Measurement of Octanol−Air Partition Coefficients for Polycyclic Aromatic Hydrocarbons and Polychlorinated Naphthalenes

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Measurements of the octanol−air partition coefficient, K_{OA}, are reported for 4 polycyclic aromatic hydrocarbons (PAHs) and 24 polychlorinated naphthalenes (PCNs) as a function of temperature over the range (0 to 50) °C. Results for PAHs are within a factor of 1.5 to 2 of values calculated as the ratio of the octanol−water and air−water partition coefficients. The enthalpies of transfer from octanol to air, $\Delta_O^A H$, for fluorene, phananthrene and pyrene are (82.9, 75.5, and 76.3) kJ/mol, respectively. Except for fluorene, these are within the range of reported values of the enthalpy of vaporization, $\Delta_{vap}H$. There is also good agreement between $\Delta_O^A H$ and the temperature coefficient for vegetation-atmosphere partitioning (Q_D). Correlations of log K_{OA} against log vapor pressure (p^o) are compared with previous results for polychlorinated biphenyls (PCBs). Values of log K_{OA} for PCNs show a stepwise change and increase by more than 3 orders of magnitude from the 2-Cl to 6-Cl homologue groups.

Introduction

Physical chemical properties and their variation with temperature control the cycling and transport of persistent organic pollutants. The octanol−air partition coefficient, K_{OA}, is thought to be the key descriptor of the partitioning of semivolatile compounds between the atmosphere and terrestrial organic phases (Wania and Mackay, 1996). These include organic carbon in soil, the waxy cuticle and lipid portion of vegetation (Bacci et al., 1990a,b; Paterson et al., 1991; Tolls and McLachlan, 1994; Simonich and Hites, 1995; Kömp and McLachlan, 1997a), and the organic film that coats atmospheric particulate matter (Finizio et al., 1997).

K_{OA} is the ratio of the solute concentration in octanol, C_O (mass/volume), to the concentration in air, C_A (mass/volume), when the octanol−air system is at equilibrium, i.e., $K_{OA} = C_O/C_A$. Hence K_{OA} is dimensionless. It is possible to calculate K_{OA} as the ratio of the octanol−water and air−water partition coefficients, i.e., $K_{OA} = K_{OW}/K_{AW}$. K_{AW} is H/RT, where H is the Henry's law constant, T is absolute temperature, and R is the ideal gas constant. However, almost no physicochemical data exist for PCNs, and the literature values of K_{OW} and H for some PAHs vary by more than an order of magnitude (Mackay et al., 1992; Sangster, 1989). These errors will be propagated in the calculation. Another problem is the absence of temperature-dependent data for H and K_{OW}. It is therefore desirable to measure K_{OA} directly as a function of temperature.

Previous papers (Harner and Mackay, 1995; Harner and Bidleman, 1996) described a novel method for measuring K_{OA} using a generator column containing glass wool coated with a solution of the chemical in octanol. Values were reported for chlorobenzenes, PCBs, and DDT over the temperature range (−10 to +30) °C. This paper reports

K_{OA} values as a function of temperature for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated naphthalenes (PCNs). PAHs and PCNs are widespread and persistent environmental contaminants. PAHs are combustion products, and the 2-4 ring compounds partition between the gas phase and vegetation according to their vapor pressures or K_{OA} values (Simonich and Hites, 1996; Tremolada et al., 1996). PCNs were introduced in the 1920s as commercial mixtures (e.g. Halowaxes) primarily as dielectric fluids (Crookes and Howe, 1993). PCNs have been reported in incinerator emissions (Oehme et al., 1987), ambient air (Harner and Bidleman, 1997; Dörr et al., 1996) and sediment and biota from the Baltic region (Falandysz et al., 1996a,b; Falandysz and Rappe, 1996; Järnberg et al., 1997). Some congeners have high tetrachlorodibenzodioxin toxic equivalents (TEQs), comparable to those for the coplanar PCBs (Järnberg et al., 1993; Harner and Bidleman, 1997).

Theoretical Background

In a previous paper (Harner and Bidleman, 1996), a number of sign errors were made in the equations describing K_{OA} theory. This section is repeated below with proper signs.

The octanol−air partition coefficient can be expressed as

$$K_{OA} = c_O/c_A = s^o/(p^o/RT) \qquad (1)$$

where p^o and s^o are solid-phase vapor pressure and solubility in octanol. The temperature variations of p^o and s^o are described by the following equations

$$\log p^o = -\Delta_{sub}H/2.303RT + b_{sub} \qquad (2)$$

$$\log s^o = -\Delta_{sol}H/2.303RT + b_{sol} \qquad (3)$$

where the ΔH terms and the b variables are assumed to be temperature independent. $\Delta_{sub}H$ (J/mol) is the enthalpy

