VAPOR PRESSURE ESTIMATES OF INDIVIDUAL POLYCHLORINATED BIPHENYLS AND COMMERCIAL FLUIDS USING GAS CHROMATOGRAPHIC RETENTION DATA

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SUMMARY

   The liquid phase vapor pressures at 25°C of 27 polychlorinated biphenyls were plotted *versus* published retention indices on two gas chromatographic stationary phases. Good fits were obtained (r^2 = 0.996–0.999) for data on an intermediate polarity (Dexsil-410) capillary and a non-polar (OV-101) packed column. Estimates of vapor pressures for 134 polychlorinated biphenyls found in five commercial Aroclor fluids were made using these two plots and published retention indices. Vapor pressure estimates of the five fluids were calculated using individual polychlorinated biphenyl vapor pressures and Aroclor compositional information, assuming Raoult's law. The resulting vapor pressures at 25°C for Aroclors 1248, 1254 and 1260 were *ca.* 2.3–3.3 times lower than values previously reported, whereas the vapor pressure of Aroclor 1242 was 1.4 times higher.

INTRODUCTION

   Predicting contaminant transport, distribution, and fate in the environment relies on accurate physical and chemical properties for developing suitable models. Required vapor pressure and water solubility data are lacking, or are in some cases questionable, particularly for components of complex mixtures.
   Only limited vapor pressure data are available for polychlorinated biphenyls (PCBs), an important class of organic pollutants. Up to a few years ago, the only vapor pressure information was for Aroclor fluids, determined in the 150–300°C range by Monsanto Corporation[1]. Mackay and Wolkoff[2] extrapolated these data to estimate Aroclor vapor pressures at 25°C, which today are the most widely quoted volatility data for PCB fluids. Aroclor mixtures contain fifty or more components and the vapor pressures referenced above are dominated by a few of the more volatile PCBs.
   Of the 209 possible PCBs, vapor pressures of only a few have been directly measured by physical methods (effusion, gas saturation, or extrapolation from boiling point data). Recently, Bidleman[3] estimated the liquid phase vapor pressures
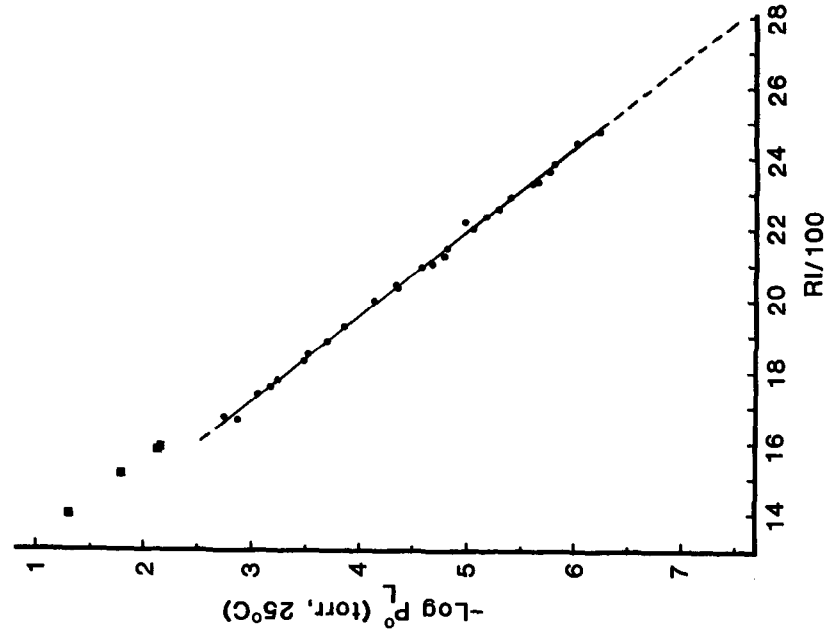
Fig. 1. Plot of $-\log P_L^0$ (Torr, 25°C) vs. retention index (RI) at 200°C on Dexsil-410 liquid phase. The solid line is the regression line, and the dashed lines show the 95% confidence interval for single predicted P_L^0 from published RI values. Data points: ■ = biphenyl and three monochlorobiphenyls (not included in regression); ● = di- through heptachlorobiphenyls.
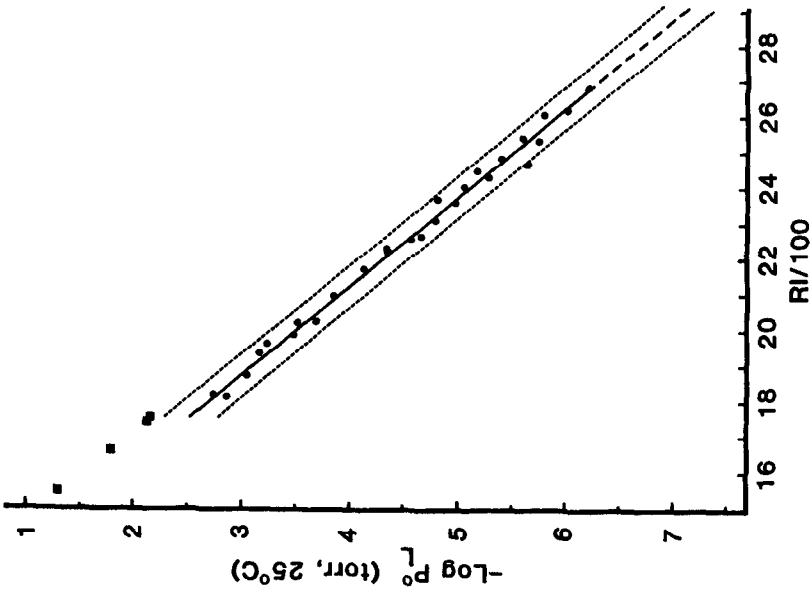
Fig. 2. Plot of $-\log P_L^0$ (Torr, 25°C) vs. retention index at 200°C on OV-101 liquid phase. The 95% confidence interval is much smaller than in Fig. 1 (Table II) and is not shown. (■ and ● same as Fig. 1.)

