The Solubility of Aroclor 1254 in Seawater

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This paper describes a determination of the solubility of Aroclor^R 1254 in seawater. Interest in this determination derived from experiments designed to test the effects of polychlorinated biphenyl (PCB) compounds on marine animals. Knowledge of solubility was needed to determine if PCB-saturated seawater could be used as a source of the pollutant at the different concentrations desired. This seemed preferable to the use of solvents or surfactants to make up the PCB-seawater treatments as they may also affect the organisms.

Polychlorinated biphenyls have been manufactured and used for a variety of industrial and agricultural purposes for many years. They have been recognized as an environmental pollutant since 1966 (JENSEN 1966). In spite of the fact that U.S. sales are limited to customers using PCBs in closed system applications such as capacitors and heat exchangers, they continue to be released into the marine environment (NISBET and SAROFIM 1972). Through accidental releases and their persistence, they are likely to continue to be of environmental concern and the subject of toxicity research for years to come.

MATERIALS AND METHODS

The study can be broken into three parts. Seawater for all three parts was collected off the coast of Oregon. Salinity was 33.1 parts per thousand. The water was filtered through 0.45 µm millipore^R filters prior to storage. The water was then refiltered and autoclaved for 15 minutes, just prior to use.

Part 1

Two five-gallon glass carboys were filled with 16 liters each of the filtered autoclaved seawater and approximately 15 grams of Aroclor^R 1254 were added. The water was then stirred for several weeks at 16.5°C. After stirring was terminated, duplicate samples of roughly 250 ml were taken from each bottle at 2 hours, 8 hours, and 4 days.

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Part 2

Stirring in one of the carboys was resumed for several weeks at 16.5°C. After stirring was terminated, duplicate samples were taken periodically from the 4th through the 42nd day.

Part 3

One carboy was filled (16-liters) with seawater which had been shaken several times with five grams of activated carbon and refiltered, after the initial 0.45 µm membrane filtering. The water was stirred at 16.5°C in the presence of 15 gm of Aroclor^{R} 1254 for one week. Samples were taken 8, 20, 31, and 75 days after stirring was terminated. Then the temperature was lowered to 10.5°C and stirring was resumed for seven days. Duplicate samples were taken at 2 hours, and at 1, 4, 7, 14, and 21 days after stirring was terminated.

All samples were drawn from carboys through a glass and teflon siphoning system directly into 1000 ml separatory funnels containing 30 ml of hexane. Each sample was extracted three tiems with 30 ml aliquots of nanograde hexane. Batches of hexane were checked for purity prior to use. The combined extract was then concentrated to 2-3 ml and analyzed on a Micro-Tek model 220 GLC equipped with a tritium foil electron capture detector. Three columns were used during the course of the work. These included: 1) an 8' x 1 mm ID pyrex tube packed with 2.7% QF-1/1.3% DC-11; 2) a 6' x 2 mm column packed with 7% OV 210/7% OV 17-4:1; and 3) a 6' x 2 mm 7% DC-11 column. Chromosorb 100/120 W(HP) was the support used in all columns.

The quantification used was a modification of the technique of WEBB and McCALL (1973). A standard solution of the Aroclor 1254 was analyzed by microcoulometric gas chromatography. The chlorine content of each major peak was determined by GLC-MS and reference to WEBB and McCALL (1972). The weight percent for each major peak in the standard was calculated from the integrated MC-GLC peak areas, the areas being corrected for the percent chlorine of each peak. These weight percent values were used for the quantitation of the water samples by electron capture GLC.

