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NOTES

PCB's in Suburban Watershed, Reston, Va.

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■ Polychlorinated biphenyl concentrations in Lake Anne basin increased from water (<0.05–0.2 ppb), to bed sediment (<2.5–105 ppb), to fish (140–700 ppb) in an average ratio of 1:500:3000. The highest concentrations were observed in the lake, which is 10 years old, and receives no sewage or industrial waste discharges. Evidence indicates that the polychlorinated biphenyls (PCB's) originate from diffuse sources associated with urban development and living.

To satisfy a growing demand for waterfront property, numerous real estate lakes have recently been contructed. Although often carefully planned, their development has fostered a host of environmental problems (*1*). Among the most interesting and perplexing of the problems was the discovery of polychlorinated biphenyls (PCB's) in Lake Anne, a 10-year-old lake in Reston, Va. (*2*).

The major sources of PCB's are believed to be sewage and industrial wastes (*3*). Thus, it was surprising in a community, such as Reston, with no industrial or sewage discharge, that significant amounts of PCB's were detected in the Lake Anne watershed. A study was designed to determine the extent of PCB distribution and to attempt to locate and identify the sources.

Experimental

Sampling. Sampling sites were selected to determine the distribution of PCB's in Lake Anne, its tributaries, and its outflow (Figure 1). For comparison, sampling was also conducted in New South Lake, an undeveloped man-made lake 3 miles (4.8 km) south of Lake Anne (not shown in Figure 1). A total of 31 sites was established: 16 in Lake Anne, 13 in the surrounding watershed, and two in New South Lake.

Sampling was done in the spring of 1972. All surface-water samples were collected unfiltered and stored in specially cleaned glass jars fitted with Teflon-lined metal screw caps. Bed sediment samples were collected with an Ekman dredge in deep sites and with a stainless steel dustpan in shallow sites. Approximately 1 kg of material was collected at each site from about the upper 2 *cm* of the sediment profile. All sediment samples were stored in glass jars. In addition to water and sediment samples, fish were collected to determine whether or not biological concentration was occurring in the lake ecosystem. Fish were wrapped in aluminum foil and frozen until analysis.

Analytical Procedure. The PCB residues in the water and bottom sediment samples were extracted using the multiple chlorinated pesticide residue methods of Goerlitz and Brown (*4*). The method of Porter et al. (*5*) was used for fish. Following extraction, all samples were cleaned up and the PCBs were separated from other co-extractives by a liquid-solid column chromatography technique developed by Goerlitz and Law (*6*). This technique involved the selective elution of the extract through a 9% deactivated alumina column and then through a 3% deactivated silica gel column. The eluate containing PCBs was subsequently analyzed using dual-column electron capture (^{63}Ni) gas chromatography, and confirmed by gas chromatography–mass spectrometry when residue amounts were sufficient.

The presence of PCBs in the samples was determined by comparing the unknown multicomponent peaks on the chromatograms (Figure 2-B) to different Aroclor standards (the trade name of commercially available PCBs in the United States). The environmental residues were found to resemble most closely a 1:1 mixture of Aroclor 1254 and 1260 (Figure 2-A).

Quantification of PCBs presented a problem because, at the time of the study, no satisfactory method had been per-

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Figure 1. Sampling sites (1–29) in Lake Anne basin

fected for measuring the amount of multicomponent, weathered, metabolized, or combined residue (*3*). In this study, the PCB concentration was calculated by comparing the total areas of the four major late-eluting peaks in each sample with those of the Aroclor standard (see Figure 2). Each total PCB content was thus expressed relative to Aroclor 1254–60. Additional quantification was carried out using J. A. Armour's perchlorination method (*7*). The accuracy of this method was within 5% of the results obtained using peak areas.

Results and Discussion

Water Samples. Analysis of unfiltered water (Table I) from Lake Anne yielded PCB concentrations of 0.1–0.2 ppb (μg/l). In contrast, water samples from Lake Anne tributaries and from New South Lake contained only traces of PCB's (<0.05 ppb). The PCB concentration in all 16 samples of Lake Anne water was more than 10 times the maximum permissible level of 0.01 ppb proposed by the Environmental Protection Agency (*3*). Nevertheless, the PCB concentrations in Lake Anne water were still lower, on the average, than concentrations (0.1–4 ppb) recently reported for other waters in the United States (*8*).

