Updated Abraham Solvation Parameters for Polychlorinated Biphenyls

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This study shows that the recently published polychlorinated biphenyl (PCB) Abraham solvation parameters predict PCB air–*n*-hexadecane and *n*-octanol–water partition coefficients very poorly, especially for highly ortho-chlorinated congeners. Therefore, an updated set of PCB solvation parameters was derived from four PCB properties and associated Abraham solvation equations. Additionally, the influence of ortho-chlorination on PCB solvent accessible volume and surface area was investigated. The updated PCB solvation parameters were tested on partitioning between five other phase combinations. Compared to the original PCB solvation parameter set, the updated PCB solvation parameters resulted in substantially improved estimates from Abraham solvation equations for (subcooled) liquid vapor pressures, aqueous solubilities, HPLC capacity factors, and for coefficients of air–*n*-hexadecane, air–water, organic carbon–water, and *n*-octanol–water partitioning. For water to polydimethyl siloxane and sodium dodecylsulphate (SDS) partitioning, the updated PCB solvation parameters yielded no improvement compared to the original data set. The main difference between the updated and the original parameter set is that updated PCB McGowan specific volumes depend on the degree of ortho-chlorination, which is qualitatively confirmed by trends in the PCB solvent accessible volumes and surface areas. The use of the updated PCB solvation parameters instead of the original values is therefore recommended.

Introduction

For organic compounds, distribution over various environmental compartments is a key process in their transport and the environmental risk. At the molecular level, organic compounds interact with their direct environment by a variety of processes: nonspecific van der Waals interactions, dipolar interactions, and hydrogen bond formation. The so-called Abraham solvation equations are often used for the estima-

tion of the distribution coefficient (K) for any two-phase system:

$$\log K = c_1 + e_1 E + s_1 S + a_1 A + b_1 B + vV \tag{1}$$

$$\log K = c_2 + e_2 E + s_2 S + a_2 A + b_2 B + lL \tag{2}$$

In eqs 1 and 2, the capital letters are solute descriptors. The values of the solute descriptor coefficients vary with the phase system. Equation 1 is used mainly for condensed systems, whereas eq 2 is mostly used for gas–solvent partitioning. V is the McGowan characteristic volume [(dm^3 mol^{-1})/100], and L is the logarithm of the gas to hexadecane partition coefficient at 298 K. Both solute descriptors are some measure of the solute's potential for van der Waals interactions and solvent cavity formation. E is the solute excess molar refractivity [(dm^3 mol^{-1})/100] relative to an alkane with the same V; S is the solute dipolarity/polarizability; A and B are the solute overall hydrogen bond acidity and basicity. Values for V are calculated from atom increments (*1*), whereas values for L have to be determined experimentally. A close inspection of eqs 1 and 2 suggests that V should be related to L. An evaluation of a large data set of solute descriptors yielded the following relation (Michael H. Abraham, personal communication):

$$L = -0.882 + 1.183E + 0.839S + 0.454A + 0.157B + 3.505V \quad n = 4785, \, r^2 = 0.992,$$
$$F = 115279, \, \text{standard deviation} = 0.31 \tag{3}$$

Abraham and Al-Hussaini (*2*) recently published solvation parameters for PCBs. They calculated E values from chlorine fragment contributions. L values were obtained from GC retention indices and S and B were calculated from two chromatographic retention index data sets for a relatively small number of PCBs. An analysis of these solvation parameter data, however, reveals the following inconsistency between these solvation parameters. Whereas eq 3 predicts L for non-ortho PCBs within 0.25 log units, it poorly predicts L for ortho-chlorinated PCBs (Figure 1). For tetra-ortho-chlorinated PCBs, L is seriously overestimated by about 1.5 log units.

An analysis of log K_{ow} data also reveals a large deviation for highly ortho-chlorinated PCBs. Recently a compound-class specific PCB log K_{ow} structure–property relation was published (*3*) that predicts log K_{ow} within 0.12 log units on average.

$$\text{Log } K_{ow} = 0.088 + 0.562E - 1.054S - 3.46B + 3.814V \tag{4}$$

Substitution of the PCB solvation parameters in eq 4 (from ref *2*) results in non-ortho PCB log K_{ow} values that are close to those calculated from the PCB log K_{ow} structure–property relation. For tetra-ortho-chlorinated PCBs, however, prediction is poor (indicated for three PCBs from each ortho-chlorination class in Figure 1).

