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Atmospheric transport of organochlorines in the North Atlantic gyre

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ABSTRACT

Chlorinated pesticides and polychlorinated biphenyls (PCB) circulating over the North Atlantic were measured during 1977-78 at Barbados and during the 1977 summer at the southern tip of Newfoundland. Total organochlorines were collected using a glass fiber filter backed up by a polyurethane foam trap, and were analyzed by electron capture gas chromatography on packed and glass capillary columns. Filter-retained organochlorines were < 10% of the total. Compounds identified at both locations were hexachlorobenzene (HCB), α - and γ -hexachlorocyclohexane (HCH), high and low molecular weight PCB, *cis*- and *trans*-chlorodane, *trans*-nonachlor, p,p'-DDE, p,p'-DDT, and dieldrin. A clear GC pattern for polychloroterpenes (toxaphene) was obtained in Newfoundland. Several Barbados samples had a GC pattern suggestive of polychloroterpenes, but the match with a toxaphene standard was not considered good enough for quantitation. Quantitative values could not be obtained for HCB, HCH, or low molecular weight PCB because of poor collection efficiency by polyurethane foam at the high air volumes sampled (1200-3500 m³). Collection efficiency tests in Columbia, SC indicated that the other organochlorines were effectively retained. Pesticide concentrations measured from shipboard on a cruise across the trades region agreed well with those from the land-based stations, indicating that our measurements were representative of North Atlantic background levels. Estimates of organochlorine residence times in the North Atlantic troposphere ranged from 45-70 days, based on Junge's (1974) relationship between residence time and concentration variability.

1. Introduction

Much of the interest in aerial pollutant input to the oceans stems from the discovery of organochlorine pesticides on dust carried in the North Atlantic trade-

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winds. The initial investigations were made by Risebrough *et al.* (1968) in 1965-66 from the east coast of Barbados (13N, 59W), which lies in the easterlies trades belt and has been the site of extensive studies of transoceanic Sahara dust movements (Prospero and Nees, 1977). Airborne dust collected by hanging glycerin-coated nylon screens in the wind contained 10^{-9} g/g concentrations of DDT, its degradation products, and dieldrin. Pesticide residues of similar magnitude were also measured in 1968 and 1970, using the same collection method (Seba and Prospero, 1971; Prospero and Seba, 1972). Pesticide concentrations measured in these studies were on the order of 10^{-15} - 10^{-13} g per cubic meter of air, and reflected only the fraction of the aerial pesticide load that was carried on dust particles larger than $1 \mu\text{m}$.

These early investigators recognized that although dust-borne pesticides have a high likelihood of being deposited in the ocean, particulate pesticides probably account for only a small fraction of the total pesticides in ocean air. The development of solid adsorbent collectors in the mid 1970's enabled large volumes of air to be sampled for vapor-phase as well as particulate organic pollutants, and measurements, in the western North Atlantic (Bidleman and Olney, 1974a, 1975; Bidleman *et al.*, 1976; Rice *et al.*, 1977; Harvey and Steinhauer, 1974; Giam *et al.*, 1978), the Gulf of Mexico (Giam *et al.*, 1978, 1980), and near the British Isles (Dawson and Riley, 1977) all showed total pesticide levels two orders of magnitude greater than particulate concentrations measured at Barbados. Concentrations of polychlorinated biphenyls (PCB) greatly exceeding those of DDT and dieldrin were also found in these later studies, although they were not detected in Barbados dust samples (Risebrough *et al.*, 1968). PCB have higher vapor pressures than DDT, and the fraction of PCB attached to airborne particles should be lower (Junge, 1977; Bidleman and Christensen, 1979).

The majority of recent measurements of PCB and pesticides in North Atlantic air have been carried out at Bermuda (32N, 65W, Fig. 1) and on cruises between Bermuda and the U.S. Bermuda is only 1100 km from North America, and pollutants are readily transported to this area by westerlies. In the case of toxaphene insecticide, a complex mixture of polychloroterpenes heavily used on cotton, higher levels measured at Bermuda have been correlated with air masses moving off the southern cotton-growing states (Rice *et al.*, 1978, 1979). However, pollutants are also transported north of Bermuda, where they can become entrained in the anticyclonic airflow around the prevailing high pressure area in the Sargasso Sea. Detailed PCB measurements in North Atlantic surface waters show that no area of the ocean is free from contamination. Minimal PCB concentrations are found in the Sargasso, with increasing concentrations in the trades region (10-20N) and in temperate latitudes (40-55N) (Harvey and Steinhauer, 1976). According to these authors, PCB may be transported out of the Sargasso Sea where net evaporation is high and rained out at the higher and lower latitudes. In the trades region

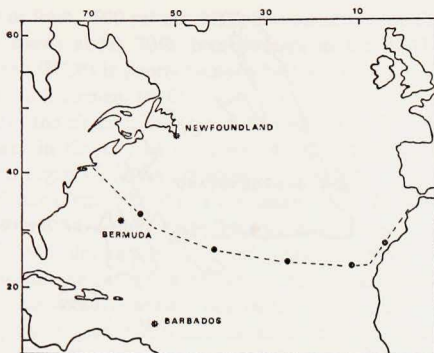


Figure 1. Sampling locations in the North Atlantic, showing land-based stations (*) used by ourselves and other investigators, and the *Atlantis II* transect showing the midpoints of the collection tracks (● --- ●).

it would also seem that PCB as well as pesticides would be scavenged by the high dust loads and deposited into the ocean.

Our interest was to measure atmospheric levels of organochlorines circulating in the North Atlantic gyre, and we selected Barbados and Newfoundland as sampling sites (Fig. 1). In 1977-78 we collected three series of high volume air samples on the east coast of Barbados. The first set was taken during the 1977 winter, while the second and third sets were collected during the summer Sahara dust transport seasons of 1977 and 1978. Due to a lack of electrical power we were not able to operate the air pumps at the wooden tower where the 1965-70 nylon screen measurements were made. Instead we used the University of Miami aerosol sampling station in Ragged Point, about one km from the tower (Fig. 2), where the winds blew consistently off the open ocean. Collection filters were white or pale grey during the winter and showed the pale yellow color typical of Sahara dust during the summer.

Measurements in Newfoundland were made in July-August 1977 at two lighthouse sites on the southern tip of the Avalon peninsula (Fig. 2). Four samples were collected at Cape Race from the roof of a metal shed on the edge of a cliff overlooking the ocean, while two were taken from atop the lighthouse at Cape Pine. Winds were from the west-south, off the ocean, and all collection filters were white or pale grey.

