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Chromatographic Determination of Octanol–Water Partition Coefficients (Kow's) for 58 Polychlorinated Biphenyl Congeners

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■ Octanol–water partition coefficients of 58 polychlorinated biphenyl (PCB) congeners have been determined by reverse-phase C_{18} high-performance liquid chromatography (HPLC) of Aroclor 1242 and 1254 mixtures. High-resolution glass capillary gas–liquid chromatography was used for the detection of the eluted individual congeners. Some PCB congeners behaved atypically from other organics on reverse-phase HPLC, and empirically derived correction factors were used to adjust K_{ow} values. Congener log K_{ow} values for PCB's ranged from an average of 4.5 for $N_{Cl} = 1$ to 8.1 for $N_{Cl} = 7$. The environmental implications of PCB K_{ow} values and congener behavior on the C_{18} reverse-phase column are discussed.

Introduction

Octanol–water partition coefficients (K_{ow}'s) are widely used in correlations concerning pollutant partitioning between water and sediments (1, 2), in aqueous solubility relationships (3, 4), in bioconcentration factor determination (4–7), and in toxicity relationships (8). K_{ow} values for polychlorinated biphenyl (PCB) congeners comprising Aroclor mixtures are especially valuable since predictions can be made concerning the equilibrium distribution of these compounds in the environment. The principal objective of this study is to provide K_{ow} values for PCB congeners comprising commercial mixtures.

Polychlorinated biphenyls are among the most studied group of organic compounds with environmental significance. A total of 209 positional congeners are possible, in addition to some sterically induced optical isomers (9–11). Eisenreich et al. (12) have combined published data (13–15) with their glass capillary gas chromatography (GC)

results to determine the percentage of each congener and its identity in Aroclor mixtures. This has provided the information necessary to identify congeners separated by reverse-phase high-performance liquid chromatography (RPHPLC) using a high-resolution capillary GC as the detector.

RPHPLC has been used to determine log K_{ow} values for a variety of environmentally important organic compounds (16–19). The K_{ow} determination is indirect, in that compounds of known log K_{ow} are chromatographed by RPHPLC and the resulting log retention time or log capacity factor (log k') is plotted against log K_{ow}. After a number of compounds have been chromatographed, a calibration curve to be used for interpolation of log K_{ow} values for unknown compounds can be constructed. Table I is a summary of the systems used in the accuracy of calibration curves constructed by several investigators.

Octanol–water partition coefficients have generally been measured by mixing the desired chemical with a 1-octanol/water mixture, shaking for an extended period to ensure equilibrium, allowing phase separation, and then carefully measuring the solute concentration in both phases. This method is problematical for highly hydrophobic molecules like PCB's, where precise concentrations in the water phase are difficult to measure in small volumes (1, 18). In addition, emulsion formation often occurs, complicating the analysis (1). Measurement of individual PCB congeners using such a system would be time consuming and expensive.

Another direct method for the accurate determination of K_{ow} values of hydrophobic compounds is based on use of a generator column (19, 20). A solid, inert support (i.e., glass beads) is coated with water-saturated octanol con-

Table I. Summary of Some Chromatographic Methods To Determine Octanol–Water Partition Coefficients (K_{ow}'s) for PCB's

investigators	solvent	system	reverse-phase	calibration curve	accuracy
19	85:15 MeOH–H$_2$O	isocratic HPLC	C$_{10}$	log K_{ow} = 5.1 log (t_R)[b] – 1.3 R^2 = 0.975 n = 5	$\overline{\Delta}$ log K_{ow}[f] = 0.16 Sy·x[g] = 0.26 1.8 × error in K_{ow}
13	75:25 MeOH–H$_2$O	isocratic HPLC	C$_{18}$	log K_{ow} = 2.7 log k'[c] + 2.37 R^2 = 0.975 n = 37	$\overline{\Delta}$ log K_{ow} = 0.19 Sy·x = 0.25 1.8 × error in K_{ow}
5	50–80% MeOH in 0.01 N HCl with 5% MeOH step changes	isocratic HPLC	C$_{18}$	log K_{ow} = 1.18 log k$^\circ$[d] + 0.36 R^2 = 0.980 n = 29	Sy·x = 0.15 α = 0.1%
4[a]	95:5 MeOH–H$_2$O	reverse-phase TLC	C$_{18}$	low K_{ow} = 4.52 R_m[e] + 5.79 R^2 = 0.90 n = 20	Sy·x = 0.51 3.2 × error in K_{ow}
this work	85:15 MeOH–H$_2$O	isocratic HPLC	C$_{18}$	low K_{ow} = 3.37 (log k') + 2.88 R^2 = 0.977 n = 12	$\overline{\Delta}$ log K_{ow} = 0.18 Sy·x = 0.25 1.8 × error in K_{ow}

[a] Regression curve for PCB congeners. [b] t_R = retention time of compound on RPHPLC system. [c] k' = (t_R – t_0)/t_0, where t_0 is the void volume. [d] k$^\circ$ is an extrapolation of K' to 100% aqueous mobile phase. [e] R_m = log (1/R_f – 1). [f] Average absolute error in log K_{ow} between curve calculated and literature-derived K_{ow} values. [g] Sy·x = standard error of estimate = (($\Sigma \Delta$ log K_{ow})^2/(n – 2))$^{1/2}$.

taining the desired solute. Water is then pumped through the column resulting in an aqueous solution in equilibrium with the octanol phase. This water is extracted on a C$_{18}$ column placed downstream of the generator column. This method has been used for the log K_{ow} determination of 10 PCB congeners with N_{Cl} = 1–3 (19). This method is experimentally limited to log K_{ow} values below 6 if the water is not saturated with octanol.

