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Vapor Pressures of the Polychlorinated Naphthalenes

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The vapor pressures of the supercooled liquid P_L for 17 polychlorinated naphthalene congeners were determined as a function of temperature with a gas chromatographic retention time technique. The method was calibrated with vapor pressure data for polychlorinated biphenyls (PCBs) which had been measured by other techniques. These data were employed to predict temperature-dependent vapor pressures for all polychlorinated naphthalenes (PCNs) from a regression with published retention time indices. Enthalpies of vaporization $\Delta_{VAP}H$ and activity coefficients in 1-octanol were calculated for the PCNs and compared with those for polychlorinated biphenyls. Data analysis suggests that the dependence of P_L and $\Delta_{VAP}H$ on molecular size, as well as the partitioning behavior into 1-octanol of the PCNs, is very similar to that of coplanar PCBs, i.e., those congeners with no or only one chlorine substitution in the ortho positions. The affinity of these chemicals to 1-octanol increases with the degree of chlorination.

Introduction

Polychlorinated naphthalenes (PCNs) (Figure 1) are emerging as an important group of persistent organic pollutants with significant toxicity (Hanberg et al., 1990) and widespread occurrence in the environment (e.g., see Falandysz et al. (1996) and Järnberg et al. (1993, 1997)) and in human tissues (Williams et al., 1993; Lundén and Norén, 1998). They even have been detected in Arctic air, where they contribute a significant fraction of the dioxin-like toxicity (Harner et al., 1998).

Apart from measurements of the octanol−air partition coefficients K_{OA} (Harner and Bidleman, 1998) and aqueous solubility (Opperhuizen et al., 1985) for selected congeners, basic physical−chemical property data for these substances are missing. In this work we report supercooled liquid vapor pressures P_L for all 75 PCN congeners. For 17 congeners these were determined as a function of temperature with the gas chromatographic retention time technique by Bidleman (1984). For the remaining congeners P_L was estimated from relative retention time indices published in the literature.

Methods

Chemicals. PCN congeners were obtained from Wellington Laboratories (Guelph, Ontario) and Ultra Scientific (Kingstown, RI). Polychlorinated biphenyls (PCBs) used for calibration of the technique were obtained from Ultra Scientific, and the reference substance 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (*p,p*′-DDT) was from ChemService. Typically, between 0.5 and 35 ng of chemical in hexane (HPLC grade) was injected, 250 ng in the case of the monochloronaphthalenes.

Instrumentation. A Hewlett-Packard 5890 gas chromatograph (GC) equipped with electron capture (ECD) and flame ionization detectors (FID) and a dimethylpolysiloxane capillary column (0.32 mm i.d. × 1.0 m length; DB-1, J&W Scientific Columns, Folsom, CA) was used. The FID was employed only for the monochlorinated PCNs. The experiment was run isothermally at four to eight temperatures in the range 323.15 to 423.15 K. The temperature of the GC oven had been calibrated with a thermocouple. The injection port and FID had a temperature of 523.15 K, the ECD was at 573.15 K, the carrier gas flow rate (helium for GC-FID, argon/methane for GC-ECD) was approximately 4 mL·min^{-1}, and the split ratio was 10:1.

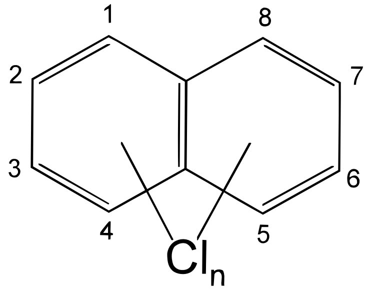

Figure 1. Generalized structure of the polychlorinated naphthalenes. The positions 1, 4, 5, and 8 are called α-positions. Positions 2, 3, 6, and 7 are *β*-positions.

Vapor Pressure of the Standard Reference Compounds. *p,p*′-DDT was used as the standard reference compound, because its temperature-dependent vapor pressure is known very accurately. To derive the best vapor pressure estimate based on all the determinations that have been reported (Balson, 1947; Spencer and Cliath, 1972; Rothman, 1980; Wania et al., 1994), the individual observed solid vapor pressure data P_S from these four studies were regressed against reciprocal absolute temperature (Figure 2), obtaining

$$\log(P_S/\text{Pa}) = 16.28 - 6148\ (T/\text{K})^{-1} \qquad r^2 = 0.998 \quad (1)$$

This relationship was converted to the vapor pressure of the supercooled liquid using an entropy of fusion $\Delta_{FUS}S$ of 72.8 J·K^{-1}·mol^{-1} and a melting point temperature T_m of