For comparison with land-based stations we also collected five samples from the bow of the Woods Hole ship R/V *Atlantis II* on a transect across the trades region in May, 1977 (Fig. 1). This cruise was the culmination of a five-month

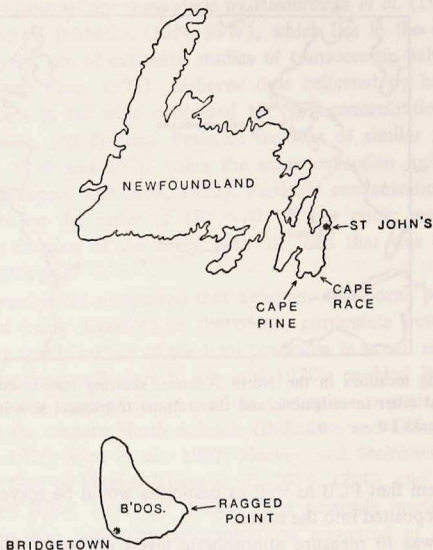


Figure 2. Sampling sites on the Avalon Peninsula, Newfoundland; and Barbados.

study to compare organochlorine levels in the northern Indian Ocean and the North Atlantic. Details of these cruises in the Arabian Sea, the Persian Gulf, and the Red Sea will be reported elsewhere (Bidleman and Leonard, in press).

2. Experimental

a. Sampling techniques. Air was pulled through a glass fiber filter followed by a single 7.6-cm diameter \times 7.6-cm thick plug of polyurethane foam using a Bendix Hurricane (brush-type) or Rotron (brushless) pump. In 1977 we used a 10-cm diameter filter in front of the foam plug and sampled about 600 m³ air in a 24-hour period. In 1978 we increased the flow rate by using a 20 \times 25-cm filter, enabling us to nearly double this volume per day. Details of foam plug preparation, sampler design, and discussions of the trapping efficiency for pesticide and PCB vapors are given in Bidleman and Olney, 1974b; Rice *et al.*, 1977; Simon and Bidleman, 1979; Bidleman *et al.*, 1981; and Billings and Bidleman, 1980). A single foam plug of the dimensions used here has 95% or better collection efficiency for high molecular weight PCB (Aroclor 1254), chlordane, toxaphene,

and DDT up to at least 1600 m³ air, while low molecular weight PCB (Aroclors 1242 or 1016) shows about 30% breakthrough in the 1300-1600 m³ range. Hexachlorobenzene (HCB) is poorly retained by foam even for air volumes below 500 m³ (Billings and Bidleman, 1980).

Because some of the air samples taken at Barbados were ≥ 3000 m³, we carried out an experiment in the city of Columbia, South Carolina to determine how effectively various organochlorines are retained by a foam plug at these high air volumes. A single air sample (3600 m³) was taken over a five-day period in June, 1980 using a 20 \times 25-cm filter backed up by three foam plugs. Temperatures ranged from 25-35°C during the run. Each plug was analyzed individually to determine organochlorine collection efficiency. The breakthrough of light PCB, HCB, and the hexachlorocyclohexane pesticides α -HCH and γ -HCH was extensive, with nearly equal quantities found on all three plugs. Less volatile organochlorines were quite well retained however. Only 16% of the Aroclor 1254 was lost to the second plug, and 2% to the third plug. More than 90% of the chlordane, DDT, and toxaphene was found on the first plug. We are thus confident that a single foam plug effectively collected Aroclor 1254, chlordane, DDT, toxaphene, and other organochlorines of comparable volatility at Barbados and Newfoundland; however, our identification of low molecular weight PCB, HCB, and HCH are only qualitative.

b. Analytical methods. Chlorinated pesticides and PCB were isolated from air samples by solvent extraction (Bidleman and Olney, 1974b). The extracts were cleaned up on an alumina column and fractionated by a silicic acid procedure described in detail elsewhere (Bidleman *et al.*, 1978). Briefly, the organochlorines were eluted in three petroleum ether fractions and a fourth dichloromethane fraction containing: 1. HCB, 2. PCB and p,p'-DDE, 3. p,p'-DDT, *cis*-, and *trans*-chlordane, and 4. p,p'-DDD, dieldrin, and endosulfan I. Polychloroterpenes (toxaphene) divide among the fractions, with 50-60% being eluted in fraction 4. The two HCH isomers α -HCH and γ -HCH are split between fractions 3 and 4, with the majority in fraction 4. The sample fractions were further cleaned up by shaking with 7% fuming H₂SO₄, which removes oxygen- and nitrogen-containing compounds (omitted during dieldrin and endosulfan analysis).

Samples were analyzed by electron capture gas chromatography (EC-GC) on at least two and occasionally three of the following packed columns (0.4 cm i.d. \times 180 cm long, glass): 1.5% SP-2250/1.95% SP-2401; 4% SE-30/6% SP-2401; 3% OV-225 (Supelco, Inc.) operated at 180-210°C, using Tracor 222 or Varian 3700 instrumentation. All of the samples from Newfoundland (1977) and Barbados (1978) were also examined by EC-GC on a 30-m glass capillary column coated with SP-2100 or SE-54 (Supelco, Inc.). Quantification of residues was based on peak height, or the sum of the peak heights for multi-component organochlorines (PCB

and polychloroterpenes). Pesticide and PCB standards were obtained from the U.S. Environmental Protection Agency Pesticide Repository, Research Triangle Park, NC.

3. Results and discussion

a. Chromatographic identification of organochlorines. The atmosphere contains a tremendous number of high molecular weight organochlorines. A commercial PCB mixture is composed of about 20 constituents (Sawyer, 1978), while nearly 180 components have been identified in toxaphene insecticide (Holmstead *et al.*, 1974). Complete resolution of these substances even using capillary GC is impossible and most analytical schemes use liquid-solid column chromatographic separations and/or chemical treatments prior to GC analysis. Our silicic acid method was designed to separate PCB from most organochlorine insecticides, and also to separate p,p'-DDT from interfering polychloroterpenes, which are predominant in the western North Atlantic atmosphere (Bidleman and Olney, 1975; Rice *et al.*; 1978, 1979). Although about 30-40% of the components of technical toxaphene coelute with p,p'-DDT from the silicic acid column and show a complex chromatographic pattern, the p,p'-DDT peak falls in a valley in this pattern and can therefore be measured (Bidleman *et al.*, 1978). Figure 3 shows a capillary chromatogram of a Newfoundland sample, silicic acid fraction 3. The three most prominent peaks in this sample were identified by retention times as *trans*-chlordane, *cis*-chlordane, and *trans*-nonachlor, all components of technical chlordane which together comprise about 50% of the mixture (Sovocool *et al.*, 1977). Directly below the sample chromatogram is the GC trace of the toxaphene components that coelute with p,p'-DDT and the chlordanes in this silicic acid fraction. It appears that a number of the smaller peaks in the air sample chromatogram can be accounted for by the presence of polychloroterpenes, and in fact chromatograms of silicic acid fraction 4 clearly showed a polychloroterpene pattern (Fig. 4). However the retention time region for p,p'-DDT is free from polychloroterpene interferences, and thus p,p'-DDT could be identified.

