Polychlorinated Biphenyls (PCB's) in the Rivers Avon and Frome

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Polychlorinated biphenyls (PCB's) which came into industrial use as early as the 1930's are so versatile that their spread is global. As the number of industries increase, their spread is yet more likely. It has been demonstrated that PCB's exert to some extent adverse effects on wildlife, fish² and phytoplankton³ as do organochlorine insecticides. It is therefore obligatory that various environments be monitored for these compounds so that remedial measures may be instituted. The investigation report here is part of a project designed to measure trace inorganic and organic substances in the Rivers Avon and Frome in the Bristol area, U.K.

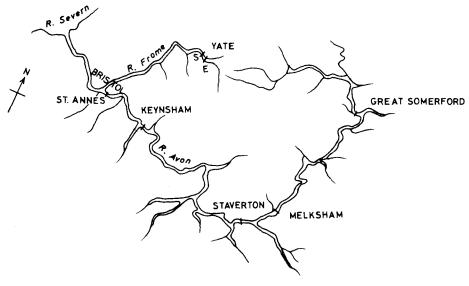
Materials and Methods

Surface water samples:

Four bridges on the River Avon and two bridges on the River Frome (see Figure 1) were sampled between October 1972 and January 1974 for chlorinated insecticides and PCB's. Duplicate surface water samples were collected at each bridge with a metal bucket and drained into Winchester bottles. Unfiltered surface water samples were adjusted to pH 7 and 1 litre was extracted twice with 60 ml 15% diethyl ether in hexane and once with 60 ml hexane. The extracts were cleaned up in Florisil columns and PCB's were separated from organochlorine insecticides on metal doped silicic acid⁴ columns. Spiked river water gave recoveries between 80.12 and 114.31% for Aroclors 1242, 1248, 1254 and 1260.

Fish samples

Various species of fish caught from different bridges on the River Avon were deep frozen. Tissues of the fish were macerated, blended with anhydrous sodium sulphate until fairly dry and Soxhlet extracted with (150 - 250 ml) purified acetone. The extract was partitioned between water and hexane. It was then cleaned in the first instance by partitioning between hexane and acetonitrile⁵, secondly on Florisil columns and finally separated into insecticide and PCB fractions on silicic acid columns in the same manner as the water samples. Fortified fish flesh gave 78.21, 84.31, 86.71 and 94.1% recoveries for Aroclors 1242, 1248, 1254 and 1260 respectively.



F1G.1. Bridges sampled on the Rivers
Avon and Frome.
S = Stover Road Bridge, YATE.

E = Engine Common Road Bridge, YATE.

The cleaned up extracts were then analysed in the Pye Unicam gas chromatograph series 104, model 134 with nickel-63 ECD and FID. Comparison of retention data of samples and standards on three different columns, 1.5% OV-17 + 1.95% QF-1 on Gas Chrom Q (100 -120 mesh), 2% OV-1 + 3% QF-1 on Gas Chrom Q (100 - 120 mesh) and 2% OV-17 on Supasorb (80 - 100 mesh) in 0.25 inch x 5.5 feet glass columns with oxygen free nitrogen as carrier gas were used for the identification of organochlorine insecticides. Their identities were confirmed by comparison of retention times on one of the columns before and after chemical treatment of both standards and samples.

The PCB's were tentatively identified by comparison of chromatograms with those of authentic standards on one of the columns and quantified by reference to peaks with retention times 0.35D, 0.80D, 1.61D and 1.83D (D is the retention time of p,p'-DDE). They were then identified and characterized in GC-MS system by reference to molecular weights and isotopic cluster of the atoms.

Results and Discussion

The presence of PCB's in the River Avon was suspected as early as October 1972 but the amount was not quantified. In the subsequent months their presence was not noticed until June 19, 1973, when very high levels of Aroclor 1254 were measured in both rivers at all the bridges, Tables 1 and 2.