RESULTS

The detailed results are presented in Table 1. The equilibrium concentration of Aroclor^{R} 1254 in membrane filtered seawater was 28.1 ± 1.8 ppb at 16.5°C (Part 2). In seawater which had been both membrane filtered and carbon filtered the equilibrium concentration was 24.7 ± 2.3 ppb at 16.5°C (Part 3). When the temperature of this water was lowered to 10.5°C the equilibrium level dropped to 22.7 ± 1.1 ppb (Part 3). The rapid 25% decrease in

TABLE 1

SUMMARY OF PCB CONCENTRATIONS IN PARTS 1, 2, AND 3 OF THE EXPERIMENT

Part 1			Part 2			Part 3					
	16.5°C			16.5°C			16.5°C			16.5°C	
	Bottle			Replicate			Replicate			Replicate	
Stirring off (days)	1 (ppb)	2 (ppb)	Stirring off (days)	1 (ppb)	2 (ppb)	Stirring off (days)	1 (ppb)	2 (ppb)	Stirring off (days)	1 (ppb)	2 (ppb)
1 hr 45 min	57.5	42.1	4	29.6	31.0	8	26.6	27.3	0	23.0	21.8
	60.3	42.4					26.7			20.6	22.8
8 hr	54.3	31.6	15	27.0	29.0	20	24.3	25.2	2 hr	23.5	22.0
	57.6	32.6		26.6	28.6		23.6	19.1		21.1	22.0
4	41.1	32.7	23	30.5	29.1	31	24.6	20.8	1	22.2	24.3
	37.8	31.5		29.6	29.4		25.5	23.5		22.1	22.7
			32	25.2	27.3	75	26.5	25.3	4	21.8	24.9
				27.8	24.3		26.7	24.8		24.8	
			42	34.6	26.9				7	20.0	23.1
				32.5	28.2					22.3	21.9
									14	24.3	21.7
									34	21.6	24.0
										23.4	23.1
Mean				28.0	28.2		25.6	23.7		22.4	22.9
Combined Mean ± One Standard Deviation				28.1 ± 1.8			24.7 ± 2.3			22.7 ± 1.1	

concentration with time observed in Part 1 is thought to be a result of PCB settling out after being thrown into suspension by stirring. While trying to center the stirring bar on the rounded bottom of the carboys, the stirring bar came in contact with PCB prior to the beginning of each part of the work. After the stirring bar was centered it did not come in contact with additional PCB.

Table 2 and Figure 1 show the relative solubilities of the major PCB isomers present. The 2,3,5,2',5'-pentachloro isomer (peak 3) reached the highest concentration (5.5 ppb). This was closely followed by peaks 1, 2, and 5. Since the weight percent of peaks 1 and 2 in the Aroclor^R 1254 are less than that of peaks 3 and 5, these tetrachloro isomers would appear to be more soluble, if present on an equal molar basis.

DISCUSSION AND CONCLUSIONS

The observed solubility values of 28.1 ± 1.8 ppb for membrane filtered seawater and 24.7 ± 2.3 ppb for carbon filtered seawater at 16.5°C are considerably lower than values cited in the literature for Aroclor^R 1254 in fresh or seawater. ZITKO (1970) reported saturation concentrations ranging between 0.3 and 1.5 ppm in seawater and 0.3 and 3.0 ppm in fresh water. HAQUE et al. (1974) have obtained a solubility of 56 ppb, for Aroclor 1254 in fresh water. NELSON (1972) reported that Monsanto Corporation also found the solubility to be close to 50 ppb in fresh water. WIESE (1975) produced Aroclor 1254 solubilities in seawater ranging between 40 and 44 ppb.

Four factors may explain the difference between the results of this work and values listed above. They are stirring, salinity, organic content, and temperature. Stirring probably has the most impact. Stirring most likely holds aggregates of PCB molecules in suspension which subsequently settle to the bottom or accumulate on the water surface once stirring is stopped. ZITKO (1970), HAQUE et al. (1974), and WIESE (1975) used blenders (ZITKO) or magnetic stirring bars to help solubilize the PCB. The experimental method of Monsanto Corporation is unknown. Settling out or surface attraction of aggregates has been mentioned as the suspected reason why the solubility of DDT in fresh water was found to drop sharply (∿60%) after centrifugation of equilibrated samples (BOWMAN et al., 1960). This would also explain why the solubilities of individual PCB isomers decreased up to 33% after stirring of equilibrated water samples was stopped for several weeks during work reported by HAQUE and SCHMEDDING (1975). Compared to earlier work done by WIESE (1975) the results of this work show a 43% reduction in the apparent solubility of Aroclor 1254, most of which must be attributed to the difference in sampling times after stirring was terminated.

