparative runs were made with a Greenburg-Smith impinger containing ethylene glycol, the system used by EPA for sampling airborne pesticides (THOMPSON 1971). The collection efficiency of the impinger for PCB vapors (Table 2) is lower than for the foam plugs and is approximately the same as reported by MILES et al. (1970) for organophosphorus insecticide vapors. Impingers are not the preferred method for sampling marine air because they are limited to relatively low flow rates.

Atmospheric samples were collected during February - March 1973 from the top of a 20-meter tower at High Point, Bermuda, with

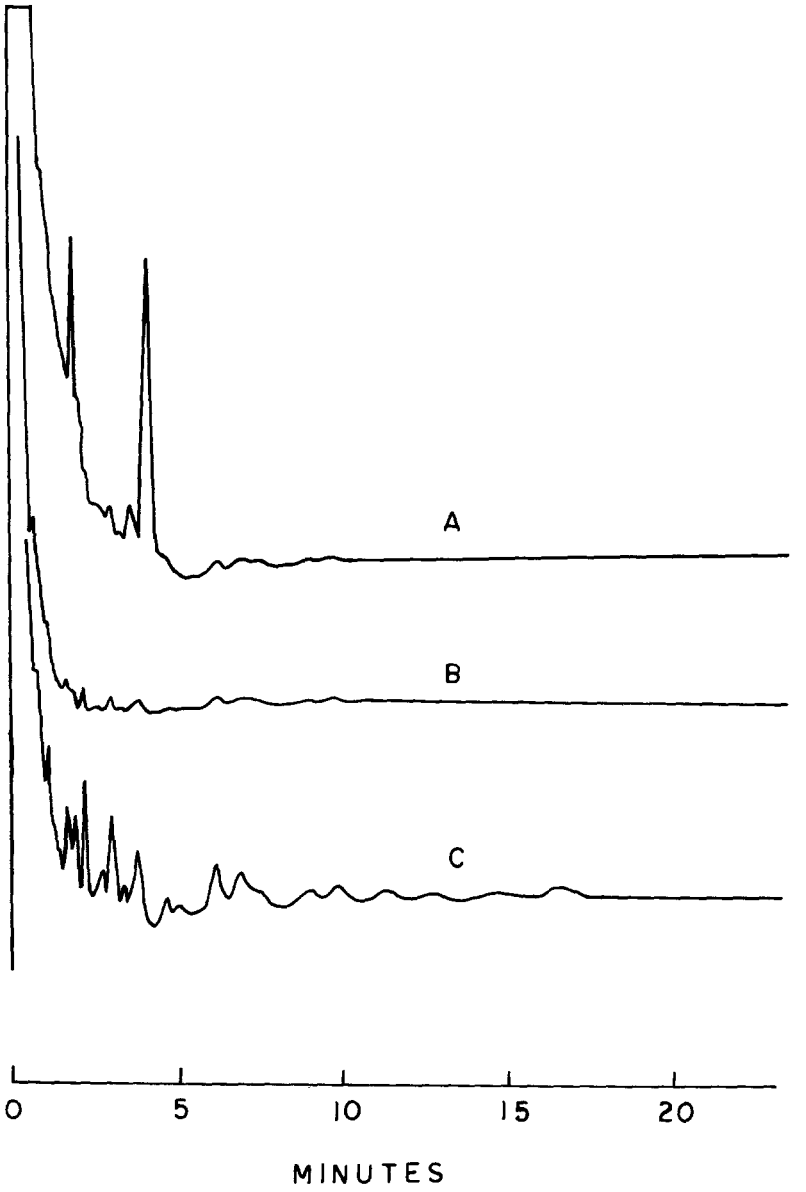

Fig. 1: Chromatograms of foam plug blanks, OV-17/QF-1

A. no cleanup, 5 ml, 10 µl injection

B. after alumina cleanup, 5 ml, 10 µl injection

C. after alumina cleanup, 1 ml, 10 µl injection

TABLE 1

Collection of PCB Vapors on Polyurethane Foam Plugs

Flow Rate	Volume air	PCB in air,[a] ng/m^3			% on first PF plug[b]			% on GFA filter		
m^3/min	m^3	tri	tetra	penta	tri	tetra	penta	tri	tetra	penta
0.48	987	- -	5.6	1.2	- -	99	96	- -	0.7	4
0.50	683	2.3	2.4	0.86	99	99	98	0.4	0.6	2
0.62	865	- -	2.4	0.47	- -	99	97	- -	0.5	2
0.68	958	- -	0.4	0.14	- -	98	96	- -	1.0	3
0.76	550	1.7	- -	- -	99	- -	- -	0.3	- -	- -

[a] Calculated from volume of air sampled and quantity of PCB trapped.