The PCB L values derived by Abraham and Al-Hussaini (*2*) from GC retention times show a strong dependence on the number of ortho-chlorines (N_{ortho}) besides the expected dependence on the total number of chlorines (N_{Cl}) (eq 5).

$$L = 6.14 + 0.71N_{Cl} - 0.37N_{ortho}$$
$$n = 208, \, r^2 = 0.98, \, \text{standard error} = 0.14 \tag{5}$$

The E, S, and B values derived by Abraham and Al-Hussaini (*2*) only slightly depend on N_{ortho}. Therefore, the large

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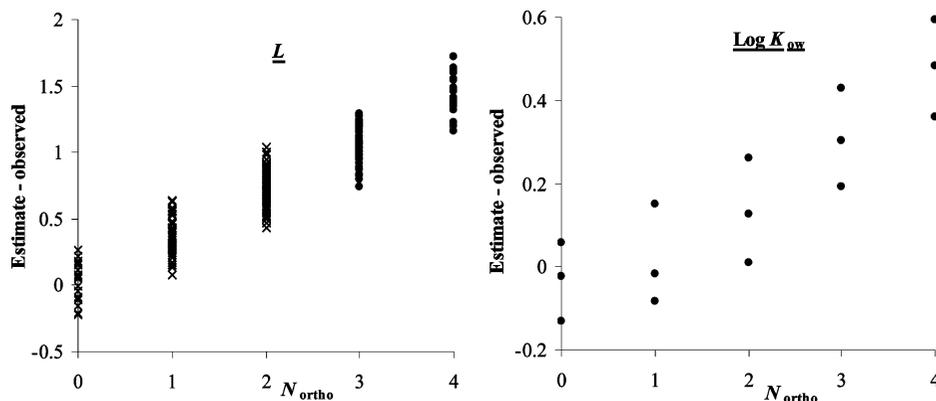† Deltares.
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FIGURE 1. Deviation plots for PCB air−n-hexadecane partition coefficients (L) and log K_{ow} values estimated using solvation parameters from Abraham and Al-Hussaini (*2*). N_{ortho} denotes the number of ortho-chlorines.

differences between estimated and observed L and log K_{ow} values for ortho-chlorinated PCBs suggest that V should decrease with increasing N_{ortho}. The procedure for the calculation of V from atom increments, however, does not account for ortho-chlorination effects. In this respect, it is interesting to note that already more than two decades ago, from the analysis of a small set of PCB log K_{ow} data, it was suggested (*4*) that the Leahy intrinsic volume, which is linearly correlated with the McGowan specific volume, is overestimated for highly chlorinated PCBs.

A close inspection of the B values derived by Abraham and Al-Hussaini (*2*) reveals another peculiarity. Namely, B for hexachlorobiphenyls is reported to be 0.07−0.11 and 0.02 for decachlorobiphenyl. For chlorobenzenes, however, B decreases by about 0.045 for each chlorine added and is zero for trichlorobenzenes. For chloronaphthalenes (*5*), B values show a similar rapid decrease on increasing chlorination: B decreases by about 0.065 for each chlorine added and is zero for the trichloronaphthalenes. Therefore, for PCBs, a similar rapid decrease would be more reasonable.

The increasing differences between Abraham solvation equation-estimated and observed partitioning data on increasing ortho-chlorination, and the relatively high B values for highly chlorinated PCBs derived by Al-Hussaini and Abraham suggest that a recalculation of PCB solvation parameters that also takes into account ortho-chlorination dependent McGowan specific volumes is necessary.