Bed Sediment Samples. Table I shows that the concentration of PCB's in bed sediments was related to the nature of the cultural and hydrologic environment. Three stream sites in Lake Anne basin (sites 1, 8, 12) and the two sites in New South Lake (sites 30, 31) were located in undeveloped areas. Bed sediments from these five unurbanized locations contained only traces (<2.5 ppb) of PCB's.

In contrast, most bed-sediment samples from urbanized sites contained appreciable levels of PCB's. At six urbanized locations, the PCB concentrations of stream-bottom sediments (sites 2, 3, 6, 7, 9, 13) ranged from a trace to 22 ppb. Concentrations were even higher in sediments from Lake Anne; the range for 16 samples was 25 to 105 ppb.

Moreover, the PCB concentrations in lake sediments appeared to vary with the intensity of adjacent urbanization. The highest levels were observed in the vicinity of the densely urbanized Village Center (sites 14–21). This area (Figure 1), the most urbanized of the basin, has a high density of commercial buildings, apartments, parking lots, and roads. The PCB concentrations in eight bed sediments from this area ranged from 41 to 105 ppb, and averaged 74 ppb. Considerably lower levels were observed in samples from the less urbanized, eastern part of the lake (Figure 1).

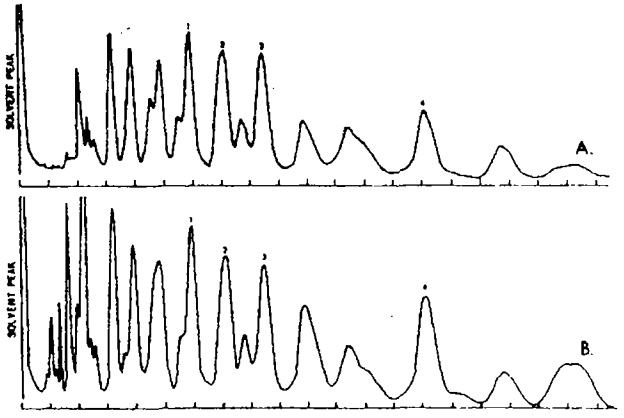


Figure 2. Gas chromatograms of
(A) 1254–1260 Aroclor standard: column, DC-200; injection volume, 5.0 ml (B) PCB fraction of a typical sediment sample: column, DC-200; injection volume, 5.0 ml

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Development in this area consists of a moderate density of houses, parking lots, and roads. PCB concentrations in seven bed sediment samples (sites 22–28) ranged from 25–39 ppb, with an average of 30 ppb.

As previously noted, there are no industrial waste or sewage discharges in Lake Anne basin. Thorough investigations discounted the possibility of accidental inputs from electrical-transformer leakage and sewer overflow. It thus appears that the PCB's originated from diffuse sources associated with urban development and living and entered the hydrologic system through storm-water runoff. Until recently, PCB's were used in the formulation of plasticizers, adhesives, surface coatings, sealants, and fire-retardant compositions (*3*, *9*). This suggests that building materials would be one possible source of PCB's. It is important to note, then, that during the period of sampling, sites 10 and 29 were receiving rainfall runoff from areas of active construction (Table I). Site 10 was in a small stream adjacent to a new housing development, whereas 29 was in a small cove of Lake Anne, immediately offshore from a partly constructed house. PCB concentrations in sediment samples from these sites were much higher than in samples from other streams or from the eastern part of the lake.

In addition to the degree of urbanization, PCB distribution in bed sediments was also related to the nature of the hydrologic environment. The most notable example was in the area defined by sites 2 through 7 (Figure 1, Table I). There, the PCB concentration in sediments of the pond (sites 4, 5) was about four times higher than in sediments from incoming streams (sites 2, 3, 6), and twice as high as in the effluent stream (site 7). This can be explained on the basis that current velocities in the pond were less than in the contributing streams, thus allowing a more complete settling of suspended fines. This rationale is consistent with size-analysis data obtained on the respective sediments.

Bed sediment in the stream receiving the lake outflow (site 11) contained only a trace amount of PCB's. Evidently, Lake Anne acts as an efficient trap for incoming sediment and, consequently, for the associated PCB's.

Fish Samples. PCB's were also detected in fish (Table II). Lake Anne was stocked 10 years ago and has never been restocked. Since the oldest fish analyzed were determined to be 5 years of age, the detected PCB levels must have derived from association of fish with the lake ecosystem. The primary food sources of bass and bluegill were not analyzed, but it is assumed that the high concentrations of PCB's resulted from food-chain magnification. PCB levels increased almost directly with the age of the fish. For example, a 5-year-old bass, the oldest fish analyzed, contained more than twice the amount of PCB's found in a 2-year-old bass.

