

Measurements of Octanol-Air Partition Coefficients for Chlorinated Dioxins / Furans: Applications to Describing Surface-Air Partitioning

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Introduction

The octanol-air partition coefficient (K_{OA}) is recognized as a key descriptor of chemical partitioning between the atmosphere and organic phases. Recently, K_{OA} -based approaches have been successfully employed to model surface-air partitioning of persistent organic pollutants (POPs) to aerosols (1-3), soil (4) and vegetation (5). The chief advantages of using K_{OA} over the subcooled liquid vapor pressure (p°_L) is that K_{OA} can be measured directly, whereas p°_L (which is a hypothetical state for most compounds at ambient temperatures) must be estimated or calculated.

This paper presents K_{OA} data for selected PCDD/Fs over the temperature range 0-40 °C.

Experimental

A detailed description of the apparatus and an outline of the experimental procedure is presented elsewhere (6). Octanol solutions were prepared from solid standards (Promochem, Hertfordshire, U.K.) by adding a known volume of octanol (0.5 – 1) mL to ~1 mg solid in a tapered vial and then sonicating overnight. An aliquot of the top, nearly-saturated, octanol solution was then taken and further diluted in a small amount of octanol to make individual solutions for all of the compounds tested. A “mixed” solution, consisting of several solutes, was made by combining aliquots of the individual solutions. The generator column consisted of glass beads coated with approximately 100 μ L of this “mixed” solution.

Octanol-saturated nitrogen was passed through a thermostically controlled generator column. Flow rates ranged from 100-150 mL min⁻¹ and measurement temperatures ranged from 0 to 40 °C. Effluent compounds were trapped on C₁₈-bonded silica (IST, Mid Glamorgan U.K.) which was extracted with 10 mL 1:1 dichloromethane:hexane. ¹³C-labelled 1,3,6,8-tetrachlorodioxin was added as the internal standard for volume correction followed by 25-50 μ L nonane. Samples were blown down into nonane using a gentle stream of nitrogen.

PCDD/Fs were determined using a Hewlett Packard 5890 Plus GC equipped with an electron capture detector (ECD). Compounds were eluted on a 60 m DB-5 capillary column (J&W Scientific) with 0.25 mm i.d. and 0.25 μ m film thickness, operated with helium carrier gas. Peaks were quantified relative to calibration solutions made from the “mixed” octanol solution.

Results

Quality Control

Steps were taken to assure the validity of the data and consistency with previous measurements in other laboratories. Firstly, equilibration tests were performed to ensure that equilibrium of the gas-

phase with the octanol solution existed over the flow rate range for these measurements. Results showed consistency over the range 100-260 mL min⁻¹. Secondly, PCB-138 was included in the octanol mixture as a check against previous measurements. Several samples (n=3-6) were collected at each temperature. Relative standard deviations values were usually below 20%.

K_{OA} measurements over the range 0-40 °C

Figure 1 is a plot of log K_{OA} versus 1/T for several dioxins (2,3,7-TriCDD, 1,2,3,4-TCDD, 1,2,3,4,7-PeCDD) and PCB-138. K_{OA} varied log-linearly with inverse absolute temperature with slopes in the range 4436 to 4581. These values are slightly higher than observed for PCBs of similar degree of chlorination (6). The regression equation for PCB-138 (i.e. log K_{OA} = 4581/T - 5.45) was in excellent agreement with a previously published value (i.e. log K_{OA} = 4584/T - 5.57) (6). This strongly suggests consistency between the two data sets.

