# Estimating Octanol–Air Partition Coefficients of Nonpolar Semivolatile Organic Compounds from Gas Chromatographic Retention Times

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**Relative gas chromatographic retention times on a nonpolar stationary phase can be used to determine the octanol–air partition coefficient ($K_{OA}$) and the energy of phase transfer between octanol and the gas phase ($\Delta_{OA}U$) for semivolatile, nonpolar organic compounds. The only prerequisites are knowledge of the temperature-dependent $K_{OA}$ of a standard reference compound and directly measured $K_{OA}$ values at one temperature for a sufficient number of calibration compounds. It is shown that the technique is capable of predicting the $K_{OA}$ of polychlorinated benzenes, biphenyls and naphthalenes as well as polybrominated diphenyl ethers within the environmentally relevant temperature range with an average deviation from directly measured values of <0.2 log units.**

The octanol–air partition coefficients ($K_{OA}$) of organic compounds is increasingly used to describe the phase partitioning between the gas phase and a variety of organic phases of environmental relevance. These phases include urban aerosol particles,[1,2] plant cuticles,[3–5] soil organic matter,[6] and the organic film formed on urban impervious surfaces.[7] The usefulness of $K_{OA}$ is based on the assumption that the interaction between the organic chemicals and the environmental organic phases sufficiently resembles the interaction between the chemical and *n*-octanol.

The classical method for determining $K_{OA}$ values for semivolatile organic compounds is the generator column method by Harner and Mackay.[8] It has been used extensively to measure the $K_{OA}$ of chlorinated benzenes (CBzs),[8] biphenyls (PCBs),[8,9]

naphthalenes (PCNs),[10] dibenzo-*p*-dioxins and dibenzofurans,[11] polybrominated diphenyl ethers (PBDEs),[12] organochlorine pesticides,[13] and polycylic aromatic hydrocarbons.[10] Kömp and McLachlan[14] used a fugacity meter technique, a method similar to the generator column method, to measure $K_{OA}$ values for selected PCB congeners. Other methods for measuring $K_{OA}$ involve headspace gas chromatography,[15] headspace analysis by SPME fibers,[16] and gas chromatography on octanol-coated packed GC columns.[17,18] However, these latter methods tend to be limited to fairly volatile organic compounds. The generator column and fugacity meter techniques are applicable to semivolatile compounds and directly measure $K_{OA}$; however, these techniques are time-consuming, especially at low temperatures, and involve several analytical steps, such as the extraction of traps, concentration of analytes, and quantification against a calibration curve, which have the potential to introduce error to the measured $K_{OA}$ value. It would thus be desirable to have a method that allows the reliable estimation of $K_{OA}$ values from easily and reproducibly measured substance properties.

To address that need, Zhang et al.[19] suggested estimating $K_{OA}$ for semivolatile organic compounds from multiple linear regressions between previously reported $K_{OA}$ values and gas chromatographic capacity factors on a number of columns of variable polarity. Specifically, they applied this interpolation technique to the PCBs, predicting $K_{OA}$ for numerous congeners at 20 and 0 °C from the $K_{OA}$ for selected congeners previously reported by Harner et al.[6,8] Recently, Su et al.[20] applied the same technique to interpolate $K_{OA}$ values reported for the PCNs and the CBzs. They further showed how this method allows the determination of the enthalpies of octanol–air phase transfer, which in turn can be

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used to estimate $K_{OA}$ as a function of temperature. Although successfully applied to PCBs, PCNs and CBzs, this multicolumn method was found to have several drawbacks.[20] Specifically, the success of the method relies on the availability of a large and highly consistent set of $K_{OA}$ values for a group of structurally very similar substances. The regression equations are valid only within this group, and cannot be used for the prediction of $K_{OA}$ of structurally different compounds. In addition, if the elution order has not previously been established, determination of capacity factors on multiple gas chromatographic columns can be time-consuming.

Interestingly, the study by Su et al.[20] revealed that capacity factors on a single nonpolar gas chromatographic column were sufficient to explain much of the variability in the $K_{OA}$ of the PCNs and CBzs. The classical gas chromatographic retention time technique for the determination of the vapor pressure of nonpolar semivolatile organic compounds[21–23] generally also relies only on retention times on a single nonpolar column. This method, which uses the retention time of an analyte relative to that of a standard reference compound with well-established temperature-dependent vapor pressure, also was shown to be applicable to structurally quite diverse substances, as long as they were fairly nonpolar and as long as a calibration with independently derived vapor pressure data is performed.[23] A recent comparison of several vapor pressure estimation methods based on gas chromatographic retention times came to the conclusion that this method gives reliable results.[24]

Here, we set out to explore whether that method may also be applicable to the determination of $K_{OA}$ values of semivolatile, nonpolar organic substances. If a reliable $K_{OA}$ value is available for the same standard reference compounds used in the vapor pressure determination, no new measurements are required, but merely a reinterpretation of previously determined retention time ratios. The method was evaluated by estimating the $K_{OA}$ values for numerous semivolatile organic compounds, including selected CBzs, PCBs, PCNs, and PBDEs.

## THEORY

The retention time of a substance on a gas chromatographic column, $t_R$, is proportional to the equilibrium partition coefficient between stationary phase and the gas-phase $K_{SA}$.

$$t_R \propto K_{SA} \qquad (1)$$

For a compound i and a reference compound eluted on the same column, we can write

$$K_{SAi}/K_{SAref} = t_{Ri}/t_{Rref} \qquad (2)$$

If an appropriate stationary phase is selected, the partitioning equilibrium between stationary phase and gas phase may resemble the partitioning equilibrium between air and n-octanol. This assumes that the molecular interactions of the eluate with the chosen stationary phase are similar to that with octanol. Specifi-

cally, we can assume that the ratio of the activity coefficients of compound i and of the reference compound in pure octanol equals the ratio of the activity coefficients of these two compounds in the stationary phase,

$$\gamma_{Oi}/\gamma_{Oref} = \gamma_{Si}/\gamma_{Sref} \qquad (3)$$

or, in terms of equilibrium partition coefficients,

$$K_{OAi}/K_{OAref} = K_{SAi}/K_{Saref} \qquad (4)$$

On the basis of eqs 2 and 4, the octanol−air partition coefficients $K_{OA}$ of a compound i and of a reference compound should, thus, be related to their retention times $t_{Ri}$ and $t_{Rref}$ on the same GC column according to

$$K_{OAi}/K_{OAref} = t_{Ri}/t_{Rref} \qquad (5)$$

Equation 5 in logarithmic form is

$$\ln K_{OAi} = \ln K_{OAref} + \ln(t_{Ri}/t_{Rref}) \qquad (6)$$

Further, the van't Hoff equation expresses the temperature dependence of $K_{OA}$,

