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DETERMINATION OF OCTANOL-AIR PARTITION COEFFICIENTS OF ORGANOPHOSPHATE FLAME RETARDANTS (PFRS) AS A FUNCTION OF TEMPERATURE

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Introduction:
Organic flame retardants (FRs) have been applied for several decades to reduce the inflammability of various industrial and commercial products [1,2]. The restrictions on the production and usage of some FRs (i.e. PBDEs) have led to the application of alternative FRs to meet the fire safety regulations for various consumer products. Among those alternatives, PFRs (organophosphate flame retardants) have been associated recently with a variety of applications in a wide range of products [1,2]. The K_{OA} is a key descriptor of chemical partitioning between the atmosphere and other environmental organic phases such as soil and vegetation [3,4]. Recent studies have indicated that relative gas chromatographic retention times or gas chromatographic capacity factors on a non-polar stationary phase can be used to determine K_{OA} and the energy of phase transfer between octanol and gas phase (ΔU_{OA}) for non-polar POPs (persistent organic pollutants) [5,6]. In the present study, temperature-dependent K_{OA} values for 10 PFRs and four of their deuterated derivatives were determined using the GC retention time method for the first time.

Materials and Methods:
A GC (Agilent 6890N) equipped with a mass selective detector (Agilent 5973N MSD) and a capillary column with a non-polar stationary phase (HP5-ms, 30 m, 0.25mm, 0.25 mm) was used to determine the isothermal retention times of PFRs. Two PFR solutions (at 2 μg mL^{-1}) were used. The first solution contained four PFRs and the second solution contained six PFRs. Reference compounds (fluorene, pyrene, and p,p'-DDT) were also added to these solutions. The first group was run at thirteen different temperatures (100 to 120 and 145 to 180 °C, respectively with 5 °C intervals) while the second group was run at eight temperatures (210–180 °C) in triplicate.
Isothermal retention times of 19 additional nonpolar compounds having directly measured K_{OA} values (i.e., organochlorine pesticides-OCPs, polycyclic aromatic hydrocarbons-PAHs, and PBDEs) were also determined. Isothermal retention times were determined at eight different temperatures in triplicate. The MSD was run in full scan mode for OCPs and PAHs and in selected ion monitoring mode for PBDEs. OCPs and PBDEs were used along with fluorene, phenanthrene, and fluoranthene for the calibration of the method. The detailed description of chromatographic retention time based calculations of K_{OA} values can be found elsewhere [8,9,10].

Results and Discussion:
The relationships between $\ln(t_R/t_{Rref})$ and $\ln K_{OAref}$ were highly linear for all compounds with very high coefficients of determination ($r^2 > 0.99$). Table 1 lists determined octanol–air partition coefficients (K_{OA-GC} and K_{OA}) of PFRs at 25°C as well as the intercepts (A) and slopes (B) of the temperature regressions. The K_{OA-GC} values were highly reproducible as indicated by the small relative standard deviations (0.4–3.3%) calculated from independent determinations (n=3).
K_{OA-GC} values for several OCPs, PBDEs, and PAHs were also determined. Figure 1 shows that there is a strong correlation between the directly measured log K_{OA} values (at 25°C) of PAHs [10], OCPs [4], and PBDEs [11] versus K_{OA-GC}. The equation showed in Figure 1 was used to correct the K_{OA-GC} values for the systematic deviations from directly measured K_{OA} values (Table 1). K_{OA} values were slightly higher than K_{OA-GC} values (1.05-1.26 times).
K_{OA} values for PFRs were also calculated as the ratio of octanol/water partition coefficient (K_{OW}) to dimensionless Henry's law constant (H') (Table 1). The $K_{OA}/K_{OA(calculated)}$ [12] ratio ranged between 0.18 (tri(2-isopropylphenyl) phosphate) and 1.48 (tris(2-chloroethyl) phosphate). Similar deviations between the calculated and directly measured K_{OA} values were reported by previous studies [4,8,9,10,13]. Table 1 shows calculated energies of phase transfer determined in this study. ΔU_{OA} values ranged between 65.0 (triethyl phosphate) and 107.3 kJ mol^{-1} (tri(2-isopropylphenyl) phosphate). ΔU_{OA} values for PFRs have not been reported previously. However, values determined in the present study were in the ranges reported for

other compound groups like PBDEs (74.5-105 kJ mol^{-1}) [11], PCBs (72.6-89.9 kJ mol^{-1}) [13-15], and OCPs (61.9-105.0 kJ mol^{-1}) [4].

In the present study f_g (gas-phase fraction) values for PFRs were estimated for summer and winter seasons. f_{OM} (organic matter fraction) and C_{TSP} (total suspended particle concentration) values were assumed as 0.50 and 50 μg m^{-3}, respectively while ambient temperatures were assumed as 5°C for winter and 25°C for summer season. Figure 2 shows the relationship between f_g and log K_{OA} for studied PFRs. Modeled gas-phase percentages ranged between 100 and 0.24% for winter, while 100 and 5.07% for summer. In both seasons, four of the ten studied PFRs were predominantly in the gas-phase (>95%) and all the compounds have higher gas phase fractions under summer conditions. The results of the present study and recent studies suggest that the factors influencing the gas-particle partitioning of PFRs should be further investigated[16].

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Table 1. Uncalibrated (K_{OA-GC}, average±SD, $n=3$) and calibrated (K_{OA}, average±propagated error) octanol–air partition coefficients for PFRs at 25 °C determined from gas chromatographic retention times using fluorene, pyrene and p,p'-DDT as reference, energies of phase transfer (ΔU_{OA}, average±propagated error), regression parameters for Eq. (9), and calculated K_{OA} values from dimensionless Henry's law constant (H') and octanol–water partition coefficient (K_{OW}).

