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Determination of Octanol−Air Partition Coefficient (K_{OA}) Values for Chlorobenzenes and Polychlorinated Naphthalenes from Gas Chromatographic Retention Times

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Isothermal capacity factors k on three gas chromatographic columns of different polarity were determined for chlorobenzenes (CBzs) and polychlorinated naphthalenes (PCNs). All possible multiple linear regressions of the logarithm of these capacity factors with previously reported temperature-dependent octanol−air partition coefficient (K_{OA}) values of selected CBzs and PCN congeners were performed to derive predictive relationships for the remaining congeners. A comparative evaluation of the regression coefficients and the standard error of the predicted K_{OA} values revealed that regressions with the capacity factor on a single nonpolar column (DB-5ms) yielded the best results for both CBzs and PCNs. Using the best regression equations, K_{OA} values for 6 CBzs and 27 PCNs were obtained for the temperature range from 10 °C to 50 °C. The internal energies of air−octanol phase transfer $\Delta_{OA}U$ for these chemicals were calculated by correlating the interpolated log K_{OA} values with reciprocal absolute temperature.

Introduction

The octanol−air partition coefficient (K_{OA}) and its temperature dependence are important descriptors of the equilibrium distribution of organic compounds between air and natural organic matter in aerosols, soils, and vegetation.[1−3] The classical method for determining K_{OA} is the generator column method.[4−6] However, the experimental determination of K_{OA} for semivolatile compounds with this technique is difficult and time-consuming, especially at low temperatures.[5,6] For environmentally important compound classes with a large number of individual congeners, such as the polychlorinated biphenyls (PCBs) or the polychlorinated naphthalenes (PCNs), measured K_{OA} values typically exist only for a selection of congeners. Recently, Zhang et al. developed a method to predict K_{OA} values for a large number of PCB congeners by interpolating known K_{OA} values for selected congeners using retention times on several gas chromatographic columns of variable polarity.[7] In the present study, this multicolumn method was applied to determine the K_{OA} values for 6 chlorobenzenes (CBzs) and 27 PCNs based on the measured values for selected congeners.[4,6,8] Individual regressions at several temperatures in the range 10 °C to 50 °C allowed the estimation of the internal energies of air−octanol phase transfer $\Delta_{OA}U$. CBzs and PCNs are common environmental pollutants and are routinely detected in various environmental samples.[9−11] The number and position of chlorine substitutions on the benzene and naphthalene structure results in 12 different CBz and 75 PCN congeners. The latter were systematically numbered by Wiedmann and Ballschmiter.[12]

Methods

Chemicals. The CBz congeners were purchased from Aldrich Chemical Co. (Milwaukee, WI) and Supelco (Bellefonte, PA). The purity of all CBz congeners was above 98%. Selected PCN congeners, CN-1, CN-2, CN-3, CN-5, CN-6, CN-12, CN-13, CN-27, CN-28, CN-31, CN-34, CN-36, CN-46, CN-48, CN-49, CN-50, CN-52, CN-53, CN-55, CN-66, CN-69, CN-71, CN-72, CN-73, CN-75, and the technical PCN mixture Halowax 1014 were obtained from Wellington Laboratories (Guelph, Ontario, Canada) and Ultra Scientific (Kingstown, RI). All CBzs and selected PCNs were separately dissolved in hexane (Caledon Laboratories Ltd., Georgetown, Ontario, Canada; 95% *n*-hexane). Halowax 1014 was dissolved into 2,2,4-trimethylpentane (Caledon Laboratories Ltd.; HPLC grade).

Instrumentation. Three gas chromatographic columns showing different intermolecular interactions with organic analytes were employed: DB-5ms (J&W Scientific; 60 m × 0.25 mm i.d., 0.10-μm film thickness) mainly interacts by dispersive forces, Rtx-2330 (Restek Corp.; 60 m × 0.25 mm i.d., 0.10-μm film thickness) has a strong induced polarity and some hydrogen-bonding acidity, whereas DB-FFAP (J&W Scientific; 60 m × 0.25 mm i.d., 0.10-μm film thickness) possesses a high polarity and the ability to hydrogen bond.[7]

Isothermal retention times of the analytes were obtained by injecting 0.1−1.0 μL of the solutions with concentrations in the μg/μL range into a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID). The Halowax mixture was additionally analyzed on the same GC with an electron capture detector (ECD) and on an Agilent 6890 GC equipped with an autosampler (Agilent 7863) and a mass spectrometric detector (Agilent 5973 MSD). The carrier gas (flow rate 1.0 mL·min^{-1}) was helium for the FID and MSD and 95% argon + 5% methane for the ECD. The split ratio was approximately 50:1. The injection port was kept at 225 °C, and the detector temperature was 250 °C for the FID and 300 °C for the ECD. The GC-MSD was run in the total ion mode (TIC) and the PCN homologues were monitored at

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the following mass-to-charge ratios (m/z): 196−198 for di-CN, 230−232 for tri-CN, 264−266 for tetra-CN, 298−300 for penta-CN, 332−334 for hexa-CN, 366−368 for hepta-CN, and 402−404 for octa-CN.

Whereas the CBzs were run at 140 °C on all three columns, the oven temperatures used for the PCNs were 185 °C in the case of the DB-5ms and Rtx-2330 and 210 °C for DB-FFAP. The retention time of pentane was measured on each of these columns to determine the dead time of the system. Pentane was injected directly using a gastight syringe. Since pentane shows no response on an ECD, a number of PCN congeners were run on both GC-ECD and GC-FID. The retention time of pentane on the GC-ECD was calculated from a perfect correlation between the retention times on the two detectors ($r^2 = 1$). The measurement of retention time had good reproducibility. Each solution was run three to five times on all three columns, and the relative standard deviation (RSD) of the retention times was always below 0.85%.