$$d \ln K_{OA}/dT = \Delta_{OA}U/(RT^2) \qquad (7)$$

where $\Delta_{OA}U$ is the internal energy of phase transfer between octanol and air, $R$ is the ideal gas constant, and $T$ is absolute temperature. Rewriting eq 7 for a substance i and a reference substance at the same temperature,

$$d \ln K_{OAi}/dT = \Delta_{OA}U_i/(RT^2)$$
$$d \ln K_{OAref}/dT = \Delta_{OA}U_{ref}/(RT^2)$$

that is, $d \ln K_{OAi} = (\Delta_{OA}U_i/\Delta_{OA}U_{ref}) \cdot d \ln K_{OAref}$. Assuming that the energies of phase transfer are independent of temperature in the temperature range of interest, which extends from the environmentally relevant range to the temperatures of the gas chromatographic runs, integration yields

$$\ln K_{OAi} = (\Delta_{OA}U_i/\Delta_{OA}U_{ref}) \cdot \ln K_{OAref} + C \qquad (8)$$

where $C$ is the constant of integration. Combining eqs 6 and 8 gives

$$\ln K_{OAref} + \ln(t_{Ri}/t_{Rref}) = (\Delta_{OA}U_i/\Delta_{OA}U_{ref}) \cdot \ln K_{OAref} + C$$

and after rearranging,

$$\ln(t_{Ri}/t_{Rref}) = (\Delta_{OA}U_i/\Delta_{OA}U_{ref} - 1) \cdot \ln K_{OAref} + C =$$
$$S \cdot \ln K_{OAref} + C \qquad (9)$$

A plot of $\ln(t_{Ri}/t_{Rref})$ versus $\ln K_{OAref}$ should give a straight line with intercept $C$ and slope $S = \Delta_{OA}U_i/\Delta_{OA}U_{ref} - 1$, where $t_{Ri}/t_{Rref}$

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is the relative retention time at the temperature where the reference compound has the octanol−air partition coefficient $K_{OAref}$. The $K_{OAi}$ of compound i at a reference temperature is then obtained by using eq 8, where $K_{OAref}$ is the $K_{OA}$ of the reference compound at that temperature. $\Delta_{OA}U_i/\Delta_{OA}U_{ref} = S + 1$ and $C$ are obtained from the slope and intercept of the regression on the basis of eq 9.

It is also possible to estimate $\Delta_{OA}U_i$ from the regressed slope $S$ of eq 9 and $\Delta_{OA}U_{ref.}$ using

$$\Delta_{OA}U_i = (S + 1)\cdot\Delta_{OA}U_{ref} \qquad (10)$$

## METHODS

**Determination of the $K_{OA}$ of the Standard Reference Compounds.** The compounds that have been most commonly employed as standard reference compounds in the GC retention time method for measuring the vapor pressure of semivolatile and nonpolar substances have been $p,p'$-DDT and the two long-chain alkanes $n$-octadecane (C-18) and eicosane (C-20). We chose to use the same chemicals and, additionally, hexachlorobenzene (HCBz) for this study, because it may allow the retrospective analysis of existing gas chromatographic retention times in terms of octanol−air partitioning. To serve as standard reference compounds, a substance has to fulfill two major conditions: it should be sufficiently similar to the compounds of interest for the assumption of eq 3 to be reasonable, and its $K_{OA}$ has to be known accurately as a function of temperature. The three reference compounds and all investigated compounds are nonpolar, semivolatile substances that should display similar interactions with nonpolar stationary phases. Whereas the $K_{OA}$ value of $p,p'$-DDT and HCBz had been measured previously,[13] no measurements for the $K_{OA}$ for C-18 and C-20 had been reported.

The $K_{OA}$ for C-18 and C-20 was measured at temperatures between 5 and 45 °C using the generator column technique as described by Shoeib and Harner.[13] Briefly, octanol-saturated nitrogen at a flow rate of 200−400 mL·min⁻¹ was passed through a generator column consisting of glass beads coated with an octanol solution of the target analyte. Equilibrated gas-phase chemicals that exit the column were trapped using $C_{18}$-bonded silica (IST Ltd, Glamoragn, U.K.). Various quality checks were performed to ensure complete extraction of chemical from the trap and to guarantee that there was no breakthrough of chemical. Sample volumes were determined by measuring flow rates at the exit of the trap. Concentrated trap extracts were analyzed using a Varian 3800 GC Saturn 2000 ion trap mass spectrometer. A DB-5 column (J&W Scientific, 30 m, 0.25-mm i.d., 0.25-$\mu$m film thickness) operated with UHP helium carrier gas at a flow of 1.3 mL·min⁻¹. The GC oven temperature program was as follows: 160 °C held for 1 min, ramped at 15 °C·min⁻¹ to 260 °C, held for 15 min. An autosampler Varian 8200 was used to inject 2 $\mu$L on splitless mode split after 1 min. The injector and transfer line were kept at 250 °C and 265 °C, respectively, whereas ion trap and manifold temperature were kept at 220 °C and 50 °C, respectively. Analysis was performed in EI-SIS mode. Retention time and the mass/charge of 71/57 (quantifier/qualifier) were used to identify and quantify both C-18 and C-20. Mirex was used as internal standard to correct for volume difference with mass/charge 272/274. Calibration standards for quantification were made from serial

**Table 1. Logarithm of the $K_{OA}$ of $n$-Octadecane and Eicosane as Determined by the Generator Column Technique (%RSD)**

|  | temp, °C | | | | |
| --- | --- | --- | --- | --- | --- |
|  | 5 | 15 | 25 | 35 | 45 |
| eicosane |  | 8.93 (26%) | 8.42 (35%) | 8.12 | 7.59 (23%) |
| $n$-octadecane | 8.65 |  | 7.87 | 7.38 (12%) | 6.95 |

dilutions of the mixed octanol solution used in the generator column, thereby eliminating the need to determine absolute concentrations.

**Determination of Retention Times.** The isothermal retention times of 15 PCN and 22 PBDE congeners on a dimethylpolysiloxane capillary column (0.32-mm i.d., 1.0-m length; DB-1, J&W Scientific Columns, Folsom, CA) relative to those of $p,p'$-DDT at a number of temperatures were taken from two previous studies aimed at estimating the subcooled liquid vapor pressure of these compounds.[25,26] For eight PCB congeners (4-monochlorobiphenyl (PCB-3), 4,4′-dichlorobiphenyl (PCB-15), 2,4,5-trichlorobiphenyl (PCB-29), 2,3,4,5-tetrachlorobiphenyl (PCB-61), 2,2′,5,5′-tetrachlorobiphenyl (PCB-52), 3,3′,4,4′-tetrachlorobiphenyl (PCB-77), 2,2′,4,5,5′-pentachlorobiphenyl (PCB-101), and 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB-153)), such retention times were determined using the same technique as described in these papers.[25,26] For all CBzs except monochlorobenzene, isothermal retention times on the same DB-1 column relative to those of C-18 and HCBz were determined at six temperatures between 60 and 110 °C, again using the same techniques as described previously. The injections were made in the split mode using a split of 1:10 and an injector temperature of 250 °C. The injected solutions contained between one and five substances in addition to the standard reference compounds. In each case, between two and six independent measurements of the retention time ratios were made.