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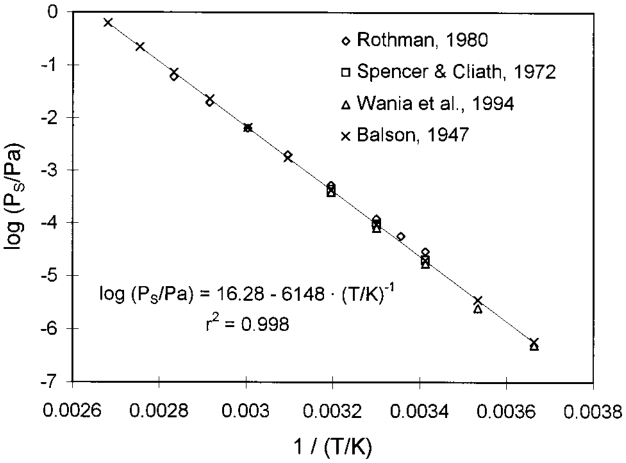

Figure 2. Vapor pressure of the solid substance P_S of reference compound *p,p′*-DDT as a function of temperature as constructed from data reported in Balson (1947), Spencer and Cliath (1972), Rothman (1980), and Wania et al. (1994).

382.05 K (Mackay et al., 1997):

$$\log(P_L/\mathrm{Pa}) = 12.48 - 4695\ (T/\mathrm{K})^{-1} \qquad (2)$$

Octadecane was used as the standard reference compound for the monochlorinated naphthalenes. Its vapor pressure is given as a function of temperature in Macknick and Prausnitz (1979).

Calibration Procedure Using Polychlorinated Biphenyls. Hamilton (1980), Bidleman (1984), and Hinckley et al. (1990) have described in detail how to calculate vapor pressures P_{GC} from gas chromatographic retention times at different temperatures. P_{GC} is not always identical to the vapor pressure of the (supercooled) liquid P_L but tends to be highly correlated with it. To obtain reliable P_L data, a calibration of the method with closely related compounds is advisable (Bidleman, 1984). This was accomplished by employing PCB congeners for which vapor pressure had been determined by the effusion and gas saturation column techniques (Table 1). P_{GC} for these PCB congeners was determined as described in Bidleman (1984) and regressed against the literature data of the vapor pressure of the supercooled liquid P_L given in Table 1. The following relationship was obtained:

$$\log(P_{GC}/\mathrm{Pa}) = 0.969 \log(P_L/\mathrm{Pa}) - 0.00015 \qquad r^2 = 0.968 \quad (3)$$

The slope close to 1, the intercept close to 0, and the high correlation coefficient indicate that the P_{GC}s are very close to the P_Ls for nonpolar aromatic compounds and only a minor correction is necessary.

Determination of the Vapor Pressure of 17 PCN Congeners. For 17 PCN congeners P_{GC} was determined from gas chromatographic retention times using the procedure given in Bidleman (1984). P_L at 298.15 K for these congeners was then calculated using the calibration eq 3. The temperature dependence of these vapor pressures, namely, slope and intercepts of Antoine type relationships,

$$\log(P_L/\mathrm{Pa}) = m_L/(T/\mathrm{K}) + b_L \qquad (4)$$

were estimated following the procedure outlined in Bidleman (1984).

Estimation of the Vapor Pressure of the Remaining PCN Congeners. For the remaining 58 congeners P_L was estimated using their retention times relative to pentachlorobenzene, t_R, on a 5% phenyl−methylpolysiloxane column reported by Järnberg et al. (1994). The predicted, rather than the measured, retention indices from that study were used, because that data set was more complete including all congeners from di- up to octachloronaphthalene. The measured P_L of the 17 PCN congeners was regressed against t_R. The relationship was not linear (Figure 3), but a very tight correlation of the following type could be established:

$$\log(P_L/\mathrm{Pa}) = -10.11 + \frac{45.99}{3.709 + t_R} \qquad r^2 = 0.996 \quad (5)$$

P_L for the other congeners was calculated using their retention index t_R and eq 5.

