A Method of Measuring the Water Solubility of Hydrophobic Chemicals: Solubility of Five Polychlorinated Biphenyls

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Hydrophobic environmental chemicals such as DDT and PCBs (polychlorinated biphenyls) possess very low solubility in water. An exact determination of aqueous solubility is quite difficult. In many cases controversies still exist regarding the true solubility values. A knowledge of the solubility may shed much light on such problems as the accumulation of the chemical in animals, transport of the compound in the hydrosphere and their mode of action. The polychlorinated biphenyls (PCBs) being strongly hydrophobic, possess the inherent problem described above.

The solubility of various PCB isomers and formulations has been reported by many workers. SÖDERGREN (1970) reported the solubility of Clophen^R A 50 as ~4 ppb in water. ZITKO (1970) published the solubility of Aroclor^R 1254 in fresh and salt water in the range of .3 to 3 ppm and .3 to 1.5 ppm, respectively. These values appear high possibly due to the formation of emulsions. NISBET and SAROFIM (1972) listed 200, 100, 50, and ~25 ppb at 20°C for the solubilities of Aroclor^R 1242, 1248, 1254, and 1260, respectively. Their data on 1254 is in good agreement with that of HAQUE et al. (1974) of ~56 ppb at room temperature. The solubility of individual biphenyl isomers containing 1 and 2 chlorines has been reported by HOOVER (1971). Recently WALLNOFER et al. (1973) have published the water solubility of 21 PCB isomers. The results reported by the above authors were not intended to yield absolute physical constants but rather relative values of reasonable accuracy.

One of the main factors associated with determining the solubility values of hydrophobic chemicals is the slow equilibration of the chemical in water. To obtain an absolute value of the water solubility one must carry out a time-dependent study. This factor has been ignored by most workers. In the present paper we describe a method which gives an absolute solubility value of five PCB isomers in water. This procedure involves the slow equilibration of the compound in water and monitoring its concentration over a long period of time. The method could be applied to other toxic hydrophobic chemicals.

Bulletin of Environmental Contamination & Toxicology,
Vol. 14, No. 1

EXPERIMENTAL

Materials

The compounds studied were 2,4'-dichlorobiphenyl, 2,2',5-trichlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, 2,2',4,5,5'-pentachlorobiphenyl, and 2,2',4,4',5,5'-hexachlorobiphenyl, all 99% standards, lot #001, obtained from Analabs, Incorporated. The hexane used for all extractions was Mallinckrodt Nanograde^R. All water was house distilled and run through a 2 x 10 cm glass column packed with XAD-2, a macroreticular resin provided by Rohm and Haas. Preliminary studies indicated this was a more efficient method of removing organics than any combination of redistilling and extracting with hexane.

Instrumentation

All samples were chromatographed on a Tracor 550 with a ^{63}Ni detector. The column used was 10' x 1/8" glass, packed with 1.5% OV-17, 1.95% OV-210 on 60/80 Gas Chrom Q. Oven temperature ranged from 190 to 245°C depending on the isomer.

Methods

Approximately 50 mg of each isomer was dissolved in 100 ml ether and swirled onto the walls of individual 25 liter carboys. Care was taken not to allow the ether solution to contact the bottom since the solution was stirred via magnetic stirrer. The residual ether was evaporated by nitrogen stream, resulting in a thin film of the compound on the container walls. Water was then added carefully near the bottom to avoid disturbing the film. Each carboy was fitted with a glass siphon tube which had a tubular fine frit that extended below the liquid level. A squeeze bulb was added to facilitate solution removal, the stirrer bar added, and the carboy was sealed. Each solution was isolated from its magnetic stirrer by a 1/2" polystyrene sheet to prevent temperature gradients from the stirrer motor. The setup is shown in Figure 1.

The solutions were stirred at ∿250 rpm and sampled at weekly intervals for one month and monthly thereafter. Initially stirring was stopped for 24 hours and three aliquots were withdrawn and extracted three times with hexane. This procedure was terminated when it was found that the concentration was slowly dropping after stirring ceased. Evidently suspended material was still making its way to the surface. To avoid this, stirring was not resumed after the third month since the concentration of PCB had already reached a plateau. The monthly measurements thereafter produced reproducable values.

