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# Passive sampling: partition coefficients for a silicone rubber reference phase.

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1 **Passive sampling: Partition coefficients for a silicone rubber reference phase**

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8  
9 **Abstract**

10 Silicone rubber sheeting can be used as a passive sampling device for hydrophobic  
11 organic contaminants in the environment to determine the available concentrations in  
12 water and sediments. Reliable sampler-water partition coefficients are required to  
13 determine the sampling rates and the dissolved contaminant concentrations in water and  
14 in sediment pore water. Log partition coefficients ( $\log K_{sr,w}$ ) for silicone rubber-water  
15 have been estimated for 32 polycyclic aromatic hydrocarbons (PAHs), 2 deuterated PAH  
16 analogues and 32 chlorobiphenyls (CBs) using the cosolvent method, with methanol as  
17 cosolvent. Strong linear relationships were found with literature values for the  
18 corresponding log octanol-water partition coefficients ( $\log K_{ow}$ ) for both CBs and PAHs,  
19 confirming that partitioning into the silicone rubber is strongly determined by the  
20 hydrophobicity of the compounds, which suggests  $\log K_{ow}$  is a good predictor of  
21  $\log K_{sr,w}$  and that absorption is the main mechanism for accumulation of analytes into  
22 the silicone rubber polymer.

# 1 Introduction

2

3 The determination of the dissolved concentrations of priority hydrophobic organic  
4 contaminants (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) and  
5 chlorobiphenyls (CBs) is a difficult task due to their low concentrations and the problem  
6 of incomplete phase separation between particle-bound and dissolved analytes <sup>1</sup>. The  
7 problems are even more pronounced when the determination is required in sediment pore  
8 waters, as large volumes of pore water are required. The development of passive  
9 sampling methods, using solid or liquid reference phases, allows direct measurement of  
10 exposure to dissolved hydrophobic organic contaminants. Single phase sampling devices,  
11 such as low density polyethylene (LDPE strips) <sup>1</sup>, polyoxymethylene strips (POM) <sup>3</sup>,  
12 Tenax <sup>4</sup>, polydimethylsiloxane (PDMS) <sup>5</sup>, and silicone rubber <sup>2, 6, 7</sup> have been developed  
13 in addition to the two-phase semi-permeable membrane devices (SPMDs) <sup>8, 9</sup> developed  
14 earlier to determine the free dissolved HOC concentrations. They are easy to construct,  
15 re-usable and of low cost <sup>6</sup>. Rusina *et al.* <sup>6</sup> discussed the properties of materials for  
16 passive samplers and proposed that silicone rubbers can be attractive reference phases  
17 due to their high partition coefficients and low transport resistances.

18

19 Using reference (sampling) phases, such as silicone rubber, that equilibrate with the  
20 surrounding medium, the partition coefficient can be used, together with the  
21 concentration in the sampler, to determine the freely dissolved concentration in the  
22 environmental medium <sup>10</sup>, to estimate the sampling rates of added performance reference  
23 compounds <sup>11</sup> that have dissipated from the passive sampling device and subsequently the  
24 equilibration rate constants which are used to determine the sampling scenario (kinetic or  
25 equilibrium), as not all compounds would have attained equilibrium. Consequently,  
26 passive sampling using a reference phase that equilibrates with the dissolved  
27 concentration in the sampling medium is attractive. The ratio of the concentration in the  
28 sampler to that in the surrounding water at equilibrium yields the sampler-water partition  
29 coefficient as described in equation 1:

30 
$$K_{s,w} = \left( \frac{C_s}{C_w} \right) \quad (1)$$

1 where  $K_{s,w}$  is the sampler-water partition coefficient,  $C_s$  and  $C_w$  is the concentration in  
2 the sampler and water respectively. The sampling rate is calculated from equation 2<sup>1</sup>:

$$3 \quad R_s = k_e K_{s,w} M_s \quad (2)$$

4 where  $R_s$  is the sampling rate,  $k_e$  is the exchange coefficient (assuming first order kinetics  
5 during sampling) and  $M_s$  is the sampler mass. The  $k_e$  can be estimated from the release of  
6 performance reference compounds, spiked onto the sampler using

$$7 \quad k_e = -\frac{\ln(N^t/N^0)}{t} \quad (3)$$

8  $N^t$  = Amount of PRC left in sampler at the end of exposure time  $t$ ,  $N^0$  = Amount of  
9 PRC spiked onto the sampler at the start of the exposure