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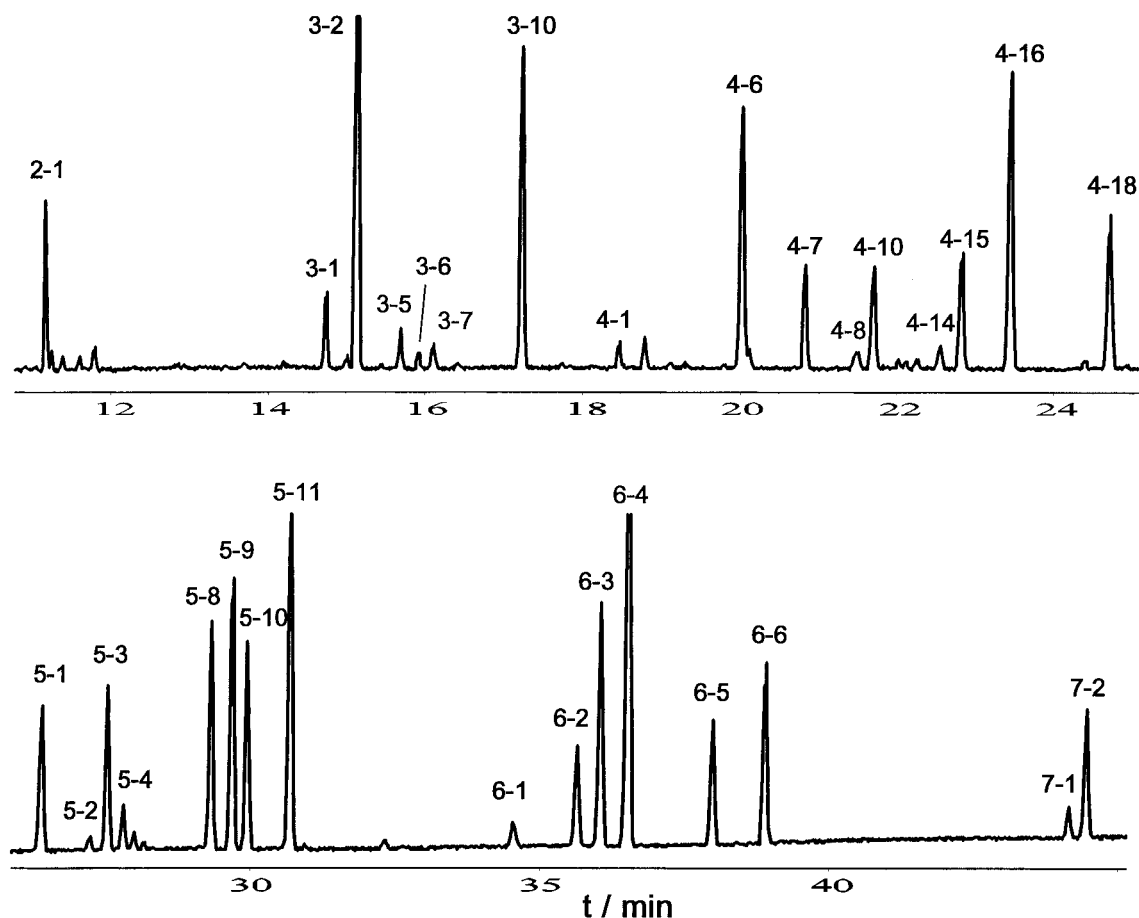[†] University of Toronto.
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Figure 1. GC-FID chromatogram of Halowax 1014 with major PCN peaks identified (see Table 1), 60 m, DB5-MS column.

of sublimation and $\Delta_{sol}H$ (J/mol) is the enthalpy of dissolution in octanol. The enthalpy associated with the transition from octanol solution to air is $\Delta_O^A H$. The temperature dependence of K_{OA} is described by

$$\log K_{OA} = (\Delta_{sub}H - \Delta_{sol}H)/2.303RT - b_{sub} + b_{sol} + \log RT \quad (4)$$

According to eq 4, a plot of $\log K_{OA}$ vs $1/T$ is only approximately linear because the term $\log RT$ is a weak function of temperature. Octanol–air partitioning can also be defined by

$$K'_{OA} = s^o/p^o = K_{OA}/RT = (\Delta_{sub}H - \Delta_{sol}H)/2.303RT - b_{sub} + b_{sol} \quad (5)$$

where K'_{OA} has units of concentration/pressure, $\Delta_O^A H = \Delta_{sub}H - \Delta_{sol}H$, and the intercept $(b_{sol} - b_{sub})$ is a constant.

Experimental Section

A description of the apparatus used to measure K_{OA} and an outline of the experimental procedure are presented in an earlier paper (Harner and Bidleman, 1996). Octanol solutions of PAHs were prepared from solids obtained from Accustandard (New Haven, CT). Solutions of PCNs in octanol were prepared by diluting pure Halowax 1014 (United States Environmental Protection Agency, Repository for Pesticides and Industrial Chemicals, Research Triangle Park, NC). Concentrations of individual PAHs ranged from (0.2 to 0.3) g/L. The octanol solution of PCNs contained 3.3 g/L of Halowax 1014. Octanol-saturated

nitrogen was passed through a thermostated generator column containing glass wool coated with the octanol solution. Effluent compounds were trapped on C_8-bonded silica (Varian Corp.), which was extracted with 30% dichloromethane in petroleum ether. Flow rates for the PAH and PCN experiments ranged from (70–100) mL/min, and measurement temperatures ranged from (0 to 50) °C for PAHs and (10 to 50) °C for PCNs.