In this study, we recalculate PCB solvation parameters using four Abraham solvation equations, for log K_{ow}, the (subcooled) liquid vapor pressure (P_l), the (subcooled) liquid aqueous solubility (S_l), and for L. Abraham solvation equations for log S_l and log P_l are not available in literature and are derived in the present study. To independently explore the possible influence of ortho-chlorination on McGowan specific volumes, solvent accessible volumes and solvent accessible surface areas for PCBs with various degrees of ortho-chlorination are calculated in this study as well. The updated PCB solvation parameters are tested on Abraham solvation equations for air−water partitioning coefficients, sodium dodecyl sulfate−water partition coefficients, water-to-polydimethylsiloxane (PDMS) sorption coefficients, HPLC capacity factors, and organic carbon−water partition coefficients (K_{oc}).

Data Collection. For the derivation of the (subcooled) liquid vapor pressure and aqueous solubility solvation equations, data were collected from various sources. Alkylbenzene, chlorinated benzene, and polycyclic aromatic hydrocarbon (PAH) (subcooled) liquid vapor pressures were taken from the compilation in ref *6*. Liquid aqueous solubilities of alkylbenzenes and subcooled PAHs are from ref *7* and those for chlorinated benzenes are from ref *3*. Vapor pressures and aqueous solubilities of alcohols, amines, and nitro

compounds were taken from Quina et al. (*8*). Vapor pressures and aqueous solubilities of the other compounds are from Mackay et al. (*9*). Thus, 216 vapor pressure (range log P_l (Pa) of +5 to −5) and 127 aqueous solubility data (log S_l (mol m^{-3}) range of +4 to −4) for organic compounds up to high molecular weight PAHs were collected. They are listed in Table S-1 (Supporting Information). E, S, A, B, and V values were obtained from Abraham et al. (*10, 11*) and a recent revision of E, S, and A values for several compounds were obtained from Poole et al. (*12*).

Abraham Solvation Equations for Subcooled Liquid Vapor Pressure and Aqueous Solubility. Equations 1 and 2 are not applicable if one of the phases is the pure compound because in the pure (liquid) compound the interaction of the solute with itself will depend on the solute. Therefore, the coefficients e, s, a, and b will not be constant for such a system. To account for hydrogen bonding in the pure state, in eq 1 the product of A and B has to be added (eq 6). That will correct the variability in a (by xB), and b (by xA). Note that both a and b in eq 6 are zero in case of vapor pressures. In this case, the Abraham solvation equation is therefore:

$$\log K = c + eE + sS + aA + bB + \nu V + xAB \qquad (6)$$

For E and S, quadratic terms could have been added to eq 6 to correct for nonconstant e and s values. Initial fitting exercises, however, showed that these quadratic terms did not improve the fit. Quadratic E and S terms were, therefore, not included on the derivation of Abraham solvation equations for subcooled liquid vapor pressure and aqueous solubility.

For the vapor pressure P_l of liquid compounds, Quina et al. (*8*) derived an amended version of eq 6 using a large data set (log P_l (Pa) ranges from +5 to −1).

They added two solvation descriptors, λ and η, to minimize systematic differences between observed and predicted vapor pressures for alcohols, amines, nitro compounds, and alkylbenzenes. For the liquid aqueous solubility (S_l), a similar amendment is possibly needed. However, for PCBs, the additional Quina parameters are difficult to estimate and may only slightly affect the fit. Therefore, for the present purpose of deriving PCB solvation parameters, eq 6 will be the basis for the derivation of Abraham solvation equations for subcooled liquid vapor pressure and aqueous solubility.

Because the A times B term in eq 6 describes hydrogen-bonding interactions in the pure liquid, the value of x in the log P_l Abraham solvation equation should be identical to the one in the log S_l Abraham solvation equation. Therefore, pressure and solubility data were fitted together to the two Abraham solvation equations. This resulted in eqs 7 and 8 (standard deviations for the coefficients are given between brackets).

$$\log P_l(\text{Pa}) = 7.88(0.07) - 5.94(0.21)AB -$$
$$0.73(0.06)E - 2.03(0.08)S - 3.43(0.06)V \quad (7)$$
$$n = 216, \; r^2 = 0.994, \; \text{standard deviation} = 0.26$$

$$\log S_l(\text{mol m}^{-3}) = 3.60(0.11) - 5.94(0.21)AB -$$
$$0.58(0.09)E + 0.78(0.15)S + 3.56(0.23)A + 4.62(0.16)B -$$
$$4.34(0.11)V \quad n = 127, \; r^2 = 0.988,$$
$$\text{standard deviation} = 0.20 \quad (8)$$