The indirect RPHPLC determination of PCB congener K_{ow} values in an Aroclor mixture is attractive for several reasons. The method is rapid, with elution of chlorinated biphenyls within minutes, and clean, since emulsion formation and other phase contaminations do not occur. In addition, quantitation of the compound(s) in either phase is not necessary, since log K_{ow} determination is only dependent on the compound retention time or a related parameter. The method is applicable to complex mixtures (i.e., an Aroclor), so that many K_{ow} values can be determined in one experimental run (18). Finally, when the method is coupled to high-resolution glass capillary GLC, it is limited only by the availability of K_{ow} values for highly hydrophobic molecules (log K_{ow} > 6). However, only a few accurate log K_{ow} values in this range are needed to establish a good calibration curve.

One disadvantage to the method is that it is indirect and is dependent on the accurate determination of K_{ow} values by direct methods. K_{ow} values for a number of compounds vary in the literature (1, 3, 4, 6, 17, 18, 21, 22). The other problem involves differences in the partitioning process of some PCB congeners on RPHPLC as a result of chlorine substitution. The mechanism of the C$_{18}$ stationary phase is not strictly analogous to octanol–water partitioning since octadecyl groups are chemically bonded in a monolayer to a silica support (23–26). The determination of K_{ow} values based on RPHPLC must therefore be interpreted carefully since the partitioning or adsorption (24, 26) of a particular solute on a reverse-phase system may differ from its octanol–water partitioning behavior.

Materials and Methods

A Waters Model 202 high-performance liquid chromatograph with U6K injector, 440 UV absorbance detector, and 6000A solvent pump was used for the RPHPLC. The column was an Altex Ultrasphere IPC$_{18}$, with a 4.6 mm i.d., and packed with 5-μm spherical particles.

The solvent for isocratic elution was 85% methanol in water. The methanol was MCB-Omnisolve chromatography grade, and the water was purified by a Milli-Q water purification system. This solvent was degassed before use by vacuum filtration. The flow rate through the system was 1.0 mL/min. This flow rate was checked daily, whenever the instrument was operated. Temperature was relatively constant at 17 °C.

Organic compounds for the calibration curve were obtained from Aldrich Chemical Co., Analabs, Mallinckrodt, and EPA Reference Standards repository. Individual PCB congeners were obtained from Analabs, and Aroclor 1242 and Aroclor 1254 were provided by Applied Science. All compounds were reported to be 99+% pure.

The calibration curve was constructed by injecting known amounts (100–1200 ppm) of the compound of interest to provide at least a 25% of scale deflection, while monitoring the UV spectra at 254 nm. The maximum scale setting was 0.1 absorbance unit. Capacity factors (k') were determined for each compound by using the relationship k' = (t_r – t_0)/t_0, where t_r is the compound retention time and t_0 is the retention time associated with the void volume. The t_0 value was obtained by measuring the retention time of formamide which is not retained by the reverse-phase column (17). At least five compounds were used for calibration whenever an experimental run was attempted.

Individual PCB standards were injected as described above, and their k' values were also determined. All of these standards were chromatographed at least twice.

One hundred microliters of either Aroclor 1242 (34 ppm) or 1254 (40 ppm) was injected into the HPLC and detected by UV absorption at 254 nm. The PCB's were unresolved, but the chromatogram established a "window" of time when elution of the PCB congeners occurred. Care was taken to include all of the time when UV absorbent material eluted. Aroclor 1242 eluted in the range 3–28 min, and the higher chlorinated biphenyls in Aroclor 1254 spanned 12–40 min. Eluent from the HPLC was sampled every 21 s (0.35 min) by using a fraction collector during the periods described above, resulting in a total of 72 and 78 fractions from liquid chromatography of Aroclor 1242 and 1254, respectively.

Following the HPLC step 3 mL of hexane and 1 mL of water were added to each fraction bottle and mixed by

Table II. Compounds and Data Used To Construct the log k' vs. log K_{ow} Calibration Curve

compound	n	$\bar{t}$, min[a]	S[b]	log k'	lit. log K_{ow}	ref	predicted log K_{ow} (est)[c]	Δ log K_{ow}[d]
formamide	6	2.40	0.013					
benzene	20	4.02	0.023	-0.171	2.11	17	2.25	0.14
toluene	6	4.90	0.058	0.018	2.69	17	2.89	0.20
naphthalene	4	5.60	0.026	0.125	3.36	17	3.26	0.10
fluorene	3	8.60	0.058	0.412	4.38	6	4.23	0.15
endrin	5	9.35	0.422	0.462	4.56	6	4.40	0.16
anthracene	11	9.60	0.191	0.477	4.54	17	4.45	0.09
pyrene	4	12.57	0.236	0.627	5.18	17	4.96	0.22
p,p'-DDT	10	13.82	0.644	0.677	5.57	17	5.13	0.44
2,2',4,5,5'-PCB	2	25.40	0.212	0.982	6.11	4	6.16	0.05
HCB	5	35.67	0.614	1.142	6.22	17	6.71	0.49
benzo[a]pyrene	3	29.73	1.33	1.056	6.50	3	6.42	0.08
benzo[ghi]perylene	3	44.37	1.63	1.243	7.10	3	7.05	0.05

[a] Average retention time. [b] Standard deviation of retention times. [c] log $K_{\mathrm{ow}} = 2.88 + 3.37$ (log k'). [d] Absolute difference in predicted and literature-derived log K_{ow} values. $\bar{\Delta}$ log $K_{\mathrm{ow}} = 0.18$, Sy·x = 0.25, and 0.488 at $\alpha = 0.05$.

using a vortex mixer for 30–45 s. An aliqout of the hexane layer was then removed for analysis by high-resolution glass capillary GLC.