PAHs were determined using a Hewlett-Packard 5890 Plus GC equipped with a flame ionization detector (FID). Compounds were eluted on a 60 m DB-5 capillary column (J&W Scientific) with 0.25 mm i.d. and 0.25 mm film thickness, operated with hydrogen carrier gas at 50 cm/s. Injections (1 mL) were splitless with the split opened after 0.5 min. The temperature program was 90 °C for 0.5 min, 10 °C/min to 160 °C, and 2 °C/min to 250 °C. Injector and detector temperatures were (250 and 300) °C. Peaks were quantified against a mixture of PAH standards (Axact Standards, Commack, NY), and PCB-110 (Accustandard, New Haven, CT) was used as internal standard for volume correction.

PCN measurements were performed using an octanol solution of Halowax 1014, a commercial mixture containing mostly 4-7 chlorinated naphthalenes. PCNs in this mixture were quantified by a method that used GC-FID to estimate the mass percent contribution of the individual peaks in the FID chromatogram (Harner and Bidleman, 1997). FID response was assumed to respond to the carbon skeleton of the PCN molecule. Mass percent contributions $(m_i\%)$ were assigned using

Table 1. Mass Percent Contribution Assignments for PCNs in Halowax 1014 (GC-FID Chromatogram Using DB-5 Column)

peak a	peak b	congener[c]	mass contribution (%)	homolog contribution (%)
		Dichloronaphthalenes		0.9
2-1		CN-5 (1,4)	0.85	
		Trichloronaphthalenes		9.9
3-1	(3a)	CN-19 (1,3,5)	0.58	
3-2	(3b)	CN-24 (1,4,6)	5.87	
		CN-14 (1,2,4)		
3-5			0.36	
3-6			0.16	
3-7			0.30	
3-10		CN-23 (1,4,5)	2.65	
		Tetrachloronaphthalenes		14.0
4-1	(4a)	CN-42 (1,3,5,7)	0.31	
4-6	(4b)	CN-33 (1,2,4,6)	3.32	
		CN-34 (1,2,4,7)		
		CN-37 (1,2,5,7)		
4-7	(4c)	CN-47 (1,4,6,7)	1.26	
4-8		CN-36 (1,2,5,6)	0.40	
4-10	(4d)	CN-28 (1,2,3,5)	1.27	
		CN-43 (1,3,5,8)		
4-14	(4f)	CN-32 (1,2,4,5)	0.32	
4-15	(4g)	CN-35 (1,2,4,8)	1.48	
4-16	(4h)	CN-38 (1,2,5,8)	3.78	
4-18	(4i)	CN-46 (1,4,5,8)	1.90	
		Pentachloronaphthalenes		33.9
5-1	(5a)	CN-52 (1,2,3,5,7)	3.57	
		CN-60 (1,2,4,6,7)		
5-2	(5b)	CN-58 (1,2,4,5,7)	0.32	
5-3	(5c)	CN-61 (1,2,4,6,8)	3.78	
5-4	(5d)	CN-50 (1,2,3,4,6)	0.97	
5-8	(5e)	CN-57 (1,2,4,5,6)	5.57	
5-9	(5f)	CN-62 (1,2,4,7,8)	6.46	
5-10	(5g)	CN-53 (1,2,3,5,8)	4.81	
5-11	(5h)	CN-59 (1,2,4,5,8)	8.41	
		Hexachloronaphthalenes		32.4
6-1	(6a)	CN-66 (1,2,3,4,6,7)	0.89	
		CN-67 (1,2,3,5,6,7)		
6-2	(6b)	CN-64 (1,2,3,4,5,7)	3.00	
		CN-68 (1,2,3,5,6,8)		
6-3	(6c)	CN-69 (1,2,3,5,7,8)	7.08	
6-4	(6d)	CN-71 (1,2,4,5,6,8)	13.3	
		CN-72 (1,2,4,5,7,8)		
6-5	(6e)	CN-63 (1,2,3,4,5,6)	3.30	
6-6	(6f)	CN-65 (1,2,3,4,5,8)	4.87	
		Heptachloronaphthalenes		4.8
7-1	(7a)	CN-73 (1,2,3,4,5,6,7)	0.92	
7-2	(7b)	CN-74 (1,2,3,4,5,6,8)	3.90	
		Octachloronaphthalene		0.1
8	(8)	CN-75 (1,2,3,4,5,6,7,8)	0.13	

[a] Labeling scheme used in this work. [b] Labeling used in Järnberg et al. (1993, 1997). [c] Peaks identified by Imagawa et al. (1993) and Falandysz et al. (1996a).