**Data Analysis.** For all chemicals, $\ln(t_R/t_{Rref})$ was regressed against $\ln K_{OAref}$ according to eq 9, yielding a slope and an intercept. Using these regression parameters and eq 8, an octanol−air partition coefficient for these chemicals was calculated, which is referred to as $K_{OA-GC}$ in the remainder of the paper.

## RESULTS

$K_{OA}$ **of the Standard Reference Compounds.** The experimental values for the $K_{OA}$ of the two long-chain alkanes are listed in Table 1. Linear regression of the data yielded the following relationships:

C-18 $\quad \log K_{OA} = (3729 \pm 218)/(T/K) -$

$$(4.72 \pm 0.73) \quad r^2 = 0.993 \quad (11)$$

C-20 $\quad \log K_{OA} = (3952 \pm 316)/(T/K) -$

$$(4.79 \pm 1.05) \quad r^2 = 0.987 \quad (12)$$

The respective equations for $p,p'$-DDT and HCBz, taken from Shoeib and Harner,[13] are

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$p,p'$-DDT $\log K_{OA} = (4603 \pm 237)/(T/K) -$

$$(5.64 \pm 0.78)\ r^2 = 0.995\quad(13)$$

HCBz $\log K_{OA} = (2914 \pm 107)/(T/K) -$

$$(2.40 \pm 0.37)\ r^2 = 0.996\quad(14)$$

These four equations were used to calculate the $K_{OAref}$ of the standard reference compound as a function of temperature. Please note that a different relationship for the $K_{OA}$ of HCBz had been reported by Harner and Mackay.[8] The more recent data from ref 13 were considered more reliable.

From the slope of eqs 11 and 14, it is possible to estimate the internal energy of phase transfer $\Delta_{OA}U$ of the standard reference compounds over the temperature range 5−45 °C. They are 71.4 ± 4.2, 75.7 ± 6.1, 88.1 ± 4.5, and 55.8 ± 2.0 kJ·mol⁻¹ for C-18, C-20, $p,p'$-DDT, and HCBz, respectively.

**GC-Retention-Time-Derived Octanol−Air Partition Coefficients $K_{OA\text{-}GC}$.** Figure 1 shows an example of the relationships between the logarithm of the retention time ratio $\ln(t_R/t_{Rref})$ and the $\ln K_{OAref}$ of the standard reference compound (eq 9). All such relationships were highly linear with very high regression coefficients. $K_{OA\text{-}GC}$ values for all compounds were derived from similar plots and are listed in Tables 2 and 3. The $K_{OA\text{-}GC}$ values are given with a standard deviation, which is derived from averaging the results of between two and six separate $\ln(t_R/t_{Rref})$ vs $\ln K_{OAref}$ regressions. This standard deviation is very small because of the excellent reproducibility of gas chromatographic retention time measurements.

**Comparison and Calibration of $K_{OA\text{-}GC}$ with Directly Measured $K_{OA}$ Values Reported in the Literature.** For approximately one-half of the investigated compounds, directly measured $K_{OA}$ values have been reported. The $K_{OA\text{-}lit}$ values for these compounds, which were calculated from the $\log K_{OA}$ vs $1/T$ relationships reported in the respective references, are also listed in Tables 2 and 3.

For the compounds for which $p,p'$-DDT served as a reference compound (Table 2), deviations between $K_{OA\text{-}GC}$ and $K_{OA\text{-}lit}$ are on average 0.2 log units, and never larger than 0.55 log units. The discrepancies are higher for the PBDEs (0.34 log units on average) than for the other two compound groups (PCNs, 0.15 log units; PCBs, 0.16 log units). In the case of the 2,2′,4,5,5′-pentaCB and 2,2′,4,4′,5,5′-hexaCB, the $K_{OA\text{-}GC}$ is somewhat closer to the $K_{OA\text{-}lit}$ reported by Harner and Bidleman[9] than the $K_{OA\text{-}lit}$ by Kömp and McLachlan,[14] which are smaller than the $K_{OA\text{-}GC}$ by ∼0.25 log units. The deviations are not entirely random. For the compounds with a $\log K_{OA\text{-}lit} < 8$, $K_{OA\text{-}GC}$ is slightly higher than the $K_{OA\text{-}lit}$, whereas for compounds with $\log K_{OA\text{-}lit} > 9$, the $K_{OA\text{-}GC}$ tends to be smaller than the $K_{OA\text{-}lit}$.

Figure 2 plots the data from Table 2, that is, regresses the $K_{OA\text{-}GC}$ against $K_{OA\text{-}lit}$ for the compounds for which $p,p'$-DDT served as a reference. The plot confirms the strong correlation between GC-derived $K_{OA\text{-}GC}$ and the $K_{OA}$ values from the literature.

$\log K_{OA\text{-}lit} = (1.105 \pm 0.032)\cdot\log K_{OA\text{-}GC} -$

$$(0.86 \pm 0.29)\ n = 26,\ r^2 = 0.980\quad(15)$$

This relationship can be interpreted as a calibration of the GC-
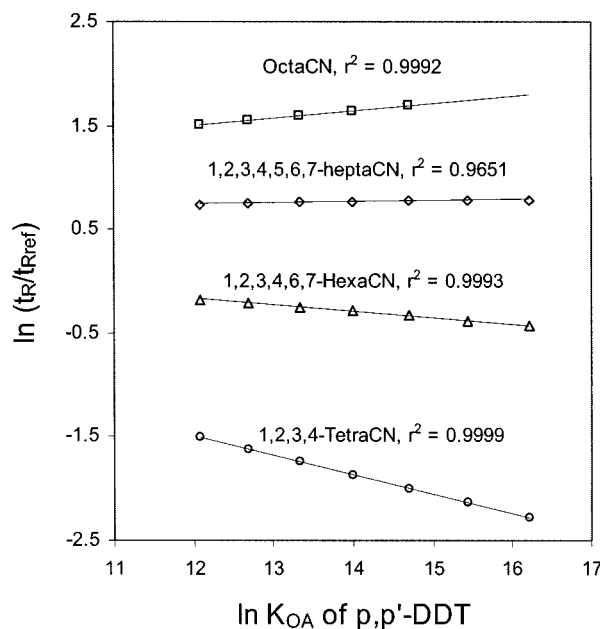


**Figure 1.** Linear relationships between the logarithm of the ratio of the retention times of four chlorinated naphthalenes to that of the standard reference compound $p,p'$-DDT at five to seven temperatures and the logarithm of the $K_{OA}$ value of $p,p'$-DDT at these temperatures as calculated from eq 13. The $K_{OA\text{-}GC}$ of the chlorinated naphthalenes can be obtained from the slope and intercept of these regressions.

derived $K_{OA\text{-}GC}$ data. With the help of that equation, the $K_{OA\text{-}GC}$ values can be corrected for the systematic deviations from directly measured $K_{OA}$ values. Calibrated $K_{OA\text{-}calc}$ values were obtained by substituting $\log K_{OA\text{-}calc}$ for $\log K_{OA\text{-}lit}$ in eq 15 and are also listed in Table 2. The standard deviation given for the $K_{OA\text{-}cal}$ values in that Table were derived from the standard error of the slope and intercept of the calibration eq 15 and the standard deviation of the $K_{OA\text{-}GC}$ values by error propagation. It is clear that the error, which is on the order of 5%, is dominated by the uncertainty of the coefficients in the calibration equation rather than by the uncertainty in the determination of $K_{OA\text{-}GC}$.