A Hewlett-Packard Model 5840A GC with integrator, Model 7672A auto sampler, and 18835B capillary inlet system with an electron capture detector was used. The carrier gas was pure N_2 applied at a linear velocity of 30 cm/s. A fused silica SE-54 capillary column was used (25 m $\times$ 0.32 mm i.d.). The injector temperature was 230 °C and the detector 340 °C. Each run was initially isothermal at 150 °C for 4 min and then temperature programmed to 200 °C at 1 °C/min. A standard of either Aroclor 1242 or 1254 was included after every six sample runs depending on which mixture was being analyzed at that time.

The area counts of each GLC peak within a sample were recorded, and a chromatogram of area counts vs. retention time was constructed for each mixture. The reconstructed HPLC chromatogram for Aroclor 1242 is shown in Figure 2 (see also Figure 1). Samples where the maximum number of counts occurred for a given congener were used as the peak concentration, and k' determination was based on the retention time represented by that sample. For a given fraction, the middle of the sampling interval (0.175 min) where a peak occurred was used for k' determination. Retention time for a congener was determined in the following manner:

$$(R_0 - t_d) + 0.35(\text{fraction no.}) - 0.175 \qquad (1)$$

where R_0 is the initial collection time (3 or 12 min) and t_d is the total dead time.

As mentioned previously some GLC peaks contain more than one congener (13). When the congener percent composition data determined by Albro et al. (14, 15) for each of these GLC peaks was used, the congener with the highest composition was selected as the eluting compound. The criteria used were that the compound must be 3-fold higher in concentration than any other compound contained in that GLC peak. The other compound(s) in the peak was (were) not considered, since it was assumed that they either coeluted with the dominant compound or were at undetectable concentrations.

In certain cases, two peaks were clearly identifiable in the reconstructed HPLC chromatogram with the same GC retention time. This GC peak was invariably reported to contain more than one congener (13). In this case a tentative identification of the compounds was based on percent composition in the mixture and in two cases on congener structure. The structural influence on retention time will be discussed in the next section. In cases where only one HPLC peak eluted and a 3-fold difference between
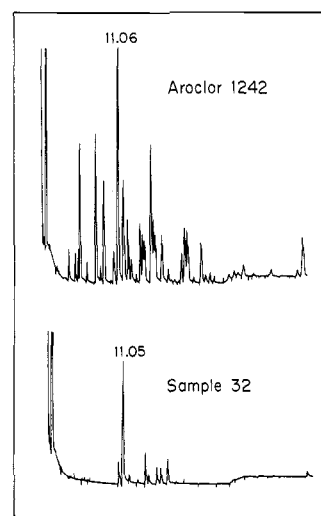

Figure 1. Comparison of Aroclor 1242 glass capillary GC chromatogram with the GC chromatogram from sample 32 eluted by RPHPLC of Aroclor 1242. To determine the number of area counts of the PCB congener 2,4,4'-TCB (11.06-min retention time), the peak in the sample at 11.05 min is identified as 2,4,4'-TCB and the number of area counts recorded. This particular sample corresponds to the circled point on the reconstructed liquid chromatogram in Figure 2. Note that several other PCB congeners are at various stages of elution in this sample.
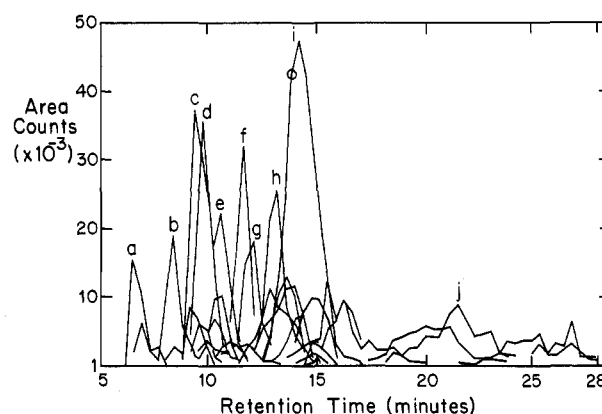

Figure 2. Reconstructed HPLC chromatogram of Aroclor 1242. (a) 2,2'-DCB; (b) 2,2',3-TCB; (c) 2,2',5-TCB; (d) 2,4'-DCB; (e) 2,2',4-TCB; (f) 2,2',3,5'-TeCB; (g) 2,3,4'-TCB; (h) 2,3,3'-TCB; (i) 2,4,4'-TCB; (j) 2,3',4,4'-TeCB.

compounds did not occur, both congeners were tentatively listed. This was often unnecessary for compounds present in both Aroclor mixtures, since one of the mixtures usually provided the required criteria for congener assignment.
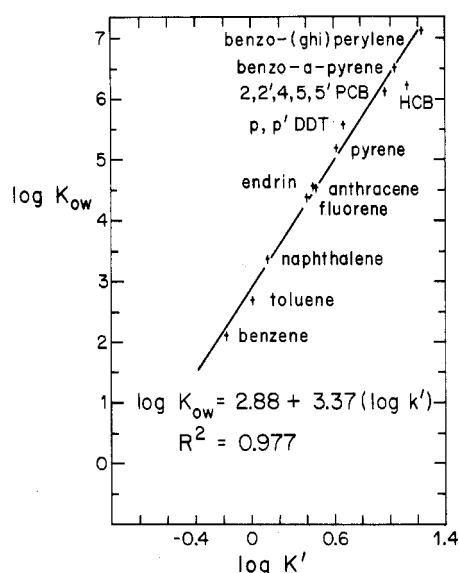
Figure 3. log K_{ow} vs. log k'.