Estimation of the Temperature Dependence of the Vapor Pressure. To estimate the temperature dependence of the vapor pressure of the remaining 58 congeners, we regressed the slopes m_L obtained for the 15 congeners, which were measured with *p,p′*-DDT as a standard reference compound, versus the number of chlorine atoms n_{Cl} per molecule (Figure 4). A very good fit was obtained with a linear regression:

$$m_L = -315.7\ n_{Cl} - 2537 \qquad r^2 = 0.993 \qquad (6)$$

Results

Table 2 lists the measured vapor pressures P_{GC} and P_L of the 17 PCN congeners at 298.15 K and the intercepts b_L and slopes m_L of the temperature regressions (eq 4), as well as the enthalpy of vaporization $\Delta_{VAP}H$ (applicable to the temperature range of the GC measurements, i.e., 323.15 to 423.15 K) derived from the slopes m_L. The results for P_{GC} were very reproducible, as seen from the small standard deviation derived from at least three independent determinations. Tables 3 and 4 list the results for P_L, b_L, and m_L obtained with the regression methods for all PCN congeners.

Discussion

Relationship between log P_L and Molecular Size. Figure 5 is a plot of vapor pressure log P_L against the Le Bas molar volume V_M for the 17 PCN congeners. For comparison, it also shows regressions for the vapor pressure of PCBs (Falconer and Bidleman, 1994) and chlorobenzenes (CBzs) (Mackay et al., 1992). Each additional chlorine substitution decreases the vapor pressure of PCNs by a factor of approximately 4 to 5. Compared to the PCBs, the PCNs and CBzs show a tight linear relationship between log P_L and molecular size; i.e., size alone accounts for a large fraction of the variability in log P_L. PCBs show much more scatter because their substitution pattern affects the orientation of the two aromatic rings, namely, their coplanarity, which in turn affects vapor pressure. PCBs with more than one chlorine substitution in ortho-positions (2, 2′, 6, 6′) (multiortho PCBs) have a higher vapor pressure than PCBs with one or no chlorine in such positions (coplanar PCBs). This difference increases with the degree of chlorination. In contrast, the number of chlorine substitutions in the α- and *β*-positions (Figure 1) has little effect on the vapor pressure of PCNs. PCNs and CBzs are always planar, independent of substitution pattern.

The slope of the log P_L versus V_M relationship for the PCNs is similar to that of the coplanar PCBs (and that of

Table 1. Vapor Pressure Data for the PCB Congeners Used in the Calibration of the GC Retention Time Method for PCNs[a]

ID	PCB congener	P_{GC}/Pa	P_L/Pa	ref
PCB-3	4-monochlorobiphenyl	0.291 ± 0.008	0.555	Burkhard et al., 1984
			0.364	Wania et al., 1994
			0.253	Ferro et al., 1983
PCB-15	4,4-dichlorobiphenyl	0.049 4 ± 0.002	0.042 3	Wania et al., 1994
PCB-33	2′,3,4-trichlorobiphenyl	0.019 9 ± 0.000 5	0.029 6	Westcott et al., 1981
PCB-61	2,3,4,5-tetrachlorobiphenyl	0.005 88 ± 0.000 03	0.002 57	Wania et al., 1994
PCB-52	2,2′,5,5′-tetrachlorobiphenyl	0.012 5 ± 0.0001	0.008 30	Westcott et al., 1981
PCB-101	2,2′,4,5,5′-pentachlorobiphenyl	0.003 45 ± 0.000 02	0.003 01	Westcott et al., 1981
PCB-155	2,2′,4,4′,6,6′-hexachlorobiphenyl	0.000 854 ± 0.000 003	0.002 66	Wania et al., 1994
PCB-202	2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl	0.000 231 ± 0.000 001	0.000 536	Burkhard et al., 1984
PCB-209	decachlorobiphenyl	0.000 0135 ± 0.000 0001	0.000 0145	Burkhard et al., 1984

[a] P_{GC}s are the uncorrected vapor pressures determined by the GC retention time method, P_Ls are vapor pressures of the supercooled liquid compiled from the literature. Solid vapor pressure data given in the reference were converted to P_L using a conversion equation based on melting point and entropy of fusion (from Mackay et al. (1992)).

Table 2. GC Determined Vapor Pressure P_{GC} with Standard Deviation from Three Independent Determinations, Supercooled Liquid Vapor Pressure P_L at 298.15 K, Slopes m_L, and Intercepts b_L of Equation 4 for 17 PCN Congeners and Enthalpies of Vaporization $\Delta_{VAP}H$ Estimated from the Slopes m_L