	Reference Compound	log K_{OA-GC}	log K_{OA}	B	A	ΔU_{OA} (kJ mol^{-1})	Log K_{OW}[a]	H'[a]	Log K_{OA} (calculated)	Factor difference
triethyl phosphate-D15	fluorene	5.04±0.003	5.15±0.30	3343	-6.07	64.0±2.7				
triethyl phosphate	fluorene	5.09±0.006	5.21±0.30	3392	-6.18	65.0±2.7	0.87	2.38 x 10^{-5}	5.49	0.59
tributyl phosphate	fluorene	7.35±0.003	7.44±0.34	4739	-8.46	90.7±3.8	3.82	1.30 x 10^{-4}	7.71	0.70
tris(2-chloroethyl) phosphate-D12	fluorene	7.77±0.005	7.86±0.35	4969	-8.82	95.1±4.0				
tris(2-chloroethyl) phosphate	fluorene	7.83±0.003	7.91±0.35	5001	-8.87	95.8±4	1.63	1.04 x 10^{-6}	7.61	1.48
tris(1-chloro-2-propyl) phosphate	fluorene	7.96±0.003	8.05±0.35	5071	-8.96	97.1±4.1	2.89	2.44 x 10^{-6}	8.20	0.83
tris(1,3-Dichloro-2-propyl) phosphate-D15	pyrene	9.94±0.006	10.01±0.39	4641	-5.57	88.9±5.3				
tris(1,3-dichloro-2-propyl) phosphate	pyrene	10.00±0.011	10.07±0.39	4674	-5.62	89.5±5.3	3.65	1.07 x 10^{-7}	10.62	0.59
triphenyl phosphate-D15	pyrene	10.21±0.009	10.28±0.40	4782	-5.77	91.6±5.4				
tris(2-butoxyethyl) phosphate	pyrene	10.67±0.002	10.73±0.41	5103	-6.39	97.7±5.8	3.00	4.91 x 10^{-10}	12.31	0.25
triphenyl phosphate	pyrene	10.25±0.006	10.32±0.40	4804	-5.80	92.0±5.4	4.70	1.63 x 10^{-6}	10.49	0.85
2-ethylhexyl diphenyl phosphate	pyrene	10.50±0.002	10.56±0.40	4961	-6.09	95.0±5.6	6.30	1.01 x 10^{-5}	11.29	0.51
tris(2-ethylhexyl) phosphate	p,p'-DDT	10.83±0.002	10.89±0.41	5211	-6.60	99.8±5.1	9.49	3.91 x 10^{-3}	11.90	0.41
tri(2-ısopropylphenyl) phosphate	p,p'-DDT	11.73±0.002	11.78±0.43	5605	-7.02	107.3±5.5	9.07	1.20 x 10^{-5}	13.99	0.18

[a] Ref. 12

$$\log K_{OA} = 0.991 \log K_{OA-GC} + 0.162$$
$$R^2 = 0.986, \; n=19, \; p<0.01$$
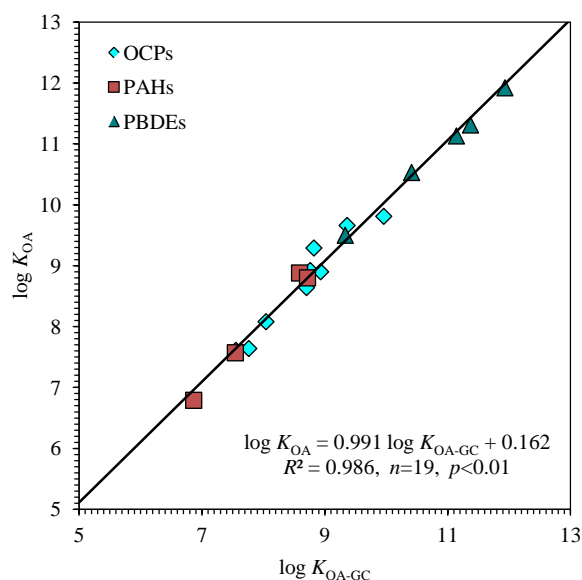
Figure 1. Relationship between the directly measured K_{OA} values for OCPs ($n=9$), PAHs ($n=5$), and PBDEs ($n=5$) at 25°C and K_{OA-GC} values derived from GC retention times.
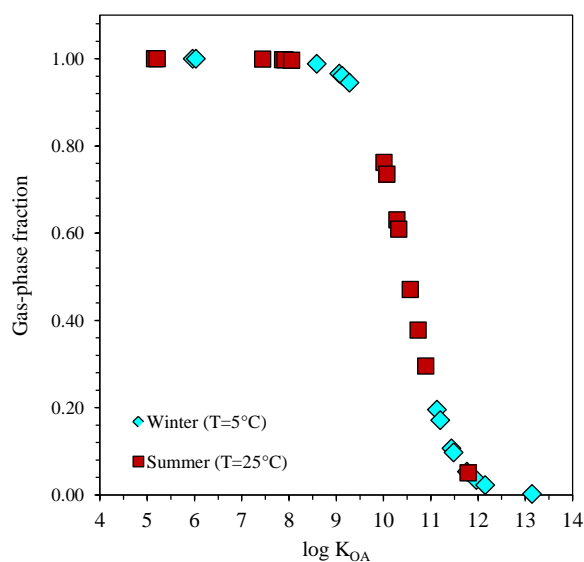
Figure 2. Modeled gas-phase fractions of PFRs.