

Measurements of Octanol-Air Partition Coefficients for Polychlorinated Biphenyls

Tom Harner* and Terry F. Bidleman

Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario M3H 5T4, Canada

The octanol-air partition coefficient, K_{OA} , is measured for 15 polychlorinated biphenyls (PCBs) over the temperature range $-10\text{ }^{\circ}\text{C}$ to $+30\text{ }^{\circ}\text{C}$ using a generator column method. The enthalpy of phase change from octanol to air, $\Delta_{\text{O}}^{\text{A}}H$, is calculated for 18 PCBs and ranges from 66 to 90 kJ/mol. Enthalpy of dissolution of the liquid phase PCB in octanol, $\Delta_{\text{SOL}}H$, calculated as $\Delta_{\text{VAP}}H - \Delta_{\text{O}}^{\text{A}}H$, has a mean value of 6.6 kJ/mol ($n = 18$) and there is no correlation of $\Delta_{\text{SOL}}H$ with homolog group or number of ortho-substituted chlorine atoms. Results show that K_{OA} values increase within a homolog group for congeners having fewer ortho chlorine atoms. A $\log_{10} - \log_{10}$ correlation of K_{OA} against liquid-phase vapor pressure (p°_L) shows enhanced partitioning into octanol for mono- and non-ortho congeners. Separate regressions for non/mono-ortho and multi-ortho groups allow K_{OA} to be estimated for other congeners.

Introduction

The octanol-air partition coefficient, K_{OA} , and its temperature dependence are important descriptors for the partitioning of hydrophobic chemicals between air and environmental lipids (Paterson et al., 1991; Tolls and McLachlan, 1994; Mackay and Wania, 1995; Simonich and Hites, 1995; Finizio et al., 1996). Examples of these compartments include organic carbon in soil, cuticular lipids in vegetation, and oily films on aerosols and other surfaces. Organic contaminants are atmospherically transported to remote, and often pristine, cold climate regions where they accumulate by means of the cold condensation effect (Wania and Mackay, 1993). Significant levels of polychlorinated biphenyls (PCBs), pesticides, and polycyclic aromatic hydrocarbons (PAHs) are found in air, water, snow, and wildlife in the Arctic (Barrie et al., 1992; Muir et al., 1994; Bidleman et al., 1995). The chromatographic migration of these chemicals from source regions to colder climates is greatly influenced by particle/gas partitioning and air/surface exchange. Knowledge of physicochemical factors such as K_{OA} and its temperature dependence can be used to explain the movement of these compounds and identify chemicals which are susceptible to this effect.

It is possible to calculate K_{OA} as the ratio of the octanol-water partition coefficient, K_{OW} , and the dimensionless air-water partition coefficient, $K_{AW} = H/RT$, where H is the Henry's law constant, T is absolute temperature, and R is the ideal gas constant. K_{OA} is calculated as

$$K_{OA} = K_{OW}RT/H \quad (1)$$

However, K_{OW} represents octanol saturated with water and water saturated with octanol whereas H represents pure water. Arbuckle (1983) estimates that this mutual solubility results in a reduction in the calculated K_{OW} by approximately half a \log_{10} unit for hydrophobic chemicals such as 1,2,3,5-tetrachlorobenzene and pentachlorobenzene. Li and Andren (1994) report a negligible increase in solubility for 4-monochlorobiphenyl (PCB-3), 2,4,6-trichlorobiphenyl (PCB-30), and 2,2',4,4',6,6'-hexachlorobiphenyl (PCB-155) in a near-saturated solution of octanol in water ($0.003\text{ }125\text{ mol L}^{-1}$). However, they report experimental difficulties when working with long chain alcohols such as 1-octanol and especially 1-nonanol and

1-decanol due to the formation of microemulsions in water which tend to increase the apparent solubility. Consequently, K_{OA} values which are calculated from K_{OW} measurements are likely to be underestimated, with the deviation increasing for chemicals with larger values of K_{OW} . Literature values of K_{OW} and H for individual PCB congeners (Sangster, 1989; Mackay et al., 1991) vary by up to 1 order of magnitude, which further contributes to the error associated with calculating K_{OA} . It is therefore desirable to measure K_{OA} directly for these compounds.