[b] 1% or less of total PCB was found on the second plug in all cases.

the high-volume equipment described. Wind direction was monitored with a recording anemometer. Samples 1 - 4 were collected without regard to wind direction while 5 and 6 were collected intermittently only while the wind blew from the open-ocean sector (90 - 240°). The GC patterns matched Aroclor 1248 (Fig. 2) and the concentrations in the air were calculated as both Aroclor 1248 and 1254 (Table 3). Most of the PCB was found on the first foam plug of the two inserted into the cylinder. Even for samples 5 and 6, which remained on the tower for a week, the collection efficiency of the first plug was approximately 80%. Negligible fractions of total PCB (< 2%) were found on the GFA filters in all cases, in agreement with the results in Table 1.

Glass fiber filters are commonly used to collect high-volume particulate samples and have been shown to be efficient collectors of DDT dusts and some organophosphorus insecticide vapors under low-flow conditions (MILES et al. 1970). This study shows that they are poor collectors for PCB vapors during high-volume sampling, but the GFA filters appear to have a slightly higher collection efficiency for the less volatile pentachlorobiphenyl than for the tri- or tetrachlorobiphenyls (Table 1). Preliminary experiments indicate that polyurethane foam plugs are also good collectors for atmospheric DDT and the extension of this method to chlorinated pesticides, phthalate esters, and hydrocarbons is currently under investigation.

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TABLE 2

Collection of PCB Vapors in Greenburg-Smith Impinger

Flow Rate m^3/min	Volume Air m^3	PCB in air, ng/m^3		% in impinger[a]	
		tetra	penta	tetra	penta
0.017	17.3	543	148	79	83
0.028	18.4	322	76	75	79
0.028	32.8	33	11	79	82

[a]Remainder trapped on polyurethane foam.

TABLE 3

PCB in Bermuda Atmospheric Samples

Sample Number	Flow Rate m^3/min	Volume Air m^3	PCB in air, ng/m^3		% on first PF plug
			as 1248	as 1254	
1	1.13	1320	0.30	0.22	94
2	1.03	1070	0.59	0.39	99
3	0.85	918	0.65	0.44	90
4	0.71	1950	0.62	0.37	86
5	0.57	1740	0.55	0.24	79
6	0.57	732	0.52	0.29	84

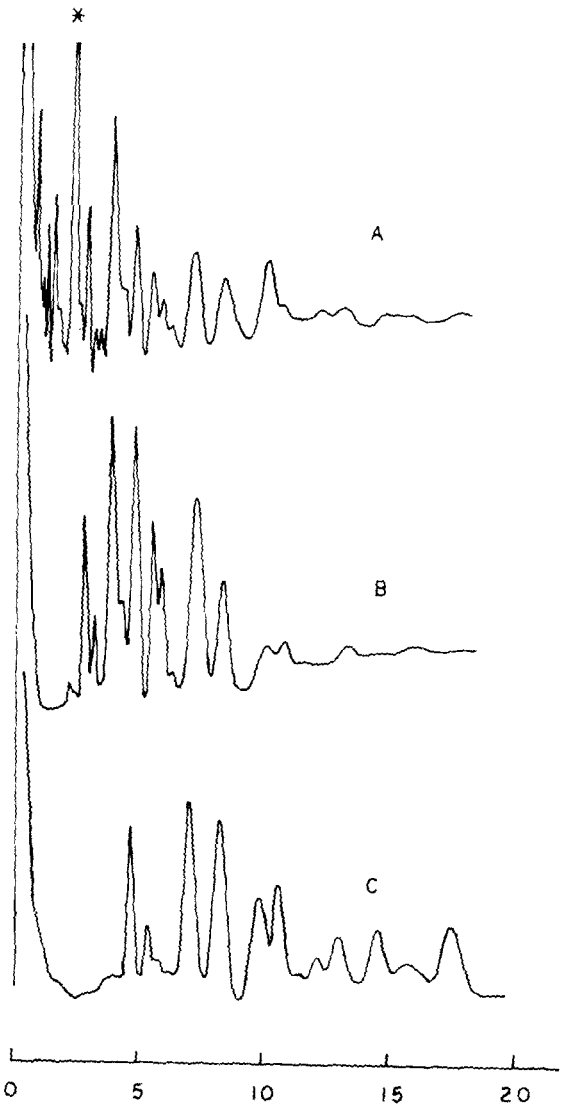

Fig. 2: Chromatograms of a Bermuda atmospheric sample extract and Aroclor standards, SE-30/QF-1

A. Bermuda sample extract, PCB fraction from silicic acid 8 ml, 7 µl injection. Peak marked * not used for quantitation.
B. Aroclor 1248, 0.53 ng
C. Aroclor 1254, 0.42 ng

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