(P_L^0) at 25°C of 30 PCBs using a capillary gas chromatographic (GC) method. This paper describes the use of this GC determined vapor pressure data set in conjunction with published retention indices of PCBs to estimate the liquid phase vapor pressures of 134 PCBs found in five Aroclor fluids.

METHOD

In 1977, Albro et al.[4] computed retention indices (RI) for all of the 209 possible PCBs and biphenyl on thirteen GC liquid phases, including 3% Dexsil-410 and 10% OV-101 at 200°C. Albro and Parker[5] subsequently determined the composition of the PCB mixtures Aroclor 1016 and 1242 using twelve packed columns containing different GC phases. In 1981, Albro et al.[6] used a capillary Dexsil-410 column to determine RI at 200°C and molar percentages of all the PCB components in Aroclors 1248, 1254 and 1260.

We plotted $-\log P_L^0$ at 25°C *versus* RI at 200°C for the 30 PCBs and biphenyl whose P_L^0 had been determined by capillary GC, using RI data on Dexsil-410 and OV-101 phases. The Dexsil-410 RI were the experimental values of Albro et al.[6] for 23 of the PCBs, and those calculated from the half-index table of Albro et al.[4] for the remaining seven and biphenyl. RI for the 30 PCBs and biphenyl on OV-101 were calculated using the half-index table.

Linear regression equations were fitted to these two plots using 27 of the PCBs, with biphenyl and the three monochlorobiphenyls being excluded (see Discussion section). From these two equations, estimates of P_L^0 at 25°C for 134 PCBs found in Aroclors 1016, 1242, 1248, 1254 and 1260 were calculated using the published RI values.

The partial pressures ($P_{L,i}$) of individual PCBs in each fluid were calculated using the percent composition information of Albro et al.[5,6] assuming Raoult's Law:

$$P_{L,i} = P_{L,i}^0 X_i \tag{1}$$

where $P_{L,i}^0$ is the P_L^0 for the pure component, and X_i is the mole fraction of an individual PCB in the fluid. Vapor pressures of the five Aroclors were estimated by summing the partial pressures of individual PCBs in each fluid.

RESULTS AND DISCUSSION

Retention index correlated vapor pressures of individual PCBs

The $-\log P_L^0$ *versus* RI correlation plot for data on the intermediate polarity Dexsil-410 phase is shown in Fig. 1. A similar plot using RI data on the non-polar OV-101 phase is presented in Fig. 2. Both of these plots reveal a marked discontinuity which occurs between the mono- and dichlorobiphenyls. Biphenyl and the three monochlorobiphenyls are shifted off a line passing through the di- to heptachlorobiphenyls. The reason for this deviation is not understood; however, the discrepancies are not likely to be due to inaccuracies in P_L^0, since the capillary GC measured P_L^0 (ref. 3) agreed well with the literature values for these compounds (Table I). Because of this obvious discontinuity only the di- to heptachlorobiphenyl points were used in calculating the $-\log P_L^0$ *versus* RI regression equations.