From eqs 7 and 8, an Abraham solvation equation for the dimensionless air−water partition coefficient ($K_{\text{air−water}}$) (eq 9) can be calculated for comparison with the 298 K Abraham solvation equations for air−water partitioning derived by Abraham et al. (*10*) (eq 10) and by Goss (*13*) (eq 11).

$$\log K_{\text{air−water}} = 0.885 - 0.15E - 2.81S - 3.56A - 4.62B +$$
$$0.91V \quad (9)$$

$$\log K_{\text{air−water}} = 0.994 - 0.577E - 2.549S - 3.813A -$$
$$4.841B + 0.869V \quad (10)$$

$$\log K_{\text{air−water}} = 0.96 - 0.67E - 2.39S - 3.77A - 4.89B + 0.85V$$
$$(11)$$

Note that the *A*, *B*, *S*, and *V* coefficients in eqs 10 and 11 are numerically comparable to those in eq 9. The *E* coefficients in eqs 10 and 11 are quite different from the one in eq 9. However, that is of less importance because of the relatively small contribution of the *E* terms to log $K_{\text{air−water}}$. The numerical similarity of the coefficients in eqs 10 and 11 to eq 9 lends additional support to the validity of eqs 7 and 8.

With eqs 7 and 8, the applicability of the PCB solvation parameters derived by Abraham and Al-Hussaini (*2*) can now be tested on PCB subcooled liquid vapor pressure and aqueous solubility values calculated from compound-class-specific structure−property relationships derived by Van Noort (*3, 6*). For non-ortho and mono-ortho PCBs, it turned out that Abraham solvation parameters reasonably estimate both PCB properties (Figure 2). For highly ortho-chlorinated PCBs, however, estimation is poor: for tetra-ortho-chlorinated PCB log P_l values the deviation is about two log units. These deviations are similar to those for *L* and log K_{ow} (see before) and once more stress the need for an update of PCB solvation parameters.

Estimation of Updated PCB Solvation Parameters. To derive updated PCB solvation parameters, the fit to Abraham solvation equations for log P_l (Pa), log S_l(mol m^{-3}), log K_{ow}, and *L* values was optimized in three steps, by minimizing squared residuals using the Excel Solver package, for a group of 15 PCBs in which the chlorine substitution at non-ortho positions was not specified. This group contained three PCBs within each of the five ortho-chlorination subgroups. The

TABLE 1. Linear Dependence of PCB *E* and *S* Solvation Parameters on N_{Cl}

	E			*S*		
N_{ortho}	intercept	slope	r^2	intercept	slope	r^2
0	1.32	0.13	0.94	1.01	0.17	0.99
1	1.36	0.13	0.90	0.87	0.16	0.97
2	1.36	0.14	0.96	0.77	0.14	0.98
3	1.37	0.15	0.98	0.7	0.13	0.995
4	1.34	0.16	0.99	0.67	0.11	0.9999

three PCBs in each subgroup had the minimum, intermediate, and maximum possible number of chlorine substituents. Log P_l(Pa), log S_l(mol m^{-3}), and log K_{ow} values were calculated from the QSPRs derived by van Noort (*3, 6*). *L* values were from Al-Hussaini and Abraham (*2*).

B was assumed equal to $0.22 - 0.055N_{\text{Cl}}$, in which the N_{Cl} coefficient was arbitrarily taken equal to the average of the chlorine decrement for the *B* values of chlorobenzenes and chloronaphthalenes. For tetra- and higher chlorinated PCBs, *B* was taken zero. This procedure is slightly different from the earlier suggested procedure (*4*) of taking the average of *B* for each separate phenyl ring, because this neglects electron-withdrawing effects of the substituted second ring.