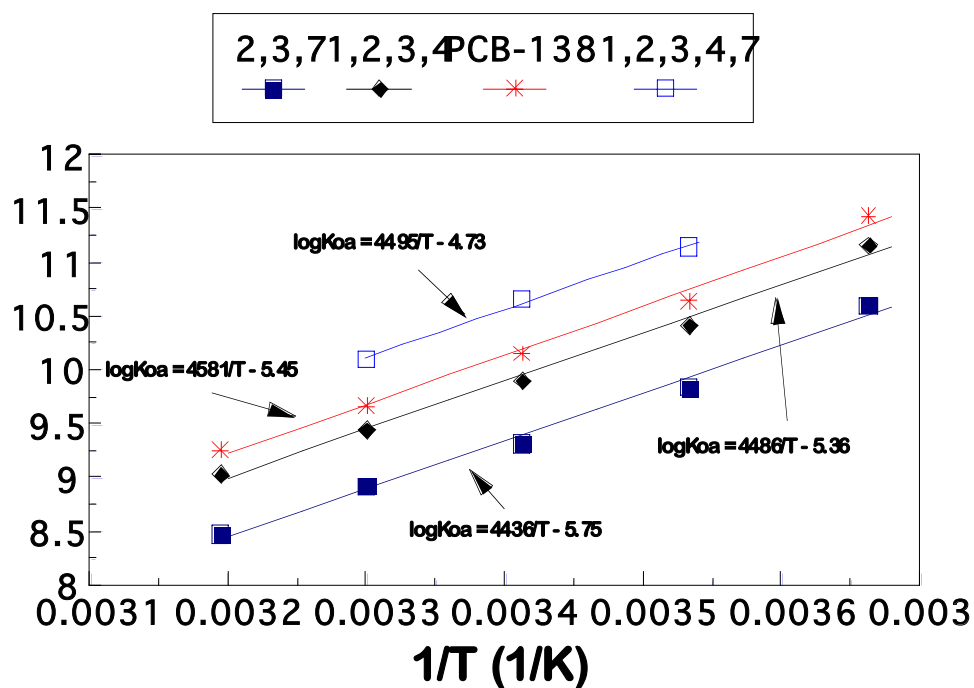


Figure 1. Measurements of K_{OA} for chlorinated dioxins and PCB-138 over the temperature range 0-40 °C.

Table 1 compares calculated values of K_{OA} at 25 °C for the PCDDs (i.e. K_{OA} = K_{OW} RT/H) (8) to measured values. For 2,3,7-TriCDD and 1,2,3,4-TCDD the calculated values exceed measured

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values by about 38% and 45% respectively. For 1,2,3,4,7-PeCDD the difference is smaller (10%) but in the opposite direction. Discrepancies between measured and calculated K_{OA} values was also noted for PCBs and was attributed to uncertainties that arise in measurements of K_{OW} for extremely hydrophobic compounds that may in part be due to the solubility of octanol in water (7). Resolution of errors such as these is important and a promotion for the direct measurement of K_{OA} .

Table 1. Calculated and measured K_{OA} values at 25⁰C.

	H ^a (m ³ Pa mol ⁻¹)	log K _{OW} ^a	log K _{OA} (calculated)	log K _{OA} ^b (measured)	factor difference
2,3,7-TriCDD	2.82	5.74	9.28	9.14	1.38
1,2,3,4-TCDD	2.75	6.34	9.86	9.70	1.45
1,2,3,4,7-PeCDD	2.24	6.89	10.32	10.36	0.91

^a ref. 8; ^b this work

Particle-gas partitioning models rely on accurate values of K_{OA} . The particle-gas partition coefficient, K_p (m³ μg⁻¹), is related to K_{OA} by (1,2),

$$K_p = 10^{-9} K_{OA} f_{OM} / \rho_{OCT} \quad \text{Eq. 1}$$

where, f_{OM} is the fraction of the particle mass that consists of absorbing organic matter, and ρ_{OCT} is the density of octanol (kg m⁻³). The fraction of chemical associated with the particle phase (ϕ) is then determined by,

$$\phi = K_p TSP / (K_p TSP + 1) \quad \text{Eq. 2}$$

where TSP is the total suspended particulate concentration (μg m⁻³ air)

Table 2 shows how the difference between calculated and measured K_{OA} is propagated in the calculation of particulate fraction. Models which rely on calculated K_{OA} values for dioxins will therefore miscalculate the proportion of dioxins on aerosols and other condensed media (e.g. soil, grass). This example further highlights the need for accurate measurements of K_{OA} for PCDDs/Fs over a range of environmentally relevant temperatures.

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Table 2. Particulate fractions of PCDDs determined using the K_{OA} absorption model (eq. 1 and eq. 2, assuming $f_{OM}=0.2$, $TSP=80$) for calculated versus measured K_{OA} values at 25 °C.

	using calculated K_{OA}		using measured K_{OA}		factor difference in $\phi \times 100$
	K_p	$\phi \times 100$	K_p	$\phi \times 100$	
2,3,7-TriCDD	0.00047	3.6	0.00034	2.6	1.38
1,2,3,4-TCDD	0.00175	12.3	0.0012	8.8	1.40
1,2,3,4,7-PeCDD	0.0051	29	0.0056	30.9	0.94

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