Peak Identification. Halowax 1014 is composed mostly of tetra- through hexachlorinated naphthalenes, with minor amounts of tri-, hepta-, and octachlorinated congeners. Whereas a lot of previous work has been devoted to identifying the peaks of this technical mixture when eluted on a DB-5ms column,[6,13−16] this information does not exist for the other two columns used in this study. The elution order of the PCNs on the Rtx-2330 and DB-FFAP columns is not necessarily the same as that on the DB-5ms. Also, some components of Halowax 1014 which coelute on the DB-5ms may be separated when run on the other two columns. Imagawa and Yamashita, for example, separated CN-64 and CN-68 on an α-DEX 120 column and CN-71 and CN-72 on a β-DEX 120 column,[16] whereas Helm et al. further separated CN-52/CN-60 and CN-66/CN-67 using a Restek Rt-βDEXcst column.[15] We used the following tiered approach to identify as many individual PCN peaks on the three Halowax 1014 chromatograms as possible:

1. If solutions of individual congeners were available, identification was based on retention time matching. This allowed us to unequivocally identify PCN congeners CN-1, CN-2, CN-3, CN-5, CN-6, CN-12, CN-13, CN-27, CN-28, CN-31, CN-34, CN-36, CN-46, CN-48, CN-49, CN-50, CN-52, CN-53, CN-55, CN-66, CN-69, CN-71, CN-72, CN-73, and CN-75 on all three columns.

2. Next, we used previously published chromatograms and peak assignments[6,13−17] to identify additional congeners CN-14, CN-15, CN-16, CN-17, CN-19, CN-23, CN-24, CN-25, CN-30, CN-32, CN-33, CN-35, CN-37, CN-38, CN-39, CN-41, CN-42, CN-43, CN-45, CN-47, CN-51, CN-54, CN-57, CN-58, CN-59, CN-60, CN-61, CN-62, CN-63, CN-64, CN-65, CN-67, CN-68, and CN-74 in the DB-5ms chromatogram.

3. Finally, the Halowax 1014 solution was run on the GC-MSD using DB-5ms, Rtx-2330, and DB-FFAP columns and the chromatograms obtained from these different columns were compared to identify some “apparent” peaks in Halowax 1014 chromatograms. One assumption was that the relative peak height on all three columns remains the same for the Halowax 1014 solution using similar GC conditions. Another 26 PCNs on Rtx-2330 and 23 PCNs on DB-FFAP were identified using this method.

In total, 59 PCN congeners were identified on the DB-5ms column, 51 PCN congeners on the Rtx-2330 column, and 48 PCN congeners on the DB-FFAP column.

Data Analysis. We performed multiple linear regression analysis (MLRA) between the measured K_{OA} values and the capacity factors k obtained on the three columns k_{DB-5ms}, $k_{Rtx-2330}$, and $k_{DB-FFAP}$. Specifically, MLRAs were performed on three data sets of measured K_{OA} values:

A: K_{OA} values for six CBzs.[4,8] In the case of hexachlorobenzene, recent measurements by Shoeib and Harner[8] were assumed more reliable than the early data by Harner and Mackay.[4]

B: K_{OA} values for 32 PCN congeners.[6] Prior to analysis a reporting error in the published data sets was corrected. Namely, the K_{OA} values for PCN 4−6 (CN-33, CN-34, CN-37) and PCN 4−7 (CN-47) at 40 °C were too high by an order of magnitude and thus should read $(2.47 \pm 0.32) \times 10^7$ and $(2.69 \pm 0.36) \times 10^7$, respectively (Harner, personal communication).

C: data sets A and B combined.

All K_{OA} values in these data sets have been measured by Harner et al. using the same method, ensuring a high degree of consistency. The experimental uncertainty of these data can be assessed from the standard deviation of replicate measurements reported by Harner and co-workers.[4,6,8] To our knowledge, no other measured K_{OA} values for CBzs and PCNs have been reported.

The correlation equations take the following forms:

$$\log K_{OA}(T) = a \log k_{DB-5ms} + d \tag{1}$$

$$\log K_{OA}(T) = b \log k_{Rtx-2330} + d \tag{2}$$

$$\log K_{OA}(T) = c \log k_{DB-FFAP} + d \tag{3}$$

$$\log K_{OA}(T) = a \log k_{DB-5ms} + b \log k_{Rtx-2330} + d \tag{4}$$

$$\log K_{OA}(T) = a \log k_{DB-5ms} + c \log k_{DB-FFAP} + d \tag{5}$$

$$\log K_{OA}(T) = b \log k_{Rtx-2330} + c \log k_{DB-FFAP} + d \tag{6}$$

$$\log K_{OA}(T) = a \log k_{DB-5ms} + b \log k_{Rtx-2330} + c \log k_{DB-FFAP} + d \tag{7}$$

Here a, b, c, and d are empirical regression parameters. As the K_{OA} values had been reported at several temperatures, these seven regressions were performed for 10, 20, 30, 40, and 50 °C, respectively. The regression coefficient r^2, adjusted regression coefficient r_{adj}^2, and standard deviation (SD) were calculated.

Results

Retention Times and Capacity Factors k. The retention times of CBzs, PCNs, and pentane on different columns using GC-ECD are listed in Tables S1 and S2 in the Supporting Information. The capacity factors were calculated using eq 8:

$$k = (t - t_{pentane})/t_{pentane} \tag{8}$$

where $t_{pentane}$ and t are the retention times of pentane and the chemical of interest, respectively. Tables 1 and 2 list the logarithm of the capacity factors k for CBz and PCN congeners on all three columns. It also gives the SD of log k derived from the standard deviation of the retention times.