Table III. Correlation of Congener log k' Values from Individual Determinations and from Aroclor Mixtures

compound	log k' of individual congener	log k' of 1242	log k' of 1254	SD of log k'	predicted log K_{ow} range[a]
2,4'	0.463	0.481		0.013	4.44–4.50
2,2',5	0.450	0.460		0.007	4.40–4.43
2,2',5,5'	0.672	0.652	0.662	0.010	5.08–5.15
2,2',4,5,5'	0.979	0.974	0.980	0.003	6.16–6.18
2,4,4'	0.700	0.679	0.662	0.019	5.11–5.24
2,3,6	0.537	0.487		0.035	4.52–4.67

[a] log K_{ow} range predicted from log k' values and regression eq 2.

Results and Discussion

The results from construction of the calibration curve are summarized in Table II. Figure 3 shows the calibration curve: log K_{ow} vs. log k'. The resulting linear regression equation is

$$\log K_{ow} = 2.88 + 3.37 \log k' \qquad (2)$$

The correlation coefficient is 0.977 and the standard error of estimate if 0.488 in log K_{ow} at the 95% confidence level.

The compounds used for the calibration curve are a heterogeneous group including benzene, toluene, six polycyclic aromatic hydrocarbons (PAH's), two aromatic chlorinated pesticides (HCB and p,p'-DDT), one PCB, and an alicyclic chlorinated pesticide, endrin. The variety of compounds should yield a curve that is unbiased toward a single group of compounds.

Two chlorinated aromatic compounds, p,p'-DDT and hexachlorobenzene, deviated markedly from the curve. We are not able to account for these differences, although literature K_{ow} values for these compounds can vary by more than an order of magnitude (4). We have noted differences in the behavior of some PCB congeners on RPHPLC, and some related differences may occur with other chlorinated compounds.

As was stated previously, it is difficult to obtain accurate K_{ow} values for highly hydrophobic molecules (log K_{ow} > 6) using liquid–liquid partitioning procedures. The literature K_{ow} values used in the calibration curve in this range are therefore somewhat less reliable than the lower K_{ow}'s. This could shift the calibration curve, resulting in slight changes in all predicted congener K_{ow} values, but
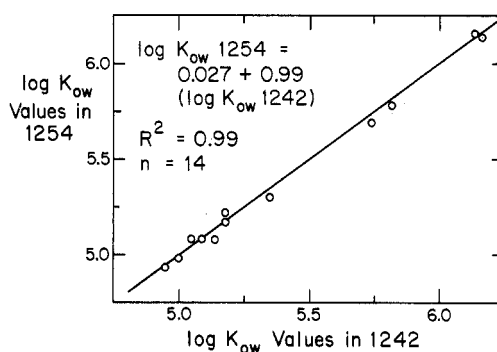

Figure 4. Comparison of congener log K_{ow} values obtained from both Aroclor 1242 and Aroclor 1254 mixtures.

Table IV. PCB log K_{ow} Values from Generator Column Data, Shake Flask Partitioning, and RPHPLC

congener	Woodburn[a]	Bruggeman[b]	Veith method[c]	this study
biphenyl	3.89		3.70	3.79
2-CBP	4.38	4.59	3.75	3.90
3-CBP	4.58	4.71	4.35	4.42
4-CBP	4.49	4.61	4.34	4.40
2,2'-DCB	4.90	5.00	3.55	3.63
2,4'-DCB	5.14		4.48	4.47
3,4-DCB	5.29		5.10	
4,4'-DCB	5.33	5.36	4.92	4.82
2,2',5-TCB	5.60		4.34	4.39
2,4',5-TCB	5.79		5.30	5.11
2,4,5-TCB	5.81		5.86	5.67

[a] Generator column (19). [b] Shake flask partitioning (23). [c] RPHPLC, determined by ref 19.

their relative position would be unchanged.

One of the major concerns of the experiment was that compounds might behave differently in a mixture than they would if injected individually on RPHPLC. For this reason, six standard PCB congeners were chromatographed for comparison to the elution of the same congeners in the Aroclor mixtures. Predicted log K_{ow} values (Table III) are well within the range permitted by statistical variation in the calibration curve. In addition when the log K_{ow} values of the congeners that are common to both Aroclor mixtures were plotted against each other, a straight line of slope 0.99 and intercept 0.03 resulted (Figure 4). Therefore, log K_{ow} values for all 14 common congeners could be predicted equally as well from either mixture.

With the k' data derived from experiments, log K_{ow} values were predicted for 58 PCB congeners found in the Aroclor 1242 and 1254 mixtures. Directly determined log K_{ow} values, reported for several PCB congeners, differed substantially from our results (19, 23). A comparison of these values appears in Table IV. The values reported by using the Veith et al. method (18) were determined by Woodburn (19) on a RPHPLC system. This procedure is very similar to that employed here, in that a reverse-phase column with an 85:15 MeOH–H₂O solvent mixture was used. The RPHPLC results for the 10 common compounds are very similar. Woodburn (19) measured log K_{ow} values using the generator column method, and Bruggeman et al. (23) used a shake flask partition method measuring concentrations in the octanol phase and toluene-extracted aqueous phase.

Woodburn (19) noted that most of the error found between the generator column and RPHPLC occurred for PCB congeners with chlorines ortho to the phenyl bridge position: that is, chlorines in the 2-, 2'-, 6-, and 6'-positions. He proposed an "ortho correction factor", to align HPLC values for these congeners with the generator column
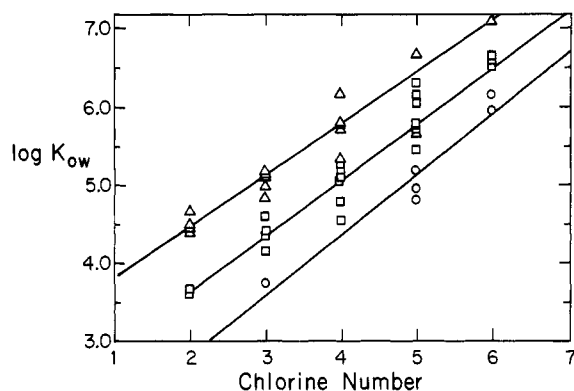
Figure 5. 2, 2,2′, and 2,2′,6 log K_{ow} values (eq 2) vs. chlorine number. Linear plots of log K_{ow} values calculated by using eq 2 vs. chlorine number for ortho-substituted congeners. (△) 2-substituted congeners, (□) 2,2′-substituted congeners, and (○) 2,2′,6-substituted congeners.