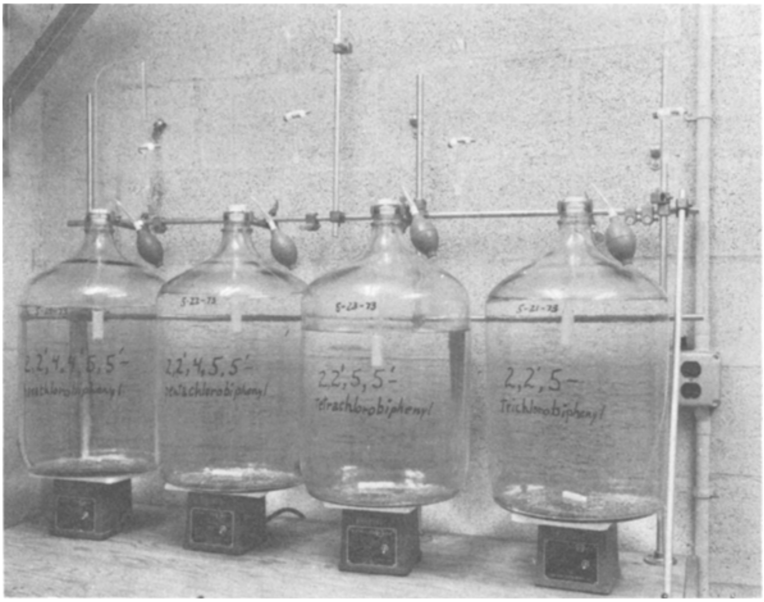

Figure 1 Experimental setup for measuring the solubility

RESULTS AND DISCUSSION

The concentration of PCB isomer in water as a function of time is shown in Figure 2. It is apparent that about a month is required to reach an equilibrium. However, when the measurements were taken after the stirring was stopped the concentration of PCB decreased slightly and reached a new equilibrium value. This decrease may be explained on the basis that during the stirring we have PCB aggregates giving a high solubility value. As we stop stirring these aggregates float to the surface and we reach the true solubility value. These findings are consistent with earlier studies of BOWMAN et al. (1960) who while determining the water solubility of DDT noticed a sharp decrease in the concentration of DDT when the equilibrated sample was centrifuged. The solubility values of the PCB isomers are given in Table 1. For comparison purposes we have included the values reported by WALLNOFER et al. (1973). The solubility data for one of the isomers is not available in the literature for comparison.

As expected, the solubility of the PCB isomers decreases with increasing chlorine atoms. One striking difference between the results reported by our studies and of WALLNOFER et al. (1973) is that the results reported by these workers is an order of magnitude higher. Several factors may contribute to this discrepancy. In our studies we have removed the organic matter which may be present in the distilled water. Any organic matter present in water could

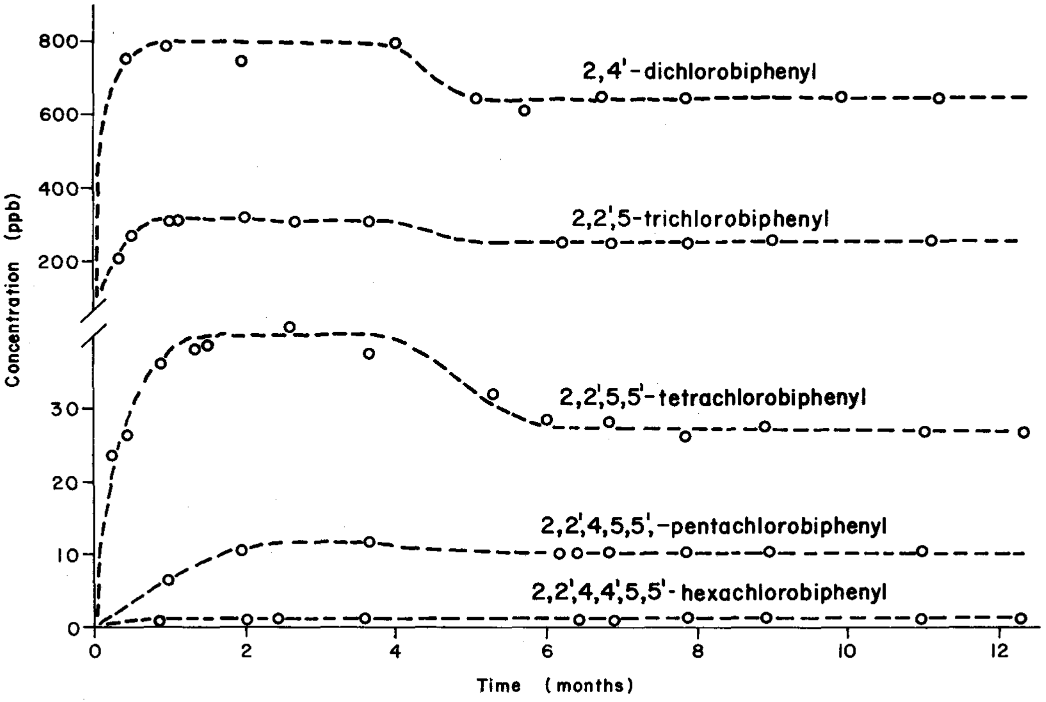

Figure 2 Concentration of PCB isomers in water as a function of time.

TABLE 1

Water Solubility of the Five PCB Isomers

	Solubility (ppb)	
Biphenyl Isomer	Wallnofer et al. (1973)	This Work
2,4'-Dichloro	1850-1900	637 ±7
2,2',5-Trichloro		248 ±4
2,2',5,5'-Tetrachloro	46	26.5±0.8
2,2',4,5,5'-Pentachloro	28-35	10.3± .2
2,2',4,4',5,5'-Hexachloro	8.8	.953± .01

increase the apparent concentration in the water. Further, WALLNOFER et al. (1973) allowed only two hours for equilibration after shaking. This time may not be sufficient for all the PCB aggregates to float to the surface. Although the adsorption of PCB on glass container surfaces may reduce its concentration in water, earlier studies have shown that PCBs are poorly adsorbed on a sand surface (HAQUE et al., 1974). Thus, it is unlikely that the material adsorbed on the glass surface would reduce the concentration by an order of magnitude. Therefore, the high values reported by WALLNOFER et al. (1973) are probably due to the formation of aggregates in the solution and the presence of organic impurities in the water.

The 8.8 ppb solubility of the 6-chlorine isomer reported by WALLNOFER et al. (1973) appears to be too high as compared to DDT, In view of the number of chlorine atoms, the molecular configuration and the hydrophobic nature of the hexa-chloro isomer one should expect its solubility to be less than that of DDT. The value reported in the present work as 0.953 ppb seems quite reasonable.

The method of determining the water solubility of PCB isomers described in this paper may be applied to other hydrophobic chemicals. The procedure takes into account such factors as the slow equilibration process in water, the settling of aggregates and the trace organic impurity present in water.

ACKNOWLEDGMENT

This research is supported by U.S. Public Health Service Grant ES-00210 from the National Institute of Environmental Health Sciences. Manuscript issued as Technical Paper No.3893 from the Oregon Agricultural Experiment Station.

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