$$m_i\% = 100(A_i)(M_i)/\sum_{i=1}^{n}(A_i)(M_i) \qquad (6)$$

where A_i is the area fraction of peak *i*, M_i is the molecular weight of compound *i*, and *n* is the total number of peaks integrated. It was not possible to assign mass percents to all of the congeners since some peaks coeluted on the DB-5 column. A series of *n*-alkanes was used to calibrate the FID response by normalizing the PCN response to an alkane having similar retention time. Concentrations of
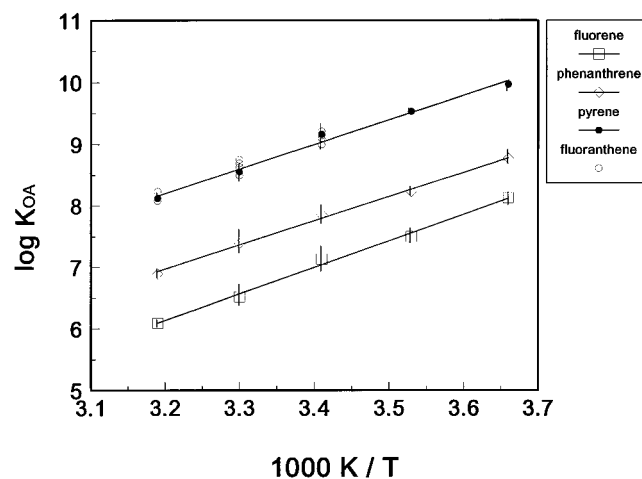

Figure 2. Summary of K_{OA} results for PAHs over the temperature range (0 to 40) °C, plot of eq 7. Symbols and bars represent mean and range of values for fluorene, phenanthrene, and pyrene; single data points are plotted for fluoranthene at (20, 30, and 40) °C.

the individual PCN congeners in octanol (0.01 to 0.44) g/L were calculated from the Halowax 1014 concentration and the mass percent contributions in Halowax 1014. GC-negative ion mass spectrometry was used to confirm the homologue identity of each peak.

Vaporized PCNs were quantified by GC using electron capture detection (GC-ECD). Halowax 1014 was used as the calibration solution, and PCB-103 (Accustandard, New Haven, CT) was used as internal standard for volume correction. Samples were analyzed on the same 60 m DB-5 column that was used for the PAH analysis with the same temperature program and other conditions.

Results and Discussion

Composition of Halowax 1014. Figure 1 is a labeled GC-FID chromatogram showing the 2 to 7 chlorinated PCN congeners. Peaks were labeled according to a new numbering scheme which accounted for peaks not previously identified in the literature. On the basis of FID response the mass percent contribution of individual congeners in Halowax 1014 was determined. Results are shown in Table 1, in which peaks are also identified by another labeling scheme used by Järnberg et al. (1993). IUPAC congener numbers and structures are also included for peaks that have been identified in the literature (Imagawa et al., 1993; Falandysz et al., 1996a).

Quality Control. The accuracy of the mass percent contribution of individual congeners relied on the accuracy of the GC-FID method for quantifying PCNs in the Halowax 1014 mixture. It was therefore important to validate this method using pure PCN solutions of known concentration. Pure compounds were obtained from the following sources. Congeners 1,2,4,7-TeCN (4b) and 1,2,3,5,7-PeCN (5a) were purchased from Larodan AB (Malmö, Sweden); 1,2,3,4,6,7-/1,2,3,5,6,7-HxCN (6a), 1,2,4,5,6,8-HxCN (6d), and 1,2,3,4,5,6,7-HeptaCN (7a) were gifts of Åke Bergman and Eva Jakobsson (Department of Environmental Chemistry, Stockholm University, Stockholm, Sweden); 1,2,3,4,5,6,7,8-OctaCN (8) was purchased from Ultra Scientific (Hope, Rhode Island). A solution containing known concentration of these congeners was quantified against the same peaks in Halowax 1014 using the percent composition information from GC-FID analysis. Results showed that the measured values were within ±22% of the true value for five out of the six congeners (Harner and Bidleman,

Table 2. Results for PAHs and PCNs ($K_{OA} \pm$ S.D.)

PAHs	0 °C ($n = 5$)	10 °C ($n = 9$)	20 °C ($n = 7$)	30 °C ($n = 4$)	40 °C ($n = 3$)
fluorene	$(1.36 \pm 0.27) \times 10^8$	$(3.17 \pm 0.60) \times 10^7$	$(1.35 \pm 0.48) \times 10^7$	$(3.28 \pm 0.77) \times 10^6$	$(1.24 \pm 0.09) \times 10^6$
phenanthrene	$(6.43 \pm 1.02) \times 10^8$	$(1.85 \pm 0.09) \times 10^8$	$(7.89 \pm 2.31) \times 10^7$	$(2.62 \pm 0.08) \times 10^7$	$(8.44 \pm 0.66) \times 10^6$
pyrene	$(9.24 \pm 1.89) \times 10^9$	$(3.37 \pm 0.29) \times 10^9$	$(1.43 \pm 0.53) \times 10^9$	$(3.52 \pm 0.78) \times 10^8$	$(1.32 \pm 0.05) \times 10^8$
fluoranthene[a]	n.d.	n.d.	$(1.33 \pm 0.25) \times 10^9$	$(4.49 \pm 1.06) \times 10^8$	$(1.45 \pm 0.35) \times 10^8$