Table V. Regression Equations for RPHPLC-Determined log K_{OW} Values vs. Chlorine Number (Figure 5) for 2-, 2,2′-, and 2,2′,6-PCB Congeners

congener group	regression equation	R^2	$\Delta \log K_{ow}{}^a$	$Sy \cdot x$ standard error
2	$\log K_{ow} = 3.20 + 0.646(\text{Cl no.})$	0.92	0.14	0.21
2′,2	$\log K_{ow} = 2.25 + 0.704(\text{Cl no.})$	0.91	0.20	0.27
2,2′,6	$\log K_{ow} = 1.30 + 0.763(\text{Cl no.})$	0.93	0.19	0.27

[a] Average difference between log K_{ow} values predicted by eq 2 and log K_{ow} values predicted from the regression equations above.

values. The correction factor was determined by subtracting the log K_{ow} value from the RPHPLC method for 2-CBP (3.75) from the generator column value (4.38). This results in an ortho correction of 0.63 in log K_{ow}. Then, all non-ortho log K_{ow} values were adjusted and averaged to derive an inherent error in the RPHPLC method of 0.23 log K_{ow}. Thus, the "ortho only" correction is 0.40 log K_{ow} unit. This correction is then added to the HPLC calculated log K_{ow} value. When this correction was used only once for all congeners containing at least one ortho chlorine, the average absolute error in log K_{ow} dropped from 0.51 to 0.29. If this value is added for each ortho chlorine in a congener, the error drops to 0.22.

In matching our log K_{ow} estimates to those of the generator column, it is obvious that the ortho position causes an effect similar to the one described above. There is also very little difference between our RPHPLC determined values for biphenyl, 4-CBP, and 3-CBP when compared to generator column values.

The great majority of PCB congeners found in Aroclor 1242 and 1254 have at least one ortho chlorine. This is undoubtedly due to the ortho–para-directing property of the biphenyl system during PCB synthesis (24). For this reason it is not possible to check if the chlorine correction factor remains constant as the congener chlorine number increases, since there are few non-ortho compounds to standardize against. However, if all 2, 2,2′, and 2,2′,6 congener log K_{ow} values determined by RPHPLC are plotted separately vs. chlorine number, a correction factor is calculated for each ortho substitution, which depends on the total number of chlorines on biphenyl. Figure 5 is a group of linear plots of log K_{ow} vs. chlorine number for PCB congeners having 2, 2,2′, and 2,2′,6 substitutions. Table V is a summary of the regression equations and correlation coefficients obtained for each line in Figure 5.

Table VI. Correction Factors for Ortho Chlorine Substituted PCB Congeners

Cl no.	2 and 2′ ortho log units	6 ortho log units
1	0.69	
2	0.63	
3	0.58	0.57
4	0.51	0.51
5	0.46	0.45
6	0.41	0.39
7	0.34	0.34

For each chlorine number from 2 to 7, the predicted log K_{ow} value of the 2,2′-position congener is subtracted from the predicted value of the 2-position congener, giving a correction for the 2′-position. Predicted values are based on the linear estimate from the appropriate linear regression equation in Table V. In a similar manner, the log K_{ow} value for the 2,2′,6 congener is subtracted from that of the 2,2′ congener, yielding the 6-position congener correction. Since there are insufficient data for non-ortho PCB congeners, the correction value for the 2′-position is also used for the 2-position. This assumption seems especially valid since the 2′- and 6-position corrections are virtually identical for each chlorine number. For single chlorinated congeners the 2,2′ correction line is extrapolated to 1 chlorine (log K_{ow} = 2.95), and this value is subtracted from the monochlorinated value from the N_{Cl} = 2 line (log K_{ow} = 3.85).

Examination of the generator column data in Table IV illustrates that the log K_{ow} values for ortho-containing congeners are about 0.2 log unit below equivalent non-ortho congeners—for each ortho chlorine present. For example 2,2′-DCB (log K_{ow} = 4.90) is about 0.4 log unit below values for the non-ortho compounds 3,4-DCB and 4,4′-DCB (log K_{ow} = 5.29 and 5.33, respectively). The difference of 0.2 unit is subtracted from each ortho correction to adjust for the inherently lower log K_{ow} values of ortho compounds. All of the correction factor results are summarized in Table VI. Table VII contains the uncorrected HPLC log K_{ow} values and the final ortho-corrected log K_{ow} values for the 58 congeners.

The final correction factors corresponding to the congener chlorine number are than added for each ortho chlorine present in the congener. For example 2,2′,3,4′,6-penta-CB contains two ortho chlorines in the 2-position, and one ortho 6-position chlorine. The correction factors for a five-chlorinated congener are 0.46 for the 2-position chlorines and 0.45 for the 6-position. The value of log K_{ow} determined from RPHPLC (regression eq 2) is 4.94. Thus, the corrected value is 4.94 + 0.46(2) + 0.45 = 6.31.

What effect do the ortho corrections have on the disparity between our RPHPLC data and the generator column data? Without correction the average error ($\Delta \log K_{ow}$) in log K_{ow} is 0.58 for the nine common congeners. When corrected, the average error is reduced to 0.18 log K_{ow} unit. This corresponds to a standard deviation of 0.435 (in log K_{ow}) before correction and 0.18 after, or reduction from a 2.7-fold to a 1.5-fold error in K_{ow} value determination. We feel that this substantial improvement justifies the use of ortho correction of RPHPLC log K_{ow} values.