In the first step, an initial estimate of the linear dependence of *V* on N_{ortho} was made on the assumption that *E* and *S* are linearly related to N_{Cl} and N_{ortho}. For biphenyl, the experimental *E* and *S* values were taken. The average contribution of *m*- and *p*-chlorines used by Abraham and Al-Hussaini (*2*) was taken as the N_{Cl} coefficient in the linear equation for *E*. The sum of the squared differences between observed and predicted log P_l, log S_l, log K_{ow}, and *L* values for the 15 PCBs together was minimized by simultaneous variation of the N_{ortho} dependence of both *V* and *E*, and the N_{ortho} and N_{Cl} dependence of *S*. This resulted in a sum of squared differences of 1.41 and showed that for the calculation of *V*, ortho chlorines should count for only 30%.

In the second step, for each of the 15 PCBs separately, optimum values of *E* and *S* were determined using the N_{ortho} dependence of *V* determined in the first step. This reduced the sum of squared differences from 1.41 to 0.63. From these optimum values for the 15 PCBs, linear relations of *E* and *S* with N_{Cl} were derived for each ortho-chlorination group (Table 1). In the third and final step, the final dependence of *V* on N_{ortho} was determined (eq 12) using *E* and *S* values calculated from the data in Table 1. Updated solvation parameters for all PCBs are listed in Table S-2 (Supporting Information).
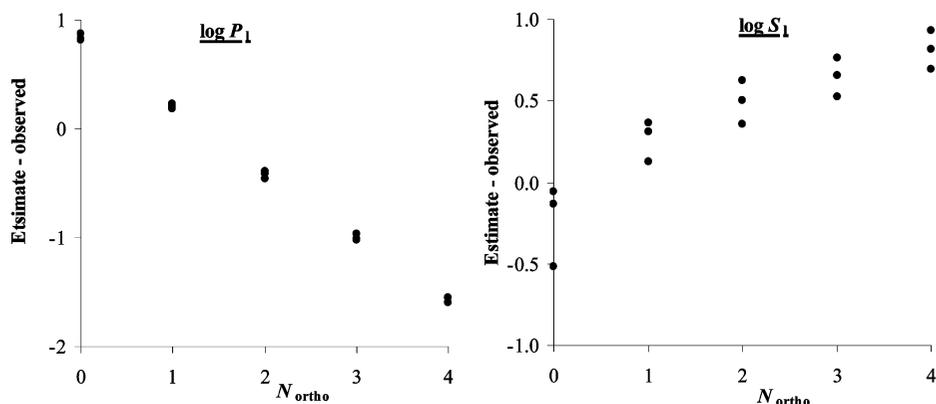

FIGURE 2. Deviation plots for the estimation of PCB subcooled liquid vapor pressure (Pa) and aqueous solubility (mol m^{-3}) from the PCB solvation parameters derived by Abraham and Al-Hussaini (*2*).

$$V = 1.324 + 0.1224(N_{Cl} - 0.71 N_{ortho}) \qquad (12)$$

The average absolute difference between estimates and observed log P_l, log S_l, log K_{ow}, and L values is 0.10, 0.14, 0.12, and 0.14, respectively, which is quite acceptable. Deviation plots are given in Figure 3. They illustrate that the strong dependence on N_{ortho} of differences between observed values and estimates using Abraham and Al-Hussaini's (*2*) original data set (see Figures 1 and 2) is almost completely removed using the updated PCB solvation parameters. The substantially reduced difference between estimated and observed values is mainly due to the introduction of the N_{ortho} dependence of V. This will be further explored, in the next section, by the examination of the dependence of solvent accessible surface areas and volumes on the degree of the PCB ortho chlorination.

PCB Solvent Accessible Surface Area and Volume. Solvent accessible volume (SAVOL) and solvent accessible surface area (SASA) for a range of PCBs were calculated with molecular modeling software (Hyperchem, v. 7.51, Hypercube Inc., Gainesville FL). Planar molecular models were geometrically optimized *in vacuo* with the Amber force field from Cornell et al. (*14*) applying a convergence limit of 0.04 kJ/mol. The atomic charges were subsequently calculated semiempirically with PM3 in Hyperchem. Torsion angles between rings were constrained at angles calculated at the density functional theory level from Dorofeeva et al. (*15*). The molecular structures were again optimized with the Amber force field. Values for SAVOL and SASA (Table 2) were calculated with the QSAR package in Hyperchem.