TABLE I

VAPOR PRESSURES OF INDIVIDUAL PCBs FOUND IN AROCLOR FLUIDS

IUPAC No.	Chlorine substitution pattern	$-\log P_L^0$ (Torr, 25°C)				
		OV-101 RI correlation	Dexsil 410 RI correlation	GC method*	Literature value	Ref.
0	Biphenyl			1.304	1.376	3
Monochlorobiphenyls						
1	2			1.782	1.860	8
2	3			2.126		
3	4			2.156	2.167**	
Dichlorobiphenyls						
4	2,2'	2.611	2.600		2.650	10
6	2,3'	2.887	2.918			
7	2,4	2.803	2.791	2.739		
8	2,4'	2.929	2.970			
9	2,5	2.761	2.759	2.860	3.237	9
10	2,6	2.598	2.556			
11***	3,3'	3.164	3.244	3.167		
12	3,4	3.231	3.331			
13	3,4'	3.205	3.299			
14	3,5	3.025	3.057			
15	4,4'	3.247	3.355	3.237	3.485	10
Trichlorobiphenyls						
16	2,3,2'	3.394	3.347			
17	2,4,2'	3.277	3.256			
18	2,5,2'	3.235	3.204			
19	2,6,2'	3.071	3.009			
20	2,3,3'	3.670	3.729			
22	2,3,4'	3.712	3.764			
25	2,4,3'	3.553	3.562			
26	2,5,3'	3.511	3.510			
27	2,6,3'	3.348	3.327			
28	2,4,4'	3.595	3.593			
29***	2,4,5	3.469	3.458	3.478		
30***	2,4,6	3.080	2.993	3.056	3.648	9
31	2,5,4'	3.553	3.586	3.520		
32	2,6,4'	3.390	3.375			
33	3,4,2'	3.704	3.784			
35	3,4,3'	3.980	4.102			
37	3,4,4'	4.022	4.150			
39	3,5,4'	3.817	3.884			
Tetrachlorobiphenyls						
40	2,3,2',3'	4.177	4.190	4.134		
41	2,3,4,2'	4.085	4.134			
42	2,3,2',4'	4.060	4.062			
43	2,3,5,2'	3.905	3.844			
44	2,3,2',5'	4.018	4.011			
45	2,3,6,2'	3.771	3.697			
46	2,3,2',6'	3.855	3.812			
47	2,4,2',4'	3.943	3.931			

TABLE I (*continued*)

IUPAC No.	Chlorine substitution pattern	$-\log P_L^0$ (Torr, 25°C)				
		OV-101 RI correlation	Dexsil 410 RI correlation	GC method*	Literature value	Ref.
48	2,4,5,2'	3.943	3.911			
49	2,4,2',5'	3.901	3.915			
52	2,5,2',5'	3.859	3.888	3.844	4.108	11
53	2,5,2',6'	3.696	3.605	3.688		
54	2,6,2',6'	3.532	3.411			
55	2,3,4,3'	4.362	4.460			
56	2,3,3',4'	4.487	4.611			
60	2,3,4,4'	4.403	4.508			
66	2,4,3',4'	4.370	4.420	4.335		
70	2,5,3',4'	4.328	4.384	4.353		
71	2,6,3',4'	4.165	4.182			
72	2,5,3',5'	4.123	4.130			
74	2,4,5,4'	4.261	4.285			
75	2,4,6,4'	3.871	3.820			
76	3,4,5,2'	4.345	4.496			
77	3,4,3',4'	4.797	4.965	4.809		
78	3,4,5,3'	4.621	4.810			
79	3,4,3',5'	4.592	4.690			
80	3,5,3',5'	4.387	4.416			
81	3,4,5,4'	4.663	4.865			
Pentachlorobiphenyls						
83	2,3,5,2',3'	4.688	4.643			
84	2,3,6,2',3'	4.554	4.480			
85	2,3,4,2',4'	4.751	4.786			
87	2,3,4,2',5'	4.709	4.738	4.770		
91	2,3,6,2',4'	4.437	4.301			
92	2,3,5,2',5'	4.529	4.464			
95	2,3,6,2',5'	4.395	4.253			
97	2,4,5,2',3'	4.726	4.702			
98	2,4,6,2',3'	4.336	4.249			
99	2,4,5,2',4'	4.609	4.551	4.658		
101	2,4,5,2',5'	4.567	4.519	4.560	4.627	11
102	2,4,5,2',6'	4.403	4.301			
103	2,4,6,2',5'	4.177	4.074			
105	2,3,4,3',4'	5.178	5.294	5.170		
106	2,3,4,5,3'	4.986	5.020			
108	2,3,4,3',5'	4.973	5.052			
110	2,3,6,3',4'	4.864	4.825			
113	2,3,6,3',5'	4.659	4.559			
114	2,3,4,5,4'	5.028	5.064			
118	2,4,5,3',4'	5.036	5.108	5.047		
120	2,4,5,3',5'	4.831	4.817			
121	2,4,6,3',5'	4.441	4.341			
122	3,4,5,2',3'	5.128	5.278			
123	3,4,5,2',4'	5.011	5.127			
126	3,4,5,3',4'	5.438	5.668			
127	3,4,5,3',5'	5.233	5.394			

TABLE I (*continued*)

