

Application of the Octanol-Air Partition Coefficient for Describing Particle/Gas Distribution of Chlorinated Aromatics

Tom Harner¹, Terry Bidleman¹, Renee Falconer², Donald Mackay³,

1. Atmospheric Environment Service, 4905 Dufferin St., Downsview, Ontario, M3H 5T4, Canada. 2. Chemistry Department, Youngstown State University, Youngstown, Ohio, 44555, U.S.A. 3. Department of Chemical Engineering, University of Toronto, Toronto, Ontario, M5S 1A4, Canada.

1. Introduction

Partitioning of chlorinated aromatics between gas and particulate phases can be explained by adsorption onto active sites on the surface of the aerosol and/or by absorption into an organic liquid film¹⁾. In both cases the particle/gas distribution coefficient, K_p , is well correlated to the subcooled vapor pressure (P_L°) of the compound. For PCBs the correlation improves by including a shape parameter which

takes into account the planarity of the molecule²⁾. It is proposed that the octanol-air partition coefficient, K_{OA} , may be used as a surrogate for K_p . A method for measuring K_{OA} is described and results are presented over the temperature range -10°C to $+30^\circ\text{C}$. The temperature dependence of K_p for PCBs to urban air particulate matter is compared to the temperature dependence of the compound's P_L° and K_{OA} values.

2. Background

The octanol-air partition coefficient, K_{OA} , is defined as,

$$K_{OA} = C_O / C_A \quad (1)$$

where C_O and C_A are the concentrations of the solute in the octanol and air phases respectively. This is analogous to the partitioning of a chemical between the atmosphere and the organic liquid film which covers many aerosols and especially urban and combustion aerosols. It is also possible to calculate K_{OA} from the octanol-water partition coefficient, K_{OW} , and the dimensionless air-water partition coefficient, K_{AW} .

$$K_{OW} / K_{AW} = (C_O / C_W) / (C_A / C_W) = C_O / C_A = K_{OA} \quad (2)$$

There is, however, a possible error inherent in this estimation procedure in addition to the obvious combination of measurement errors in K_{OW} and K_{AW} . K_{OW} represents

the partitioning of chemical between octanol saturated with water and water saturated with octanol, whereas K_{AW} represents partitioning between air and pure water. For these reasons it is desirable to measure K_{OA} directly.

3. Methods

Octanol-Air Partition Coefficient

The octanol-air partition coefficient was measured for five PCBs over the temperature range -10 to +20 °C and five PCBs at -10 to +30 °C using the apparatus shown in Fig.1. A more detailed account of the method was previously described³⁾.

Air from a cylinder was saturated with octanol by sparging through an octanol column approximately 30 cm in length at temperature T_1 and then passed through a heat exchanger coil which reduced the air temperature from T_1 to the desired measurement temperature, T_2 , which was -10 to +30°C. The bath temperature, T_2 , was always lower than the temperature of the octanol column to ensure that the air remained saturated with octanol. As the temperature was reduced from T_1 to T_2 , octanol condensed and the excess liquid was collected at the bottom of a glass mineral oil bubbler. The air saturated with octanol then passed through the glass wool column which consisted of a glass tube approximately 10cm in length with outside diameter 6mm or 12mm. The glass wool was coated with a solution of the chemicals in octanol at typical concentrations of 0.1 to 1 g/L.