A previous paper by Harner and Mackay (1995) introduced a novel approach for measuring K_{OA} which utilized a generator column. Air was passed through a glass wool column coated with octanol containing 0.5 to 2 g/L of solute (c_0). The vaporized solute was collected on Tenax TA adsorbent traps which were thermally desorbed and analyzed by gas chromatography. The vapor concentration (c_A) was calculated from the amount of chemical desorbed and the total air volume sampled, and K_{OA} was calculated as c_0/c_A . Results were presented for six chlorobenzenes, five PCB congeners, and *p,p'*-DDT over the temperature range $-10\text{ }^{\circ}\text{C}$ to $+20\text{ }^{\circ}\text{C}$. Theoretical concepts including mass transfer and equilibrium criteria were discussed. This paper describes a modified and improved method for measuring K_{OA} . Results are presented over the temperature range $-10\text{ }^{\circ}\text{C}$ to $+30\text{ }^{\circ}\text{C}$.

Theoretical Background

The octanol-air partition coefficient can be expressed as

$$K_{OA} = c_0/c_A = s^{\circ}_L/(p^{\circ}_L/RT) \quad (2)$$

where p°_L and s°_L are liquid-phase vapor pressure and solubility in octanol. Units of K_{OA} are mass/volume of octanol divided by mass/volume of air. The temperature variation of p°_L and s°_L are described by the following equations:

$$\log_{10} p^{\circ}_L = \Delta_{\text{VAP}}H/2.303RT + b_{\text{VAP}} \quad (3)$$

$$\log_{10} s^{\circ}_L = \Delta_{\text{SOL}}H/2.303RT + b_{\text{SOL}} \quad (4)$$

where the ΔH terms and the b variables are temperature

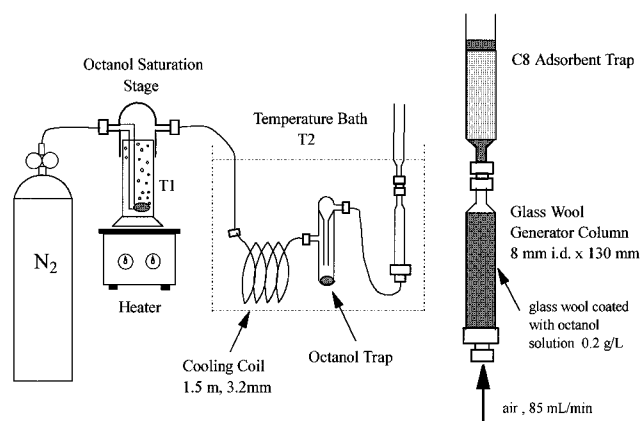


Figure 1. Schematic diagram of K_{OA} apparatus, modified from Harner and Mackay (1995).

independent. $\Delta_{VAP}H$ (J/mol) represents the enthalpy of vaporization and $\Delta_{SOL}H$ (J/mol) is the enthalpy of dissolution of the liquid phase compound in octanol. The enthalpy associated with the transition from octanol solution to air Δ_OH . The temperature dependence of K_{OA} is described

$$\log_{10} K_{OA} = \Delta_OH/2.303RT + b_{OA} \quad (5)$$

$${}_{10}K_{OA} = (\Delta_{VAP}H - \Delta_{SOL}H)/2.303RT + b_{VAP} + b_{SOL} - \log_{10} RT \quad (6)$$

where $\Delta_OH = \Delta_{VAP}H - \Delta_{SOL}H$ and $b_{OA} = b_{VAP} - b_{SOL} - \log_{10} RT$. The temperature dependence of K_{OA} is reduced relative to that of p^*_L because of the enthalpy required for dissolution in octanol, $\Delta_{SOL}H$.