IUPAC No.	Chlorine substitution pattern	$-log\ P_L^0$ (Torr, 25°C)				
		OV-101 RI correlation	Dexsil 410 RI correlation	GC method*	Literature value	Ref.
Hexachlorobiphenyls						
128	2,3,4,2',3',4'	5.560	5.660	5.592		
131	2,3,4,6,2',3'	5.023	4.905			
132	2,3,4,2',3',6'	5.245	5.167			
133	2,3,5,2',3',5'	5.199	5.084			
134	2,3,5,6,2',3'	5.036	4.857			
135	2,3,5,2',3',6'	5.065	4.861			
136	2,3,6,2',3',6'	4.931	4.659			
138	2,3,4,2',4',5'	5.417	5.429	5.397		
143	2,3,4,5,2',6'	5.170	5.143			
146	2,3,5,2',4',5'	5.237	5.143			
148	2,3,5,2',4',6'	4.847	4.682			
149	2,3,6,2',4',5'	5.103	4.925	4.968		
151	2,3,5,6,2',5'	4.877	4.718			
153	2,4,5,2',4',5'	5.275	5.215	5.280		
154	2,4,5,2',4',6'	4.885	4.778			
156	2,3,4,5,3',4'	5.803	5.922	5.793		
157	2,3,4,3',4',5'	5.819	6.022			
158	2,3,4,6,3',4'	5.333	5.473			
163	2,3,5,6,3',4'	5.346	5.433			
167	2,4,5,3',4',5'	5.677	5.747			
168	2,4,6,3',4',5'	5.287	5.330			
Heptachlorobiphenyls						
170	2,3,4,5,2',3',4'	6.184	6.216	6.202		
171	2,3,4,6,2',3',4'	5.715	5.624	5.752		
174	2,3,4,5,2',3',6'	5.870	5.755			
176	2,3,4,6,2',3',6'	5.400	5.179			
177	2,3,5,6,2',3',4'	5.727	5.596			
179	2,3,5,6,2',3',6'	5.413	5.123			
180	2,3,4,5,2',4',5'	6.041	5.970	6.013		
181	2,3,4,5,6,2',4'	5.660	5.501			
182	2,3,4,5,2',4',6'	5.652	5.573			
183	2,3,4,6,2',4',5'	5.572	5.418			
185	2,3,4,5,6,2',5'	5.618	5.445			
186	2.3.4,5,6,2',6'	5.455	5.247			
187	2,3,5,6,2',4',5'	5.585	5.366	5.640		
188	2,3,5,6,2',4',6'	5.195	4.949			
189	2,3,4,5,3',4',5'	6.443	6.606			
190	2,3,4,5,6,3',4'	6.087	5.958			
192	2,3,4,5,6,3',5'	5.882	5.728			
193	2,3,5,6,3',4',5'	5.987	6.181			
Octachlorobiphenyls						
194	2,3,4,5,2',3',4',5'	6.808	6.872			
195	2,3,4,5,6,2',3',4'	6.469	6.252			
196	2,3,4,5,2',3',4',6'	6.339	6.200			
197	2,3,4,6,2',3',4',6'	5.870	5.807			
198	2,3,4,5,6,2',3',5'	6.289	6.037			

TABLE I

IUPAC No.	Chlorine substitution pattern	$-\log P_L^0$ (Torr, 25°C)				
		OV-101 RI correlation	Dexsil 410 RI correlation	GC method*	Literature value	Ref.
199	2,3,4,5,6,2',3',6'	6.154	5.902			
200	2,3,4,6,2',3',5',6'	5.882	5.604			
201	2,3,4,5,2',3',5',6'	6.351	6.125			
202	2,3,5,6,2',3',5',6'	5.895	5.533		5.306	12
203	2,3,4,5,6,2',4',5'	6.326	6.105			
204	2,3,4,5,6,2',4',6'	5.937	5.684			
205	2,3,4,5,6,3',4',5'	6.728	6.661			
Nonachlorobiphenyls						
206	2,3,4,5,6,2',3',4',5'	7.093	6.940			
207	2,3,4,5,6,2',3',4',6'	6.624	6.427			
208	2,3,4,5,6,2',3',5',6'	6.636	6.304			
209	Decachlorobiphenyl	7.378	7.003		7.414	12

* Average of P_L values determined on Apolane 87 and BP-1 liquid phases using the GC method of Bidleman (ref. 3).
** Average of values reported in refs. 8 and 12.
*** Not found in Aroclor fluids.