The one exception to this analysis comes from a small set of non-ortho congeners, present in the Aroclor mixtures. These are 3,3′,5 (log K_{ow} = 4.15), 3,4,4′ (log K_{ow} = 4.94), 3,3′,4,5′ (log K_{ow} = 6.08), and 3,3′,4,4′ (log K_{ow} = 5.62). The 3,3′,4,5′ congener is consistent with ortho correction, but the others are not. However, Brinkman and DeVries (27) found that 3,4,3′,4′-TeCB eluted similarly to several 2,2′

Table VII. Uncorrected log K_{ow} Values for PCB Congeners Based on Regression Equation 2 (See Figure 3) and the Final Corrected Values for 58 PCB Congeners

compound	systematic no.	% 1242	% 1254	RPHPLC uncorrected pred log K_{ow}	final corrected[g] low K_{ow}	lit. log K_{ow}
biphenyl[a]				3.79	3.79	3.89 (*19*)
2[a]	1			3.90	4.60	4.38 (*19*)
						4.59 (*23*)
3[a]	2			4.42	4.42	4.58 (*19*)
						4.71 (*23*)
4[a]	3			4.40	4.40	4.49 (*19*)
						4.61 (*23*)
2,2′	4	3.41		3.63	4.89	4.90 (*19*)
						5.00 (*23*)
2,4′	8	7.66		4.47	5.10	5.14 (*19*)
4,4′ [a]	15	0.84		4.82	4.82	5.33 (*19*)
						5.36 (*23*)
2,3′	6	1.06	0.05	4.39	5.02	
2,4[c]	7	0.89		4.67	5.30	5.15 (*23*)[f]
2,5[c]	9	0.26		4.67	5.30	5.18 (*23*)[f]
2,6[a]	10	0.11		4.05	5.31	
2,2′,5[b]	18	9.23	0.06	4.39	5.55	5.60 (*19*)
						5.64 (*23*)[f]
2,4′,5[c]	31	4.29	0.57	5.11	5.69	5.79 (*19*)
						5.77 (*23*)[f]
2,4,5	29			5.67	6.25	5.81 (*19*)
						5.77 (*23*)[f]
2,3,6	24			4.52	5.67	
2,2′,6	19	0.96		3.75	5.48	
2,2′,4[b]	17	2.88		4.60	5.76	
2,2′,3[b]	16	3.21		4.15	5.31	
2,4′,6[b]	32	2.12		4.60	5.75	
2,4,4′ [c]	28	13.12		5.11	5.69	5.74 (*23*)[f]
2,3,3′	20	3.59		4.99	5.57	
2,3,4′	22	2.60		4.84	5.42	
3,3′,5	36			4.15	4.15	
3,4,4′	37	1.59	0.16	4.94	4.94	5.90 (*23*)[f]
2,3′,5	26	0.54		5.18	5.76	
2,2′,5,5′	52	4.56	3.89	5.07	6.09	6.26 (*23*)[f]
2,2′,4,5′	49	3.67	1.47	5.20	6.22	
2,2′,4,4′	47	1.85	0.46	5.27	6.29	5.68 (*17*)
2,2′,3,5′	44	1.19		4.79	5.81	
2,2′,3,4	41	1.87		5.09	6.11	
2,2′,3,3′	40	0.17	0.23	4.54	5.56	
2,4,4′,5	74	2.26	0.27	6.16	6.67	
2,3′,4,4′	66	0.91	2.00	5.80	6.31	
2,3,4,4′	60	0.23		5.33	5.84	
2,3′,4′,5	70	1.24	4.24	5.72	6.23	6.39 (*23*)[f]
						5.95 (*17*)
3,3′,4,4′	77	0.43	0.11	5.62	5.62	
2,2′,3,4′,6	91		5.00	4.94	6.31	
2,2′,3,5′,6	95	0.66		5.18	6.55	
2,2′,4,5,5′	101	0.34	6.98	6.15	7.07	6.85 (*23*)[f]
2,2′,3,5,5′	92	0.15	0.63	6.05	6.97	
2,2′,4,4′,5	99	0.69	6.10	6.29	7.21	
2,2′,3′,4,5	97		2.59	5.75	6.67	
2,2′,3,4,5′	87	0.11	3.81	5.45	6.37	6.85 (*23*)[f]
2,2′,3,4,4′	85	0.50	2.15	5.69	6.61	
2,3′,4,5,5′	120	0.39	0.15	5.22	5.68	
2,3′,4,4′,5[d]	118		8.09	6.66	7.12	
2,2′,3,4′,5′,6[d]	149		3.96	6.14	7.28	
2,2′,4,4′,5,5′ [e]	153	0.03	3.67	6.93 (>6.89)	7.75	7.44 (*23*)[f]
						6.72 (*4*)
2,2′,3,4,4′,5[e]	137			>6.89	>7.71	
2,2′,3,3′,4,5′ [c]	130			6.57	7.39	
2,3,3′,5,5′,6[c]	165			6.57	7.37	
2,2′,3,4,4′,5	138	0.11	4.60	6.62	7.44	
2,2′,3,3′,4,5	129			6.50	7.32	
2,2′,3,3′,4,4′	128		1.45	6.14	6.96	7.44 (*23*)[f]
2,2′,3,3′,5,6′	135		0.22	5.94	7.15	
2,2′,3,3′,6,6′	136			4.91	6.51	
2,2′,3,3′,5,6,6′	179		0.68	6.77	8.13	
2,2′,3,3′,6	84	0.48	1.72	4.73	6.04	