In addition to capillary GC, two other approaches were used to confirm the presence of p,p'-DDT (which was always a small inconspicuous peak in the chromatograms, as in Fig. 3): Silicic acid fractions containing p,p'-DDT from four winter 1977 Barbados samples were pooled, transferred to hexane, and partitioned with an equal volume of acetonitrile. Injection of the hexane layer before and after partitioning yielded a partition coefficient "p-value" of 0.37, which agreed excellently with the literature "p-value" for p,p'-DDT of 0.38 in this solvent pair (Bowman and Beroza, 1965) and also with the 0.37 value obtained in our laboratory with an authentic p,p'-DDT standard. Six other samples (two from Barbados, two from Newfoundland, and two from the *Atlantis II*) were

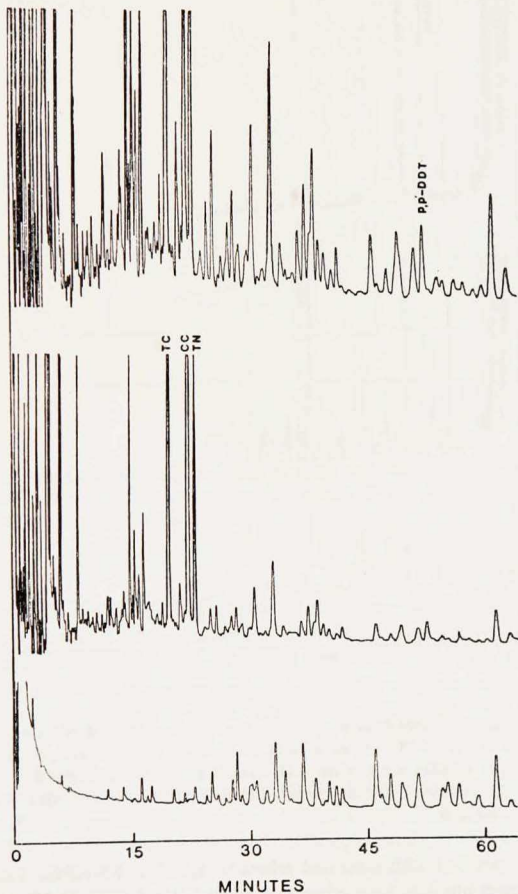


Figure 3. Capillary GC identification of *p,p'*-DDT, *trans*-chlordane (TC), *cis*-chlordane (CC), and *trans*-nonachlor (TN) in Newfoundland air (7/18-21/77) silicic acid fraction 3. Top: air sample extract; middle: same, diluted 3 times; bottom: components of a technical toxaphene standard which elute in silicic acid fraction 3. Conditions: 30-m SE-54 column, direct injection, 170°C, H₂ carrier gas, 2.5 ml/min.

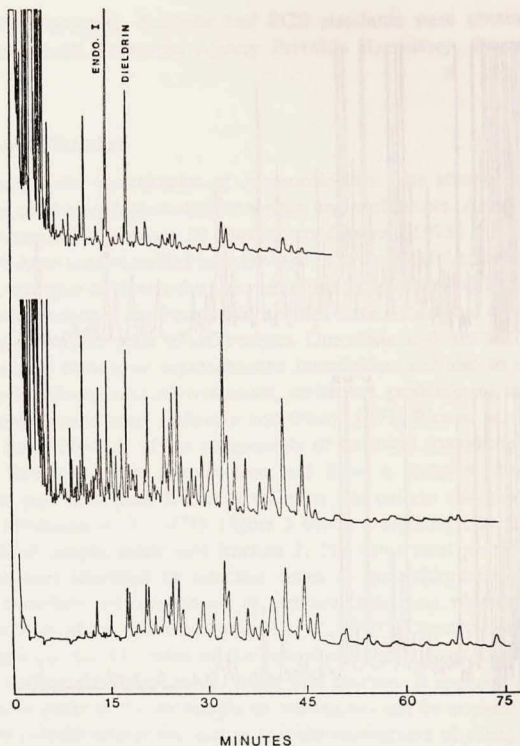


Figure 4. Capillary GC identification of endosulfan, I, dieldrin, and polychloroterpenes in Newfoundland air (7/21-23/77), silicic acid fraction 4. Top: air sample extract, before H_2SO_4 treatment; middle: same, after acid treatment and concentrated 6 times; bottom: components of a technical toxaphene standard eluting in silicic acid fraction 4. Conditions: $180^\circ C$, rest as in Fig. 3.

individually saponified with saturated ethanolic KOH at $85-90^\circ C$. The products were re-extracted into petroleum ether, treated with 7% fuming H_2SO_4 to eliminate artifacts, and analyzed by GC. In all cases we obtained a good confirmation of *p,p'*-DDT and *cis*-chlordane by observing their dehydrochlorination to *p,p'*-DDE and 3-chlorochlordene (Chau and Cochrane, 1969).

Identification of pesticides eluting in the fourth (dichloromethane) fraction from the silicic acid column is depicted in a series of chromatograms in Figure 4. Two

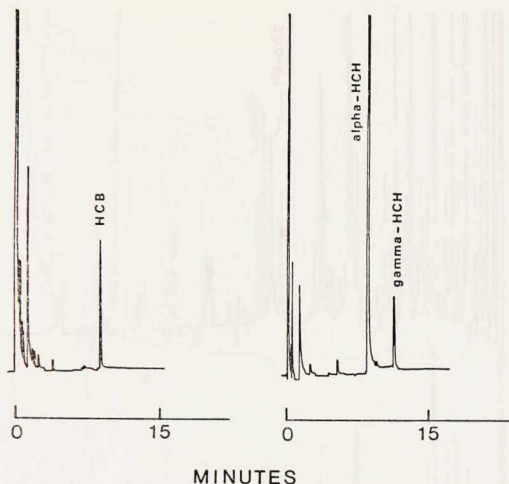


Figure 5. Capillary GC identification of HCB in silicic acid fraction 1 and HCH isomers in silicic acid fraction 4 of a Newfoundland air extract (7/21-23/77), treated with H_2SO_4 . Conditions: $150^\circ C$, rest as in Fig. 3.

of the prominent peaks before treatment of the sample extract with 7% fuming H_2SO_4 , were identified as endosulfan I and dieldrin on packed and capillary columns. After the sample was acid-treated and concentrated, the remaining pattern of peaks resembled a chromatogram of standard toxaphene components which elute in the fourth column fraction. Lindane (γ -HCH) and α -HCH were also identified in all samples after acid treatment, by diluting the sample and chromatographing at a lower temperature (Fig. 5).