In the case of the CBzs, two sets of $K_{OA\text{-}GC}$ were derived on the basis of the use of the reference compounds C-18 and HCBz (Table 3). The $K_{OA\text{-}GC}$ values derived using HCBz as a reference are consistently higher than those derived using C-18 by ∼0.6 log units, showing that the value of $K_{OA\text{-}GC}$ depends on the standard reference compound. This had also been observed with the GC-based determination of vapor pressure.[22,23] A comparison shows that the $K_{OA\text{-}GC}$ for the CBzs derived with C-18 as reference are much closer to the $K_{OA\text{-}lit}$ values in ref 8 than the $K_{OA\text{-}GC}$ derived with HCBz as a reference. Whereas the latter are ∼0.1 log units lower, the former are 0.5 log units higher than the directly measured values. The respective calibration relationships are depicted in Figure 3 and read

HCBz $\log K_{OA\text{-}lit} = (1.056 \pm 0.081)\cdot\log K_{OA\text{-}GC} -$

$$(0.84 \pm 0.48)\quad n = 5,\ r^2 = 0.983\quad(16)$$

C-18 $\log K_{OA\text{-}lit} = (1.050 \pm 0.077)\cdot\log K_{OA\text{-}GC} -$

$$(0.15 \pm 0.41)\quad n = 5,\ r^2 = 0.984\quad(17)$$

The $K_{OA\text{-}calc}$ values obtained with these two equations are virtually

**Table 2. Uncalibrated ($K_{OA\text{-}GC}$) and Calibrated ($K_{OA\text{-}Cal}$) Octanol−Air Partition Coefficients for Various Halogenated Aromatic Compounds at 25 °C Determined from Gas Chromatographic Retention Times Using $p,p'$-DDT as a Reference, Octanol−Air Partition Coefficients from the Literature ($K_{OA\text{-}lit}$), and Energies of Phase Transfer, $\Delta_{OA}U$, Obtained from the Literature and Gas Chromatographic Retention Times**