[a] log K_{ow} determination by individual congener chromatography. [b] Compounds coelute on GLC but have different retention times on HPLC. [c] Compounds coelute on GLC and HPLC and have less than a 3-fold difference in percent composition. They are assigned the same log k'. [d] Tentatively identified compounds, due to ambiguity in GLC identification. [e] Compound maxima elute after 40-min collection time (Aroclor 1254). 2,2′,4,4′,5,5′ was measured individually. [f] log K_{ow} values for PCB congeners determined by experimentally determined Π_{Cl} values added to the log K_{ow} value for biphenyl. Π_{Cl} values were derived from direct measurements of mono- and dichloro PCB's. [g] When ortho correction factors are used, a sum of squares analysis (based on the standard error of prediction) of the regression lines in Figure 5 yields an overall standard error of 0.5–0.7 in log K_{ow} for each PCB congener.

congeners on silica gel, whereas 3,5,3′,5′ eluted much earlier.

There is no obvious reason for the ortho effect on RPHPLC and the less pronounced effect in octanol–water partitioning. Operationally, the ortho-chlorinated PCB congener becomes more polar. Restriction of rotation about the 1,1′ bond by opposing chlorines (i.e., 2,2′) (9–11, 27, 28) does not seem to explain why each ortho chlorine has an additive effect on log K_{ow} and on the reduction of RPHPLC retention time. Interestingly, the effect of the ortho position has been noted on other HPLC systems (23, 27, 28). Bruggeman et al. (23) noted a similar elution pattern with respect to ortho substitution of PCBs on their RPTLC system. Brinkman and DeVries (27) observed little or no effect of PCB planarity (i.e., restricted rotation) on silica gel retention but did observe an obvious increase in retention time (increased polarity) with ortho substitution. This increase was noted for 2, 2,2′, and 2,6,2′,6′ congeners compared to other PCB's with the same chlorine number. Experiments of Dekok et al. (28) produced similar results.

The fact that ortho-substituted PCB compounds behave atypically and cannot be accurately predicted from a correlation curve may be a function of the mechanism of RPHPLC. Horvath and Melander (24) and Telepchak (25) have concluded that the most likely mechanism for C_{18} HPLC is adsorption, rather than solvent–solute partitioning. The former study examines RPHPLC, recognizing that octadecyl groups are covalently bonded to a silica surface, reducing the number of translational and rotational degrees of freedom that an unbonded liquid phase would have.

For nonionized solutes in the same solvent, the main factors influencing retention are the extent of solute polarity and the size of the contact area between solute and the hydrocarbon ligand (24). Two possible explanations for the pronounced ortho effect on C_{18} are increased polarity due to ortho chlorine substitution or a decrease in contact area resulting from persistence of the biphenyl moiety in a nonplanar form. Nonplanarity increases with ortho substitution (11). Therefore, the increasing effect of ortho substitution might reflect a decrease in substrate–compound contact area and/or increased congener polarity.

One further effect was observed with PCB congeners containing 2,2′ substitutions. When these compounds contained a 3-position chlorine substituent, the retention time on RPHPLC was consistently lower than for congeners without this substitution. For 2,2′-substituted congeners, it was possible to predict the RPHPLC elution order for 13 out of 15 compounds, with a reversal in order for the other two. Compounds were ordered by the presence or absence of 3-position chlorines and a similar, less striking 5-position effect.

The reason for the 3-position effect appears to be a conformational one. It has been proposed that when a bulky substituent is introduced next to a large ortho group (2- or 6-position) in a biphenyl, the 3-position substituent exerts a steric, "pushing" effect on the proximate ortho group, thereby forcing it toward the 1,1′ bond. The ortho group will then interfere more strongly with the opposing (2′ or 6′) ortho group (11). The atomic radius of chlorine is compatible with such an effect (11). The net effect of this pushing is to force the compound into a more dominant nonplanar configuration. Since the congener becomes more nonplanar, its decreased elution time might be a function of reduced surface contact area. An additional 3-position addition (3′) and/or another ortho addition

would enhance this effect. This is evident, as is seen by the following:

	HPLC log K_{ow}		HPLC log K_{ow}
2,2′,3	4.2	2,2′,3,4,5′	5.5
2,2′,4	4.6	2,2′,3,4′,6	4.9
2,2′,3,4	5.1	2,2′,3,3′,6	4.7
2,2′,3,3′	4.5	2,2′,3,3′,6,6′	4.9
2,2′,4,5,5′	6.2		

It cannot be determined whether this 3-position effect is noticeable in directly determined partition coefficients, due to the lack of data at this time.

The obvious differences in the behavior of PCB congeners on RPHPLC lead to the following question: Are $k′$ values determined on RPHPLC better indicators of environmental behavior than congener K_{ow}'s?

Several studies have shown that natural organic matter adsorbs readily to inorganic particles (29–32) and exerts a substantial influence on the subsequent adsorption of other materials. Changes have been noted in the electrophoretic mobility (29, 33), ζ potential (29), and phosphate adsorption (29) of particles. In addition, recent investigations (29, 34) support a surface complexation mechanism between phenolic or carboxylic acid groups on organic molecules and hydroxyl groups on the metal oxide surface. Functional groups not included in complexation are largely protonated and uncharged after adsorption on geothite and alumina (29, 30).

The amount of surface coverage in natural systems is compatible with the quantity of coverage on ODS. Surface coverage of alumina by an organic fraction derived from lake water can be calculated from the data of Davis (29) in the following manner (from ref 35):

$$\alpha \ (\mu mol/m^2) = \frac{W}{M_r S} 1000 \qquad (3)$$

where W = weight of organic bound per weight of adsorbent (0.04 × 2), M_r = molar weight of the bound carbon (850), and S = specific surface area (120 m²/g). Assuming that M_r is an average of 850 (29) and that the amount of organic matter on the particles determined by TOC (4% by weight) is 50% of the total organic weight, then the calculated α is 0.8 $\mu mol/m^2$. Maximum surface coverage of alkyl-bonded phases are generally considered to be 2.9–3.4 $\mu mol/m^2$ (35). Therefore, about a 4-fold difference in surface coverage between the two systems exists. This difference is consistent with the larger area per molecule displaced by the higher molecular weight environmental organics and/or by increased steric effects with natural organics when compared to C_{18} molecules.