PCNs	10 °C ($n = 1$)	20 °C ($n = 5$)	30 °C ($n = 2$)	40 °C ($n = 3$)	50 °C ($n = 3$)
2-1	3.34×10^7	$(1.36 \pm 0.24) \times 10^7$	5.20×10^6	$(2.40 \pm 0.28) \times 10^6$	$(1.35 \pm 0.20) \times 10^6$
3-1	9.24×10^7	$(4.25 \pm 0.78) \times 10^7$	1.10×10^7	$(4.61 \pm 0.63) \times 10^6$	$(2.39 \pm 0.05) \times 10^6$
3-2	8.04×10^7	$(3.53 \pm 0.86) \times 10^7$	1.08×10^7	$(4.38 \pm 0.37) \times 10^6$	$(2.29 \pm 0.01) \times 10^6$
3-10	1.73×10^8	$(7.09 \pm 1.63) \times 10^7$	1.94×10^7	$(7.64 \pm 0.87) \times 10^6$	$(3.92 \pm 0.09) \times 10^6$
4-6	6.14×10^8	$(2.29 \pm 0.45) \times 10^8$	6.57×10^7	$(2.47 \pm 0.32) \times 10^6$	$(1.22 \pm 0.03) \times 10^7$
4-7	7.00×10^8	$(2.62 \pm 0.56) \times 10^8$	7.38×10^7	$(2.69 \pm 0.36) \times 10^6$	$(1.32 \pm 0.03) \times 10^7$
4-14	n.d.	$(7.36 \pm 1.69) \times 10^8$	1.97×10^8	$(7.60 \pm 0.70) \times 10^7$	$(3.31 \pm 0.09) \times 10^7$
4-15	1.46×10^9	$(4.90 \pm 1.22) \times 10^8$	1.38×10^8	$(4.88 \pm 0.62) \times 10^7$	$(2.32 \pm 0.04) \times 10^7$
4-16	1.38×10^9	$(5.00 \pm 1.28) \times 10^8$	1.39×10^8	$(4.84 \pm 0.59) \times 10^7$	$(2.30 \pm 0.05) \times 10^7$
4-18	1.54×10^9	$(5.62 \pm 1.77) \times 10^8$	1.55×10^8	$(5.30 \pm 0.55) \times 10^7$	$(2.49 \pm 0.05) \times 10^7$
5-1	3.18×10^9	$(1.10 \pm 0.37) \times 10^9$	2.92×10^8	$(9.29 \pm 1.07) \times 10^7$	$(4.29 \pm 0.10) \times 10^7$
5-2	4.30×10^9	$(1.47 \pm 0.41) \times 10^9$	3.92×10^8	$(1.27 \pm 0.14) \times 10^8$	$(5.69 \pm 0.12) \times 10^7$
5-3	3.44×10^9	$(1.29 \pm 0.47) \times 10^9$	3.33×10^8	$(1.01 \pm 0.07) \times 10^8$	$(4.64 \pm 0.05) \times 10^7$
5-4	5.54×10^9	$(1.59 \pm 0.52) \times 10^9$	4.22×10^8	$(1.31 \pm 0.17) \times 10^8$	$(5.67 \pm 0.09) \times 10^7$
5-5	1.20×10^{10}	$(3.02 \pm 0.99) \times 10^9$	6.37×10^8	$(2.00 \pm 0.43) \times 10^8$	$(8.13 \pm 0.31) \times 10^7$
5-9	6.41×10^9	$(2.65 \pm 1.11) \times 10^9$	6.77×10^8	$(1.88 \pm 0.07) \times 10^8$	$(8.59 \pm 0.13) \times 10^7$
5-10	9.40×10^9	$(2.74 \pm 1.01) \times 10^9$	7.20×10^8	$(2.18 \pm 0.33) \times 10^8$	$(9.06 \pm 0.05) \times 10^7$
5-11	n.d.	$(3.11 \pm 1.35) \times 10^9$	7.78×10^8	$(2.25 \pm 0.17) \times 10^8$	$(9.57 \pm 0.19) \times 10^7$
6-1	3.77×10^{10}	$(1.03 \pm 0.27) \times 10^{10}$	2.90×10^9	$(6.88 \pm 0.31) \times 10^8$	$(2.65 \pm 0.07) \times 10^8$
6-2	n.d.	$(1.18 \pm 0.30) \times 10^{10}$	3.73×10^9	$(8.92 \pm 0.21) \times 10^8$	$(3.48 \pm 0.09) \times 10^8$
6-3	n.d.	$(1.23 \pm 0.24) \times 10^{10}$	4.13×10^9	$(9.73 \pm 0.22) \times 10^8$	$(3.71 \pm 0.10) \times 10^8$
6-4	n.d.	$(1.38 \pm 0.48) \times 10^{10}$	4.68×10^9	$(1.13 \pm 0.11) \times 10^9$	$(4.08 \pm 0.18) \times 10^8$
6-5	n.d.	$(2.12 \pm 0.46) \times 10^{10}$	8.81×10^9	$(2.22 \pm 0.28) \times 10^9$	$(7.49 \pm 0.51) \times 10^8$
6-6	n.d.	$(4.19 \pm 1.78) \times 10^{10}$	1.61×10^{10}	$(3.62 \pm 0.77) \times 10^9$	$(1.08 \pm 0.08) \times 10^9$

[a] For fluoranthene at (20, 30, and 40) °C, $n = 5$, 4, and 2 respectively; n.d. = not determined.