A good fit ($r^2 = 0.996$) was obtained using the Dexsil-410 RI data with the model:

$$-\log P_L^0 = (-3.974 \cdot 10^{-3})RI + 4.434 \tag{2}$$

Further improvement was obtained ($r^2 = 0.999$) with the model:

$$-\log P_L^0 = (-4.189 \cdot 10^{-3})RI + 4.184 \tag{3}$$

using the RI data on OV-101. Vapor pressure estimates of the 134 PCBs found in five Aroclor fluids were calculated using these two equations and the RI data of Albro et al.[4,6] (Table I). Vapor pressure estimates of the other 75 PCBs not found in the Aroclor fluids can be obtained by using eqn. 2 or 3 and the half-index table of Albro et al.[4].

Values of P_L^0 obtained by correlation from the two sets of RI data differed on the average by 22.7% and in the worst case (decachlorobiphenyl) by a factor of 2.4, with the heavier PCBs exhibiting a slightly greater overall difference. These differences were due to changes in elution order for some PCBs on the two liquid phases.

Within a given series of isomers, P_L^0 generally increased with the number of *ortho*-chlorines. This "*ortho*-effect" produces large differences in volatilities of PCBs having the same chlorine content as observed by Bidleman[3]. Mullin et al.[7] also found that retention times of isomeric PCBs increased with decreasing number of *ortho*-substituted chlorines.

Accuracy of RI-correlated vapor pressures
Vapor pressures of only a few PCBs have been measured by methods other

than GC. Boiling point data[8,9] were extrapolated to estimate vapor pressures of 2-chlorobiphenyl, 4-chlorobiphenyl, 2,5-dichlorobiphenyl, and 2,4,6-trichlorobiphenyl. The resulting vapor pressures at 25°C were P_L^0, since extrapolations were made from above the melting points. Vapor pressures of the crystalline solids (P_S^0) at 25°C were determined by effusion[10] for 2,2'-dichlorobiphenyl and 4,4'-dichlorobiphenyl, and by gas saturation[11,12] for 2,5,2',5'-tetrachlorobiphenyl, 2,4,5,2',5'-pentachlorobiphenyl, 4-chlorobiphenyl, 2,3,5,6,2',3',5',6'-octachlorobiphenyl, and decachlorobiphenyl. For these, P_L^0 were estimated from P_S^0 using[13]:

$$\ln P_L^0/P_S^0 = 6.8\ (T_m - 298)/298 \tag{4}$$

where T_m is the melting point (°K). The resulting P_L^0 for the above PCBs and the average of several experimental results for biphenyl[3] are listed in Tables I and II under "Literature value".

Average PCB P_L^0 values from OV-101 and Dexsil-410 correlations are compared with literature values in Table II. In all cases but one, the correlated results are slightly higher. The worst agreements occur with 2,5-dichlorobiphenyl and 2,4,6-trichlorobiphenyl, for which the correlated P_L^0 are 3.0 and 4.1 times higher than P_L^0 estimated from boiling point data. However, the extrapolated P_L^0 at 25°C were based on only three boiling points above 100°C, and thus their accuracies are uncertain. Including the two worst cases, the average agreement between correlated and literature P_L^0 was about a factor of two.

The 95% confidence intervals of P_L^0 (Fig. 1 and Table II) were calculated using the method described in Draper and Smith[14]. Confidence bands for the OV-101 plot were very narrow (Table II), and these bands were omitted from Fig. 2 for clarity. Since GC-determined P_L^0 were available only up to the heptachlorobiphenyls, extrapolation was necessary to calculate P_L^0 for the octa-through decachlorobiphenyls, and whether linearity holds in this region remains uncertain. However, the fairly good agreement between predicted and literature P_L^0 for the one octachlorobiphenyl and decachlorobiphenyl (Table II) suggests the same level of accuracy for the other octa- and nonachlorobiphenyls.

TABLE II

COMPARISON OF PCB VAPOR PRESSURES CALCULATED USING RI CORRELATION WITH VALUES REPORTED IN THE LITERATURE

Compound	P_L^0 (Torr, 25°C) ± 95% confidence limits		
	OV-101	Dexsil-410	Literature value
2,2'	$2.4 \pm 0.29 \cdot 10^{-3}$	$2.5 \pm 1.9 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$
2,5	$1.7 \pm 0.20 \cdot 10^{-3}$	$1.7 \pm 1.3 \cdot 10^{-3}$	$5.8 \cdot 10^{-4}$
4,4'	$5.7 \pm 0.65 \cdot 10^{-4}$	$4.4 \pm 3.2 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$
2,4,6	$8.3 \pm 0.96 \cdot 10^{-4}$	$1.0 \pm 0.75 \cdot 10^{-3}$	$2.2 \cdot 10^{-4}$
2,5,2',5'	$1.4 \pm 0.16 \cdot 10^{-4}$	$1.3 \pm 0.92 \cdot 10^{-4}$	$7.8 \cdot 10^{-5}$
2,4,5,2',5'	$2.7 \pm 0.30 \cdot 10^{-5}$	$3.0 \pm 2.1 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$
2,3,5,6,2',3',5',6'	$1.3 \pm 0.15 \cdot 10^{-6}$	$2.9 \pm 2.1 \cdot 10^{-6}$	$4.9 \cdot 10^{-6}$
Decachlorobiphenyl	$4.2 \pm 0.53 \cdot 10^{-8}$	$9.9 \pm 7.9 \cdot 10^{-8}$	$3.8 \cdot 10^{-8}$