Regression between log K_{OA} and Capacity Factors k. Equations 1−7 were used to regress log K_{OA} and the capacity factors k. Tables S3 (data set A), S4 (data set B), and S5 (data set C) in the Supporting Information list the regression parameters a, b, c, and d and their standard deviations as well as r^2, r_{adj}^2, and SD for all regressions at all temperatures. The SD of the log K_{OA} estimated with a

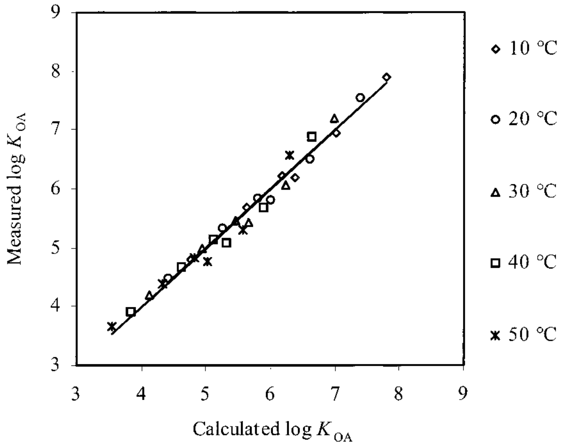

Figure 1. Correlation between the measured and calculated log K_{OA} values for CBzs at different temperatures.

Table 1. Capacity Factors of All Chlorobenzenes on Three Gas Chromatographic Columns and Their Standard Deviation

	$\log k_{DB-5ms}$	$\log k_{Rtx-2330}$	$\log k_{DB-FFAP}$
CB	−1.114 ± 0.006	−1.083 ± 0.025	−0.906 ± 0.002
1,3-diCB	−0.725 ± 0.003	−0.784 ± 0.015	−0.516 ± 0.001
1,4-diCB	−0.702 ± 0.001	−0.736 ± 0.015	−0.467 ± 0.001
1,2-diCB	−0.651 ± 0.001	−0.620 ± 0.013	−0.373 ± 0.001
1,3,5-triCB	−0.431 ± 0.001	−0.654 ± 0.013	−0.329 ± 0.001
1,2,4-triCB	−0.329 ± 0.001	−0.425 ± 0.011	−0.098 ± 0.001
1,2,3-triCB	−0.252 ± 0.001	−0.263 ± 0.011	0.058 ± 0.001
1,2,3,5-tetraCB	−0.006 ± 0.001	−0.207 ± 0.011	0.152 ± 0.001
1,2,4,5-tetraCB	−0.0004 ± 0.0004	−0.184 ± 0.011	0.170 ± 0.001
1,2,3,4-tetraCB	0.102 ± 0.001	0.014 ± 0.010	0.390 ± 0.001
penta-CB	0.390 ± 0.001	0.178 ± 0.010	0.563 ± 0.001
hexa-CB	0.759 ± 0.001	0.516 ± 0.010	0.910 ± 0.001

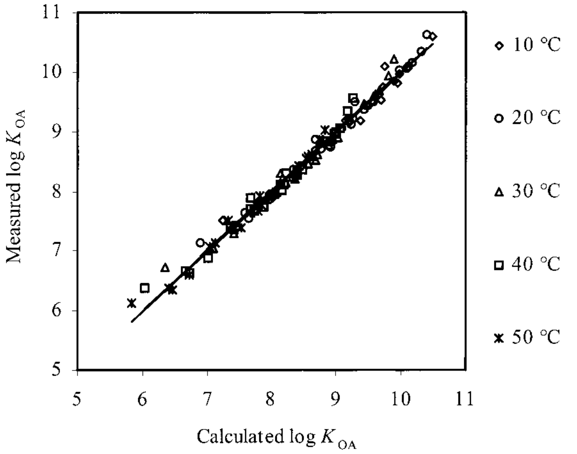

Figure 2. Correlation between the measured and calculated log K_{OA} values for PCNs at different temperatures.

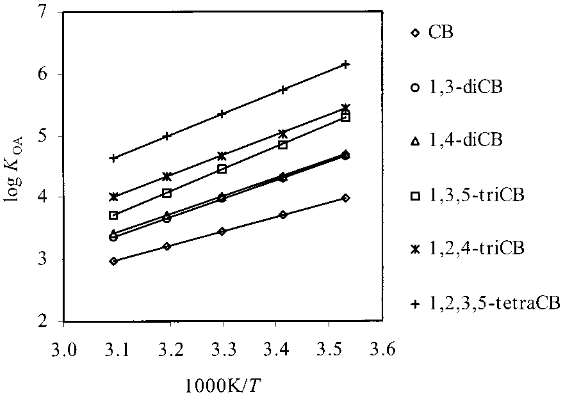

Figure 3. The log K_{OA} values of CBzs vs reciprocal absolute temperature over the temperature range 10 °C to 50 °C.

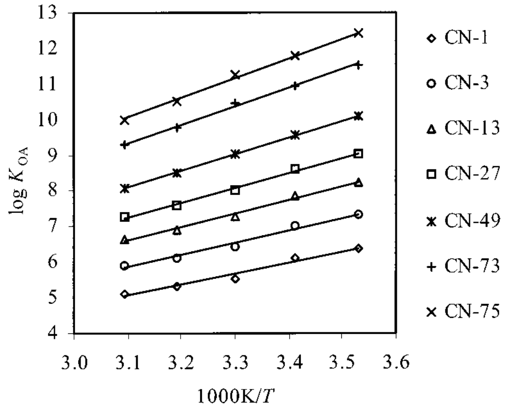

Figure 4. The log K_{OA} values of the selected PCNs vs reciprocal absolute temperature over the temperature range 10 °C to 50 °C.

particular regression equation was also calculated using appropriate error propagation methods that take into account the uncertainty of the regression parameters $a-d$ and that of the capacity factors k. For each compound group at each temperature, the best regression equation was identified by choosing the equation with the highest r_{adj}^2 and the lowest SD of the predicted log K_{OA}. The selected equations are listed in Table 3. In the case of the two separate data sets A and B, eq 1 based on the capacity factors on the DB-5MS column gave the best results. In the case of the combined data set C, the three column equation, (7), was superior.

The relationship between measured K_{OA} values and those calculated using the equations for the separate data sets A and B in Table 3 is shown in Figures 1 and 2 for CBzs and PCNs, respectively. The slopes of the correlation equations are close to 1, and the intercepts are close to 0. It is apparent that the regression equations explain most of the variability in the measured K_{OA} values at all temperatures. This indicates that the regression equations in Table 3 are well suited to interpolate the log K_{OA} values for other CBz and PCN congeners. They were thus employed to calculate log K_{OA} values for 6 CBzs and 27 PCNs at different temperatures. These values are listed in Tables 4 and 5.