Conclusions

Tables I and II show that in Lake Anne there is approximately a 500-fold increase in the concentration of PCB's from water to bed sediment and about a 3000-fold increase from water to fish. The results indicate that low levels of PCB's detected in water or bed sediment provide no assurance that ecosystem animals might not be contaminated. In the case of Lake Anne, PCB residues found in fish were still below 5000 ppb, the safe action level established by the Food and Drug Administration (*3*).

The results of this investigation support the studies de-

Table I. PCB Residues in Lake Anne Basin and New South Lake According to Cultural and Hydrologic Environment

Site[a]	PCB residue (ppb)	
	Water	Bed sediment
Unurbanized Surroundings		
1	Trace[b]	Trace[c]
8	Trace	Trace
12	Trace	Trace
30	Trace	Trace
31	Trace	Trace
Urbanized Streams		
2	Trace	10
3	0.1	Trace
6	0.1	10
7	Trace	20
9	Trace	16
13	Trace	22
Lake Anne—Densely Urbanized Section		
14	0.1	90
15	0.1	41
16	0.1	105
17	0.2	105
18	0.1	63
19	0.2	69
20	0.1	41
21	0.1	80
Lake Anne—Moderately Urbanized Section		
22	0.1	26
23	0.1	26
24	0.1	29
25	0.1	36
26	0.1	39
27	0.1	25
28	0.1	27
Near Active Construction		
10	Trace	74
29	0.1	63
Sedimentation Pond		
4	Trace	36
5	Trace	48
Lake Anne Outflow		
11	Trace	Trace

[a] All sites except 30 and 31 are shown in Figure 1. [b] Trace in water = <0.05 ppb. [c] Trace in bed sediment = <2.5 ppb.

Table II. PCB Residues in Fish Samples

	Length, cm	Age, yr	PCB residue, ppb
Bluegill (*Lepomis Macrochirus*)	10	1	140
Bluegill	14	2	440
Bluegill	17	3	550
Largemouth bass (*Micropterus Salmoides*)	16	2	280
Largemouth bass	17	3	340
Largemouth bass	20	3	380
Largemouth bass	30	5	700

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scribing the tendencies of PCB's to spread and persist in the aquatic environment. In 1971, Monsanto Co., the sole manufacturer of PCB's in the United States, decided to restrict their use in all applications except dielectrics, where they are vital in decreasing the risk of fire and explosion. This action, if followed by manufacturers in other nations, should ensure only minimal input of these pollutants into our environment.

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Fluorocarbon Air Pollutants

Measurements in Lower Stratosphere

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■ Fluorocarbon 11 and fluorocarbon 12 concentrations are reported for three altitudes in the atmosphere, 21,000, 40,000, and 60,000 ft. At 60,000 ft, the fluorocarbon 11 concentration was 60 ppt (10^{-12} v/v) and the fluorocarbon 12 concentration was 98 ppt (10^{-12} v/v). The data for fluorocarbon 11 are in agreement with the values reported by other workers, and the fluorocarbon 12 concentrations are the first values reported for the stratosphere.

Several research groups have demonstrated with theoretical models that fluorocarbon air pollutants, primarily fluorocarbon 11 (CCl_3F) and fluorocarbon 12 (CCl_2F_2), are diffusing into the stratosphere and that the concentrations of these chemicals in the stratosphere are likely to increase for the next few years, even if production is stopped immediately (*1–4*). The theoretical work proposed that the fluorocarbons will be broken down in the stratosphere by ultraviolet light, and that this breakdown will produce chlorine atoms. The chlorine atoms can act as a catalyst for the destruction of some of the ozone in the stratosphere. This, in turn, means that harmful radiation which previously was screened from the earth by the ozone shield will now be striking the surface.

To confirm or disprove the results of the theoretical odel, a considerable amount of experimental evidence is ecessary. As an initial step to supplying part of the experiental evidence necessary, fluorocarbon concentrations aken from high-altitude aircraft, including measurements in the lower stratosphere, are reported in this paper.