ID	compound	P_{GC}/Pa	P_L/Pa	m_L	b_L
PCN-1	1-monochloronaphthalene	3.75 ± 0.01	3.597	−3058	10.81
PCN-2	2-monochloronaphthalene	3.84 ± 0.03	3.679	−3054	10.81
PCN-3	1,2-dichloronaphthalene	0.333 ± 0.023	0.344	−3172	10.18
PCN-5	1,4-dichloronaphthalene	0.416 ± 0.012	0.428	−3067	9.92
PCN-13	1,2,3 -trichloronaphthalene	0.065 2 ± 0.000 7	0.071 0	−3551	10.76
PCN-27	1,2,3,4-tetrachloronaphthalene	0.017 3 ± 0.000 1	0.019 7	−3825	11.12
PCN-28	1,2,3,5-tetrachloronaphthalene	0.017 9 ± 0.000 1	0.020 3	−3836	11.17
PCN-34	1,2,4,7-tetrachloronaphthalene	0.024 8 ± 0.000 4	0.027 8	−3763	11.06
PCN-50	1,2,3,4,6-pentachloronaphthalene	0.004 75 ± 0.000 10	0.005 62	−4123	11.58
PCN-52	1,2,3,5,7-pentachloronaphthalene	0.005 93 ± 0.000 04	0.006 96	−4082	11.53
PCN-53	1,2,3,5,8-pentachloronaphthalene	0.003 29 ± 0.000 01	0.003 94	−4204	11.70
PCN-66	1,2,3,4,6,7-hexachloronaphthalene	0.001 21 ± 0.000 00	0.001 50	−4411	11.97
PCN-67	1,2,3,5,6,7-hexachloronaphthalene	0.001 21 ± 0.000 00	0.001 50	−4411	11.97
PCN-69	1,2,3,5,7,8-hexachloronaphthalene	0.001 00 ± 0.000 03	0.001 24	−4441	11.99
PCN-71	1,2,4,5,6,8-hexachloronaphthalene	0.000 957 ± 0.000 006	0.001 19	−4456	12.02
PCN-73	1,2,3,4,5,6,7- heptachloronaphthalene	0.000 225 ± 0.000 002	0.000 293	−4745	12.38
PCN-75	octachloronaphthalene	0.000 0560 ± 0.000 0008	0.000 0761	−5021	12.72

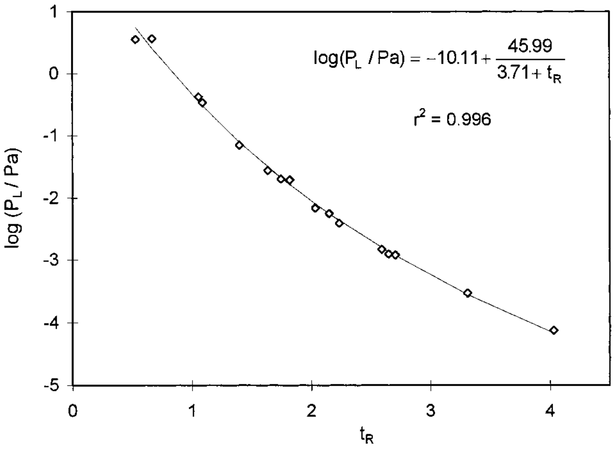

Figure 3. Regression of the measured vapor pressure log P_L at 298.15 K for 17 polychlorinated naphthalene congeners (Table 2) with the relative retention time indices reported by Järnberg et al. (1994).

the CBzs) but steeper than that for the multiortho PCBs. The larger size of the biphenyl relative to the naphthalene structure thus results in vapor pressures of the PCNs which are higher by a factor of approximately 4 relative to that of coplanar PCBs with the same number of chlorines. The comparison between PCNs and multiortho PCBs is more complex: A dichloronaphthalene tends to have twice the vapor pressure of a multiortho dichlorobiphenyl, but octachloronaphthalene has approximately the same vapor pressure as multiortho octachlorobiphenyls.

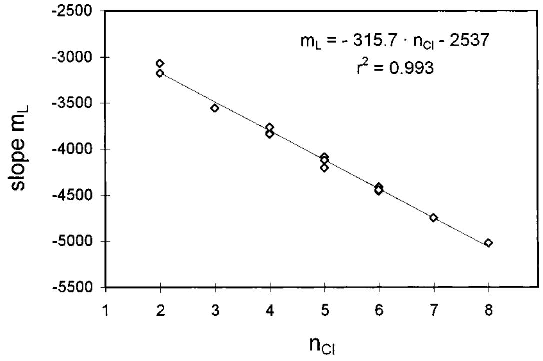

Figure 4. Regression of the measured slope m_L of eq 4 (Table 2) with the number of chlorine substitutions for 15 polychlorinated naphthalene congeners.