Estimation of the Temperature Dependence of K_{OA}. Over relatively small temperature ranges log K_{OA} is a linear function of reciprocal absolute temperature T according to[6]

$$\log K_{OA} = \Delta_{OA}U/(\ln 10 \cdot R \cdot T) + b \qquad (9)$$

where $\Delta_{OA}U$ is the internal energy of air−octanol phase transfer in J·mol^{-1} and R is the ideal gas constant in J·mol^{-1}·K^{-1}. The log K_{OA} values from Tables 4 and 5 were regressed versus 1/T. Good linear relationships between log K_{OA} and 1/T in the temperature range 10 °C to 50 °C were obtained (r^2 ranged from 0.953 to 0.990). Figures 3 and 4 show such relationships for the CBzs and selected PCNs. The $\Delta_{OA}U$ values were calculated from the product of the slopes, ln 10 and R, and are listed in Tables 4 and 5 together with the intercept b. Using these $\Delta_{OA}U$ and b values and eq 9, K_{OA} values of CBzs and PCNs can be calculated at any temperature within this range. When combined with the original data by Harner and Bidleman,[6] this constitutes a data set of temperature-dependent K_{OA} values for all CBzs and 59 out of 75 PCNs.

Table 2. Capacity Factors of Polychlorinated Naphthalenes (ID Numbers Follow the System by Wiedmann and Ballschmiter[12]) on Three Gas Chromatographic Columns and Their Standard Deviation; Superscripts Indicate the Method Used for Peak Identification[a]

ID	congener	log $k_{\mathrm{DB-5ms}}$	log $k_{\mathrm{Rtx-2330}}$	log $k_{\mathrm{DB-FFAP}}$
1	1-monoCN	-0.485 ± 0.005^{a}	-0.368 ± 0.004^{a}	-0.468 ± 0.003^{a}
2	2-monoCN	-0.494 ± 0.005^{a}	-0.359 ± 0.003^{a}	-0.469 ± 0.003^{a}
3	1,2-diCN	-0.145 ± 0.003^{a}	-0.052 ± 0.002^{a}	-0.092 ± 0.001^{a}
5	1,4-diCN	-0.183 ± 0.003^{a}	-0.174 ± 0.005^{a}	-0.188 ± 0.002^{a}
6	1,5-diCN	-0.177 ± 0.003^{a}	-0.164 ± 0.002^{a}	-0.173 ± 0.002^{a}
12	2,7-diCN	-0.168 ± 0.003^{a}	-0.211 ± 0.002^{a}	-0.102 ± 0.001^{a}
13	1,2,3-triCN	0.172 ± 0.003^{a}	0.213 ± 0.001^{a}	0.221 ± 0.001^{a}
14	1,2,4-triCN	0.095 ± 0.002^{b}	0.015 ± 0.005^{c}	0.064 ± 0.001^{c}
15	1,2,5-triCN	0.131 ± 0.002^{b}		
16	1,2,6-triCN	0.142 ± 0.002^{b}		
17	1,2,7-triCN	0.153 ± 0.002^{b}		
19	1,3,5-triCN	0.072 ± 0.002^{b}	-0.054 ± 0.005^{c}	-0.010 ± 0.001^{c}
23	1,4,5-triCN	0.217 ± 0.002^{b}	0.283 ± 0.004^{c}	0.292 ± 0.001^{c}
24	1,4,6-triCN	0.095 ± 0.002^{b}	0.007 ± 0.005^{c}	0.045 ± 0.001^{c}
25	1,6,7-triCN	0.153 ± 0.002^{b}		
27	1,2,3,4-tetraCN	0.451 ± 0.002^{a}	0.365 ± 0.001^{a}	0.427 ± 0.001^{a}
28	1,2,3,5-tetraCN	0.434 ± 0.002^{a}	0.305 ± 0.005^{a}	0.391 ± 0.001^{a}
30	1,2,3,7-tetraCN	0.459 ± 0.002^{b}		
31	1,2,3,8-tetraCN	0.572 ± 0.002^{a}	0.694 ± 0.001^{a}	0.427 ± 0.001^{a}
32	1,2,4,5-tetraCN	0.478 ± 0.002^{b}	0.312 ± 0.005^{c}	0.475 ± 0.001^{c}