Vapor pressures of Aroclor fluids

Partial pressures ($P_{L,i}$) of individual PCBs found in the five Aroclors were estimated by assuming that the solutions behaved ideally. $P_{L,i}$ for di- through nonachlorobiphenyls were calculated using Dexsil-410 correlated P_L^0 and are presented in Table III. A similar table of $P_{L,i}$ values computed using OV-101 correlated P_L^0 is omitted from this paper to save space, but can be obtained from the authors. $P_{L,i}$ of biphenyl and the monochlorobiphenyls (Table III) were calculated using literature P_L^0 (Table I). No entry in Table III indicates that either the PCB was not found in the Aroclor fluid, or that its $P_{L,i}$ contribution to the overall vapor pressure was insignificant (less than 10^{-9} Torr). Vapor pressures of the Aroclor fluids are largely dominated by a small number of PCBs in each mixture. The high partial pressures of some PCBs are due to high vapor pressures and/or large mole fractions.

Vapor pressures of each Aroclor fluid were calculated by summing the partial pressures of individual PCBs found in the fluid. Resulting overall vapor pressures for Aroclors 1016, 1242, 1248, 1254, and 1260 are presented in Table IV, along with Aroclor vapor pressures calculated by extrapolation of Monsanto data[1] from 150–300°C to 25°C using the Antoine equation by Mackay and Wolkoff[2].

Aroclor vapor pressures calculated using Dexsil-410 and OV-101 correlated P_L^0 values exhibited good agreement, and decreased in the order 1016 > 1242 > 1248 > 1254 > 1260. The values reported by Mackay and Wolkoff[2] decreased in the order 1248 > 1242 > 1254 > 1260, with 1016 not reported. The higher vapor pressure reported[2] for 1248 *versus* 1242 is surprising, especially considering the predominance of more volatile mono-, di- and trichlorobiphenyls in Aroclor 1242 (Table III). The reason for this discrepancy may be due to the data originally published by Monsanto[1]. Monsanto reported the Aroclor vapor pressure order 1242 > 1248 > 1254 > 1260 at 100°C, with the Aroclor 1242, 1254, and 1260 vapor pressure *versus* $1/T$ plots exhibiting very similar slopes. However, the Aroclor 1248 slope was different[1], and as a consequence when the data were extrapolated to 25°C by Mackay and Wolkoff[2] the 1248 vapor pressure was higher.

Vapor pressures of Aroclors 1248, 1254, and 1260 were *ca.* 2.4–3.3 times lower than values previously reported by Mackay and Wolkoff (Table IV). The lower values found here may be due to several reasons:

(1) Extrapolation of vapor pressures from high temperature data using the Antoine equation tends to overestimate the vapor pressure[13], and thus the values reported by Mackay and Wolkoff[2] may be too high.

(2) There is no experimental evidence to support ideal behavior of Aroclor fluids. Therefore in the calculation of PCB partial pressures, our assumption that these solutions behave ideally has possibly resulted in an underestimation of the Aroclor vapor pressures. According to Reid *et al.*[15] vapor pressures calculated using Raoult's Law generally are lower than those determined experimentally, since activity coefficients are usually greater than unity. Eggertsen *et al.*[16] also cited deviation from ideal solution behavior as a factor which may influence the accuracy of the GC method for estimating vapor pressures of petroleum distillate fractions.

(3) Differences in composition of technical PCB mixtures are known to exist and have been reported in the literature[17,18].