Table 3. Slopes m_L of Equation 4 for PCN Homologues Based on a Regression of Measured Slopes m_L (Table 2) versus the Number of Chlorine Atoms per Molecule n_{Cl}

n_{Cl}	m_L	n_{Cl}	m_L
1	−2853	5	−4116
2	−3169	6	−4432
3	−3485	7	−4748
4	−3800	8	−5063

Relationship between $\Delta_{VAP}H$ and Molecular Size. Figure 6 shows the relationship between the regressed enthalpy of vaporization (calculated from the slopes m_L in Table 3) and molecular size for PCNs, and various groups of PCBs (data from Falconer and Bidleman (1994). Each additional chlorine substitution decreases the heat of

Table 4. Supercooled Liquid Vapor Pressure P_L (Pa) at 298.15 K for All 75 PCN Congeners Determined by Regression with Retention Time Indices t_R Reported by Järnberg et al. (1994) and Intercepts b_L of Equation 4 If the Regressed Slopes m_L from Table 3 are Used[a]

ID	substitution	n_{Cl}	α-Cl	t_R	P_L	b_L	ID	substitution	n_{Cl}	α-Cl	t_R	P_L	b_L
PCN-1	*1*	*1*	*1*	*0.528*	*5.588*	*10.32*	PCN-39	1,2,6,7	4	1	1.754	0.020 5	11.06
PCN-2	*2*	*1*	*0*	*0.667*	*2.526*	*9.97*	PCN-40	1,2,6,8	4	2	1.832	0.015 6	10.94
PCN-3	*1,2*	*2*	*1*	*1.089*	*0.301*	*10.11*	PCN-41	1,2,7,8	4	2	1.907	0.012 1	10.83
PCN-4	*1,3*	*2*	*1*	*1.058*	*0.347*	*10.17*	PCN-42	1,3,5,7	4	2	1.562	0.041 5	11.36
PCN-5	1,4	2	2	1.055	0.352	10.17	PCN-43	1,3,5,8	4	3	1.749	0.020 8	11.07
PCN-6	1,5	2	2	1.055	0.352	10.17	PCN-44	1,3,6,7	4	1	1.679	0.026 8	11.17
PCN-7	1,6	2	1	1.055	0.352	10.17	PCN-45	1,3,6,8	4	2	1.758	0.020 2	11.05
PCN-8	1,7	2	1	1.055	0.352	10.17	PCN-46	1,4,5,8	4	4	1.936	0.011 0	10.79
PCN-9	1,8	2	2	1.181	0.198	9.93	PCN-47	1,4,6,7	4	2	1.67	0.027 7	11.19
PCN-10	2,3	2	0	1.067	0.333	10.15	PCN-48	2,3,6,7	4	2	1.796	0.017 7	10.99
PCN-11	2,6	2	0	1.06	0.344	10.16	PCN-49	1,2,3,4,5	5	3	2.352	0.003 02	11.29
PCN-12	2,7	2	0	1.06	0.344	10.16	*PCN-50*	*1,2,3,4,6*	*5*	*2*	*2.151*	*0.005 50*	*11.55*
PCN-13	*1,2,3*	*3*	*1*	*1.398*	*0.0791*	*10.59*	PCN-51	1,2,3,5,6	5	2	2.151	0.005 50	11.55
PCN-14	1,2,4	3	2	1.371	0.0883	10.63	*PCN-52*	*1,2,3,5,7*	*5*	*2*	*2.033*	*0.007 98*	*11.71*
PCN-15	1,2,5	3	2	1.371	0.0883	10.63	*PCN-53*	*1,2,3,5,8*	*5*	*3*	*2.234*	*0.004 28*	*11.44*
PCN-16	1,2,6	3	1	1.366	0.0901	10.64	PCN-54	1,2,3,6,7	5	1	2.199	0.004 75	11.48
PCN-17	1,2,7	3	1	1.366	0.0901	10.64	PCN-55	1,2,3,6,8	5	2	2.267	0.003 88	11.39
PCN-18	1,2,8	3	2	1.436	0.0678	10.52	PCN-56	1,2,3,7,8	5	2	2.385	0.002 75	11.24
PCN-19	1,3,5	3	2	1.315	0.111	10.73	PCN-57	1,2,4,5,6	5	3	2.219	0.004 47	11.46
PCN-20	1,3,6	3	1	1.31	0.114	10.74	PCN-58	1,2,4,5,7	5	3	2.101	0.006 43	11.61
PCN-21	1,3,7	3	1	1.31	0.114	10.74	PCN-59	1,2,4,5,8	5	4	2.302	0.003 50	11.35
PCN-22	1,3,8	3	2	1.379	0.0854	10.62	PCN-60	1,2,4,6,7	5	2	2.033	0.007 98	11.71
PCN-23	1,4,5	3	3	1.384	0.0837	10.61	PCN-61	1,2,4,6,8	5	3	2.101	0.006 43	11.61
PCN-24	1,4,6	3	2	1.315	0.111	10.73	PCN-62	1,2,4,7,8	5	3	2.219	0.004 47	11.46
PCN-25	1,6,7	3	1	1.342	0.0995	10.69	PCN-63	1,2,3,4,5,6	6	3	2.809	0.000 888	11.81
PCN-26	2,3,6	3	0	1.393	0.0807	10.59	PCN-64	1,2,3,4,5,7	6	3	2.647	0.001 34	11.99
PCN-27	*1,2,3,4*	*4*	*2*	*1.82*	*0.0162*	*10.96*	PCN-65	1,2,3,4,5,8	6	4	2.861	0.000 781	11.76
PCN-28	*1,2,3,5*	*4*	*2*	*1.754*	*0.0205*	*11.06*	*PCN-66*	*1,2,3,4,6,7*	*6*	*2*	*2.589*	*0.001 57*	*12.06*
PCN-29	1,2,3,6	4	1	1.754	0.0205	11.06	*PCN-67*	*1,2,3,5,6,7*	*6*	*2*	*2.589*	*0.001 57*	*12.06*
PCN-30	1,2,3,7	4	1	1.754	0.0205	11.06	PCN-68	1,2,3,5,6,8	6	3	2.647	0.001 34	11.99
PCN-31	1,2,3,8	4	2	1.941	0.0108	10.78	PCN-69	1,2,3,5,7,8	6	3	2.647	0.001 34	11.99
PCN-32	1,2,4,5	4	3	1.824	0.0160	10.95	PCN-70	1,2,3,6,7,8	6	2	2.886	0.000 734	11.73
PCN-33	1,2,4,6	4	2	1.637	0.0313	11.24	*PCN-71*	*1,2,4,5,6,8*	*6*	*4*	*2.705*	*0.001 16*	*11.93*
PCN-34	*1,2,4,7*	*4*	*2*	*1.637*	*0.0313*	*11.24*	PCN-72	1,2,4,5,7,8	6	4	2.705	0.00116	11.93
PCN-35	1,2,4,8	4	3	1.824	0.0160	10.95	*PCN-73*	*1,2,3,4,5,6,7*	*7*	*3*	*3.31*	*0.000 278*	*12.37*
PCN-36	1,2,5,6	4	2	1.711	0.0239	11.12	PCN-74	1,2,3,4,5,6,8	7	4	3.368	0.000 246	12.31
PCN-37	1,2,5,7	4	2	1.637	0.0313	11.24	*PCN-75*	*1,2,3,4,5,6,7,8*	*8*	*4*	*4.03*	*0.000 0684*	*12.82*
PCN-38	1,2,5,8	4	3	1.824	0.0160	10.95							