1997). The deviation for the sixth peak, CN-52 (1,2,3,5,7-PeCN, may be due to an underlying peak (CN-60) in the Halowax mixture as identified by Imagawa et al. (1993). Overestimation would occur if the response factor for CN-60 were less than for CN-52. However, small errors in estimating the mass percent contribution of individual congeners would not affect the accuracy of K_{OA}, since K_{OA} is a ratio of two concentrations.

In both PCN and PAH determinations of K_{OA}, the C_8 trap extracts were reduced to 0.2 mL by evaporation using a gentle stream of clean nitrogen. To correct for losses due to volatilization of the sample during this "blow-down" procedure, a series of spike recovery tests were performed. Recoveries for PCNs ($n = 3$) ranged from 65 to 85% with good reproducibility ($\pm 10\%$) for individual congeners. PAH recoveries were fluorene $89 \pm 2.6\%$, phenanthrene $93 \pm 2.3\%$, fluoranthene $102 \pm 0.6\%$, and pyrene $103 \pm 2.3\%$. Recovery factors for PCNs, fluorene, and phenanthrene were applied to trap extract results.

Large air volumes and hence sampling times were required to obtain a quantifiable amount of chemical in the air phase, especially for compounds with large K_{OA} values. In general, the sampling time approximately tripled for every 10 °C decrease in temperature. All experimental determinations of K_{OA} used an octanol solution consisting of several solutes; 2 to 4 compounds in the case of PAHs and approximately 30 components in the Halowax 1014 technical mixture. Earlier work showed no difference in K_{OA} value for a PCB in octanol solution as a single compound or as a component in a mixture (Harner and Bidleman, 1996). This test was repeated with phenanthrene. At 20 °C the K_{OA} value for phenanthrene alone in octanol was 7.78 ± 0.05 ($n = 6$), which was in good agreement with a value of 7.80 from the regression line for phenanthrene measured in the four-component PAH mixture.

Inherent in the measurement of K_{OA} values is the assumption that C_O remains constant. A decrease in C_O is expected due to the depletion of solute as it partitions into the air phase for extended periods of time. However, this change is quantifiable and occurs very slowly. To avoid errors due to a changing C_O, generator columns were replaced when more than 10% of the solute was depleted. This is only necessary for compounds with low K_{OA} values. Another process that can alter C_O (and result in anomalous K_{OA} values) is the accumulation or loss of pure octanol in the generator column. The assumption of a constant C_O was checked by extracting the generator column with a 30% dichloromethane in petroleum ether solvent mixture after several weeks of operation. Analysis of the extract gave values that were (10 to 20)% greater than the original octanol concentrations for a three-component mix of fluorene, pyrene, and chrysene. This result validates the assumption that C_O remains relatively constant over the duration of the K_{OA} measurement. However, more significant losses may occur for longer experiments despite presaturation of the generator column.

Results of K_{OA} Measurements. Values of K_{OA} as a function of temperature are presented in Figure 2 for fluorene, phenanthrene, and pyrene over the temperature range (0 to 40) °C and for fluoranthene at (20, 30, and 40) °C. PCN results are presented over the range (10 to 50) °C. Experimental data (Table 2) demonstrate good reproducibility. Standard deviations were less than 10% for most determinations and never exceeded 50%. The parameters of eq 7, which describes the temperature dependence of K_{OA}, are listed in Table 3 (PAHs) and Table 4 (PCNs).

$$\log K_{OA} = A + B/T \tag{7}$$

As explained in the Theoretical Background section, this

Table 3. Regression Parameters for Eq 7 (PAHs) and Measured versus Calculated K_{OA} Values at 25 °C

compound, PAHs	r^2	A	B	range (°C)	log K_{OW}[a]	H (Pa m^3 mol^{-1})	log K_{OA} (calcd)	log K_{OA} (measd)	factor difference
fluorene	0.995	−7.74	4332	0 to 40	4.18a	9.75[b]	6.59	6.79	1.58
phenanthrene	0.996	−5.62	3942	0 to 40	4.57a	3.61[b]	7.41	7.57	1.45
pyrene	0.990	−4.56	3985	0 to 40	5.18a	1.21[b]	8.49	8.80	2.04
fluoranthene	0.999	−5.94	4417	20 to 40	5.22a	1.04[c]	8.60	8.88	1.91

[a] Miller et al., 1985. [b] Shiu and Mackay, 1997. [c] Mackay et al., 1992.