Experimental Section

Chemicals. The chemicals, solvents, and PCB standards used in this work are as follows: 1-octanol (Fisher Chemical); glass distilled petroleum ether, dichloromethane, and isooctane (BDH Inc.) PCB standards and 2,2',5-tribromobiphenyl were purchased from AccuStandard (IUPAC number in parentheses): 3-monochlorobiphenyl (3-monoCBP) (PCB-3), 2,2',4,5'-tetraCBP (PCB-49), 2,2,5,6'-tetraCBP (PCB-53), 2,3',4,4'-tetraCBP (PCB-66), 3,3',4,4'-tetraCBP (PCB-77), 2,2',3,5',6-pentaCBP (PCB-95), 2,2',3,6,6'-pentaCBP (PCB-96), 2,2',4,5,5'-pentaCBP (PCB-101), 2,3,3',4,4'-pentaCBP (PCB-105), 2,3',4,4',5-pentaCBP (PCB-118), 3,3',4,4',5-pentaCBP (PCB-126), 2,2',3,4,4',5'-hexaCBP (PCB-138), 2,2',4,4',5,5'-hexaCBP (PCB-153), 2,2',3,3',4,4',6-heptaCBP (PCB-171), 2,2',3,4,4',5,6-heptaCBP (PCB-180).

Apparatus. The apparatus shown in Figure 1 has several modifications over the original design (Harner and Mackay, 1995). Nitrogen from a compressed cylinder and at a controlled flow rate was sparged through an octanol column approximately 20 cm in height. When performing measurements above room temperature, it was necessary to heat the octanol to a temperature T_1 which was at least 10 deg greater than the temperature, T_2 , of the bath. The readout accuracy for the bath was ± 0.25 deg. From the octanol saturation stage the air was cooled to the operating temperature, T_2 , by means of a cooling coil. This ensured the delivery of an octanol-saturated air stream to the generator column. Excess octanol was trapped to prevent any liquid from entering the generator column. The addition of the octanol trap shown in Figure 1 was a technical improvement over the previous "U-tube" design. The octanol-saturated air was passed through the generator column and then through an adsorbent trap which

collected the PCBs. An improved design allowed both the generator column and trap to be submerged in the temperature bath to avoid any hot or cold spots which could act as sources or sinks for chemicals. Connections were made with vacuum fittings (Swagelok, Weston Valve & Fitting Ltd.) ensuring air- and watertight seals.

The generator column consisted of a glass tube 130 mm long \times 8 mm i.d. and tapered to 4 mm i.d. at the inlet. Solvent-rinsed glass wool was moderately packed into the column to a length of 90 mm. Increased dimensions of the generator column were another modification which allowed higher flow rates and hence shorter experimental times. However, even at these higher flow rates long sampling times were required to trap a sufficient quantity of gaseous PCB for a single determination. For example, at $+30^\circ\text{C}$ the sampling time for tetrachlorinated and heptachlorinated congeners was approximately 1 and 3 h, respectively, but at -10°C this increased to 48 and 216 h. A syringe was used to apply the octanol solution evenly onto the surface of the glass wool. This was done by inserting the syringe into the glass wool packing and slowly turning and withdrawing it while delivering 400 μL of solution. Solute concentrations ranged from 0.2 g/L to 0.5 g/L. Traps were 130 mm long \times 11 mm i.d. and tapered to 4 mm i.d. at the inlet and packed with 50 mm of C_8 -bonded silica (Varian Corp.) sandwiched between glass wool plugs.

Experimental flow rates ranged from 70 to 100 mL/min and were measured at the outlet of the system and at ambient pressure. The system itself was under positive pressure caused by resistance to flow through the adsorbent traps. As a result, the true flow through the generator column was less than the flow measured at the outlet. To correct for this effect the system pressure was measured by attaching a pressure gauge (Magnehelic) through a "Tee" connector between the generator column and the adsorbent trap. From this information a pressure correction of approximately 50 cm of water was applied, which decreased the flow rate of each sample by 5%. This translated to higher values for C_A and a negative adjustment of 5% or 0.02 \log_{10} units to all K_{OA} measurements.