| compd | log $K_{OA\text{-}GC}$ | log $K_{OA\text{-}cal}$ | log $K_{OA\text{-}lit}$[i] | $\Delta_{OA}U$, kJ·mol$^{-1}$ literature[i] | this study |
|---|---|---|---|---|---|
| | | | Chlorobiphenyls | | |
| 4-monoCB | 6.93 ± 0.02 | 6.80 ± 0.37 | 6.77,[a] 6.82,[c] 6.85,[h] 6.79*[f] | 75.9,[a] 66.4,[c] 66.7*[f] | 54.9 ± 2.9 |
| 4,4'-diCB | 7.77 ± 0.01 | 7.73 ± 0.39 | 7.66,[a] 7.65*[f] | 72.6,[a] 75.9*[f] | 66.2 ± 3.4 |
| 2,4,5-triCB | 8.03 ± 0.01 | 8.01 ± 0.39 | 7.95,[a] 7.80*[f] | 72.6,[a] 84.3*[f] | 69.3 ± 3.6 |
| 2,3,4,5-tetraCB | 8.75 ± 0.01 | 8.80 ± 0.41 | 8.73,[a] 8.64*[f] | 66.3,[a] 96.6*[f] | 76.9 ± 4.0 |
| 2,2',5,5'-tetraCB | 8.44 ± 0.02 | 8.47 ± 0.40 | 8.22,[d] 8.27*[f] | 83.1,[d] 74.4*[f] | 74.6 ± 3.9 |
| 3,3',4,4'-tetraCB | 9.19 ± 0.01 | 9.29 ± 0.42 | 9.70,[c] 9.68*[f] | 73.3,[c] 79.7*[f] | 81.4 ± 4.2 |
| 2,2',4,5,5'-pentaCB | 9.05 ± 0.00 | 9.14 ± 0.41 | 9.06,[c] 8.78,[d] 9.06*[f] | 73.5,[c] 83.5,[d] 74.4*[f] | 80.6 ± 4.2 |
| 2,2',4,4',5,5'-hexaCB | 9.65 ± 0.01 | 9.80 ± 0.43 | 9.73,[c] 9.37,[d] 9.75*[f] | 89.9,[c] 84.8,[d] 79.7*[f] | 86.5 ± 4.5 |
| | | | Chloronaphthalenes | | |
| 1,2-diCN | 7.01 ± 0.03 | 6.89 ± 0.37 | 6.76*[g] | 66.0*[g] | 58.9 ± 3.1 |
| 1,4-diCN | 6.91 ± 0.01 | 6.78 ± 0.37 | 6.92[b] | 62.2[b] | 56.9 ± 2.9 |
| 1,2,3-triCN | 7.72 ± 0.00 | 7.66 ± 0.38 | 7.62*[g] | 73.2*[g] | 66.1 ± 3.4 |
| 1,2,3,4-tetraCN | 8.29 ± 0.00 | 8.30 ± 0.40 | 8.33*[g] | 79.5*[g] | 71.5 ± 3.7 |
| 1,2,3,5-tetraCN | 8.28 ± 0.00 | 8.29 ± 0.40 | 8.26*[g] | 79.1*[g] | 71.6 ± 3.7 |
| 1,2,4,7-tetraCN | 8.14 ± 0.01 | 8.13 ± 0.39 | 8.08[b] | 76.6[b] | 70.2 ± 3.6 |
| 1,2,3,4,6-pentaCN | 8.85 ± 0.01 | 8.92 ± 0.42 | 8.90[b] | 88.6[b] | 77.1 ± 4.0 |
| 1,2,3,5,7-pentaCN | 8.76 ± 0.01 | 8.82 ± 0.41 | 8.72[b] | 84.1[b] | 76.3 ± 3.9 |
| 1,2,3,5,8-pentaCN | 9.01 ± 0.00 | 9.10 ± 0.41 | 9.12[b] | 89.7[b] | 78.6 ± 4.1 |
| 1,2,3,4,6,7-hexaCN | 9.45 ± 0.00 | 9.58 ± 0.42 | 9.69[b] | 95.8[b] | 82.6 ± 4.3 |
| 1,2,3,5,6,7-hexaCN | 9.45 ± 0.00 | 9.58 ± 0.42 | 9.69[b] | 95.8[b] | 82.6 ± 4.3 |
| 1,2,3,5,7,8-hexaCN | 9.53 ± 0.01 | 9.67 ± 0.42 | 9.82[b] | 94.0[b] | 83.2 ± 4.3 |
| 1,2,4,5,6,8-hexaCN | 9.55 ± 0.00 | 9.69 ± 0.42 | 9.88[b] | 94.3[b] | 83.5 ± 4.3 |
| 1,2,3,4,5,6,7-heptaCN | 10.18 ± 0.00 | 10.38 ± 0.44 | 10.63*[g] | 99.5*[g] | 89.0 ± 4.6 |
| octaCN | 10.78 ± 0.01 | 11.05 ± 0.45 | 11.48*[g] | 106.6*[g] | 94.3 ± 4.9 |
| | | | Bromodiphenyl Ethers | | |
| 2-monoBDE | 7.34 ± 0.01 | 7.24 ± 0.38 | | | 61.9 ± 3.2 |
| 3-monoBDE | 7.44 ± 0.01 | 7.36 ± 0.38 | | | 63.6 ± 3.3 |
| 2,4-diBDE | 8.36 ± 0.01 | 8.37 ± 0.40 | | | 73.6 ± 3.8 |
| 3,4-diBDE | 8.52 ± 0.00 | 8.55 ± 0.40 | | | 75.3 ± 3.9 |
| 2,6-diBDE | 8.13 ± 0.01 | 8.12 ± 0.39 | | | 71.3 ± 3.7 |
| 4,4'-diBDE | 8.60 ± 0.01 | 8.64 ± 0.40 | | | 76.1 ± 3.9 |
| 2,4'-diBDE | 8.45 ± 0.00 | 8.47 ± 0.40 | | | 74.6 ± 3.8 |
| 3,4'-diBDE | 8.54 ± 0.01 | 8.57 ± 0.40 | | | 75.6 ± 3.9 |
| 2,3,4-triBDE | 9.37 ± 0.01 | 9.49 ± 0.42 | | | 83.2 ± 4.3 |
| 2,4,6-triBDE | 8.94 ± 0.01 | 9.02 ± 0.41 | | | 79.2 ± 4.1 |
| 3,3',4-triBDE | 9.48 ± 0.00 | 9.61 ± 0.42 | | | 84.5 ± 4.4 |
| 2,4',6-triBDE | 9.18 ± 0.00 | 9.28 ± 0.42 | | | 81.4 ± 4.2 |
| 3,4,4'-triBDE | 9.54 ± 0.01 | 9.68 ± 0.42 | | | 84.9 ± 4.4 |
| 2,3',4,6-tetraBDE | 10.04 ± 0.02 | 10.23 ± 0.44 | | | 89.2 ± 4.6 |
| 2,4,4',6-tetraDE | 9.95 ± 0.01 | 10.13 ± 0.43 | | | 88.3 ± 4.6 |
| 2,2',4,4'-tetraBDE | 10.14 ± 0.01 | 10.34 ± 0.44 | 10.53[e] | 97.0[e] | 90.1 ± 4.7 |
| 2,3',4,4'-tetraBDE | 10.28 ± 0.02 | 10.49 ± 0.44 | 10.82[e] | 106.8[e] | 91.6 ± 4.8 |
| 3,3',4,4'-tetraBDE | 10.46 ± 0.02 | 10.70 ± 0.45 | 10.87[e] | 94.5[e] | 93.4 ± 4.8 |
| 2,2',4,4',5-pentaBDE | 10.99 ± 0.01 | 11.28 ± 0.46 | 11.32[e] | 91.1[e] | 98.5 ± 5.1 |
| 2,2',3,3',4-pentaDE | 10.86 ± 0.01 | 11.14 ± 0.46 | | | 97.2 ± 5.0 |
| 2,3',4,4',6-pentaDE | 11.20 ± 0.01 | 11.52 ± 0.46 | | | 100.0 ± 5.2 |
| 2,2',4,4',5,5'-hexaBDE | 11.78 ± 0.02 | 12.15 ± 0.48 | 11.82[e] | 98.2[e] | 105.7 ± 5.5 |

[a] Ref 8. [b] Ref 10. [c] Ref 9. [d] Ref 14. [e] Ref 12. [f] Derived from data reported in ref 19. [g] Ref 20. [h] Ref 13. [i] Those values with an asterisk (*) were determined indirectly by interpolating regression using gas chromatographic capacity factors.

identical (Table 3). The relatively high estimated standard errors of the $K_{OA\text{-}calc}$ for the CBzs of 10 to 14% are due to the small number of compounds used in the derivation of eqs 16 and 17, and not due to a poor relationship between $K_{OA\text{-}GC}$ and $K_{OA\text{-}lit}$, as can be seen in Figure 3 and is evident from the high $r^2$ values.

The large discrepancy between $K_{OA\text{-}GC}$ obtained with HCBz as a reference and $K_{OA\text{-}lit}$ is somewhat surprising considering the smaller deviations observed for $K_{OA\text{-}GC}$ values obtained with C-18 and $p,p'$-DDT as a reference. This suggests that the condition of eq 3 is not fulfilled well for HCBz and the CBzs; i.e., the ratio of the activity coefficients of the not fully chlorinated CBzs and HCBz

in pure octanol does not equal the ratio of the activity coefficients in the DB-1 stationary phase. Whereas that may be appear peculiar, the octanol−air partition coefficient as well as the subcooled liquid vapor pressure of HCBz does, indeed, seem to be unusual when compared to the other CBzs. Simple linear regressions between size-related molecular descriptors, such as molar mass or the number of chlorine substituents, and log $K_{OA}$ and log $P_L$ for the chlorinated benzenes suggests that the $P_L$ for HCBz is unusally low and the $K_{OA}$ for HCBz unusually high by the same extent. For that reason, the $K_{OA\text{-}lit}$ for HCBz was also not included in the regression eq 17. We therefore believe that