Table 4. Regression Parameters for Eq 7 (PCNs) and K_{OA} Values at 25 °C

compound, PCNs	r^2	A	B	range (°C)	log K_{OA}
2-1	0.997	-3.97	3248	10 to 50	6.93
3-1	0.990	-5.39	3786	10 to 50	7.32
3-2	0.995	-4.98	3651	10 to 50	7.27
3-10	0.994	-5.52	3896	10 to 50	7.56
4-6	0.996	-5.34	4000	10 to 50	8.08
4-7	0.996	-5.49	4059	10 to 50	8.13
4-14	0.991	-5.73	4263	20 to 50	8.58
4-15	0.997	-5.70	4206	10 to 50	8.41
4-16	0.997	-5.62	4181	10 to 50	8.40
4-18	0.997	-5.66	4206	10 to 50	8.45
5-1	0.997	-6.02	4394	10 to 50	8.73
5-2	0.997	-5.92	4404	10 to 50	8.86
5-3	0.996	-6.05	4417	10 to 50	8.78
5-4	0.998	-6.63	4629	10 to 50	8.91
5-5	0.996	-7.78	5044	10 to 50	9.15
5-9	0.994	-5.88	4452	10 to 50	9.06
5-10	0.996	-6.59	4684	10 to 50	9.13
5-11	0.995	-6.96	4811	20 to 50	9.18
6-1	0.998	-7.09	5003	10 to 50	9.70
6-2	0.996	-6.77	4939	20 to 50	9.80
6-3	0.995	-6.64	4909	20 to 50	9.83
6-4	0.996	-6.63	4923	20 to 50	9.89
6-5	0.990	-5.55	4666	20 to 50	10.11
6-6	0.987	-6.54	5040	20 to 50	10.37

**Table 5. Comparison of $\Delta_{vap}H$ and $\Delta_O^A H$ and Q_D for PAHs**

compound	$\Delta_O^A H$ (kJ/mol)	$\Delta_{vap}H$ (kJ/mol)	Q_D[d] (kJ/mol)
fluorene	82.9	65.3,[a] 69.5[b]	n.d.
phenanthrene	75.5	72.8,[a] 76.2,[b] 71.1[c]	81.8
pyrene	76.3	72.0,[a] 86.7,[b] 78.6[c]	79.4

[a] Heat of sublimation for the solid, converted to heat of vaporization for the liquid using the experimentally determined heat of fusion. Literature values from articles cited in Bidleman *Anal. Chem.* **1984**, *56*, 2490−2496 and Hinckley et al. *J. Chem. Eng. Data* **1990**, *35*, 232−237 (1990) [b] Enthalpy of vaporization determined by GC (Yamasaki et al., 1984). [c] Enthalpy of vaporization determined by GC (Hinckley et al., 1990). [d] Temperature coefficient of PAH−vegetation binding (Simonich and Hites, 1994); n.d. = not determined.

equation is only approximately linear. Nevertheless, it has been previously used to describe the temperature dependence of K_{OA} (Harner and Bidleman, 1996; Harner and Mackay, 1995; Kömp and McLachlan, 1997b). Alternatively, the octanol−air partitioning data can be treated by plotting log K'_{OA} vs $1/T$ (eq 5) and then multiplying the fitted K'_{OA} values at each temperature by RT to yield K_{OA}. Values of K_{OA} obtained in this way differed by less than 1% from those calculated from eq 7 using the parameters A and B in Tables 3 and 4. Enthalpies of transfer from octanol to air, $\Delta_O^A H = \Delta_{sub}H - \Delta_{sol}H$, were on the average only 3% higher when the data were plotted by eq 5. Thus the approximation of linearity in plots of log K_{OA} vs $1/T$ (eq 7) is satisfactory over the temperature range involved.

Table 3 also compares measured K_{OA} results for PAHs at 25 °C with values calculated using the relation $K_{OA} =$
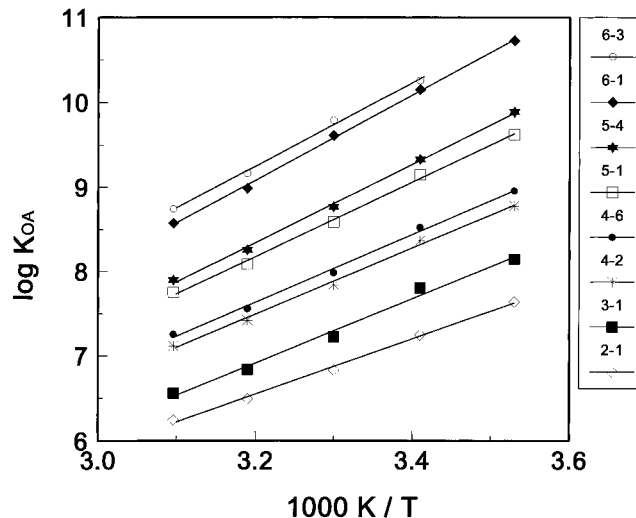
Figure 3. Selected K_{OA} results for PCNs over the temperature range (10 to 50) °C, plot of eq 2.
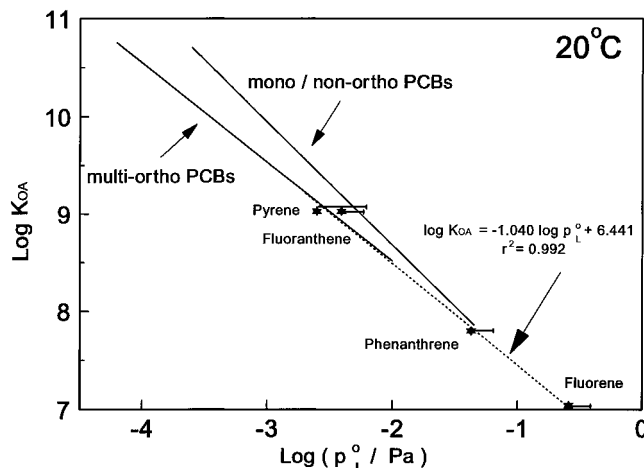
Figure 4. Log−log correlation of K_{OA} against p^o_L at 20 °C for mono/nonortho PCBs, multiortho PCBs, and PAHs. Range bars represent variability in literature values of p^o_L. Symbols and regression line are for data from Yamasaki et al. (1984).