33	1,2,4,6-tetraCN	0.355 ± 0.002^{b}	0.182 ± 0.005^{c}	0.247 ± 0.001^{c}
34	1,2,4,7-tetraCN	0.355 ± 0.002^{a}	0.182 ± 0.001^{a}	0.247 ± 0.001^{a}
35	1,2,4,8-tetraCN	0.485 ± 0.002^{b}	0.463 ± 0.004^{c}	0.505 ± 0.001^{c}
36	1,2,5,6-tetraCN	0.426 ± 0.002^{a}	0.340 ± 0.005^{a}	0.369 ± 0.001^{a}
37	1,2,5,7-tetraCN	0.355 ± 0.002^{b}	0.182 ± 0.005^{c}	0.247 ± 0.001^{c}
38	1,2,5,8-tetraCN	0.513 ± 0.002^{b}	0.526 ± 0.004^{c}	0.565 ± 0.001^{c}
39	1,2,6,7-tetraCN	0.459 ± 0.002^{b}		
41	1,2,7,8-tetraCN	0.598 ± 0.002^{b}	0.427 ± 0.004^{c}	0.773 ± 0.001^{c}
42	1,3,5,7-tetraCN	0.293 ± 0.002^{b}	0.034 ± 0.005^{c}	0.111 ± 0.001^{c}
43	1,3,5,8-tetraCN	0.434 ± 0.002^{b}	0.305 ± 0.001^{c}	0.391 ± 0.001^{c}
45	1,3,6,8-tetraCN	0.426 ± 0.002^{b}		
46	1,4,5,8-tetraCN	0.567 ± 0.002^{a}	0.643 ± 0.004^{a}	0.676 ± 0.001^{a}
47	1,4,6,7-tetraCN	0.393 ± 0.002^{b}	0.240 ± 0.005^{c}	0.298 ± 0.001^{c}
48	2,3,6,7-tetraCN	0.497 ± 0.002^{a}	0.596 ± 0.001^{a}	0.612 ± 0.001^{a}
49	1,2,3,4,5-pentaCN	0.820 ± 0.002^{a}	0.778 ± 0.001^{a}	0.597 ± 0.001^{a}
50	1,2,3,4,6-pentaCN	0.695 ± 0.002^{a}	0.520 ± 0.005^{a}	0.598 ± 0.001^{a}
51	1,2,3,5,6-pentaCN	0.703 ± 0.002^{b}	0.535 ± 0.005^{c}	0.608 ± 0.001^{c}
52	1,2,3,5,7-pentaCN	0.635 ± 0.002^{a}	0.395 ± 0.005^{a}	0.462 ± 0.001^{a}
53	1,2,3,5,8-pentaCN	0.782 ± 0.002^{a}	0.694 ± 0.004^{a}	0.759 ± 0.001^{a}
54	1,2,3,6,7-pentaCN	0.749 ± 0.002^{b}		
55	1,2,3,6,8-pentaCN	0.789 ± 0.002^{a}	0.510 ± 0.001^{a}	0.474 ± 0.001^{a}
57	1,2,4,5,6-pentaCN	0.757 ± 0.002^{b}	0.661 ± 0.004^{c}	0.726 ± 0.001^{c}
58	1,2,4,5,7-pentaCN	0.671 ± 0.002^{b}	0.459 ± 0.004^{c}	0.538 ± 0.001^{c}
59	1,2,4,5,8-pentaCN	0.812 ± 0.002^{b}	0.778 ± 0.004^{c}	0.836 ± 0.001^{c}
60	1,2,4,6,7-pentaCN	0.635 ± 0.002^{b}	0.395 ± 0.001^{c}	0.467 ± 0.001^{c}
61	1,2,4,6,8-pentaCN	0.684 ± 0.002^{b}	0.500 ± 0.005^{c}	0.573 ± 0.001^{c}
62	1,2,4,7,8-pentaCN	0.771 ± 0.002^{b}	0.701 ± 0.004^{c}	0.759 ± 0.001^{c}
63	1,2,3,4,5,6-hexaCN	1.096 ± 0.002^{b}	1.012 ± 0.004^{c}	1.154 ± 0.001^{c}
64	1,2,3,4,5,7-hexaCN	1.007 ± 0.002^{b}	0.810 ± 0.004^{c}	0.886 ± 0.001^{c}
65	1,2,3,4,5,8-hexaCN	1.132 ± 0.002^{b}	1.093 ± 0.004^{c}	1.081 ± 0.001^{c}
66	1,2,3,4,6,7-hexaCN	0.964 ± 0.002^{a}	0.720 ± 0.005^{a}	0.797 ± 0.001^{a}
67	1,2,3,5,6,7-hexaCN	0.964 ± 0.002^{b}	0.720 ± 0.001^{c}	0.797 ± 0.001^{c}
68	1,2,3,5,6,8-hexaCN	1.007 ± 0.002^{b}	0.810 ± 0.004^{c}	0.886 ± 0.001^{c}
69	1,2,3,5,7,8-hexaCN	1.023 ± 0.002^{a}	0.855 ± 0.004^{a}	0.925 ± 0.001^{a}
71	1,2,4,5,6,8-hexaCN	1.042 ± 0.003^{a}	0.906 ± 0.004^{a}	0.925 ± 0.001^{a}
72	1,2,4,5,7,8-hexaCN	1.042 ± 0.003^{a}	0.906 ± 0.004^{a}	0.971 ± 0.001^{a}
73	1,2,3,4,5,6,7-heptaCN	1.336 ± 0.002^{a}	1.152 ± 0.004^{a}	
74	1,2,3,4,5,6,8-heptaCN	1.349 ± 0.002^{b}	1.210 ± 0.004^{c}	
75	1,2,3,4,5,6,7,8-octaCN	1.645 ± 0.002^{a}	1.480 ± 0.001^{a}	