Analysis. The C_8 traps were eluted with 5 mL of 30% dichloromethane in petroleum ether. Prior to their next use the traps were washed with 3 mL of 2% toluene in dichloromethane and dried using a stream of nitrogen. Sample extracts were blown down under a gentle stream of nitrogen, and the solvent was exchanged into 2,2,4-trimethylpentane. Typical final blow-down volumes ranged from 0.2 mL to 1.0 mL, at which point 2,2',5-tribromobiphenyl was added as an internal standard for volume correction. Recovery tests were performed to correct for blow-down losses. Extraction of the C_8 traps versus thermal desorption was another improvement. It eliminated problems associated with thermal desorption efficiency for heavier compounds from Tenax TA traps and allowed for multiple analyses on trap extracts from an experiment. Samples were analyzed by gas chromatography-electron capture detection (GC-ECD). The GC was equipped with either a 30 m DB-5 or DB-5MS column (J & W Scientific) with 0.25 mm i.d. and 0.25 μm film thickness, operated with hydrogen carrier gas at 50 cm/s. Injections (1 μL) were splitless with the split opened after 0.5 min. The temperature program was 90°C for 0.5 min, $10^\circ\text{C}/\text{min}$ to 160°C , and $2^\circ\text{C}/\text{min}$ to 250°C with the detector at 300°C .

Results and Discussion

Quality Control. Extraction efficiency tests were performed on several traps and showed that essentially all of

Table 1. K_{OA} Results of Equilibration Experiments

congener	90 mm bed ^a			10 mm bed ^b		
	mean	log ₁₀ mean	<i>n</i>	mean	log ₁₀ mean	<i>n</i>
3	$(1.02 \pm 0.05) \times 10^7$	7.01	9	$(1.11 \pm 0.25) \times 10^7$	7.05	5
53	$(1.74 \pm 0.04) \times 10^8$	8.24	9	$(1.80 \pm 0.26) \times 10^8$	8.26	5
49	$(3.75 \pm 0.22) \times 10^8$	8.57	9	$(4.21 \pm 0.81) \times 10^8$	8.62	5
66	$(1.67 \pm 0.23) \times 10^9$	9.22	9	$(2.04 \pm 0.38) \times 10^9$	9.31	5
77	$(9.16 \pm 1.57) \times 10^9$	9.96	5	$(1.30 \pm 0.39) \times 10^{10}$	10.11	5

^a Flow = 70 to 85 mL/min. ^b Flow = 77 to 241 mL/min.

Table 2. Regression Constants for Eq 7

congener	r^2	<i>A</i>	<i>B</i>	range (°C)	+20 °C		
					$K_{OA} \pm$ S.D.	log ₁₀ K_{OA}	log ₁₀ $p^{\circ}L$ (Pa) ^b
3	0.9991	-4.82	3470	-10 to +30	$(1.02 \pm 0.05) \times 10^7$	7.01	-0.23
3 ^a	0.9999	-6.52	3962	-10 to +20	$(1.03 \pm 0.05) \times 10^7$	7.01	-0.23
15 ^a	0.9999	-5.06	3792	-10 to +20	$(7.54 \pm 0.31) \times 10^7$	7.88	-1.37
29 ^a	0.9996	-4.77	3792	-10 to +20	$(1.07 \pm 0.37) \times 10^8$	8.03	-1.58
49	0.9965	-4.96	3981	-10 to +20	$(3.75 \pm 0.22) \times 10^8$	8.57	-2.02
53	0.9974	-5.26	3965	-10 to +20	$(1.74 \pm 0.04) \times 10^8$	8.24	-1.79
61 ^a	0.9964	-2.89	3464	-10 to +20	$(7.96 \pm 0.72) \times 10^8$	8.90	-2.42
66	0.9974	-3.82	3827	-10 to +20	$(1.67 \pm 0.23) \times 10^9$	9.22	-2.46
77	0.9997	-3.14	3828	-10 to +20	$(9.16 \pm 1.57) \times 10^9$	9.96	-2.92
95	0.9983	-4.30	3904	-10 to +30	$(1.14 \pm 0.09) \times 10^9$	9.06	-2.53
96	0.9997	-4.60	3913	-10 to +30	$(5.91 \pm 0.54) \times 10^8$	8.77	n.a.
101	0.9923	-3.82	3841	-10 to +30	$(2.06 \pm 0.20) \times 10^9$	9.31	-2.73
105	0.9997	-5.68	4678	-10 to +30	$(1.87 \pm 0.13) \times 10^{10}$	10.27	-3.17
118	0.9996	-5.92	4693	-10 to +30	$(1.21 \pm 0.10) \times 10^{10}$	10.08	-3.19
126	0.9992	-5.98	4870	-10 to +30	$(4.08 \pm 0.40) \times 10^{10}$	10.61	-3.60
138	0.9982	-5.57	4584	-10 to +30	$(1.24 \pm 0.21) \times 10^{10}$	10.09	-3.56
153	0.9925	-6.02	4695	-10 to +30	$(1.11 \pm 0.08) \times 10^{10}$	10.04	-3.44
155 ^a	0.9944	-2.21	3954	-10 to +20	$(1.44 \pm 0.15) \times 10^9$	9.16	-2.66
171	0.9965	-5.71	4757	-10 to +30	$(3.22 \pm 0.23) \times 10^{10}$	10.51	-4.01
180	0.9943	-4.70	4535	-10 to +30	$(5.64 \pm 0.71) \times 10^{10}$	10.75	-4.17