From the data in Table 2, it can be derived that the non-ortho PCB SASA increases by 26.2 Å² for the first chlorine added. For the next two non-ortho PCBs in the data set (which show increasing crowding of chlorines) the increase is 24.4 and 20.5 Å². For the 3 groups of ortho-chlorinated compounds with increasing crowding of the chlorine substituents (one without substituents at the 3, 4, and 5 positions, one with a

TABLE 2. Calculated Values of PCB Solvent Accessible Volume (SAVOL) and Solvent Accessible Surface Area (SASA) along with the Bond Torsion

substitution pattern	SAVOL (Å³)	SASA (Å²)	bond torsion (degrees)
none	544.68	349.74	38.5
4	588.66	375.92	38.3
3,4,4′	672.83	424.64	38.3
3,3′,4,4′,5,5′	792.56	486.07	37.9
2	585.93	377.48	56.0
2,2′	630.16	395.73	82.7
2,2′,6	663.99	409.49	90.8
2,2′,6,6′	697.24	422.77	90.0
2,3′,4,4′	716.78	448.14	55.7
2,2′,3,4,4′	753.88	465.40	83.0
2,2′,3,3′,4,6′	782.97	471.53	90.9
2,2′,3,3′,4,6,6′	816.62	486.84	90.4
2,3,3′,4,4′,5,5′	833.94	506.98	59.4
2,2′,3,3′,4,4′,5,5′	870.42	521.71	85.9
2,2′,3,3′,4,4′,5,5′,6	899.01	527.15	90.9
2,2′,3,3′,4,4′,5,5′,6,6′	929.67	538.96	90.0

3,4,4′ substitution pattern, and one with a 3,3′,4,4′,5,5′ substitution pattern) the increase is 14.8, 15.0, and 12.6 Å² for each chlorine added, respectively. That suggests that the contribution of ortho-chlorines to the SASA is 58−61% of the non-ortho-chlorine contribution. A similar analysis of the SAVOL data suggests that the ortho-chlorine contribution is 82 to 89% of the non-ortho-chlorine contribution to the SAVOL.

The McGowan specific volume is thought to account for energy costs associated with cavity formation as well as the energy gained by general nonspecific solute−solvent van der Waals forces. The first aspect is proportional to the SAVOL, whereas the second aspect is proportional to the SASA. The analysis above suggests that the PCB McGowan specific
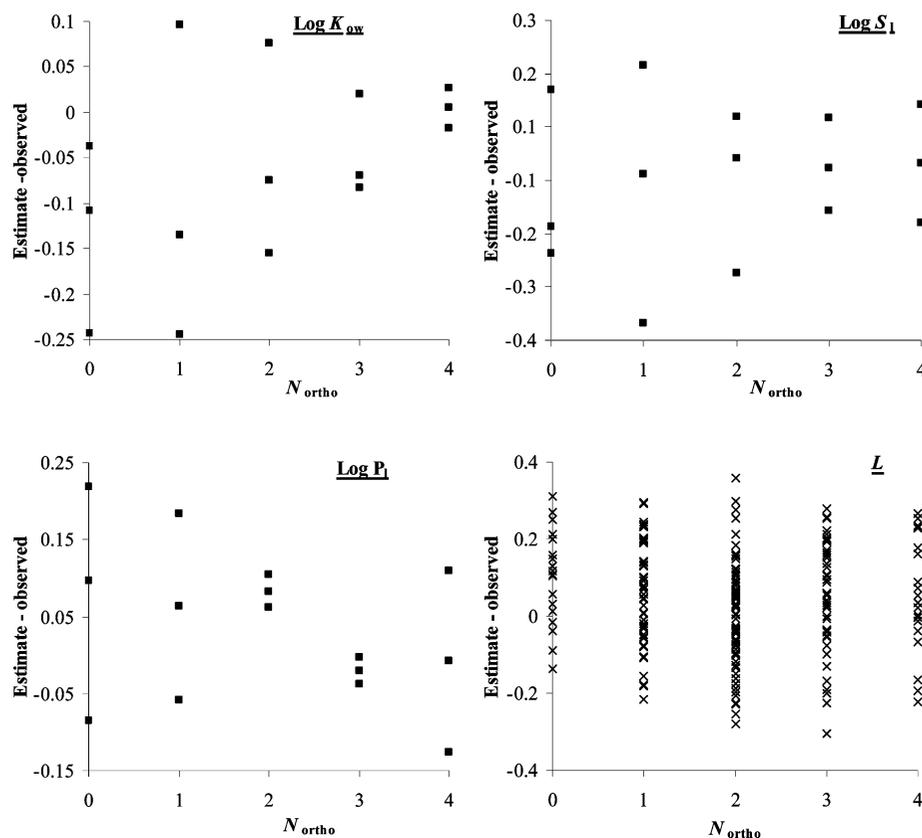