TABLE 1

Levels of Aroclor 1254 in the River Avon in µg/l

	Bridge				
	St. Annes	Staverton	Melksham	Gr. Somerford	
June 19, 1973	431.0	138.0	380.0	316.0	
July 26	21.8	8.5	1.5	0.38	
August 16	3.8	1.38	6.5	-	
October 3	0.21	12.15	0.84	6.63	
October 25	0 <i>.</i> 75	3.55	1.33	8.25	
November 22	0.40	0。13	0.3	5 . 58	
December 20	0.46	0.70	0.9	0.25	
January 25, 1974	0.29	0.25	0.17	0.17	

TABLE 2
Levels of Aroclor 1254 in the River Frome in µg/l

	Bridge			
	Stover Rd. Bridge, Yate	Engine Common Rd。 Yate		
June 19, 1973	119.0	0.15		
July	_	-		
August	_	-		
October	0.13	-		
November	1.08			
December	0.86	0.72		
January 1974	0.42	0,29		

Levels as high as 431 µg per litre were determined at St. Annes, Bristol. The presence of higher levels of Aroclor 1254 at Great Somerford on October 25 and November 22, Table 1, than at other stations downstream indicates that the PCB entered the river at a point near Great Somerford. The source of PCB in the River Avon might have been from a factory near Great Somerford which cleaned its systems or a leak might have occurred. However it is not improbable that the Aroclor is used in a number of towns along the length of the river. The simultaneous occurrence of high levels of the same PCB in the River Frome (See Table 2) supports the idea of the prevalent use of PCB's in the area. There were indications that an Aroclor higher than 1254 probably Aroclor 1260 was also present in the rivers. This has been substantiated by the types of PCB residues found in fish samples.

TABLE 3

Amounts of PCB's in p.p.m. wet weight in tissues of different species of fish from the River Avon

Fish and Tissue	% Lipid	Aroclor	Type of Aroclor
Roach		,	
Flesh	3.3	0.427	1254
Liver	0.1	0.066	1254
Brain	31.0	1.29	1254
Dace			
			1254
			1254
Brain	4.2	0.75	1254
Pike			
Flesh	1.4	1.20	1254
Liver	11.3	10.6	1254
Brain	14.3	1.63	1254
Roach			
	0.3	0.042	1254
			1254
Brain	40.2	0.425	1254
Dace			
Flesh	2.7	0.237	1254
Liver	10.0	0.30	1254
Brain	17.8	0.201	1254
Bleak			
Flesh	4.3	0.23	1254
Liver	12.6	2.06	1242
		29.4	1260
Brain	8.3	5.66	1254
Pike			
	3.4	3.77	1254
	V.T		1260
Visceral fat	87.0		1254
	, •	11.0	1260
Dileo			
	4.39	6.5	1260
	Roach Flesh Liver Brain Dace Flesh Liver Brain Pike Flesh Liver Brain Roach Flesh Liver Brain Dace Flesh Liver Brain Bleak Flesh Liver Brain	Roach Flesh Jiver Flesh Jiver Flesh Liver	Roach Flesh 3.3 0.427 Liver 0.1 0.066 Brain 31.0 1.29 Dace Flesh 4.2 0.161 Liver 0.2 0.239 Brain 4.2 0.75 Pike Flesh 1.4 1.20 Liver 11.3 10.6 Brain 14.3 1.63 Roach Flesh 0.3 0.042 Liver 15.2 0.135 Brain 40.2 0.425 Dace Flesh 2.7 0.237 Liver 10.0 0.30 Brain 17.8 0.201 Bleak Flesh 4.3 0.23 Liver 12.6 2.06 29.4 Brain 8.3 5.66 Pike Liver 3.4 3.77 0.80 Visceral fat 87.0 26.6 11.0

All species of fish from the River Avon contained various levels of PCB's (see Table 3). The highest levels were 29.4, 26.6 and 10.6 p.p.m. of Aroclors 1260 and 1254 in the livers and visceral fat from bleak and pikes respectively. Of the tissues analysed those with higher percentage of lipid tended to accumulate more PCB. This may be due to the fact that PCB's are very soluble in fat.

The organochlorine insecticides determined in surface water samples were BHC's, dieldrin, DDT and its metabolities. The levels were in nanograms or 1×10^{-9} gm per litre. These same insecticides were determined in tissues of fish from the River Avon. With the exception of a few cases the amounts were generally a few fractions of p.p.m. wet weight. No other insecticides were encountered.

Summary

On June 19, 1973 very high levels of Aroclor 1254 were determined in the River Avon and Frome. The source might have been cleaning of systems in factories which use them. The levels decreased with time. In fish from the River Avon three types of Aroclors were determined.

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