From Harner and Mackay (1995). ^b From Falconer and Bidleman (1994).

the chemical was eluted in the first 5 mL of the dichloromethane–petroleum ether solvent mixture with less than 1% carryover to a second 5 mL fraction. The possibility of nonextractable PCBs being retained on the traps was checked by further extraction using dichloromethane alone. Results showed no detectable PCBs in this third fraction, thus confirming the adequacy of using 5 mL of the solvent mixture for extraction.

Losses incurred during blow down were quantified by spiking 5 mL of the dichloromethane–petroleum ether solvent mixture with known amounts of PCBs and reducing the volume to 0.2 mL. The percentages lost were reproducible and ranged from 25% for PCB-3 to 10% for PCB-77 and were less than 10% for the heavier congeners. The analytical results were corrected for these recovery factors. The possibility of PCB vapors breaking through the traps was also of concern, especially when air sample volumes exceeded 1000 L. This was investigated by occasionally adding a second trap in series for the higher volume samples. In all cases back-up traps contained less than 1% of the total, indicating that a single C₈ trap was sufficient for collecting the gas-phase PCBs.

Equilibration Experiments. Tests were performed to ensure that equilibrium was achieved between air and octanol by comparing the K_{OA} results obtained with two different lengths of generator column. The “standard” column was the 90 mm glass wool bed and was compared to a 10 mm bed. Table 1 shows the results from the 90 mm bed at 70 to 85 mL/min flow and the 10 mm bed at 77 to 240 mL/min flow. The agreement between the two sets of measurements indicates that equilibrium is established in these experiments.

A study was also performed to compare K_{OA} measurements for a single-congener octanol solution with those

using an octanol solution containing a mixture of congeners. At +20 °C the log₁₀ K_{OA} value for PCB-3 measured individually was 6.95. This agreed well with a value of 7.01 measured for an octanol solution which contained PCB-3 and four tetrachlorinated congeners.

Results of K_{OA} Measurements. The K_{OA} measurements over the temperature range -10 °C to +30 °C are summarized in Figure 2 and Table 2. K_{OA} increased log-linearly with reciprocal temperature, with values increasing by factors of 50 to 300 over the temperature range, clearly illustrating enhanced partitioning to lipid phases at cold temperatures. Equation 7 can be used to calculate K_{OA} at different temperatures using the coefficients in Table 2.

$$\log_{10} K_{OA} = A + B/T \quad (7)$$

where $B = \Delta_{\circ}^{\Delta}H/2.303R$ and $A = b_{OA}$ (eq 5).