PCB were identified by comparing sample GC fingerprints with those of Aroclor standards. Sample peaks in the high molecular weight PCB region matched the Aroclor 1254 pattern reasonably well, although capillary GC revealed some consistent differences between the samples and standard for both Newfoundland and Barbados. Noticeable in both groups of samples, for example, were the "double peak" at 35 minutes and the peak ratio reversal at 42 minutes (Figs. 6 and 7). None of the peaks quantified as Aroclor 1254 were affected by 7% fuming H_2SO_4 treatment nor by saponification with ethanolic KOH. The *p,p'*-DDT metabolite *p,p'*-DDE coelutes with PCB from the silicic acid column and was resolved from PCB interferences on the capillary column (Figs. 6 and 7).

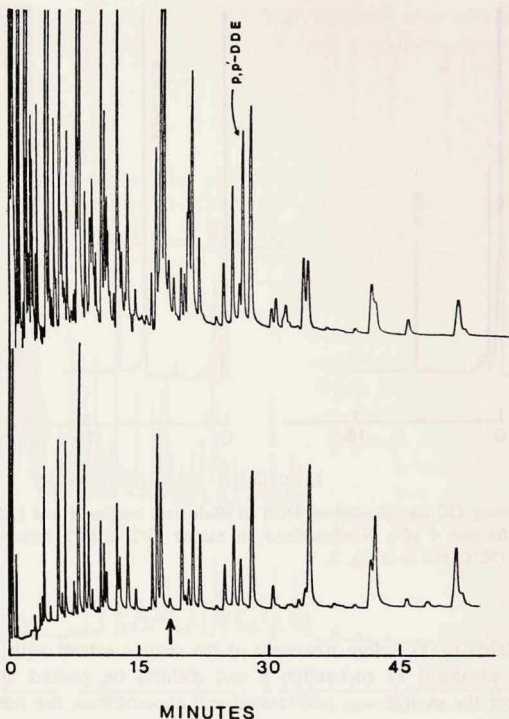


Figure 6. Capillary GC identification of PCB and *p,p'*-DDE in Newfoundland air (7/18-21/77). Top: air sample extract, treated with H_2SO_4 and ethanolic KOH; bottom: mixed standard containing equal proportions of Aroclors 1242 and 1254. The arrow indicates the end of the 1242 and the beginning of the 1254 patterns. Conditions: as in Fig. 3.

Identification of low molecular weight PCB was not as certain. Although many sample peaks matched those in an Aroclor 1242 chromatogram, numerous other peaks did not, even after H_2SO_4 and KOH treatment (Figs. 6 and 7). For this reason, plus the poor retention efficiency of light PCB at high air volumes, we did not assign quantitative values for Aroclor 1242.

HCB was separated from PCB and the chlorinated pesticides on the silicic acid column and was identified by packed and capillary GC (Fig. 5). All samples contained HCB, but because of its poor retention on foam we could not determine HCB quantitatively.

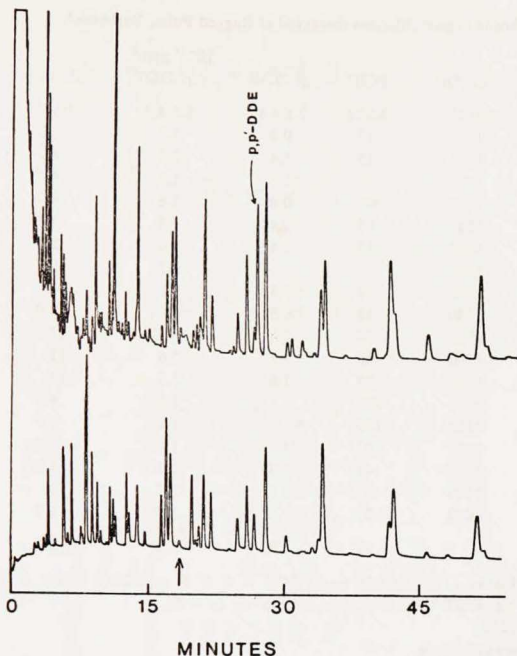


Figure 7. Capillary GC identification of PCB and p,p'-DDE in Barbados air (pooled extracts from 8/8-11, 8/11-14, and 8/17-21/78). Top: air sample extract, treated with H₂SO₄ and ethanolic KOH; bottom: mixed Aroclor 1242-1254 standard. Conditions: as in Fig. 3.

b. Organochlorine concentrations in North Atlantic air. Concentrations of high molecular weight PCB (Aroclor 1254) and chlorinated pesticides which were effectively retained by the polyurethane foam plug are presented in Tables 1-3. For comparison, we have also included in Table 4 a summary of measurements in the North Atlantic in other investigations. PCB concentrations at Barbados were generally below 100 pg/m³, with the exception of two values in 1978, and the mean (arithmetic) of all 18 Barbados PCB measurements was 57 pg/m³. PCB levels at Newfoundland were slightly higher (mean = 115 pg/m³) as might be expected from the clockwise transport of PCB around the gyre from the industrial centers in the northeastern U.S. Our PCB values from Cape Race and Cape Pine agree excellently with the 50-160 (mean = 86) pg/m³ levels of Aroclor 1254

Table 1. Airborne organochlorines measured at Ragged Point, Barbados*.

Collection Dates	m ³ Air	PCB ^b	p,p'-DDE	10 ⁻¹² g/m ³ p,p'-DDT	Chlordane ^c	Dieldrin
1/12-13/77	250-530 ^d	34-72	2.1-4.4	2.3-4.9	10-22	2.4-5.2
1/13-15/77	1150	13	0.8	1.7	6.3	4.1
1/15-18/77	1800	15	1.4	2.6	6.7	1.6
1/18-20/77	1200	9	<1	1.7	4.8	1.3
1/20-22/77	1300	<8	0.8	1.6	4.9	2.4
1/22-24/77	1200	<5	<0.4	1.5	5.7	3.1
1/24-26/77	1050	13	1.4	2.6	5.1	1.1
6/25-28/77	1550			4.3	19	
6/28-7/1/77	1300	42	<0.5	1.5	14	
7/1-4/77	1500	38	<0.3	1.0	8.0	
7/4-7/77	1900	64	1.5	4.4	17	
7/7-10/77	1500	46	1.1	5.6	11	
7/10-13/77	1300	39	1.6	3.8	12	
8/2-5/78	3400	370		1.8	4.5	2.6
8/5-8/78	3200	130	<1	1.8	6.7	6.8
8/8-11/78	2900	82	<1	1.6	3.9	7.5
8/11-14/78	3300	41	0.8	2.7	5.3	7.2
8/14-17/78	3500	37	3.3	2.5	21	13
8/17-21/78	4050	37	1.6	1.7	6.7	13
MEAN*		57	1.0	2.5	9.4	5.2

*Average blanks (10⁻¹² g/m³) were: PCB = 6 ± 5, p,p'-DDE = 0.2 ± 0.1, chlordane = 0.6 ± 0.2, p,p'-DDT = 0.2 ± 0.1 for 1500 m³ air (n = 5).