**Table 3. Uncalibrated ($K_{OA\text{-}GC}$) and Calibrated ($K_{OA\text{-}cal}$) Octanol−Air Partition Coefficients for the Chlorinated Benzenes at 25 °C Determined from Gas Chromatographic Retention Times Using Either Hexachlorobenzene (HCBz) or n-Octadecane (C-18) as a Reference, Octanol−Air Partition Coefficients from the Literature ($K_{OA\text{-}lit}$), and Energies of Phase Transfer $\Delta_{OA}U$ Obtained from the Literature and Gas Chromatographic Retention Times**

| compd | log $K_{OA\text{-}GC}$ | | log $K_{OA\text{-}cal}$ | | log $K_{OA\text{-}lit}$[a] | $\Delta_{OA}U$, kJ·mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| reference | HCBz | C-18 | HCBz | C-18 | | literature | HCBz | C-18 |
| 1,2-diCBz | 4.96 ± 0.02 | 4.33 ± 0.00 | 4.40 ± 0.63 | 4.39 ± 0.53 | 4.33[b] | 49.3[b] | 29.0 ± 1.3 | 28.2 ± 1.7 |
| 1,3-diCBz | 4.82 ± 0.00 | 4.23 ± 0.01 | 4.25 ± 0.62 | 4.29 ± 0.52 | 4.13*[c] | 57.0*[c] | 25.9 ± 0.9 | 27.1 ± 1.7 |
| 1,4-diCBz | 4.83 ± 0.00 | 4.25 ± 0.01 | 4.27 ± 0.62 | 4.32 ± 0.52 | 4.18*[c] | 55.6*[c] | 26.0 ± 0.9 | 27.9 ± 1.7 |
| 1,2,3-triCBz | 5.58 ± 0.01 | 4.96 ± 0.00 | 5.06 ± 0.66 | 5.06 ± 0.56 | 5.16[b] | 55.7[b] | 35.7 ± 1.3 | 35.7 ± 2.1 |
| 1,3,5-triCBz | 5.31 ± 0.00 | 4.69 ± 0.00 | 4.77 ± 0.64 | 4.77 ± 0.54 | 4.64*[c] | 68.6*[c] | 32.6 ± 1.2 | 32.3 ± 1.9 |
| 1,2,4-triCBz | 5.46 ± 0.00 | 4.84 ± 0.00 | 4.93 ± 0.65 | 4.93 ± 0.55 | 4.84*[c] | 62.1*[c] | 34.3 ± 1.3 | 34.1 ± 2.0 |
| 1,2,3,4-tetraCBz | 6.22 ± 0.00 | 5.60 ± 0.00 | 5.73 ± 0.70 | 5.73 ± 0.59 | 5.61[b] | 62.3[b] | 44.1 ± 1.6 | 43.9 ± 2.6 |
| 1,2,4,5-tetraCBz | 6.07 ± 0.01 | 5.45 ± 0.00 | 5.57 ± 0.69 | 5.57 ± 0.58 | 5.65[b] | 60.8[b] | 42.3 ± 1.6 | 42.2 ± 2.5 |
| 1,2,3,5-tetraCBz | 6.06 ± 0.00 | 5.44 ± 0.01 | 5.56 ± 0.69 | 5.56 ± 0.58 | 5.53*[c] | 66.3*[c] | 42.2 ± 1.5 | 42.0 ± 2.5 |
| pentaCBz | 6.75 ± 0.01 | 6.13 ± 0.00 | 6.29 ± 0.73 | 6.29 ± 0.62 | 6.28[b] | 71.3[b] | 49.7 ± 1.8 | 49.6 ± 2.9 |
| hexaCBz | | 6.77 ± 0.02 | | (6.95 ± 0.66) | 7.38[d] | 55.8[d] | | 55.6 ± 3.3 |

[a] Those values with an asterisk (*) were determined indirectly by interpolating regression using gas chromatographic capacity factor. [b] ref 8. [c] ref 20. [d] ref 13.
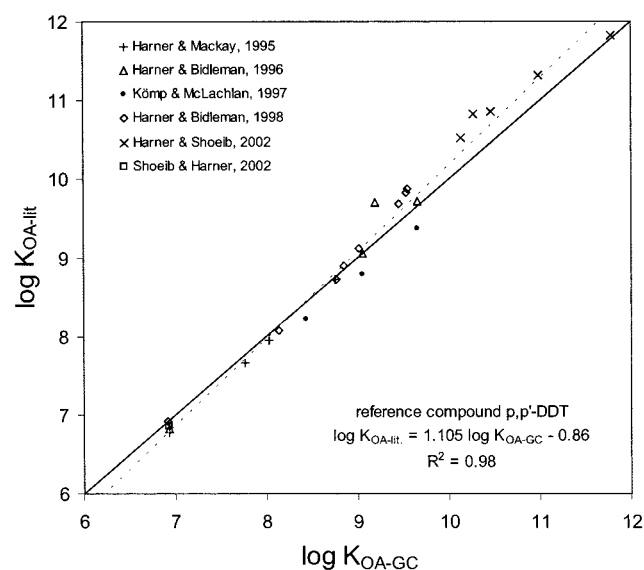


**Figure 2.** Relationship between the $K_{OA\text{-}GC}$ values at 25 °C derived from gas chromatographic retention times relative to p,p′-DDT and directly measured $K_{OA}$ values for polychlorinated biphenyls and naphthalenes, as well as polybrominated diphenyl ethers. The solid line represents a 1:1 relationship; the broken line is the linear fit through the data points.

for HCBz, the interactions with the DB-1 phase do not resemble those with the octanol or pure liquid phase, suggesting that HCBz is not a highly suitable reference compound in the presented method. However, it should be stressed that after calibration, the calculations relying on reference compound HCBz gave the same final $K_{OA}$ values as those using the reference compound C-18, highlighting the usefulness and strength of the calibration procedure.

**Comparison of $K_{OA\text{-}GC}$ with $K_{OA}$ Values Determined by a Multicolumn Regression Method.** For some of the compounds in Table 2, Zhang et al.[19] and Su et al.[20] used multiple linear regression analysis between previously measured $K_{OA}$ values and capacity factors on multiple gas chromatographic columns of different polarity to interpolate $K_{OA}$ values for structurally related substances. The $K_{OA\text{-}lit*}$ values obtained with this multicolumn regression are included in Tables 2 and 3 and are identified by
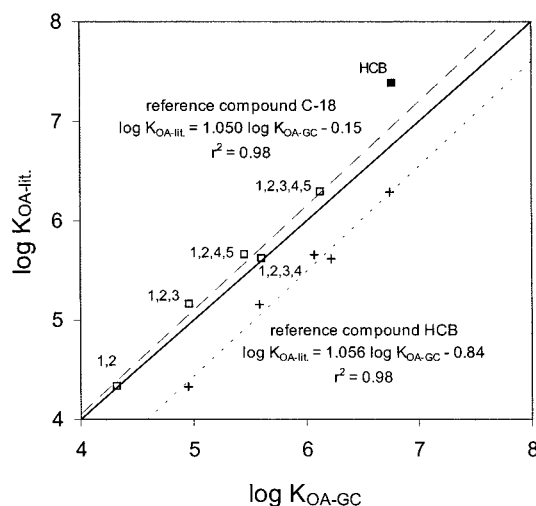


**Figure 3.** Relationship between the $K_{OA\text{-}GC}$ values at 25 °C derived from gas chromatographic retention times relative to hexachlorobenzene and n-octadecane and directly measured $K_{OA}$ values for chlorinated benzenes.

an asteriks. Figure 4 compares these values with the $K_{OA\text{-}calc}$ values obtained in this study (using eq 17 for the CBzs). This is a truly independent evaluation of the method, because the data from refs 19 and 20 had not been used in the derivation of the calibration eqs 15−17. The agreement is good, with deviations averaging at 0.14 log units. Somewhat larger deviations are observed at very high and low $K_{OA}$ values.