The enthalpy of phase change from octanol to air, $\Delta_{\circ}^{\Delta}H$ is calculated from the temperature coefficient as $2.303BR/1000$. Values of $\Delta_{\circ}^{\Delta}H$ range from 66 to 93 kJ/mol and average 79 kJ/mol (Table 3). $\Delta_{\text{VAP}}H - \Delta_{\circ}^{\Delta}H$ is the enthalpy of solution in octanol, $\Delta_{\text{SOL}}H$, as discussed earlier. Table 3 summarizes $\Delta_{\text{SOL}}H$ values for individual congeners. The $\Delta_{\text{VAP}}H$ values were estimated from gas chromatographic retention data (Falconer and Bidleman, 1994). Hinckley et al. (1990) compared log vapor pressure–temperature slopes ($\Delta H_{\text{VAP}}/2.303R$, eq 3) determined by GC with those measured by other techniques. The average absolute difference was 8.5% for 17 PAHs, PCBs, and chlorinated pesticides. The mean value of $\Delta_{\text{SOL}}H$ for all PCBs is 6.6 ± 5.9 kJ/mol ($n = 18$). There appears to be no correlation with homolog group or ortho-Cl group (considering PCBs with four or more Cl atoms) as shown below.

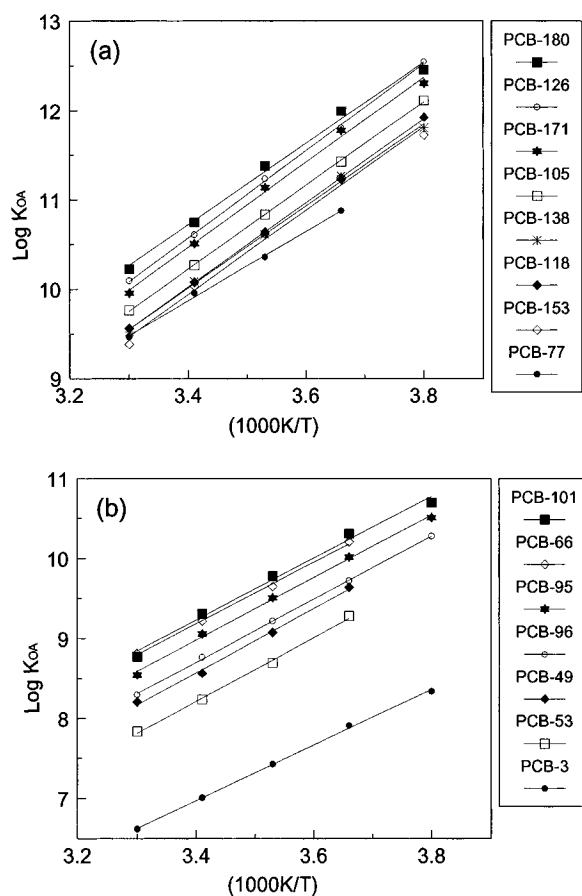


Figure 2. Summary of K_{OA} results over the temperature range 10 °C to +30 °C, plot of eq 7. (a) tetra- to heptachlorobiphenyls; (b) mono- to pentachlorobiphenyls.

$$\text{tetra: } \Delta_{SOL}H = (9.5 \pm 6.0) \text{ kJ/mol } (n = 5)$$

$$\text{penta: } \Delta_{SOL}H = (4.7 \pm 6.1) \text{ kJ/mol } (n = 5)$$

$$\text{hexa/hepta: } \Delta_{SOL}H = (7.7 \pm 6.7) \text{ kJ/mol } (n = 5)$$

$$\text{non/mono-ortho: } \Delta_{SOL}H = (6.9 \pm 7.5) \text{ kJ/mol } (n = 6)$$

$$\text{multi-ortho: } \Delta_{SOL}H = (7.6 \pm 5.5) \text{ kJ/mol } (n = 9)$$

$\Delta_{SOL}H$ is thus a small term, and $\Delta_{O}^{\Delta}H$ is on the average only 7% lower than $\Delta_{VAP}H$. PCB-3 is the only congener which is common to this work and previous measurements (Harner and Mackay, 1995). Although the temperature slopes differ somewhat, a comparison of $\log_{10} K_{OA}$ values +20 °C shows excellent agreement: 7.01 and 7.01, respectively.