[a] Using individual solutions and peak matching. [b] Comparison with published chromatograms. [c] Comparison of relative peak heights.

Discussion

Multicolumn versus One-Column Regressions. In the case of the CBzs (data set A), only six measured K_{OA} values were available. Although eq 7 showed the highest r_{adj}^{2} at each of the temperatures from 10 °C to 50 °C (Table S3), it contains four fitting parameters a, b, c, and d. These four parameters are as a result highly uncertain, rendering eq 7 useless for estimating K_{OA} values of CBzs. For illustration, Table S6 lists the log K_{OA} values and their SD obtained using eq 7. Whereas the r_{adj}^{2} was slightly higher when using eq 7 rather than eq 1 (see Table S3), the SD of the log K_{OA} values obtained using eq 7 are much higher than those obtained using eq 1 (Table 4). This highlights that if only a limited number of measured K_{OA} values exist for a particular group of related compounds, a multicolumn regression is not meaningful.

K_{OA} values measured over the temperature range 20 °C to 50 °C were available for 32 PCN congeners, whereas K_{OA} values at 10 °C were reported for only 23 PCN congeners.[6] The regression with the capacity factors on the DB-5ms

Table 3. Best Regression Equations for Interpolating the log K_{OA} Values of CBzs, PCNs, and PCNs/CBzs at Different Temperatures

data set	equation	n	r^2	r_{adj}^2	SD
CBzs at 10 °C	$\log K_{OA}(T) = 2.154 \log k_{DB-5ms} + 6.161$	6	0.995	0.988	0.115
CBzs at 20 °C	$\log K_{OA}(T) = 2.097 \log k_{DB-5ms} + 5.789$	6	0.993	0.982	0.138
CBzs at 30 °C	$\log K_{OA}(T) = 2.042 \log k_{DB-5ms} + 5.443$	6	0.989	0.973	0.165
CBzs at 40 °C	$\log K_{OA}(T) = 1.992 \log k_{DB-5ms} + 5.118$	6	0.985	0.963	0.193
CBzs at 50 °C	$\log K_{OA}(T) = 1.944 \log k_{DB-5ms} + 4.814$	6	0.980	0.949	0.220
PCNs at 10 °C	$\log K_{OA}(T) = 2.817 \log k_{DB-5ms} + 7.756$	23	0.983	0.981	0.119
PCNs at 20 °C	$\log K_{OA}(T) = 2.667 \log k_{DB-5ms} + 7.393$	32	0.989	0.989	0.096
PCNs at 30 °C	$\log K_{OA}(T) = 2.699 \log k_{DB-5ms} + 6.833$	32	0.983	0.983	0.123
PCNs at 40 °C	$\log K_{OA}(T) = 2.445 \log k_{DB-5ms} + 6.488$	32	0.980	0.980	0.121
PCNs at 50 °C	$\log K_{OA}(T) = 2.276 \log k_{DB-5ms} + 6.237$	32	0.983	0.983	0.104
PCNs/CBzs at 10 °C	$3.888 \log k_{DB-5ms} + 4.567 \log k_{Rtx-2330} - 5.653 \log k_{DB-FFAP} + 7.948$	29	0.992	0.991	0.138
PCNs/CBzs at 20 °C	$3.638 \log k_{DB-5ms} + 4.397 \log k_{Rtx-2330} - 5.304 \log k_{DB-FFAP} + 7.548$	38	0.986	0.985	0.184
PCNs/CBzs at 30 °C	$3.333 \log k_{DB-5ms} + 4.110 \log k_{Rtx-2330} - 4.707 \log k_{DB-FFAP} + 7.011$	38	0.985	0.984	0.185
PCNs/CBzs at 40 °C	$3.135 \log k_{DB-5ms} + 3.871 \log k_{Rtx-2330} - 4.482 \log k_{DB-FFAP} + 6.623$	38	0.983	0.982	0.183
PCNs/CBzs at 50 °C	$3.102 \log k_{DB-5ms} + 3.850 \log k_{Rtx-2330} - 4.571 \log k_{DB-FFAP} + 6.347$	38	0.983	0.981	0.177

Table 4. log K_{OA} Values of Selected CBzs at Different Temperatures Calculated Using the Regression Equations in Table 3 and the $\Delta_{OA}U$ and Intercept b Values Derived from Regressions of These K_{OA} Values against Reciprocal Temperature (Eq 9)

	log K_{OA}					$\Delta_{OA}U$	
	10 °C	20 °C	30 °C	40 °C	50 °C	(kJ·mol^{-1})	b
CB	3.76 ± 0.13	3.45 ± 0.16	3.17 ± 0.19	2.90 ± 0.23	2.65 ± 0.26	43.91 ± 0.04	−4.107 ± 0.007
1,3-diCB	4.60 ± 0.09	4.27 ± 0.11	3.96 ± 0.14	3.67 ± 0.16	3.40 ± 0.18	57.02 ± 0.02	−5.856 ± 0.004
1,4-diCB	4.65 ± 0.09	4.32 ± 0.11	4.01 ± 0.13	3.72 ± 0.16	3.45 ± 0.18	55.59 ± 0.02	−5.556 ± 0.003
1,2,4-triCB	5.45 ± 0.06	5.10 ± 0.07	4.77 ± 0.09	4.46 ± 0.11	4.17 ± 0.12	62.08 ± 0.01	−6.031 ± 0.002
1,3,5-triCB	5.23 ± 0.07	4.89 ± 0.08	4.56 ± 0.10	4.26 ± 0.12	3.98 ± 0.14	68.55 ± 0.03	−7.368 ± 0.005
1,2,3,5-tetraCB	6.15 ± 0.05	5.78 ± 0.06	5.43 ± 0.07	5.11 ± 0.09	4.80 ± 0.10	66.32 ± 0.01	−6.086 ± 0.002

Table 5. log K_{OA} Values of Selected PCNs at Different Temperatures Calculated Using the Regression Equations in Table 3 and the $\Delta_{OA}U$ and Intercept b Values Derived from Regressions of These K_{OA} Values against Reciprocal Temperature (Eq 9)