**Temperature Dependence of the $K_{OA}$.** Equation 10 suggests that it is also possible to estimate the temperature dependence of the $K_{OA}$ values from the slope of eq 9. The energies of octanol−air transfer $\Delta_{OA}U$ for all experimental chemicals estimated using eq 10 are listed in Tables 2 and 3. The standard deviations reported for these energies take into account the uncertainty of the factor $(S + 1)$ as obtained from replicate $\ln(t_R/t_{Rref})$ vs ln $K_{OAref}$ regressions and the uncertainty of the energy of phase transfer of the standard reference compound $\Delta_{OA}U_{ref}$ as estimated from the error of the slopes in eqs 11−14. It is the latter uncertainty that dominates the error of the estimated $\Delta_{OA}U$ values.
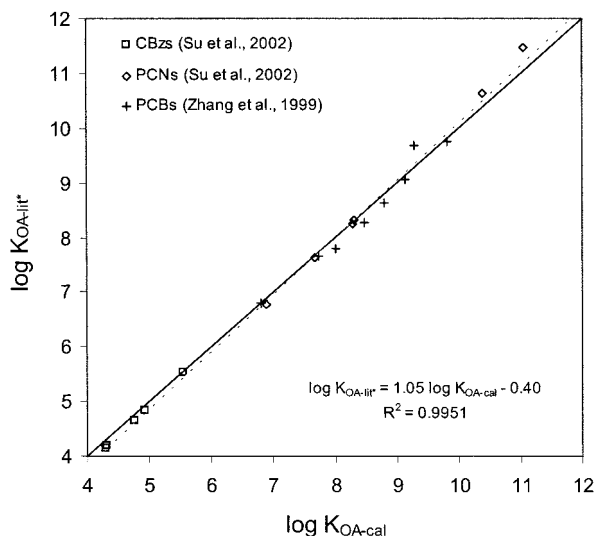
**Figure 4.** Comparison between the $K_{OA}$ values at 25 °C determined in this study with $K_{OA}$ values derived by a GC-based interpolation method. The data set includes chlorinated benzenes, biphenyls, and naphthalenes. The solid line represents a 1:1 relationship; the broken line is the linear fit through the data points.

The energies of phase transfer allow the estimation of $K_{OA}$ as a function of temperature using

$$\log K_{OA}(T) = \log K_{OA}(T_{ref}) + \Delta_{OA}U/(R \cdot \ln(10)) \cdot (1/T - 1/T_{ref}) \quad (18)$$

where $T_{ref} = 298.15$ K. Previous publications report parameters $m$ and $b$ for the equation.

$$\log K_{OA} = m/T + b \quad (19)$$

These parameters correspond to $m = \Delta_{OA}U/(R \cdot \ln(10))$ and $b = \log K_{OA}(T_{ref}) + \Delta_{OA}U/(R \cdot \ln(10) \cdot T_{ref})$.

Figure 5 compares the $\Delta_{OA}U$ from this study with directly measured values reported previously.[8–10,12,14] $\Delta_{OA}U$ values for the same compound reported by different authors often show significant deviations (Table 2). An example is the energies of phase transfer for the PCBs reported by Harner and Bidleman[9] and Kömp and McLachlan.[14] Even replicate experiments by the same authors have sometimes yielded significantly different values of $\Delta_{OA}U$, as illustrated by the case of 4-monochlorobiphenyl.[8,9] Considering this uncertainty of the directly determined energies of phase transfer, the $\Delta_{OA}U$ estimated from gas chromatographic retention times agree reasonably well with those reported in the literature. Most encouraging is the observation that the $\Delta_{OA}U$ for 2,2′,4,5,5′-pentaCB and 2,2′,4,4′,5,5′-hexaCB fall between those reported in refs 9 and 14. Exceptions to the generally good agreement are the $\Delta_{OA}U$s for the CBzs, which are not included in Figure 5. Although the $\Delta_{OA}U$ values for the CBzs obtained with HCBz and C-18 as a reference compound agree exceptionally well with each other, they are ~20 kJ/mol lower than those reported in ref 8.

It can be quite deceptive to compare and evaluate $\Delta_{OA}U$ or the temperature slopes $m$ in isolation, because they are very dependent on the log $K_{OA}$ at the reference temperature or the
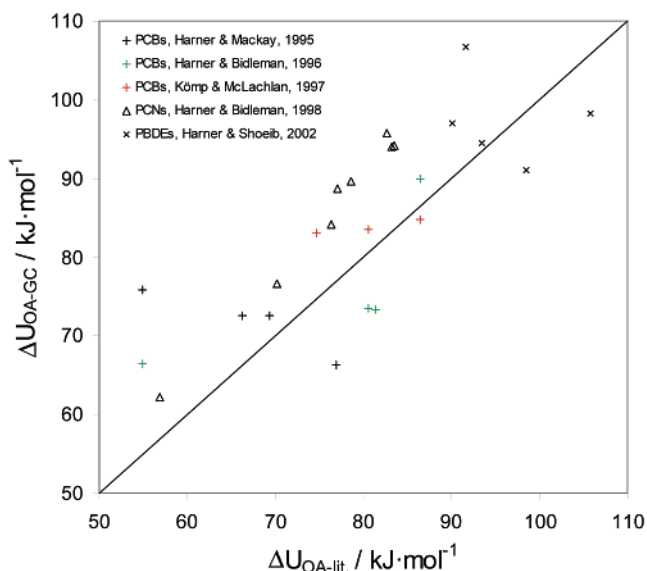
**Figure 5.** Comparison between energy of phase transfer between *n*-octanol and air $\Delta_{OA}U$ determined in this study and $\Delta_{OA}U$ values reported in the literature. The solid line represents a 1:1 relationship.
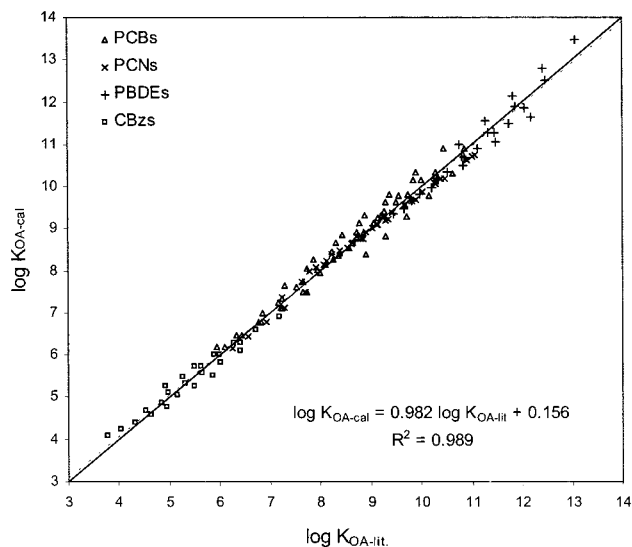