^b Aroclor 1254

^c *cis*- + *trans*-chlordane

^d Air volume uncertain due to pump failure.

* Undetectable values counted as zero.

measured from shipboard on the Grand Banks (45N, 52W) by Harvey and Steinhauer (1974) in the summer of 1973. Atlas and Giam (1981) also reported an average Aroclor 1254 concentration of 60 pg/m³ at Enewetak Atoll in the North Pacific. By contrast, PCB concentrations measured at Bermuda, between Bermuda and the U.S., and in the Gulf of Mexico are considerably higher (Table 4).

Apparent PCB concentrations measured from the *Atlantis II* were 2-3 times higher than those at Barbados or Newfoundland; but we have reason to doubt the accuracy of the shipboard PCB measurements. Even though all shipboard blanks were clean, we obtained inexplicably high PCB concentrations for some samples taken in the Arabian Sea at a considerable distance from land. We suspect that shipboard contamination might be responsible, and that we were sampling an "aura" of PCB vapors surrounding the ship. We have thus not included shipboard PCB measurements in Tables 3 and 4. On the other hand, pesticide mea-

Table 2. Airborne organochlorines measured at the Avalon Peninsula, Newfoundland.

Collection		10 ⁻¹² g/m ³							
Dates	Location	m ³ Air	PCB ^a	p,p'-DDE	p,p'-DDT	Chlordane ^b	Dieldrin	Endosulfan I	Polychloro- terpenes ^c
7/11-13/77	Cape Race	1150	150	4.3	3.9	64	7.2	8.3	57
7/13-15/77	Cape Race	1170	70	<0.9	2.1	25	7.0	6.7	121
7/15-18/77	Cape Race	1870	91	6.4	2.3	51	7.0	16	99
7/18-21/77	Cape Race	1730	84	1.1	3.0	23	8.1	38	120
7/21-23/77	Cape Pine	1820	42	0.6	2.5	26	7.1	20	99
8/30-9/2/77	Cape Pine	1790	140	0.9	2.3	20	7.3	13	160
MEAN ^d			115	2.2	3.2	42	8.7	20	109

^a. Aroclor 1254^b. *cis*- + *trans*-chlordane^c. toxaphene^d. undetectable values counted as zero

Table 3. Airborne organochlorines measured from the *Atlantis II*.

Collection Dates	Location ^a	m ^a Air	10 ⁻¹² g/m ³				
			p,p'-DDT	Chlordane ^b	Dieldrin	Endosulfan I	Polychloro- terpenes ^c
5/6-8/77	30°47'N, 11°09'W	920	14	21			
	23°47'N, 17°21'W						
5/8-10/77	23°40'N, 17°26'W	980	5.0	13	10	5.2	<110
	25°29'N, 26°50'W						
5/10-14/77	25°33'N, 27°01'W	1430	1.1	13			< 40
	26°59'N, 41°12'W						
5/14-16/77	27°00'N, 41°21'W	1230	2.4	18	15		100
	28°04'N, 54°00'W						
5/17-19/77	30°28'N, 58°42'W	970	2.6	32	24	27	
	34°59'N, 66°29'W						
MEAN			5.0	19	16	16	

^a Ship location at start and finish of sample

^b *cis*- + *trans*-chlordane

^c toxaphene

Table 4. Organochlorines in the North Atlantic atmosphere.

Location	Date	10^{-12} g/m ³					Polychloro- terpenes	Reference
		PCB	p,p'-DDT	p,p'-DDE	dieldrin	chlordan		
Barbados*	1965-66		0.007-0.16	0.002-0.072	0.002-0.016	3.9-21	≤100	Risebrough <i>et al.</i> , 1968
Barbados*	1968-70		0.012-0.57	0.009-0.029	<0.01 -0.19	20-64 13-32	57-160 <40-100	Seba and Prospero, 1971 Prospero and Seba, 1972
Barbados	1977-78	<5-370	1.0-5.6	<0.3-3.3	1.1-13			This work
Newfoundland	1977	42-150	2.1-3.9	0.6-6.4	7.0-8.1			This work
Cruise, across N. Atlantic	1977		1.1-14		10-24			This work
Bermuda	1973	150-500	17-53					Harvey and Steinhauer, 1974
Bermuda	1973	190-660	9-22			27-53	<20-1100	Bidleman <i>et al.</i> , 1976
Bermuda	1974	80-480	<3-62		<3-77	10-140	110-1100	Bidleman <i>et al.</i> , 1976
Cruises, Bermuda-USA	1973-74	<50-1600	<1-58		3-48	<2-170	<40-1600	Bidleman <i>et al.</i> , 1976
Off Delaware coast, 38°N, 69°W	1976	100-940	2-14					Giam <i>et al.</i> , 1978
Grand Banks 45°N, 52°W	1973	50-160	<1					Harvey and Steinhauer, 1974
British coastal waters	1974	<200-800	10-20					Dawson and Riley, 1977
Gulf of Mexico	1977	170-790	10-78	9-180				Giam <i>et al.</i> , 1980

* Particulate values only.

surements from the *Atlantis II* agreed quite well with those from the land stations (Tables 1-3).

DDT and dieldrin concentrations at Barbados were 1-2 orders of magnitude higher than the particulate values measured in earlier studies. We analyzed the glass fiber filters for about two-thirds of the samples and found average organochlorine residues <10% of the total, with this figure representing the detection limit in many cases. Theoretical considerations based on vapor pressure and available particle surface area indicate that little DDT or PCB should remain particle-associated under the aerosol concentration conditions typical of clean air (Junge, 1977). Other workers have also failed to find any significant percentage of filter-retained organochlorines over the open ocean (Bidleman *et al.*, 1976); Bidleman and Olney, 1974a; Harvey and Steinhauer, 1974; Dawson and Riley, 1977; Giam *et al.*, 1980; Atlas and Giam, 1981). While this fact strongly suggests that organochlorines are transported primarily in the vapor phase, the percentage of filter-retained organochlorines cannot be equated with "particulate" organochlorines because of possible volatilization from particles trapped on the filter.