$K_{OW}RT/H$. Measured results exceeded calculated values by a factor of approximately 1.5 to 2. This is consistent with a previous comparison for PCB data (Harner and Mackay, 1995) and suggests that K_{OA} values calculated using K_{OW} and H systematically underpredict the true value.

K_{OA} has a strong temperature dependence with slopes of approximately 4000−4500 for the PAHs and 3248−5040 for the 2-Cl to 6-Cl PCNs. This slope is related to the enthalpy associated with the transfer from octanol to air, $\Delta_O^A H$ (eq 4), which is calculated as $2.303BR$, where R is the ideal gas constant. Enthalpies associated with vaporization from the subcooled liquid to air, $\Delta_{vap}H$, have been reported for PAHs (Yamasaki et al., 1984; Hinckley et al., 1990). Values of $\Delta_O^A H$ and $\Delta_{vap}H$ are listed in Table 5.
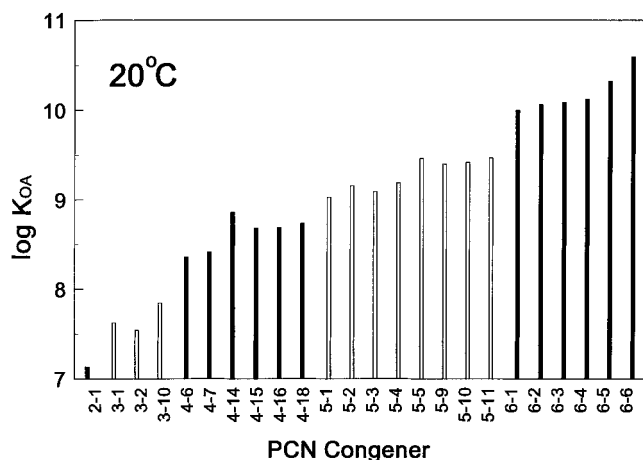
Figure 5. Plot of log K_{OA} values for PCN congeners at 20 °C.

Except for fluorene, the $\Delta_O^A H$ values are within the range of reported $\Delta_{vap}H$ values. For fluorene, $\Delta_O^A H$ exceeds $\Delta_{vap}H$ by (13 to 18) kJ/mol. Harner and Bidleman (1996) found that values of $\Delta_O^A H$ for PCBs were on average about 7% lower than $\Delta_{vap}H$. There is also good agreement between $\Delta_O^A H$ and the temperature coefficient (Q_D) associated with vegetation–atmosphere partitioning of phenanthrene and pyrene, as reported by Simonich and Hites (1994).

In earlier work with PCBs (Harner and Bidleman, 1996), the more nearly planar, mono-ortho and non-ortho PCBs exhibited greater partitioning into octanol compared to the less planar multi-ortho congeners of the same vapor pressure. In Figure 4, PAHs were added to the log–log plot of K_{OA} against $p°_L$ for PCBs (Harner and Bidleman, 1996). Values of $p°_L$ were obtained from refs 1–3 in Table 5. From the variability in the $p°_L$ data, it was inconclusive whether PAHs showed any significant "enrichment" in octanol as was previously observed for mono- and non-ortho PCBs containing more than four chlorine atoms The symbols in Figure 4 represent $p°_L$ values from Yamasaki et al. (1984) and result in the regression line: log K_{OA} = -1.040 log $p°_L$ + 6.441 (r^2 = 0.992).

This comparison cannot presently be made for PCNs since unfortunately there are no reported temperature-dependent values of $p°_L$. Instead the log K_{OA} values for PCNs were plotted against congener elution order in Figure 5. There is a clear trend of increasing K_{OA} values with PCN homolog, and within a homologue grouping, K_{OA} values increase with congener retention time. The difference between the 2-Cl and the 6-Cl homologs is a factor of more than 1000. Because of their similar shape and size and wide range of partitioning behavior, PCNs are ideal candidates for studies of particle–gas partitioning, long-range transport, and global fractionation, and the octanol–air partition coefficient should be a useful descriptor for these processes.

Conclusions

Measurements of K_{OA} as a function of temperature are reported for 24 PCN congeners and 4 PAHs. Measured values for PAHs exceed values calculated using the Henry's Law constant (H) and K_{OW} by a factor of approximately 1.5 to 2. Because of the variability in literature values of $p°_L$, it is difficult to conclude whether PAHs show enhanced partitioning into octanol as was previously observed for coplanar PCBs (Harner and Bidleman, 1996).

The enthalpy of transfer from octanol to air, $\Delta_O^A H$, for PAHs ranges from 75.5 to 82.9 kJ/mol. This agrees well with the temperature coefficient for vegetation–atmosphere partitioning for PAHs, Q_D, and (except for fluorene) with reported values of the enthalpy of vaporization, $\Delta_{vap}H$.

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