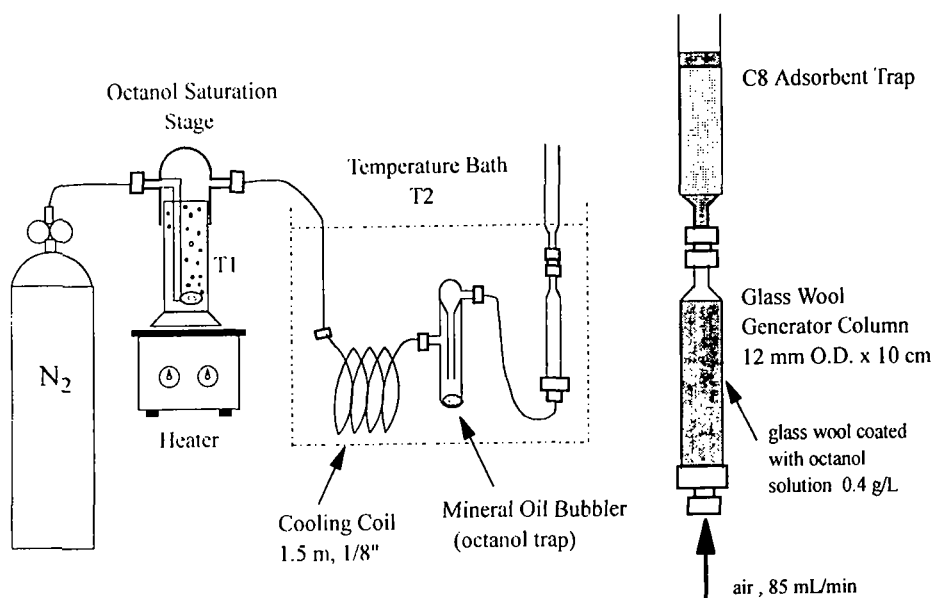


Figure 1. Apparatus used to measure K_{OA} .

Chemical in the outlet air was collected using two types of adsorbent traps. In the earlier experiments TENAX TA (35/60 mesh) was used and the traps were analyzed by thermal desorption and gas chromatography-electron capture detection (GC-ECD). The new method uses C8 cartridges which are solvent extracted and then analyzed by GC-ECD.

Particle/Gas Equilibration Experiments

The equilibration experiments were performed in a thermally insulated box at controlled temperature and humidity over the temperature range +5 to +25 °C. A generator column was used to introduce PCBs into an air stream which was pulled at 15-16 L/min through a 47 mm diameter glass fibre filter (GFF) loaded with urban air particulate matter. The system was allowed to equilibrate for 30-40 h. The air concentration C_A was monitored using polyurethane foam plugs which were changed periodically to give an average C_A . Results are presented for eight PCB congeners. K_p was calculated as C_p/C_A where C_p is the PCB concentration in or on particles (ng/ μ g particles) and C_A is the gas-phase PCB concentration (ng/m³ air). Further details of these experiments are presented elsewhere ²⁾.

4. Results and Discussion

For both the particle/gas equilibration experiments and the octanol-air experiments plots of $\log K_p$ and $\log K_{OA}$ against $1/T$ (1/K) were linear. Table 1 lists the temperature slopes, m , for K_p and K_{OA} and compares them to the slope for vapor pressure ⁴⁾.

The temperature slope of K_{OA} is lower than for P_L° for all of the PCBs with the exception of PCB-3. The temperature slope is calculated as,

$$m = -Q/2.303R \quad (3)$$

For P_L° , $Q = Q_v$, the enthalpy of vaporization of the liquid PCB. For K_{OA} , $Q = Q_v - Q_s$, where Q_s is the enthalpy of solution in octanol.

The mean values and standard deviations of the temperature slopes are 3600 ± 424 for K_p , 4406 ± 411 for P_L° , and 3754 ± 218 for K_{OA} . The slopes for K_{OA} come closer to K_p slopes than do the vapor pressure slopes. This supports the hypothesis that absorption into an organic liquid film is a plausible mechanism for sorption of chlorinated aromatics to urban aerosols.

Table 1. Temperature slopes for K_p , P_L° , and K_{OA} for PCB congeners.

Congener	# Cl	# ortho Cl	$\log K_p$ <u>m</u>	$\log P_L^\circ$ <u>m</u>	$\log K_{OA}$ <u>m</u>
PCB-3	1	0		3488	3757
-15	2	0		3971	3792
-29	3	1		4007	3792
-49	4	2	2711	4229	3979
-53	4	3		4114	3961
-61	4	1		4382	3464
-66	4	1		4349	3811
-77	4	0	3349	4552	3899
-101	5	2	3457	4514	
-105	5	1	3876	4758	
-118	5	1	3888	4664	
-126	5	0	3739	4956	
-138	6	2	4025	4800	
-155	6	4		4303	3337
-171	7	3	3756	5008	

5. References

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