In addition to DDT, DDE, and dieldrin, we also found chlordane and HCH isomers at Barbados as well as at other sampling locations. During the winter and summer of 1977 we obtained what appeared to be a polychloroterpene GC pattern for some of the Barbados samples. In many cases, however, the patterns were distorted from the standard toxaphene GC fingerprint, making identification and quantification unreliable. If present, polychloroterpene residues at Barbados would not have exceeded 100 pg/m³. Inquiries to the Barbados Ministry of Agriculture, Food and Consumer Affairs revealed that organochlorine pesticides received limited usage in Barbados during 1977-78. Estimates of DDT use on the island in 1977-78 ranged from 160-190 kg, and chlordane is popular for termite control. Some dieldrin is also used in termite control. Lindane or technical HCH is registered for application, but was "hardly used" in 1977-78. Toxaphene has not been used since the early 1970's. Although we cannot be certain that the organochlorine levels measured at Barbados do not result from local air circulation around the island, the fact that comparable pesticide levels were also measured in Newfoundland and from the *Atlantis II* (Tables 2 and 3) strongly indicates that our Barbados values are typical of the North Atlantic air background.

Concentrations of p,p'-DDT measured at all locations were very similar (Tables 1-3). The overall average, 3.0 pg/m³, is thus probably representative of the DDT background over the North Atlantic in the late 1970's. By comparison, DDT concentrations over the Arabian Sea, the Persian Gulf, and the Red Sea in 1977 averaged 30 times higher than those in the North Atlantic, apparently because DDT is still heavily used in countries bordering these seas (Bidleman and Leonard, *in press*) and DDT levels 3-30 times higher were found in the Gulf of Mexico in 1977 (Giam *et al.*, 1980, Table 4).

Polychloroterpene residues, quantified as toxaphene, were identified in all Newfoundland air samples at concentrations ranging from 57-160 $\mu\text{g}/\text{m}^3$ (Table 2, Fig. 4). Previous investigations have shown that polychloroterpenes are transported at least as far as Bermuda (Bidleman and Olney, 1975) and that higher levels at Bermuda could be correlated with air mass trajectories from the U.S. cotton belt (Rice *et al.*, 1978, 1979). However, this is the first report of polychloroterpene translocation so far north. Recently polychloroterpene residues have been identified in fish collected from Lake Michigan (Stalling, 1979) and the Baltic Sea (Jansson *et al.*, 1979), areas far removed from sites of toxaphene application. Air transport seems the most likely explanation for these residues, especially considering that polychloroterpenes have been found in rainfall along the southeastern U.S. coast and even several hundred kilometers out to sea (Munson, 1976; Harder *et al.*, 1980). Polychloroterpenes are exceedingly harmful to aquatic life. Toxaphene is acutely toxic to several estuarine organisms at low $\mu\text{g}/\text{liter}$ concentrations, with bioaccumulation factors for fish and oysters exceeding 10^4 (Schimmel *et al.*, 1977), and low ng/liter (part-per-trillion) levels have been reported to produce growth inhibition and bone composition changes in three species of freshwater fish (Mehrl and Mayer, 1975a,b, 1977).

Polychloroterpenes will probably continue to be transported over the North Atlantic for years to come. Toxaphene is extensively used in the southern U.S. on cotton and other crops, the peak application being during the late summer. In 1978 the U.S. toxaphene production was 18×10^6 kg, a slight increase over 1977 (Fowler and Mahan, 1980). In the city of Columbia, S.C. we have monitored airborne toxaphene through late 1979. Concentrations have remained essentially unchanged since 1977 and show a marked increase during the late summer, with a yearly average of 15×10^{-9} g/m^3 , nearly 150 times the average Newfoundland value (Billings and Bidleman, 1980).

The two HCH isomers α -HCH and γ -HCH (lindane) were found in all samples. Because these compounds were not quantitatively retained by polyurethane foam, we cannot report their concentrations. Nevertheless, it is evident that their presence is widespread over the North Atlantic. In all cases we found much more α -HCH than γ -HCH, a fact that cannot be related to sampling since the γ -isomer is collected with slightly better efficiency than the α -isomer. Technical HCH contains approximately 70% α -HCH and 10-15% γ -HCH (Metcalf, 1955), however, only γ -HCH is insecticidal and has been produced for years in pure form as lindane. Other investigators have noted higher concentrations of the α -HCH isomer in the environment. Rain samples collected in Great Britain during 1975-76 contained about equal concentrations of α -HCH and γ -HCH (Wells and Johnstone, 1978), while results from a Canadian precipitation network showed considerably higher levels of α -HCH (Strachan *et al.*, 1980). Atlas and Giam (1981) found α -HCH concentrations over ten times higher than γ -HCH levels at Enewetak Atoll.

Whether the predominance of α -HCH is related to the continued usage of technical HCH formulations (possibly as a wood preservative, Harper *et al.*, 1977) or to isomerization of γ -HCH to α -HCH in the environment (Benzet and Matsu-mura, 1973) remains unknown.

4. Aerial deposition and atmospheric lifetimes

Since the first measurements of pesticide transport over the ocean in the late 1960's and early 1970's, a quantitative connection between aerial concentrations and ocean deposition has been sought. Quantitative flux measurements show that atmospheric input by rainfall and dry deposition contributes significantly to the pollutant budgets of lakes and coastal areas: Sodergren (1973) found that rainfall and dry deposition provided most of the PCB and DDT input to 15 km² Lake Havgård in southern Sweden. Murphy and Rzeszutko (1977) collected rain and snow samples in Chicago, Illinois and on Beaver Island, Lake Michigan and estimated that PCB washout into Lake Michigan in 1977 was 5 metric tons, exceeding stream and wastewater effluent sources. Eisenreich *et al.* (1979) noted the uniform spatial concentration of PCB in Lake Superior sediments and suggested that atmospheric deposition may dominate the PCB input to the lake. Direct flux measurements in northern Minnesota led to an estimated 5 metric tons per year PCB input to the lake by dry deposition (Eisenreich and Hollod, 1979). Young *et al.* (1975, 1976) collected over 1000 dry deposition samples in southern California from 1973-74. Concurrent sampling of major rivers and sewage outfalls showed that aerial fallout contributed approximately 25% of the PCB and 50% of the DDT input to the Southern California Bight. A network of seven precipitation stations on the eastern coastline of Great Britain was monitored for organochlorine residues from 1975-76 and an annual inputs of 0.3-2.1 metric tons PCB and several chlorinated pesticides were estimated for the North Sea (Wells and Johnstone, 1978).