		log K_{OA}					$\Delta_{OA}U$	
ID	congener	10 °C	20 °C	30 °C	40 °C	50 °C	(kJ·mol^{-1})	b
1	1-monoCN	6.39 ± 0.07	6.10 ± 0.05	5.52 ± 0.06	5.30 ± 0.06	5.13 ± 0.05	58.3 ± 6.3	−4.4 ± 1.1
2	2-monoCN	6.36 ± 0.07	6.08 ± 0.05	5.50 ± 0.06	5.28 ± 0.06	5.11 ± 0.05	58.0 ± 6.3	−4.4 ± 1.1
3	1,2-diCN	7.35 ± 0.11	7.01 ± 0.04	6.44 ± 0.05	6.13 ± 0.05	5.91 ± 0.04	66.0 ± 4.8	−4.8 ± 0.8
6	1,5-diCN	7.26 ± 0.13	6.92 ± 0.04	6.36 ± 0.05	6.06 ± 0.05	5.83 ± 0.04	65.2 ± 4.9	−4.8 ± 0.9
12	2,7-diCN	7.28 ± 0.12	6.95 ± 0.04	6.38 ± 0.05	6.08 ± 0.05	5.85 ± 0.04	65.4 ± 4.9	−4.8 ± 0.8
13	1,2,3-triCN	8.24 ± 0.12	7.85 ± 0.04	7.30 ± 0.05	6.91 ± 0.05	6.63 ± 0.04	73.2 ± 3.6	−5.2 ± 0.6
15	1,2,5-triCN	8.12 ± 0.11	7.74 ± 0.04	7.19 ± 0.05	6.81 ± 0.05	6.53 ± 0.04	72.2 ± 3.7	−5.2 ± 0.6
16	1,2,6-triCN	8.16 ± 0.11	7.77 ± 0.04	7.22 ± 0.05	6.83 ± 0.05	6.56 ± 0.04	72.5 ± 3.7	−5.2 ± 0.6
17	1,2,7-triCN	8.19 ± 0.12	7.80 ± 0.04	7.25 ± 0.05	6.86 ± 0.05	6.58 ± 0.04	72.7 ± 3.7	−5.2 ± 0.6
25	1,6,7-triCN	8.19 ± 0.12	7.80 ± 0.04	7.25 ± 0.05	6.86 ± 0.05	6.58 ± 0.04	72.7 ± 3.7	−5.2 ± 0.6
27	1,2,3,4-tetraCN	9.03 ± 0.27	8.59 ± 0.04	8.05 ± 0.05	7.59 ± 0.05	7.26 ± 0.05	79.5 ± 2.7	−5.6 ± 0.5
28	1,2,3,5-tetraCN	8.98 ± 0.26	8.55 ± 0.04	8.00 ± 0.05	7.55 ± 0.05	7.22 ± 0.05	79.1 ± 2.8	−5.6 ± 0.5
30	1,2,3,7-tetraCN	9.05 ± 0.27	8.62 ± 0.04	8.07 ± 0.06	7.61 ± 0.05	7.28 ± 0.05	79.6 ± 2.7	−5.6 ± 0.5
31	1,2,3,8-tetraCN	9.37 ± 0.34	8.92 ± 0.05	8.38 ± 0.06	7.89 ± 0.06	7.54 ± 0.05	82.2 ± 2.5	−5.8 ± 0.4
36	1,2,5,6-tetraCN	8.95 ± 0.26	8.53 ± 0.04	7.98 ± 0.05	7.53 ± 0.05	7.21 ± 0.05	78.9 ± 2.8	−5.6 ± 0.5
39	1,2,6,7-tetraCN	9.05 ± 0.27	8.62 ± 0.04	8.07 ± 0.06	7.61 ± 0.05	7.28 ± 0.05	79.6 ± 2.7	−5.6 ± 0.5
41	1,2,7,8-tetraCN	9.44 ± 0.35	8.99 ± 0.05	8.45 ± 0.06	7.95 ± 0.06	7.60 ± 0.05	82.8 ± 2.4	−5.8 ± 0.4
42	1,3,5,7-tetraCN	8.58 ± 0.18	8.18 ± 0.04	7.62 ± 0.05	7.21 ± 0.05	6.90 ± 0.04	75.9 ± 3.2	−5.4 ± 0.5
43	1,3,5,8-tetraCN	8.98 ± 0.26	8.55 ± 0.04	8.00 ± 0.05	7.55 ± 0.05	7.22 ± 0.05	79.1 ± 2.8	−5.6 ± 0.5
45	1,3,6,8-tetraCN	8.95 ± 0.26	8.53 ± 0.04	7.98 ± 0.05	7.53 ± 0.05	7.21 ± 0.05	78.9 ± 2.8	−5.6 ± 0.5
48	2,3,6,7-tetraCN	9.16 ± 0.30	8.72 ± 0.04	8.17 ± 0.06	7.70 ± 0.06	7.37 ± 0.05	80.5 ± 2.6	−5.7 ± 0.5
49	1,2,3,4,5-pentaCN	10.07 ± 0.48	9.58 ± 0.06	9.05 ± 0.07	8.49 ± 0.07	8.10 ± 0.06	87.8 ± 2.3	−6.1 ± 0.4
54	1,2,3,6,7-pentaCN	9.87 ± 0.44	9.39 ± 0.05	8.85 ± 0.07	8.32 ± 0.07	7.94 ± 0.06	86.2 ± 2.3	−6.0 ± 0.4
55	1,2,3,6,8-pentaCN	9.98 ± 0.46	9.50 ± 0.05	8.96 ± 0.07	8.42 ± 0.07	8.03 ± 0.06	87.1 ± 2.3	−6.1 ± 0.4
73	1,2,3,4,5,6,7-heptaCN	11.52 ± 0.77	10.96 ± 0.08	10.44 ± 0.10	9.75 ± 0.10	9.28 ± 0.08	99.5 ± 3.6	−6.8 ± 0.6
74	1,2,3,4,5,6,8-heptaCN	11.56 ± 0.78	10.99 ± 0.08	10.47 ± 0.10	9.79 ± 0.10	9.31 ± 0.08	99.8 ± 3.6	−6.8 ± 0.6
75	1,2,3,4,5,6,7,8-octaCN	12.39 ± 0.95	11.78 ± 0.09	11.27 ± 0.12	10.51 ± 0.11	9.98 ± 0.10	106.6 ± 4.8	−7.2 ± 0.8

column (eq 1) showed the highest r_{adj}^2 (Table S4), implying that the accuracy of the prediction was not improved by adding capacity factors obtained on additional columns. The regression of the log K_{OA} at 10 °C was an exception in that eq 7 had a slightly higher r_{adj}^2. However, as was case for the regression of CBzs, the SD of log K_{OA} became very high when this three column regression equation was used instead of the regression based on k_{DB-5ms} only (see Table S7). This is why eq 1 was again judged to provide the most reliable interpolation of the K_{OA} values in dataset B at all temperatures (Table 2).

The increase in r_{adj}^2 that occurred when eq 7 is used instead of eq 1 indicates that there is some variability in the K_{OA} values of the PCNs at 10 °C that cannot be explained by the capacity factors on a DB-5ms column. It seems somewhat strange that such variability should occur only at the lowest experimental temperature. Interestingly, not only did Harner and Bidleman[6] report fewer K_{OA} values for 10 °C than for the other temperatures, but the values at 10 °C are also based on a single determination only. They are thus likely to be somewhat less reliable than those reported for higher temperatures, which were the result of replicate determinations. One may thus suspect that the variability in K_{OA} at 10 °C that is not explained by k_{DB5-ms} is more a result of uncertain measurements than of structural factors.