Experimental

Air samples were collected with a WB-57-F aircraft flown by the 58th Weather Reconnaissance Squadron at Kirtland Air Force Base, N.M. The air was collected in 15-liter, nickel-lined steel spheres pressurized to 3000 lb/in.^{2} by compressors in the nose of the aircraft which drew the air from the jet engine compressors. The spheres had been prepared by repeated evacuation to less than 0.1 mm and then filled to slightly positive pressure with clean nitrogen. Two samples were taken simultaneously at each altitude; however, one bottle failed to pressurize at 40,000 ft. The samples were returned to the laboratory at Riverside, Calif., for analysis. Previously described instruments and techniques were used for analysis (*5, 6*). The air samples were collected on May 23, 1974, over New Mexico and Colorado, and precise locations are given in Table I.

At least two samples were analyzed from each bottle of air, and the values reported in Table I represent the average of all samples taken from each bottle. The precision between measurements from the same bottle was ±4% for fluorocarbon 11 and ±10% for fluorocarbon 12. The data for fluorocarbon 12 are poorer in quality than those for fluorocarbon 11 because fluorocarbon 12 is an order of magnitude less sensitive to the analytical technique than fluorocarbon 11.

Results and Discussion

The model results of Cicerone predict that fluorocarbon concentrations will decrease only a few percent as a function of altitude until heights greater than 65,000 ft are reached. Within experimental error, the data presented in Table I agree with the trends predicted by the model. The drop in concentration observed for fluorocarbon 11 as the altitude increased from 21,000–60,000 ft may represent a real trend; however, the errors associated with the fluorocarbon 11 and 12 measurements, especially in the case of fluorocarbon 12, are too large, and the number of samples is too small to allow a more detailed interpretation.

The values reported for 21,000 ft in Table I are higher than data reported for background levels for fluorocarbon 11 (60×10^{-12}) and fluorocarbon 12 (90×10^{-12}) measured in mid-1973 by this lab (*7*). An increase in background concentration on the order of 10–20% is expected owing to an increase in fluorocarbon production and release (*8*). A comparison of the data taken in 1973 with the present data reflects such a trend.

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Table I. Altitude vs. Fluorocarbon Concentrations, May 23, 1974

Altitude	Start time, Greenwich mean	Latitude / longitude	Stop time, Greenwich mean	Latitude / longitude	Concentrations FC-12	Concentrations FC-11
21,000 ft (6.4 km)	0152	34.45 / 106.20	0215	33.43 / 105.00	120×10^{-12} v/v	82×10^{-12} v/v
21,000 ft	0152	34.45 / 106.20	0212	33.50 / 105.10	130×10^{-12}	78×10^{-12}
				Av	$(125 \pm 7) \times 10^{-12}$	$(80 \pm 3) \times 10^{-12}$
40,000 ft (12.2 km)	0223	33.10 / 104.30	0255	34.45 / 106.20	140×10^{-12}	75×10^{-12}
60,000 ft (18.3 km)	0313	36.15 / 106.17	0353	39.36 / 106.00	110×10^{-12}	57×10^{-12}
60,000 ft	0313	36.15 / 106.17	0359	39.30 / 106.45	85×10^{-12}	62×10^{-12}
				Av	$(98 \pm 18) \times 10^{-12}$	$(60 \pm 4) \times 10^{-12}$

The concentrations measured at 21,000 ft agree within experimental errors with ground level background values measured by two other groups (*9, 10*). Wilkniss et al. have reported values for background levels of $(83 \pm 6) \times 10^{-12}$ v/v for fluorocarbon 11 measurements taken earlier this year (*9*). Lovelock has recently reported background levels for fluorocarbon 11 of $(79.8 \pm 4.9) \times 10^{-12}$ v/v and for fluorocarbon 12 of $(101\ 7 \pm 27.3) \times 10^{-12}$ taken in Western Ireland in June and July of this year (1974) (*10*).

The high-altitude measurements of fluorocarbon 11 agree extremely well with the values reported by two other workers. Lovelock has reported measurements of fluorocarbon 11 concentrations taken at altitudes up to 33,000 ft over England of 70–75 ppt (10^{-12} v/v) (*10*). These values compare favorably with the value reported in Table I taken at 40,000 ft. Krey has made a number of measurements of fluorocarbon 11 at 60,000–63,000 ft. These values for fluorocarbon 11 were in the range of 55–65 ppt, good agreement with the values in Table I taken at 60,000 ft (*11*).

Krey's samples were collected using the same techniques reported for this work, but Lovelock's samples were taken in evacuated glass bottles through a tube to the outside of an aircraft. The fact that there is such close agreement between three laboratories working independently of each other supports the validity of the data and confirms the migration of fluorocarbons into the stratosphere.

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