**Figure 6.** Comparison between log $K_{OA}$ values at 5, 15, 25, 35, and 45 °C derived in this study and the respective log $K_{OA}$ values derived from relationships reported in previous studies.

parameter *b*. We thus evaluated the capability of the parameters determined in this study to predict $K_{OA}$ values within the environmental temperature range that are comparable to values measured as a function of temperature with the generator column technique. We thus calculated $K_{OA}$ values at 5, 15, 25, 35, and 45 °C using eq 18 and the parameters log $K_{OA-calc}$ and $\Delta_{OA}U$ from Tables 2 and 3. We further did a similar calculation with the *m*'s and *b*'s reported in refs 8, 9, 10, 12, and 14 and plotted the results against each other in Figure 5. This graph shows that despite the relatively large discrepancies in the reported $\Delta_{OA}U$, the technique used in this study is capable of predicting the $K_{OA}$ of the investigated substances within the environmentally relevant temperature range with an average deviation from directly measured values of <0.2 log units. The maximum deviation is one-half of a log unit.

## DISCUSSION

The uncalibrated $K_{OA\text{-}GC}$ values obtained with the method presented here were all within 0.6 log units of directly measured $K_{OA}$ values reported in the literature. Even in the absence of calibration data, the method, thus, could serve as a quick and easy first approximation of the $K_{OA}$ value of a nonpolar and semivolatile compound. There are several potential reasons why $K_{OA\text{-}GC}$ deviates from directly measured $K_{OA\text{-}lit}$ values. Discrepancies may be due to the difficulty in reliably measuring extreme partition coefficients with the generator column technique. The largest differences between $K_{OA\text{-}GC}$ and $K_{OA\text{-}lit}$ occurred for the PBDEs, which have extremely high log $K_{OA}$ values of above 10. Another possibility is that the condition of eq 3 is not being met, because the compounds of interest may be too dissimilar from the standard reference compound in terms of their partitioning properties. As discussed above, this is likely the reason for the discrepancy between $K_{OA\text{-}GC}$ and $K_{OA\text{-}lit}$ when HCBz is used as a reference compound for the not fully chlorinated CBzs. The third potential reason is that the $K_{OA}$ of the standard reference compound may not be known accurate enough, that is, relationships 11 through 14 may not provide entirely correct $K_{OAref}$ estimates for use in the regressions based on eq 9.

The discrepancies between GC-derived $K_{OA}$ values and those measured directly could be eliminated through a simple calibration procedure. Over the environmentally relevant temperature range of 5−45 °C, the calibrated GC-derived $K_{OA}$ values were on average within 0.2 log units of the directly measured $K_{OA}$ values and, thus, likely within the measurement uncertainty of these values. Direct measurements of the $K_{OA}$ of semivolatile substances are difficult and subject to considerable uncertainties. For example, replicate measurements of the log $K_{OA}$ of the same compound by the same research group reveals deviation on the order of 0.2 log units and less.[13,14] In addition, log $K_{OA}$ for the PCBs measured by both Harner and Bidleman[9] and Kömp and McLachlan[14] showed discrepancies on the order of 0.3 log units. In light of these inherent uncertainties, the observed agreement between $K_{OA\text{-}calc}$ and $K_{OA\text{-}lit}$ is very good and suggests that the method presented here can indeed serve to estimate the $K_{OA}$ of semivolatile substances quickly and easily.

**Relative Merits of This Method Compared with the Multiple Column Regression Technique.** Zhang et al.'s method[19] is essentially an interpolation technique and thus relies on the availability of a relatively large data set of high-quality $K_{OA}$ data of structurally highly related compounds.[20] Temperature-dependent $K_{OA}$ data or $\Delta_{OA}U$ values can be obtained only if that entire data set is available as a function of temperature.[20] It also can be quite labor-intensive and difficult to determine capacity factors of a large number of structurally related substances on several gas chromatographic columns. The method presented here requires only previous accurate knowledge of the temperature-dependent $K_{OA}$ of a single standard reference compound as well as directly measured $K_{OA}$ values at 25 °C for a sufficient number of calibration compounds. These calibration compounds need not be structurally very similar to the compounds of interest, although they should be subject to similar intermolecular interactions. Information on the temperature-dependence of the $K_{OA}$ can be readily obtained.

**Comparison of GC-Retention-Time-Based Estimation of $K_{OA}$ with the GC-Retention -Time-Based Estimation of $P_L$.** In the analogous gas chromatographic retention time technique for vapor pressure, significant deviations of GC-derived vapor pressures $P_{GC}$ from liquid vapor pressures $P_L$ obtained otherwise are common and also necessitate the use of an analogous calibration procedure[23,25,26]. The regressions between log $P_L$ and log $P_{GC}$ usually show more scatter and lower $r^2$ values than those obtained in this study (Figures 2 and 3, eqs 15−17). There are two likely reasons for this.

Literature data sets for the vapor pressure of semivolatile compounds are typically not as consistent as the data set for $K_{OA}$ used in this study. Data sets of vapor pressures usually need to rely on measurements from more than one research group, even for a group of closely related compounds, such as the PCBs.[25] On the other hand, most of the $K_{OA}$ literature values in this study have been measured by Harner and co-workers. Furthermore, to be comparable to GC-derived vapor pressures, vapor pressure values measured for the solid substance often have to be converted to the respective subcooled liquid value, introducing additional uncertainty to the data set. No such conversion is required for directly measured $K_{OA}$ values.

The other, possibly more important, reason is that the basic assumption underlying the GC-retention time method may be more appropriate for $K_{OA}$ than for $P_L$. Specifically, the GC-retention time method for $P_L$ requires the assumption that the activity coefficients of the target compound and the standard reference compound in the stationary phase are identical ($\gamma_{Si} = \gamma_{Sref}$), whereas the method introduced here requires only the assumption that the ratio of the activity coefficients of these two compounds in the stationary phase is the same as the ratio of the activity coefficients in $n$-octanol (see eq 3 above). It appears reasonable that the latter assumption is more likely to be fulfilled than the former. It also suggests that the requirement of a structurally related standard reference compound is less stringent when estimating $K_{OA}$ from GC-retention data than when estimating $P_L$, although either assumption is more likely to be appropriate if target compounds and standard reference compound are structurally related.