FIGURE 3. Deviation plots for log P_l, log S_l, L, and log K_{ow} estimated using the updated PCB solvation parameters.
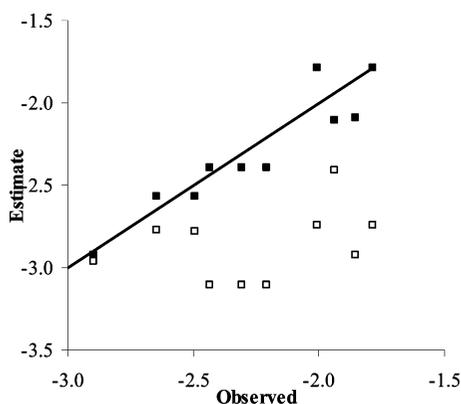
FIGURE 4. Estimated versus observed PCB log $K_{air-water}$ values at 293 K. Open symbols: solvation parameters from Abraham and Al-Hussaini (2). Closed symbols: solvation parameters from this study. The line represents $y = x$.
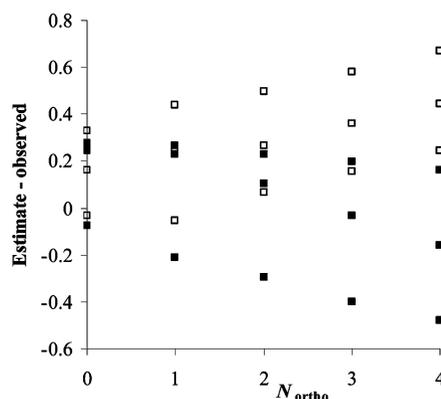

FIGURE 5. Deviation plot for PCB log K_{oc} values estimated using solvation parameters from Abraham and Al-Hussaini (2) (open symbols) and from this study (closed symbols).

volume V may substantially depend on the degree of ortho-chlorination, especially if general nonspecific solute−solvent van der Waals forces contribute to V. In the previous section, it was found that in the calculation of PCB V values, ortho chlorines should count for 29% of a non-ortho chlorine. One might speculate that the substantial dependence of PCB V values on N_{ortho} suggests that mainly general nonspecific solute−solvent van der Waals forces contribute to V.

Application of Updated Solvation Parameters to Various Phase Distributions. Recently, experimental mono- and di-ortho-chlorinated PCB log $K_{air-water}$ values at 293 K were published by ten Hulscher et al. (16), which were judged relatively accurate among a large number of experimental determinations using the gas-stripping method (17). Log $K_{air-water}$ values at 298 K can be estimated from the solvation equation given in eq 9. This equation will overpredict values at 293 K by 0.14 log units as can be derived from the temperature dependence of Henry's law constants using solvation equations reported by Goss (13). Figure 4 shows that the experimental 293 K log $K_{air-water}$ values are much better predicted using the updated PCB solvation parameters and the correction of 0.14 log units for the 298−293 K temperature difference than by using the original solvation parameter values. For the updated solvation parameters, the average difference between prediction and experimental values is 0.01; the average absolute difference is 0.13.