TABLE III

PARTIAL PRESSURES OF INDIVIDUAL PCBs IN AROCLOR FLUIDS FROM DEXSIL 410 RE-
TENTION INDEX CORRELATION DATA

IUPAC No.	Chlorine substitution pattern	$P_{L,i}$ (10^{-6} Torr, 25°C)				
		1016	1242	1248	1254	1260
0	Biphenyl	210.36*	4.21*			
Monochlorobiphenyls						
1	2	110.43*	93.87*			
2	3	7.48*	2.99*			
3	4	68.08*	14.98*			
Dichlorobiphenyls						
4	2,2′	109.52	100.22	6.28		
6	2,3′	16.55	14.98	8.33	0.85	
7	2,4	18.77	16.83			
8	2,4′	110.37	96.12	1.93		
9	2,5	5.92	5.40			
10	2,6	5.56	3.61			
12	3,4	0.51	0.42			
13	3,4′	0.60	0.60			
14	3,5	3.24	3.07			
15	4,4′	4.72	4.37			
Trichlorobiphenyls						
16	2,3,2′	15.74	14.62	3.78		
17	2,4,2′	17.42	16.20	1.05		
18	2,5,2′	67.96	58.52	62.20	0.44	
19	2,6,2′	10.58	9.50			
20	2,3,3′	7.45	6.79			
22	2,3,4′	4.82	4.55	2.13		
25	2,4,3′	4.91	4.61			
26	2,5,3′	1.92	1.70	2.32		
27	2,6,3′	2.73	2.54			
28	2,4,4′	36.96	33.95			
31	2,5,4′	12.24	11.75	24.15	1.87	
32	2,6,4′	9.74	9.07	6.16		
33	3,4,2′	5.06	4.65			
35	3,4,3′	0.30	0.52			
37	3,4,4′	1.34	1.15	0.91	0.14	0.064
39	3,5,4′	1.41	1.34			
Tetrachlorobiphenyls						
40	2,3,2′,3′	0.12	0.097	0.72	0.17	0.026
41	2,3,4,2′	1.47	1.23			
42	2,3,2′,4′			6.11	1.89	0.57
43	2,3,5,2′	0.67	0.63			
44	2,3,2′,5′	1.11	1.03			
45	2,3,6,2′	2.01	1.81	11.51	0.30	
46	2,3,2′,6′	0.51	0.48			
47	2,4,2′,4′	2.12	1.93	3.73	0.61	0.094
48	2,4,5,2′	1.73	1.63			
49	2,4,2′,5′	4.23	3.99	4.63	1.98	0.53
52	2,5,2′,5′	5.63	5.28	10.82	5.64	2.47
53	2,5,2′,6′	2.66	2.41	15.64	0.32	
54	2,6,2′,6′	0.74	0.66			

TABLE III (*continued*)

IUPAC No.	Chlorine substitution pattern	$P_{L,i}$ (10^{-6} Torr, 25°C)				
		1016	1242	1248	1254	1260
55	2,3,4,3'			0.038	0.15	0.042
56	2,3,3',4'		0.15		0.044	0.007
60	2,3,4,4'		0.065			
66	2,4,3',4'	0.053	0.31	1.88	0.85	0.084
70	2,5,3',4'		0.46	2.63	1.96	0.35
71	2,6,3',4'			0.43		
72	2,5,3',5'		0.24	1.56	0.75	0.21
74	2,4,5,4'	0.70	1.05	0.13	0.16	0.047
75	2,4,6,4'	3.63	3.30			
76	3,4,5,2'				0.057	0.003
77	3,4,3',4'		0.037	0.051	0.013	0.004
78	3,4,5,3'		0.081			
79	3,4,3',5'		0.049		0.047	0.008
80	3,5,3',5'					
81	3,4,5,4'		0.038			
Pentachlorobiphenyls						
83	2,3,5,2',3'				0.073	0.020
84	2,3,6,2',3'	0.003	0.13	0.23	0.57	0.23
85	2,3,4,2',4'		0.065	0.090	0.35	0.051
87	2,3,4,2',5'		0.016	0.19	0.70	0.20
91	2,3,6,2',4'			0.89	2.50	1.61
92	2,3,5,2',5'		0.041	0.069	0.22	0.072
95	2,3,6,2',5'	0.10	0.30			
97	2,4,5,2',3'			0.15	0.51	0.12
98	2,4,6,2',3'	0.022	0.073			
99	2,4,5,2',4'		0.15	0.71	1.71	0.23
101	2,4,5,2',5'		0.082	0.45	2.11	1.53
102	2,4,5,2',6'					
103	2,4,6,2',5'			1.59	0.24	0.084
105	2,3,4,3',4'		0.013			
106	2,3,4,5,3'				0.038	0.006
108	2,3,4,3',5'	0.014	0.041	0.002	0.049	0.012
110	2,3,6,3',4'			0.25	1.27	0.53
113	2,3,6,3',5'	0.003	0.11	0.86		0.003
114	2,3,4,5,4'				0.022	0.003
118	2,4,5,3',4'				0.63	0.16
120	2,4,5,3',5'		0.047		0.023	0.46
121	2,4,6,3',5'		0.42	1.97	1.60	0.26
122	3,4,5,2',3'				0.040	0.099
123	3,4,5,2',4'		0.027			
126	3,4,5,3',4'		0.001		0.003	0.034
127	3,4,5,3',5'		0.002			
Hexachlorobiphenyls						
128	2,3,4,2',3',4'				0.029	0.010
131	2,3,4,6,2',3'				0.017	0.001
132	2,3,4,2',3',6'				0.14	0.19
133	2,3,5,2',3',5'			0.093	0.002	0.005
134	2,3,5,6,2',3'			0.015	0.053	0.14
135	2,3,5,2',3',6'				0.027	0.040