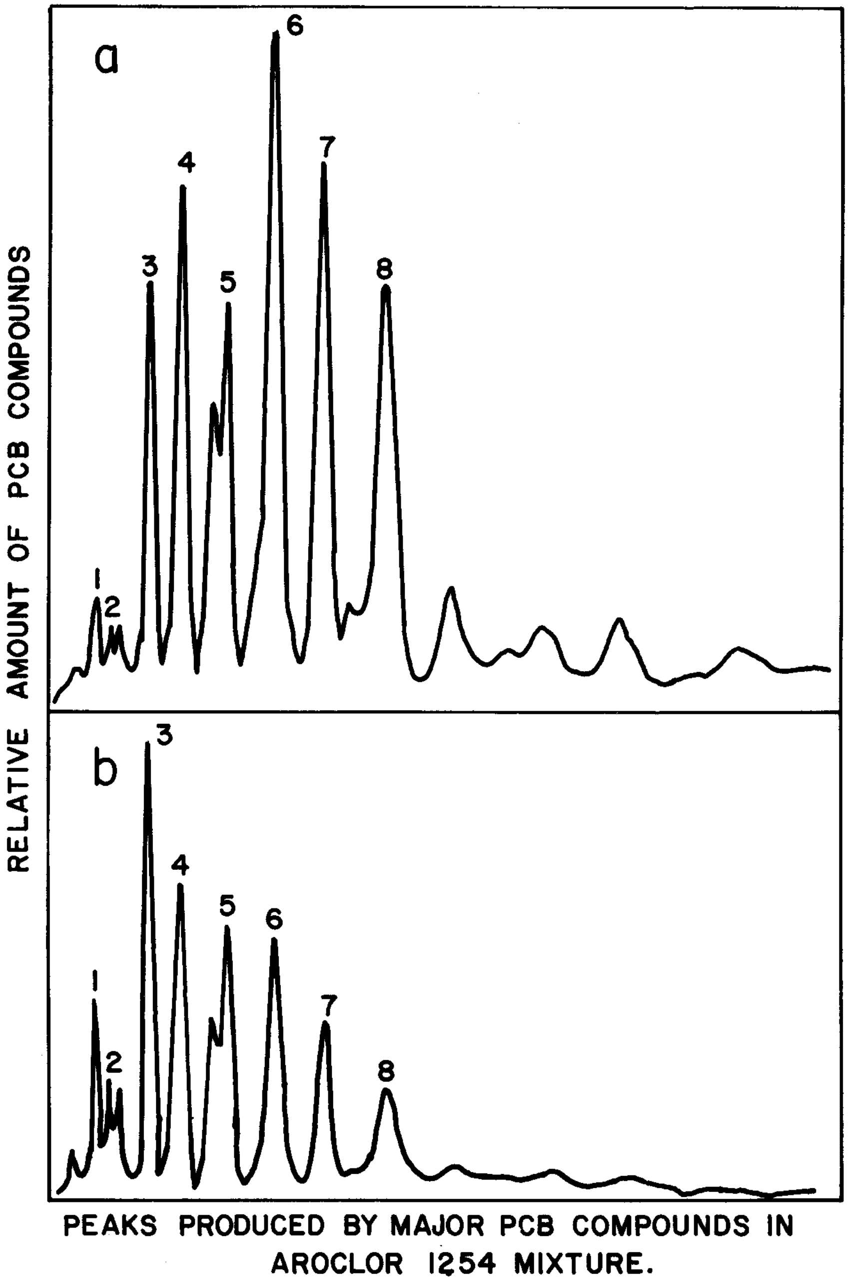

Figure 1. Chromatograms of a) Aroclor 1254 standard; b) PCB/seawater extract.