Similar quantitative estimates are not yet available for the open ocean. Only two rain samples have been collected from shipboard in the North Atlantic and analyzed for organochlorines. These were taken by us approximately 300 km off the Delaware coast in July, 1976 on the Woods Hole ship *Knorr*. Polychloroterpenes dominated the samples, with a concentration of 50 ng/liter. A washout ratio of 33 (ng/kg rain \div ng/kg air) was calculated from concurrently measured aerial concentrations (Harder *et al.*, 1980). Recently Atlas and Giam (1981) reported several organic contaminants in air and rain at Enewetak Atoll in the North Pacific. Measureable concentrations of phthalate esters and HCH isomers were found in precipitation samples; but although PCB, chlordane, dieldrin, and p,p'-DDE were found in air, they were not identified in rainfall. During the *Atlantis II* cruise across the equatorial Arabian Sea we collected several rain samples which

contained measurable quantities of p,p'-DDT and HCH isomers (Bidleman and Leonard, in press).

Organochlorine flux by dry deposition has not been reported for the open ocean. Bidleman and Christensen (1979) measured average dry deposition velocities for Aroclor 1254, chlordane, and p,p'-DDT of 0.16, \leq 0.04, and 0.28 cm/sec respectively at a pristine salt marsh on the coast of South Carolina. The value for Aroclor 1254 agreed well with 0.15 cm/sec determined by Eisenreich and Holod (1979) at several sites in Minnesota. Extrapolation of these values to dry deposition estimates over the open ocean is risky; however a deposition velocity of 0.1 cm/sec leads to a residence time due to dry deposition of 115 days in the troposphere (10 km thickness, pollutant distribution assumed vertically uniform). As discussed below, this value is not in bad agreement with residence times estimated by a different method.

Several years ago Junge (1974) showed that for several trace gases the tropospheric residence time was inversely related to the spatial variability. Coefficients of variation (CV) for all 1977-78 PCB and pesticide measurements over the North Atlantic ranged from 75-113% which, using Junge's relationship, lead to estimates of tropospheric lifetimes in the range of 45-67 days. A similar calculation, based on two years' data collected in Bermuda, yielded 60-90 day residence times for PCB and p,p'-DDT (Bidleman *et al.*, 1976). Residence time estimates using this method are likely to be too short because the above CV include sampling and analytical precisions as well as temporal and spatial differences. Analysis of many duplicate and triplicate air samples taken in Columbia, SC allowed us to determine values for the procedural CV, which were on the order of 10-20% for the various organochlorines (Billings and Bidleman, 1980). Precisions for collection and analysis of the lower concentration samples over the ocean are probably nearer the upper end of this range, and perhaps higher. If a 20% CV is accepted for the combined sampling and analytical precision and the CV for the North Atlantic samples are corrected for this factor using a propagation of errors treatment, the residence time estimates are negligibly lengthened, to 46-70 days.

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REFERENCES

- Atlas, E. L. and C. S. Giam. 1981. Global transport of organic pollutants; ambient concentrations in the remote marine atmosphere. *Science*, 211, 163-165.

- Benezet, H. J. and F. Matsumura. 1973. Isomerization of γ -BHC to α -BHC in the environment. *Nature* (London), 243, 480-481.
- Bidleman, T. F. and C. E. Olney. 1974a. Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. *Science*, 183, 516-518.
- 1974b. High volume collection of atmospheric polychlorinated biphenyls. *Bull. Environ. Contam. Toxicol.*, 11, 442-450.
- 1975. Long range transport of toxaphene insecticide in the western North Atlantic atmosphere. *Nature* (London), 257, 475-476.
- Bidleman, T. F., C. P. Rice, and C. E. Olney. 1976. High molecular weight chlorinated hydrocarbons in the air and sea: rates and mechanisms of air/sea transfer, in *Marine Pollutant Transfer*, H. L. Windom and R. A. Duce (eds.), Chap. 13, D.C. Heath and Co., Lexington, MA, p. 323-351.
- Bidleman, T. F., J. R. Matthews, C. E. Olney, and C. P. Rice. 1979. Separation of polychlorinated biphenyls, chlordane, and p,p'-DDT from toxaphene by silicic acid column chromatography. *J. Assoc. Offic. Anal. Chem.*, 61, 820-828.
- Bidleman, T. F. and E. J. Christensen. 1979. Atmospheric removal processes for high molecular weight organochlorines. *J. Geophys. Res.*, 84, 7857-7862.
- Bidleman, T. F., W. N. Billings, and C. G. Simon. 1981. Evaluation of solid adsorbents for collecting atmospheric chlorinated hydrocarbons. Final Report to EPA Grant No. 804716, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1-58.
- Bidleman, T. F. and R. Leonard. 1981. Aerial transport of pesticides over the northern Indian Ocean and adjacent seas. *Atmos. Environ.*, (in press).
- Billings, W. N. and T. F. Bidleman. 1980. Field comparison of polyurethane foam and Tenax-GC resin for high volume sampling of chlorinated hydrocarbons. *Environ. Sci. Technol.*, 14, 679-683.
- Bowman, M. C. and M. Beroza. 1965. Extraction p-values of pesticides and related compounds in six binary solvent systems. *J. Assoc. Offic. Anal. Chem.*, 48, 943-952.
- Chau, A. S. Y. and W. P. Cochrane. 1969. Cyclodiene chemistry I. derivative formation for the identification of heptachlor, heptachlor epoxide, cis-chlordane, trans-chlordane, and aldrin pesticide residues by gas chromatography. *J. Assoc. Offic. Anal. Chem.*, 52, 1092-1100.
- Dawson, R. and J. P. Riley. 1977. Chlorine-containing pesticides and polychlorinated biphenyls in British coastal waters. *Estuar. Coast. Mar. Sci.*, 4, 55-69.
- Eisenreich, S. J., G. J. Hollod, and T. C. Johnson. 1979. Accumulation of PCB in surficial Lake Superior sediments, atmospheric deposition. *Environ. Sci. Technol.*, 13, 569-573.
- Eisenreich, S. J. and G. J. Hollod. 1979. Atmospheric input of PCB to the Great Lakes: impact on the Lake Superior ecosystem. Presented at the 178th national American Chemical Society meeting, Washington, D.C., September 9-14.
- Fowler, D. L. and J. N. Mahan. 1980. The Pesticide Review-1978. U.S. Department of Agriculture, Washington, D.C. 42 pp.
- Giam, C. S., H. S. Chan, G. S. Neff, and E. L. Atlas. 1978. Phthalate ester plasticizers: a new class of marine pollutant. *Science*, 199, 419-421.
- Giam, C. S., E. Atlas, H. S. Chan, and G. S. Neff. 1980. Phthalate esters, PCB, and DDT residues in the Gulf of Mexico atmosphere. *Atmos. Environ.*, 14, 65-69.
- Harder, H. W., E. J. Christensen, J. R. Matthews, and T. F. Bidleman. 1980. Rainfall input of toxaphene to a South Carolina estuary. *Estuaries*, 3, 142-147.
- Harper, D. B., R. V. Smith, and D. M. Gotto. 1977. BHC residues of domestic origin: a significant factor in pollution of freshwater in northern Ireland. *Environ. Pollut.*, 12, 223-233.