TABLE III (continued)

IUPAC No.	Chlorine substitution pattern	$P_{L,i}$ (10^{-6} Torr, 25°C)				
		1016	1242	1248	1254	1260
136	2,3,6,2',3',6'			0.044	0.074	0.24
138	2,3,4,2',4',5'		0.003	0.007	0.15	0.19
143	2,3,4,5,2',6'		0.005			
146	2,3,5,2',4',5'				0.054	0.11
148	2,3,5,2',4',6'					
149	2,3,6,2',4',5'			0.091	0.43	1.13
151	2,3,5,6,2',5'				0.063	0.011
153	2,4,5,2',4',5'		0.001	0.008	0.20	0.50
154	2,4,5,2',4',6'					0.023
156	2,3,4,5,3',4'					0.005
157	2,3,4,3',4',5'				0.002	
158	2,3,4,6,3',4'				0.015	0.006
163	2,3,5,6,3',4'					
167	2,4,5,3',4',5'				0.004	0.003
168	2,4,6,3',4',5'			0.026	0.20	0.028
Heptachlorobiphenyls						
170	2,3,4,5,2',3',4'				0.003	0.004
171	2,3,4,6,2',3',4'				0.007	0.10
174	2,3,4,5,2',3',6'					0.002
176	2,3,4,6,2',3',6'			0.006		0.038
177	2,3,5,6,2',3',4'					
179	2,3,5,6,2',3',6'				0.042	0.062
180	2,3,4,5,2',4',5'				0.008	0.077
181	2,3,4,5,6,2',4'				0.009	0.086
182	2,3,4,5,2',4',6'					0.013
183	2,3,4,6,2',4',5'				0.044	0.098
185	2,3,4,5,6,2',5'				0.040	0.20
186	2,3,4,5,6,2',6'					0.021
187	2,3,5,6,2',4',5'				0.021	0.048
188	2,3,5,6,2',4',6'			0.13	0.008	0.007
189	2,3,4,5,3',4',5'					
190	2,3,4,5,6,3',4'					
192	2,3,4,5,6,3',5'				0.004	0.018
193	2,3,5,6,3',4',5'					0.015
Octachlorobiphenyls						
194	2,3,4,5,2',3',4',5'					0.003
195	2,3,4,5,6,2',3',4'					
196	2,3,4,5,2',3',4',6'					0.005
197	2,3,4,6,2',3',4',6'					0.005
198	2,3,4,5,6,2',3',5'				0.009	0.001
199	2,3,4,5,6,2',3',6'					0.005
200	2,3,4,6,2',3',5',6'					0.004
201	2,3,4,5,2',3',5',6'					0.012
202	2,3,5,6,2',3',5',6'					0.009
203	2,3,4,5,6,2',4',5'					0.001
204	2,3,4,5,6,2',4',6'					0.003
205	2,3,4,5,6,3',4',5'					
Nonachlorobiphenyls						
206	2,3,4,5,6,2',3',4',5'					0.001
207	2,3,4,5,6,2',3',4',6'					0.004
208	2,3,4,5,6,2',3',5',6'					0.001

* These partial pressures were calculated from literature P_L^0 values (Table I).

TABLE IV

VAPOR PRESSURES OF AROCLOR FLUIDS

Aroclor fluid	P_L (Torr, 25°C)		
	Dexsil 410 RI Correlation	OV-101 RI Correlation	Mackay and Wolkoff (ref. 2)
1016	$9.01 \cdot 10^{-4}$	$9.05 \cdot 10^{-4}$	Not reported
1242	$5.72 \cdot 10^{-4}$	$5.76 \cdot 10^{-4}$	$4.06 \cdot 10^{-4}$
1248	$1.87 \cdot 10^{-4}$	$1.80 \cdot 10^{-4}$	$4.94 \cdot 10^{-4}$
1254	$3.26 \cdot 10^{-5}$	$3.18 \cdot 10^{-5}$	$7.71 \cdot 10^{-5}$
1260	$1.37 \cdot 10^{-5}$	$1.24 \cdot 10^{-5}$	$4.05 \cdot 10^{-5}$

CONCLUSIONS

The vapor pressure data reported in this study are useful from two aspects. First, vapor pressure estimates are now available for all the PCBs found in commercial Aroclor fluids. When modeling PCB transport phenomena, such as air–water exchange and adsorption to airborne particles, it is the individual PCB vapor pressures which are needed. Second, calculations of vapor pressures for the commercial fluids show which PCBs in the mixtures dominate the "overall" vapor pressure. It is these components that are most likely to be enriched in gaseous PCB emissions from spills and disposal sites. The approach used in this study shows promise in estimating the volatilities of other complex mixtures from known vapor pressures of a limited number of components in the mixtures, coupled with GC retention data.

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