To test the updated PCB solvation parameters on the estimation of organic carbon−water partition coefficients (log K_{oc}), first a log K_{oc} Abraham solvation equation has to be derived. Recently, Niederer et al. (18) derived Abraham solvation equations for the Leonardite humic acid/air partition coefficient at various temperatures in terms of S, A, B, V, and L. From their experimental data for the Leonardite humic acid/water partition coefficient at 298 K (calculated from experimental humic acid/air partition coefficients and Henry's law coefficients) an Abraham solvation equation in terms of E, S, A, B, and V can be derived as well. To this data set, log K_{oc} values for thirteen 2- to 5-membered ring PAHs were added, because the original data set hardly contained data for highly hydrophobic compounds. These PAH log K_{oc} values were calculated from the QSPR derived by van Noort (7), which predicts PAH log K_{oc} up to a value of 6 within 0.11 log units on average. Table S-3 (Supporting Information) lists log K_{oc} values and solvation parameters used for the derivation of the log K_{oc} Abraham solvation equation. The resulting Abraham solvation equation is presented in eq 13.

$$\text{Log } K_{oc} = -0.42(0.14) + 0.53(0.08)E - 0.48(0.15)S - 0.28(0.14)A - 2.46(0.15)B + 3.25(0.10)V \quad n = 117,$$
$$r^2 = 0.967, \text{ standard error} = 0.27 \quad (13)$$

For the 15 PCBs used for the derivation of solvation parameters in this study, Figure 5 compares the deviations between estimates from eq 13 and log K_{oc} values calculated from the QSPR derived by van Noort (3) using updated solvation parameters from this study and solvation parameters from Abraham and Al-Hussaini (2). The average difference between estimates and QSPR calculated values is 0.00 using the updated solvation parameters, whereas it is 0.29 using the original values. The average absolute differences were 0.22 and 0.30, respectively. This shows that the updated PCB solvation parameters predict log K_{oc} values slightly better.

Opperhuizen (19) reported HPLC capacity factors for 57 organic compounds including 21 non-ortho to tetra-ortho-chlorinated PCBs. The average difference between observed capacity factors and estimated values from the Abraham solvation equation derived from the 36 non-PCB capacity factors was 0.00 and −0.22 log units using the updated solvation parameters and the original solvation parameters, respectively. The improvement for the average absolute differences between estimates and observed values was less: it was 0.31 log units for the updated parameters and 0.38 log units for the original parameters. The main advantage of the updated solvation parameters is that the bias in the capacity factors was removed.

For water to polydimethyl siloxane and sodium dodecyl sulfate (SDS) micelle partitioning, the updated PCB solvation parameters yielded no improvement at all compared to the original data set. From water-to-polydimethyl siloxane partition coefficients for 107 organic compounds including 16 PCBs, Sprunger et al. (20) derived an Abraham solvation equation. For PCBs, the average difference between experimental and predicted values from this solvation equation is −0.03 using the updated solvation parameters; the average absolute difference is 0.12. The fit does not deteriorate at all using the original PCB solvation parameters: the average difference between experimental and prediction is 0.01, the average absolute difference is 0.08. The Abraham solvation equation by Sprunger et al. (21) predicts the average PCB SDS micelle−water partitioning data from Dulfer (22), using the updated solvation parameters, with an average difference between experimental and predicted values of 0.20 log units and an average absolute difference of 0.28 log units. Using the original PCB solvation parameters, the average difference between experimental and predicted values is −0.08; the average absolute difference is 0.28.

Compared to the original PCB solvation parameter set, the updated PCB solvation parameters result in substantially improved estimates from Abraham solvation equations for (subcooled) liquid vapor pressures, aqueous solubilities, HPLC capacity factors, and for coefficients of air−n-hexadecane, air−water, organic carbon−water, and n-octanol−

water partitioning. For water to polydimethyl siloxane and sodium dodecyl sulfate (SDS) partitioning, the updated PCB solvation parameters yielded no improvement compared to the original data set. The main difference between the updated and the original parameter set is that updated PCB McGowan specific volumes depend on the degree of ortho-chlorination, which is qualitatively confirmed by trends in the PCB solvent accessible volumes and surface areas with increasing degree of ortho-chlorination. The use of the updated PCB solvation parameters instead of the original values in other Abraham solvation equations is therefore recommended.

Supporting Information Available

Tables with subcooled liquid vapor pressures, aqueous solubilities, and log K_{oc} values at 298 K and Abraham solvation parameters used for the derivation of Abraham solvation equations; a table with the updated solvation parameters for all 209 PCBs. This material is available free of charge via the Internet at http://pubs.acs.org.

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