TABLE 2

COMPARISON OF THE SOLUBILITY IN SEAWATER OF PCB COMPOUNDS PRODUCING THE EIGHT MAJOR AROCLOR 1254 PEAKS

Peak Number	Chlorobiphenyl Identity	Aroclor 1254 Standard Wt. % PCB	Experimental Wt. % PCB in Solution	Concentration ppb
1	2,5,2',5'-tetra	6.1	18.3	4.52
2	2,3,2',5'-tetra	5.7	18.3	4.52
	2,2',3',4'-tetra			
3	2,3,6,2',5'-penta	15.2	22.2	5.48
4	2,4,5,2',5'-penta	18.0	12.9	3.19
5	2,4,5,2',3'-penta	21.4	18.4	4.54
	2,3,6,3',4'-penta			
6	2,4,5,3',4'-penta	7.1	5.2	1.28
	2,4,5,2',3',6'-hexa			
7	2,4,5,2',4',5'-hexa	5.2	3.2	0.79
8	2,3,4,2',4',6'-hexa	3.8	1.7	0.42
TOTAL				24.7 ± 2.3 ppb

Owing to the extremely non-polar nature of PCBs, their solubility in water decreases as water salinity is increased. The magnitude of this relationship can be predicted using the equation of SETSCHENOW (1899):

$$\operatorname{Log} (S_o/S) = KC_s \qquad (1)$$

where S_o and S are the molar solubilities of a non-electrolyte in pure water (S_o) and a salt solution (S); C_s is the molar concentration of the relevant salt, and K is a constant whose value is dependent upon the salt. It has been shown that SETSCHENOW relation provides a good representation of the salting-out effect of a non-polar, non-electrolyte in aqueous salt solutions (McDEVIT and LONG 1952; GORDON and THORNE 1967; and WIESS 1970). GORDON and THRONE determined a value for K of 0.2583 ± 0.0134 by solubilizing naphthalene in seawater for differing salinities. With this value for K, and a solubility of Aroclor^R 1254 in seawater (33 parts per thousand salinity) of 26 ppb (an average of Part 2 and Part 3 results), the SETSCHENOW equation (equation 1) predicts a freshwater solubility of 35 ppb. A 25% reduction in solubility is thus predicted for a 33 part per thousand increase in salinity. If an effect for stirring is taken into consideration, the results of HAQUE et al. (1974) for fresh water (56 ppb) and this predicted solubility value (35 ppb) are in fairly good agreement.

From our Part 3 results the effect of temperature on PCB solubility in water appears to be small, compared to the effects of stirring and salinity. In fact there is no significant difference between the solubilities observed at 16.5°C and 10.5°C in Part 3. Removal of organics by carbon filtering appears to have caused a small but measurable reduction in solubility (comparison of Parts 2 and 3 at 16.5°C).

Three of the PCB isomers used by HAQUE and SCHMEDDING (1975) in their solubility tests produced individual peaks which were measured in our solubility analyses. WEIL et al. (1974) have also measured solubilities for two of the isomers. A direct comparison of the solubility of individual isomers has limited meaning because HAQUE and SCHMEDDING tested isomers singly, whereas our tests involved competition among many isomers. WEIL et al. also measured the solubilities for individual isomers, as well as using a completely different method. The comparison (Table 3) may nevertheless be instructive. Our isomer solubilities are extracted from Table 2 by multiplying the average percent by weight of PCB in peaks 1, 4, and 7 by our observed Aroclor 1254 solubility of 24.7 ppb. The calculated isomer solubilities were then multiplied by 1.33 (from equation 1) to account for the fact that our experiments were conducted using seawater. Some consideration must be given also to the fact that the peaks we have measured contain smaller amounts of other unresolved isomers.

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TABLE 3

SOLUBILITY (ppb) OF INDIVIDUAL PCB ISOMERS

Biphenyl Isomer	This Work Corrected for Fresh Water	Haque and Schmedding	Weil et al.
2,5,2',5'	4.52 x 1.33 = 6.01	26.5	--
2,4,5,2',5'	3.19 x 1.33 = 4.24	10.3	4.2
2,4,5,2',4',5'	0.79 x 1.33 = 1.05	0.95	1.2

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