Effect of Ortho-Chlorine Substitution on K_{OA} . It is interesting to compare K_{OA} on the basis of the number of chlorine (Cl) atoms occupying ortho positions. Ortho positions refer to the four sites adjacent to the biphenyl bond having designations 2, 2', 6, and 6'. PCBs with no ortho Cl atoms, also known as "coplanar PCBs", are able to obtain a configuration in which both phenyl rings lie approximately in the same plane. The planarity decreases as the ortho Cl atoms are added to the ring. Dihedral angles for different ortho-Cl groups are approximately non-ortho 40–42°, mono-ortho 57–59°, di-ortho 77–79°, and almost 90° for tri- and tetra-ortho congeners (Falconer et al., 1995, Ong and Hites, 1991). Within the same homolog group non- and mono-ortho congeners have lower vapor pressures than congeners with two or more ortho-Cl (Falconer and Bidleman, 1994). We refer to the lowering

Table 3. Estimation of $\Delta_{SOL}H$ from $\Delta_{VAP}H$ and $\Delta_{O}^{\Delta}H$

congener	no. of Cl atoms	no. of ortho Cl	$\Delta_{VAP}H^b$ /kJ/mol	$\Delta_{O}^{\Delta}H$ /kJ/mol	$\Delta_{SOL}H$ /kJ/mol
3 ^a	1	0	66.79	75.86	-9.08
3	1	0	66.79	66.44	0.35
15 ^a	2	0	76.03	72.61	3.43
29 ^a	3	1	76.72	72.61	4.12
49	4	2	80.97	76.23	4.75
53	4	3	78.77	75.92	2.85
61 ^a	4	1	83.90	66.33	17.6
66	4	1	83.27	73.28	9.99
77	4	0	87.16	73.30	13.86
95	5	3	84.23	74.75	9.48
101	5	2	86.43	73.54	12.9
105	5	1	89.76	89.57	0.19
118	5	1	89.30	89.86	-0.55
126	5	0	94.89	93.25	1.65
155 ^a	6	4	82.39	63.89	18.5
153	6	2	91.43	89.90	1.53
138	6	2	91.91	87.77	4.14
171	7	3	95.89	91.08	4.81
180	7	2	96.54	86.83	9.71

^a From Harner and Mackay (1995). ^b From Falconer and Bidleman (1994).

Table 4. Increase in K_{OA} for PCBs with Fewer Ortho Chlorines: "Primary Ortho Effect"

no. ortho Cl atoms	congener	$\log_{10} K_{OA}$	
		+20 °C	+0 °C
Tetra Homolog			
3	53	8.24	9.28
2	49	8.57	9.64
1	66	9.22	10.21
0	77	9.96	10.88
Penta Homolog			
4	96	8.77	9.72
3	95	9.06	10.02
2	101	9.31	10.31
1	105	10.27	11.43
0	126	10.61	11.81

of vapor pressures as the "primary ortho effect". Because of their lower vapor pressures non- and mono-ortho PCBs sorb to airborne particles to a greater extent (Falconer and Bidleman, 1994).

Table 4 lists K_{OA} values at +20 °C and 0 °C for the tetra and penta homologs and compares them according to the number of ortho Cl atoms. K_{OA} values increase by about 1 order of magnitude from +20 °C to 0 °C. This strong temperature dependence points to a significantly greater retention of PCBs by environmental lipids at cold temperatures. The "primary ortho effect" is also apparent when comparing K_{OA} values for PCBs in the same homolog group. PCBs with fewer ortho chlorines have higher K_{OA} values. For example in the tetra homolog, congener 77 which is non-ortho has a K_{OA} value approximately 40 times greater than congener 53 which is tri-ortho. In the penta homolog, non-ortho congener 126 has a K_{OA} value approximately 70 times higher than for tetra-ortho congener 96.