[a] In italics are those congeners for which measured P_L and b_L are given in Table 2.

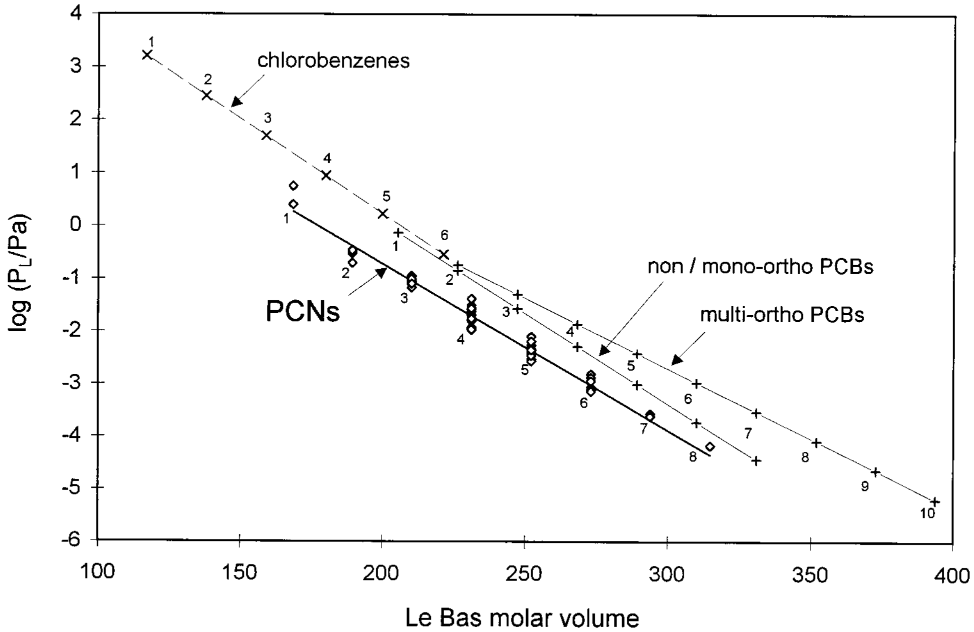

Figure 5. Relationship between regressed vapor pressure log P_L (Table 4) and the Le Bas molar volume for all 75 PCN congeners. For comparison regression lines for PCBs and chlorobenzenes are also shown (P_L data from Falconer and Bidleman (1994) and Mackay et al. (1992)). The small numbers indicate the number of chlorine substitutions.