This indicates the importance of using a highly consistent property data set of good quality when trying to use capacity factors for interpolating these properties. Otherwise the "information" contained in the capacity factors on several columns may inadvertently be used to "explain" experimental variability rather than variability caused by molecular structure. In particular, it may not be feasible to combine property data derived by different methods or different research groups. All K_{OA} data used in the present study were measured by one researcher using an essentially unchanged experimental setup. In that respect, it may be noteworthy that Zhang et al.[7] chose to ignore the log K_{OA} values reported for many PCB congeners by Kömp and McLachlan,[18] instead relying solely on the data reported by Harner and co-workers.[4,5] One may suspect that the regressions would have been considerably worse if both data sets had been combined.

Despite the strong structural similarity of the CBzs and PCNs, capacity factors on a single column were incapable of explaining a significant part of the variability of the K_{OA} of the combined data set C, yielding r_{adj}^2 of only 0.48 to 0.87 (Table S5). Among the three single-column regressions, eq 1 using k_{DB-5ms} was usually the best and eq 3 using $k_{DB-FFAP}$ the worst. Interestingly, among the two column regressions, eq 6 using both $k_{Rtx-2330}$ and $k_{DB-FFAP}$ was superior ($r_{adj}^2 = 0.94$) to any combinations involving $k_{DB-5ms.}$ The three-column regression equation, (7), gave significantly higher r_{adj}^2 (Table 4) than the best combination of two columns. This indicates that more "information", i.e., retention data on several columns, is needed to describe the variability in a K_{OA} data set that includes chemicals from more than one substance group. It also highlights that it is inappropriate to use a relationship between K_{OA} and k derived for one group of substances to predict the K_{OA} values for another group of chemicals, even if they have a fairly similar structure. This also applies to the multiple column regressions, as the regression parameters obtained for eq 7 differ substantially between the two data sets A and B (see Tables S3 and S4). Equation 7 for data set C could be used to predict K_{OA} for both chlorobenzenes and PCNs. However, for the prediction of additional K_{OA} values the regressions obtained for the separate data sets A and B were judged to be more appropriate than the regressions for the combined data set C because the latter tended to give higher SD for the calculated log K_{OA} values. For comparison, Table S8 lists the log K_{OA} values of CBzs and PCNs calculated using the three-column equation for the combined data set. Multiple column regressions that are applicable to a more varied set of substances are conceivable, but would require a similarly varied data set of measured K_{OA} and capacity factors.

One Column Regressions Using Different Columns. In all cases the regressions with k_{DB-5ms} were better than those with $k_{Rtx-2330}$ or $k_{DB-FFAP}$. DB-5ms is the most nonpolar of the three columns and is believed to interact with analytes mainly by dispersive forces.[7] The interaction of CBzs and PCNs with *n*-octanol molecules is likely also dominated by dispersive intermolecular forces and resembles therefore quite closely the interactions occurring between the chlorinated aromatics and a nonpolar stationary phase such as a DB-5ms. H-bonding interactions of the chlorinated aromatic with *n*-octanol are obviously not so dependent on the chlorine substitution pattern that they could explain a significant amount of the variability in the measured K_{OA} values of the investigated compounds.

Comparison with PCBs. Using a multicolumn method to estimate K_{OA} values for various PCB congeners, Zhang et al. reported that the r^2 increased if capacity factors k on additional columns were added to the linear regression equations.[7] However, as r^2 will always increase if more variables are introduced, the r_{adj}^2 is better suited to judge the fit of various regression equations. In our study we noted no improvement in r_{adj}^2 when the number of columns was increased from one to two or three for the regression of the K_{OA} values of PCNs over the temperature range 20 °C to 50 °C. Unfortunately, Zhang et al. did report neither the r_{adj}^2 nor the actual capacity factors of the PCBs, making it impossible to assess whether the r_{adj}^2 actually increased when using a multi-parameter equation rather than a regression based only on the capacity factors on the DB-5ms column.

However, even the r_{adj}^2 on its own is insufficient to evaluate the relative merit of the various regression equations. On the basis of r_{adj}^2 alone, the three column regression (eq 7) should have been the preferred equation for the CBzs at all temperatures and the PCNs at 10 °C. However, the error propagation calculations revealed that the log K_{OA} values determined using eq 7 had unreasonably large standard deviations. In conclusion, a regression with the capacity factors on a single column (DB-5ms) proved to be the best model to interpolate the measured K_{OA} values of both CBzs and PCNs. The information provided in Zhang et al.'s study is insufficient to assess whether the multicolumn equation is indeed superior to eq 1 for interpolating the K_{OA} values of the PCBs, in particular whether the predicted K_{OA} values are also subject to a very high uncertainty. Because of the possibility of the two aromatic rings in the PCBs rotating relative to each other, PCB congeners are likely to display a larger structural diversity than the planar PCN congeners. It is thus possible that more information, i.e., retention behavior on more than one column, is needed to describe the variability of the K_{OA} values of the PCBs than that of the PCNs.

Evaluation of the Multicolumn Method. To derive octanol−air partition coefficients from gas chromatographic retention times using simple regressions such as those presented here, a data set of K_{OA} values is required that has been measured with a classical method. Our study has shown that such a data set not only needs to apply to a group of structurally similar substances but also should be very consistent, sufficiently large, and subject to only minor experimental errors. Multicolumn regression equations that are applicable to a structurally more diverse set of substances would require empirical data on K_{OA} and capacity factors k for a very large and equally diverse set of substances. This method has thus limited applicability and its role is strictly complementary to existing techniques. However, the method may serve to fill data gaps by interpolation and identify where the original data may be subject to unusual experimental errors, as is shown in the case of the K_{OA} data for the PCNs at 10 °C. The key step of the gas chromatographic method is the identification and determination of the retention times of the chemicals of interest. If the retention order on a particular column has not previously been established and if individual congeners that would allow peak matching are not available, peak identification can be a difficult and lengthy process. Considerable time may be saved if retention on a single column can explain most of the variability in the observed partition coefficient.

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Supporting Information Available:

Additional tables of data. This material is available free of charge via the Internet at http://pubs.acs.org.

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