- Harvey, G. R. and W. G. Steinhauer. 1974. Atmospheric transport of polychlorobiphenyls to the North Atlantic. *Atmos. Environ.*, **8**, 777-782.
- 1976. Transport pathways of polychlorinated biphenyls in Atlantic water. *J. Mar. Res.*, **34**, 561-575.
- Holmstead, R. L., S. Khalifa, and J. E. Casida. 1974. Toxaphene composition analyzed by combined gas chromatography-chemical ionization mass spectrometry. *J. Agric. Food Chem.*, **22**, 939-944.
- Jansson, B., R. Vag, G. Blomkvist, S. Jensen, and M. Olsson. 1979. Chlorinated terpenes and chlordane components found in fish, guillemot, and seal from Swedish waters. *Chemosphere*, **4**, 181.
- Junge, C. E. 1974. Residence time and variability of tropospheric trace gases. *Tellus XXVI*, 477-488.
- 1977. Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants, in *Fate of Pollutants in the Air and Water Environments*, I.H. Suffet (ed.), *Advances in Environmental Science and Technology Series*, Vol. 8, Part 1, Wiley-Interscience, NY, 7-25.
- Mehrle, P. M. and F. L. Mayer, Jr. 1975a. Toxaphene effects on growth and bone development of fathead minnows, *Pimephales promelas*. *J. Fish. Res. Bd. Can.*, **32**, 593-598.
- 1975b. Toxaphene effects on growth and development of brook trout, *Salvelinus fontinalis*. *J. Fish. Res. Bd. Can.*, **32**, 609-613.
- 1977. Bone development and growth of fish as affected by toxaphene, in *Fate of Pollutants in the Air and Water Environments*, I.H. Suffet (ed.), *Advances in Environmental Science and Technology Series*, Vol. 8, Part 2, Wiley-Interscience, NY, 301-314.
- Metcalf, R. L. 1955. *Organic Insecticides, Their Chemistry and Mode of Action*. Interscience Publishers, Inc., NY, 392 pp.
- Munson, T. O. 1976. A note on toxaphene in environmental samples from the Chesapeake Bay region. *Bull. Environ. Contam. Toxicol.*, **16**, 491-494.
- Murphy, T. J. and C. P. Rzeszutko. 1977. Precipitation inputs of PCB to Lake Michigan. *J. Gt. Lakes Res.*, **3**, 305-312.
- Prospero, J. M., and R. T. Nees. 1977. Dust concentration in the atmosphere of the equatorial North Atlantic: possible relationship to the Sahelian drought. *Science*, **196**, 1196-1198.
- Prospero, J. M., and D. B. Seba. 1972. Some additional measurements of pesticides in the lower atmosphere of the northern equatorial Atlantic Ocean. *Atmos. Environ.*, **6**, 363-364.
- Rice, C. P., C. E. Olney, and T. F. Bidleman. 1977. Use of polyurethane foam to collect trace amounts of chlorinated hydrocarbons and other organics from air. *Special Environmental Report No. 10*, World Meteorological Organization, Geneva, Switzerland, WMO-460, 216-224.
- Rice, C. P. and C. E. Olney. 1978. Air mass transport of toxaphene. Presented at the 176th national American Chemical Society meeting, Miami Beach, FL, Sept. 10-15.
- Rice, C. P., T. F. Bidleman, E. J. Christensen, and C. E. Olney. 1979. Processes of dispersion and removal of toxaphene over the North Atlantic. Presented at the 178th national American Chemical Society meeting, Washington, D.C., Sept. 9-14.
- Risebrough, R. W., R. J. Huggett, J. J. Griffin, and E. D. Goldberg. 1968. Pesticides: transatlantic movements in the northeast trades. *Science*, **159**, 1233-1235.
- Sawyer, L. D. 1978. Quantitation of polychlorinated biphenyl residues by electron capture gas-liquid chromatography: reference material characterization and preliminary study. *J. Assoc. Offic. Anal. Chem.*, **61**, 272-281.

- Schimmel, S. C., J. M. Patrick, Jr., and J. Forester. 1977. Uptake and toxicity of toxaphene in several estuarine organisms. *Arch. Environ. Contam. Toxicol.*, 5, 353-367.
- Seba, D. B. and J. M. Prospero. 1971. Pesticides in the lower atmosphere of the northern equatorial Atlantic Ocean. *Atmos. Environ.*, 5, 1043-1050.
- Simon, C. G. and T. F. Bidleman. 1979. Sampling airborne polychlorinated biphenyls with polyurethane foam: a chromatographic approach to determining retention efficiencies. *Anal. Chem.*, 51, 1110-1113.
- Sodergren, A. 1973. Transport, distribution, and degradation of DDT and PCB in a south Swedish lake ecosystem. *Vatten*, 2, 90-108.
- Sovocool, G. W., R. G. Lewis, R. L. Harless, N. K. Wilson, and R. D. Zehr. 1977. Analysis of technical chlordane by gas chromatography/mass spectrometry. *Anal. Chem.*, 49, 734-740.
- Stalling, D. L. 1979. Personal communication, Columbia National Fisheries Research Laboratory, Columbia, Missouri, October.
- Strachan, W. M. J., H. Huneaul, W. M. Schertzer, and F. C. Elder. 1980. Organochlorines in precipitation in the Great Lakes region, in *Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment*, B. K. Afghan and D. MacKay (eds.), Plenum Publishing Corp., NY, p. 387-396.
- Wells, D. E. and S. J. Johnstone. 1978. The occurrence of organochlorine residues in rainwater. *Water Air, and Soil Pollut.*, 9, 271-280.
- Young, D. R., D. J. McDermott, T. C. Heesen and T. K. Jan. 1975. Pollutant inputs and distributions off southern California, in *Marine Chemistry in the Coastal Environment*, T. Church (ed.), ACS Symposium Series, Vol. 18, American Chemistry Society, Washington, DC, p. 424-439.
- Young, D. R., D. J. McDermott and T. C. Heesen. 1976. Aerial fallout of DDT in Southern California. *Bull. Environ. Contam. Toxicol.*, 16, 604-611.