vaporization of PCNs by approximately 6 kJ·mol^{-1}. The $\Delta_{VAP}H$ of the PCNs are very similar to that of monoortho PCBs of the same size, but lower than those of PCBs with more than one ortho-chlorine.

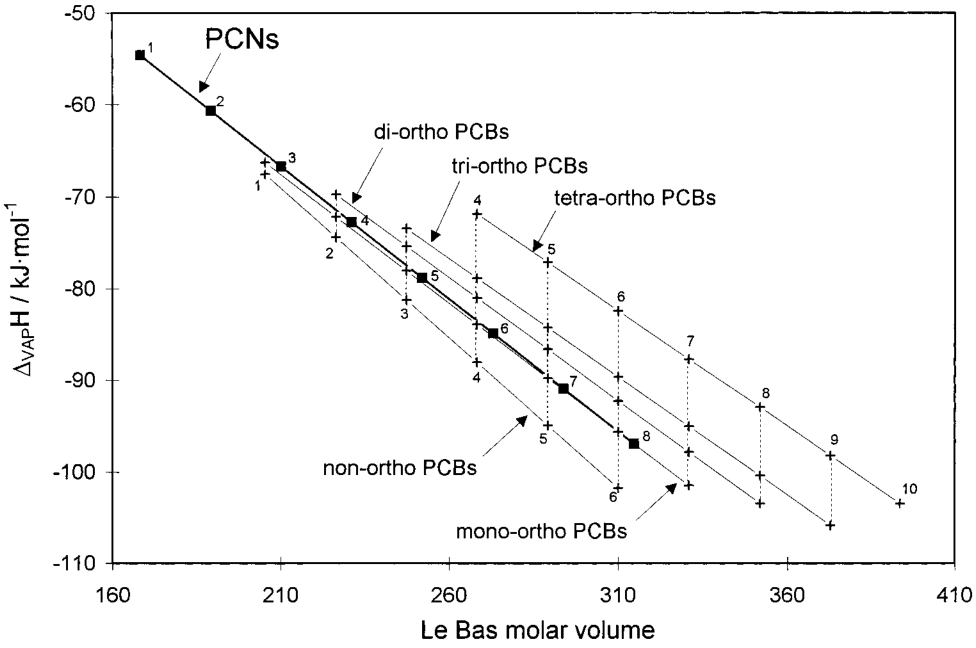

Figure 6. Relationship between regressed heats of vaporization $\Delta_{VAP}H$ (from m_L in Table 3) and the Le Bas molar volume V_M for PCNs and various groups of PCBs. The small numbers indicate the number of chlorine substitutions.

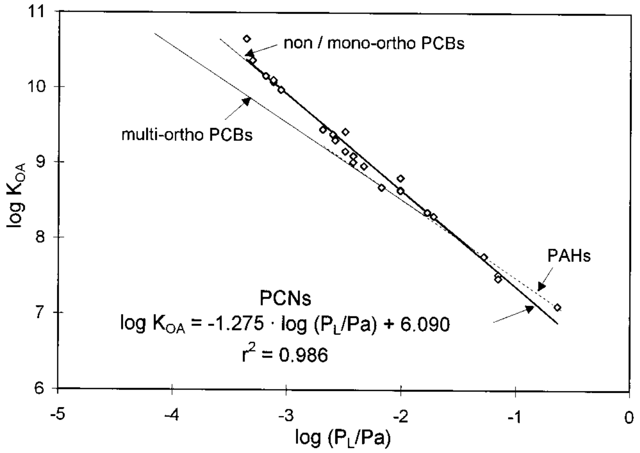

Figure 7. Correlation between measured log K_{OA} (Harner and Bidleman, 1998) and regressed log P_L (Table 4) at 293.15 K for PCNs. Regression lines for two groups of PCBs (Harner and Bidleman, 1996) and PAHs (Harner and Bidleman, 1998) are also shown.