Subcooled liquid vapor pressure (p_L^o , Pa) is often used to relate PCB concentrations in air and condensed phases. Figure 3 is a plot of $\log_{10} K_{OA}$ against $\log p_L^o$ at +20 °C for congeners containing two to seven Cl atoms. The values of p_L^o were taken from Falconer and Bidleman (1994). The difference between the non/mono-ortho PCBs and the multi-ortho PCBs increases for the higher chlorinated congeners. We refer to this as a "secondary ortho effect" which causes an enhancement of K_{OA} values in addition to the "primary ortho effect" of lower vapor pressure. The secondary effect indicates that non/mono-ortho PCBs have greater K_{OA} values than multi-ortho PCBs of the same

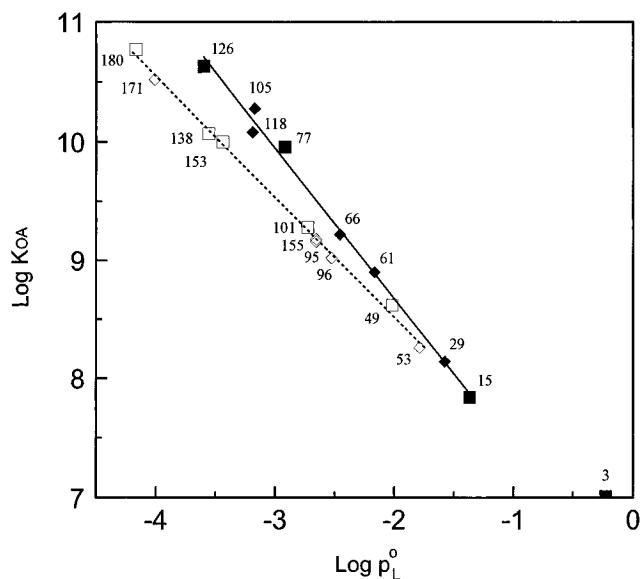


Figure 3. \log_{10} – \log_{10} correlation of K_{OA} against p_L^o at +20 °C for non/mono-ortho and multi-ortho congeners for PCBs containing two to seven chlorines, numbered according to congener (Tables 2 and 3). Key: (■) non-ortho; (◆) mono-ortho; (□) di-ortho; (◇) tri/tetra-ortho; (●) non/mono; (○) multi.

vapor pressure. The ratio of these values is defined as the enhancement factor. Studies of particle/gas partitioning also show this secondary ortho effect for non/mono-ortho PCBs (Falconer et al., 1995). The secondary effect K_{OA} values is substantial for PCBs 77, 126, 105, and 118 which contribute heavily to 2,3,7,8-tetrachlorodibenzo-dioxin toxic equivalents (TEQ) in biota (Ahlborg et al., 1994). K_{OA} enhancement factors for these congeners range from 2 to 4.

Liquid-phase vapor pressures have been reported for 180 PCB congeners (Falconer and Bidleman, 1994). Separate regressions were performed on the non/mono-ortho and multi-ortho groups of congeners containing two to seven Cl atoms, which allows K_{OA} at 20 °C to be estimated from for other congeners.

(i) non/mono-ortho:

$$\log_{10} K_{OA} = (-1.268) \log p_L^o + 6.135 \quad r^2 = 0.995$$

(ii) multi-ortho:

$$\log_{10} K_{OA} = (-1.015) \log p_L^o + 6.490 \quad r^2 = 0.997$$

PCB-3, the only monochlorobiphenyl which has a measured K_{OA} value, deviates from both the mono- and multi-ortho regression lines. Foreman and Bidleman (1985) reported abnormal behavior for biphenyl and monochlorobiphenyls compared to the di- to heptachlorinated congener based correlations of p_L^o against chromatographic retention indices. This discrepancy is consistent with the deviation for PCB-3 in Figure 3.

Conclusions

The mono-ortho and non-ortho PCBs, which are the most toxic, show enhanced partitioning into octanol relative to the multi-ortho congeners. This may explain observations of enhanced partitioning onto aerosols for coplanar PCBs which ultimately facilitates their removal from the atmosphere by wet and dry particle deposition (Falconer et al., 1995). The temperature dependence of K_{OA} may explain the movement of chemicals to colder climates by the cold

condensation effect. Until now the “chromatographic” migration of contaminants to cold regions, as they partition between the atmosphere and condensed phases such as soil and vegetation, has been explained using vapor pressure (Wania and Mackay, 1993; Mackay and Wania, 1995). K_{OA} has been proposed as a modeling parameter for air–vegetation exchange (Simonich and Hites, 1995), and the results presented here suggest that K_{OA} is able to resolve different classes of PCBs.

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