The evidence of surface complexation, relative neutrality of the adsorbed organic layer and the extent of surface coverage, suggests a similarity to the octadecyl groups attached to silica on ODS particles. There are undoubtedly differences in the nature of the organic phase covering the surfaces, especially due to the heterogeneity of natural organics; however, the relationship between $k′$ on ODS systems and environmental partition coefficients seems worthy of further investigation.

On the basis of this hypothesis environmental partition coefficients would be expected to decrease in the following order: non-ortho substituted > 2 substituted > 3,2′ substituted > 2,2′,6 substituted. In addition 2,2′,3-substituted compounds should have lower environmental partition coefficients than other PCB congeners.

Since changes in reverse stationary phase and eluting solvent will change $k′$ values (17), a calibration curve similar to one used in this study would be necessary to report

operational log K_{ow} values. These values should be comparable between different RPHPLC systems, since they would be based on compounds that provided a linear response when log K_{ow} is plotted vs. log k'. Bruggeman et al. (23) recommended the use of a relationship between log K_{ow} or capacity factor and the number of carbon atoms of components in an n-alkyl-substituted homologous series, for the determination of apparent log K_{ow} values.

Conclusions

(1) The elution behavior of PCB congeners on C_{18} RPHPLC is reproducible in Aroclor mixtures and virtually identical with the behavior of individually chromatographed congeners. (2) The atypical log K_{ow} values resulting from chromatography of ortho-substituted PCB congeners can be corrected for each ortho substitution, depending on the total congener chlorine number. (3) Chromatography of Aroclors 1242 and 1254 on RPHPLC coupled with high-resolution glass capillary gas chromatography enabled the calculation of K_{ow} values for 58 PCB congeners after ortho substitution correction. (4) A substantial reduction in RPHPLC elution time is evident with three chlorine substituted 2,2'-PCB congeners containing up to six chlorines. (5) Behavior of PCB congeners on RPHPLC may be useful in predicting individual congener partitioning in environmental systems.

Acknowledgments

Registry No. 2-CBP, 2051-60-7; 3-CBP, 2051-61-8; 4-CBP, 2051-62-9; 2,2'-DCB, 13029-08-8; 2,4'-DCB, 34883-43-7; 4,4'-DCB, 2050-68-2; 2,3'-DCB, 25569-80-6; 2,4-DCB, 33284-50-3; 2,5-DCB, 34883-39-1; 2,6-DCB, 33146-45-1; 2,2',5-TCB, 37680-65-2; 2,4',5-TCB, 16606-02-3; 2,4,5-TCB, 15862-07-4; 2,3,6-TCB, 55702-45-9; 2,2',6-TCB, 38444-73-4; 2,2',4-TCB, 37680-66-3; 2,2',3-TCB, 38444-78-9; 2,4',6-TCB, 38444-77-8; 2,4,4'-TCB, 7012-37-5; 2,3,3'-TCB, 38444-84-7; 2,3,4'-TCB, 38444-85-8; 3,3',5-TCB, 38444-87-0; 3,4,4'-TCB, 38444-90-5; 2,3',5-TCB, 38444-81-4; 2,2',5,5'-TeCB, 35693-99-3; 2,2',4,5'-TeCB, 41464-40-8; 2,2',4,4'-TeCB, 2437-79-8; 2,2',3,5'-TeCB, 41464-39-5; 2,2'3,4-TeCB, 52663-59-9; 2,2',3,3'-TeCB, 38444-93-8; 2,4,4',5-TeCB, 32690-93-0; 2,3',4,4'-TeCB, 32598-10-0; 2,3,4,4'-TeCB, 33025-41-1; 2,3',4',5-TeCB, 32598-11-1; 3,3',4,4'-TeCB, 32598-13-3; 2,2',3,4',6-penta-CB, 68194-05-8; 2,2',3,5',6-penta-CB, 38379-99-6; 2,2'4,5,5'-penta-CB, 37680-73-2; 2,2',3,5,5'-penta-CB, 52663-61-3; 2,2',4,4',5-penta-CB, 38380-01-7; 2,2',3',4,5-penta-CB, 41464-51-1; 2,2',3,4,5'-penta-CB, 38380-02-8; 2,2',3,4,4'-penta-CB, 65510-45-4; 2,3',4,5,5'-penta-CB, 68194-12-7; 2,3',4,4',5-penta-CB, 31508-00-6; 2,2',3,4',5',6-HCB, 38380-04-0; 2,2',4,4',5,5'-HCB, 35065-27-1; 2,2',3,4,4',5-HCB, 35694-06-5; 2,2',3,3',4,5'-HCB, 52663-66-8; 2,3,3',5,5',6-HCB, 74472-46-1; 2,2',3,3',4,5-HCB, 55215-18-4; 2,2',3,3',4,4'-HCB, 38380-07-3; 2,2',3,3',5,6'-HCB, 52744-13-5; 2,2',3,3'6,6'-HCB, 38411-22-2; 2,2',3,3',5,6,6'-hepta-CB, 52663-64-6; 2,2'3,3'6-penta-CB, 52663-60-2; Aroclor 1242, 53469-21-9; Aroclor 1254, 11097-69-1; biphenyl, 92-52-4; octanol, 111-87-5; water, 7732-18-5.

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