Relationship of P_L with 1-Octanol−Air Partition Coefficients K_{OA}. Measured K_{OA} for many PCN congeners have been reported (Harner and Bidleman, 1998). A strong linear relationship between log K_{OA} and log P_L, both at 293.15 K, exists for the PCNs (Figure 7):

$$\log K_{OA} = -1.241 \log(P_L/\text{Pa}) + 6.146 \qquad r^2 = 0.988 \quad (7)$$

Such relationships have previously been reported for PCB congeners (Harner and Bidleman, 1996) and PAHs (Harner and Bidleman, 1998), and these regression lines are included in Figure 6 for comparison. The regression line for PCNs is virtually identical with the one reported for the nonortho and monoortho chlorinated PCBs; i.e., at higher degrees of chlorination they have a significantly higher K_{OA} than multiortho PCBs of the same vapor pressure.

According to Goss and Schwarzenbach (1998), the fact that the relationship between log K_{OA} and log P_L is linear for the PCNs indicates that the change in the activity coefficient in octanol upon adding a chlorine, $\Delta \log \gamma$, is proportional to the change in vapor pressure, $\Delta \log P_L$. They argue further that the extent to which the slope in eq 7 deviates from −1 indicates the affinity of the chlorine substituents to 1-octanol relative to the pure liquid PCN phase. The slope −1.24 thus implies that the higher chlorinated PCNs (and coplanar PCBs) have a greater affinity for octanol (relative to the pure phase) than the lower chlorinated PCNs (and coplanar PCBs). This is confirmed by calculating activity coefficients in 1-octanol from K_{OA} and P_L using:

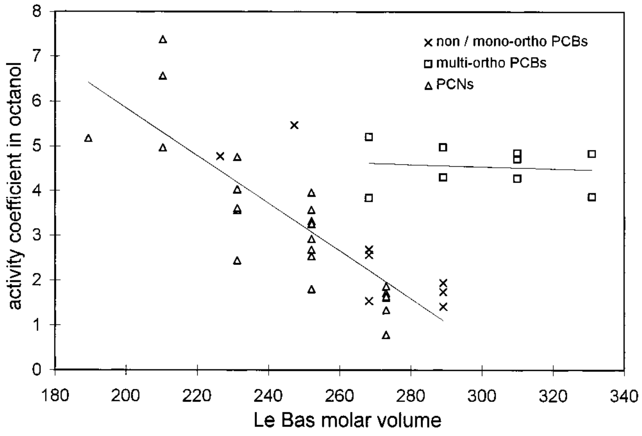

Figure 8. Relationship of the estimated activity coefficients in octanol and the Le Bas molar volume for selected PCN and PCB congeners.

$$\gamma = RT/(P_L K_{OA} V_{Oct}) \quad (8)$$

where R is ideal gas constant, T absolute temperature, and V_{Oct} the molar volume of 1-octanol (0.000 158 m^3·mol^{-1}). Activity coefficients in 1-octanol γ for the PCN and PCB congeners for which K_{OA} had been reported (Harner and Bidleman, 1996, 1998) are plotted against molecular size in Figure 8. Whereas the activity coefficients of the multiortho PCBs are not changing with the degree of chlorination (but are constant at around 4 to 5), those of the PCNs and non-/monoortho PCBs are decreasing with an increasing degree of chlorination. With more than six chlorine substituents the planar PCBs and PCNs may actually have a similar affinity to the octanol phase than to their own pure liquid phase.

The planarity of the two-ring aromatic structures of both the PCNs and non-/monoortho PCBs obviously enhances partitioning into octanol at higher degrees of chlorination, whereas this is not the case for the multiortho PCBs. Highly substituted planar aromatic two-ring molecular structures are bulky and inflexible, which may impede their ability to interact with each other. If there are too many chlorine substituents, it may become sterically preferable to interact with the more flexible, and smaller, 1-octanol molecules. Intermolecular interactions are decreasing rapidly with increasing distance and should thus be notably smaller if the molecules keep a greater distance because of their size and inflexibility.

P_L as a Criterion for Long-Range Transport Potential. Wania and Mackay (1996) have suggested that persistent chemicals have the tendency to be transported as far as, and be preferentially deposited in, polar regions if their log P_L at 298.15 K is between 0 and -2. Among the PCNs the di -through tetrachlorinated homologues fall into this vapor pressure range (Tables 2 and 4). Indeed, Harner et al. (1998) observed that the tri- and tetrachlorinated homologues accounted for 90−95% of the total mass of PCNs detected in the Arctic atmosphere, lending further credibility to this criterion of long-range transport potential.

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