10

11 It is therefore necessary to determine the partition coefficients that accurately describe  
12 partitioning in multi-compartment systems<sup>5, 10-13</sup>, particularly those between the  
13 reference sampling phase (e.g. silicone rubber) and water. The dissolution of PAHs and  
14 CBs in water is quite difficult due to their hydrophobic nature, and as a consequence may  
15 adhere to glass surfaces used in the experimental set up and yield variable water  
16 concentrations, which complicates the determination of partition coefficients. The  
17 partitioning of HOCs between environmental media is mainly determined by the aqueous  
18 solubility of the HOCs which may be modified (increased) by the addition of organic  
19 solvents<sup>14</sup>. Therefore, we have measured the silicone rubber-water partition coefficients  
20 of a series of HOCs (PAHs and CBs) with  $\log K_{ow}$  values for the compounds studied  
21 ranging from 3.3 to 8.2 using the cosolvent method, with methanol as cosolvent. This was  
22 carried out by determining log partition coefficients at different co-solvent-water volume  
23 percentages and extrapolating the > 20 % v/v methanol portion of the linear curve of log  
24 partition coefficient versus percent methanol to zero percent methanol which yields the  
25 true partition coefficient of the HOC between silicone rubber and water<sup>15-17</sup>. The  
26 estimation of partition coefficients over a wide range of methanol percentages reduces  
27 some of the errors normally associated with measurements of partition coefficients.

28

# 1 **Materials and methods**

## 3 **Materials**

4  
5 AlteSil™ Silicone rubber sheet manufactured from translucent, food grade silicone  
6 rubber, with a hardness of 60 Shore A, (600 × 600 mm, 0.5 mm thick) were purchased  
7 from Altec Products, Ltd, Cornwall, UK. HPLC grade solvents (ethyl acetate, acetone,  
8 methanol and 2-methylpentane) were purchased from Rathburn Chemicals Ltd, Scotland,  
9 UK. Certified solid standards for PAHs (including deuterated PAHs) and CBs were  
10 obtained from QMX Laboratories, Essex, UK and dissolved in 2-methylpentane (PAHs)  
11 and 2, 2, 4-trimethylpentane (CBs) to obtain required concentrations of spiking solutions.  
12 The silicone rubber sheets were cut into 6 × 4 cm pieces and pre-extracted with ethyl  
13 acetate in a Soxhlet apparatus for 4 days to remove any low molecular weight oligomers  
14 or residues that may interfere with subsequent analyses. Milli-Q water (18.2 MΩ.cm) was  
15 used throughout.

## 17 **Loading of Compounds on silicone rubber**

18  
19 Test compounds (PAHs and CBs) were loaded onto the silicone rubber sheets using the  
20 spiking method described by Booij *et al.*<sup>2</sup>. Briefly, 100 ml of methanol in an amber glass  
21 jar was spiked with known concentrations of the PAHs and CBs of interest (Table 1) and  
22 silicone rubber sheets added. The glass jar was shaken for 2 h on an orbital shaker at 200  
23 rpm followed by addition of water to obtain 80 % v/v methanol solution and further  
24 shaken for 6 h with a subsequent addition of water to obtain 50 % v/v methanol solution.  
25 This was followed by a final shaking overnight at room temperature. Reproducibility of  
26 the spiking method was always better than 5 % within each batch of spiked silicone  
27 rubber.

## 1 Partition coefficient determination

2  
3 The co-solvent method <sup>15, 16</sup> was used with methanol as co-solvent. The silicone rubber  
4 sheets, loaded with appropriate amounts of test PAHs and CBs, were introduced into 1 l  
5 glass bottles (one sheet per bottle) containing 900 ml of the water-methanol mixture at a  
6 range of 7 fractions (20-50 % <sup>v/v</sup> methanol). An un-spiked sheet was added to a bottle  
7 containing 900 ml of 20 % <sup>v/v</sup> methanol solution as procedural blank. Duplicate bottles  
8 were then placed on an orbital shaker at 150 rpm for 15 days <sup>17, 18</sup> (Smedes <sup>17</sup> used 20  
9 days in his work) during which time equilibrium can be assumed to have been attained.  
10 Other studies have shown organic compounds, e.g. CB29, D<sub>10</sub>-phenanthrene, phenol,  
11 benzene, dichlorobenzene, etc to equilibrate in silicone membranes within hours <sup>1, 19</sup>.  
12 Sorption of analytes to the glass container is considered negligible <sup>16, 17</sup> and the  
13 concentrations in the water phase were generally measurable. The bottle caps were lined  
14 with solvent-washed aluminium foil to prevent sorption onto the plastic caps. The  
15 silicone rubber sheets were removed from the bottles and gently wiped dry with paper  
16 rolls before extraction.

17  
18 Deuterated PAH internal standards (D<sub>8</sub>-naphthalene, D<sub>10</sub>-biphenyl, D<sub>10</sub>-anthracene, D<sub>8</sub>-  
19 dibenzothiophene, D<sub>10</sub>-pyrene and D<sub>12</sub>-benzo[*a*]pyrene) were added to the methanol-  
20 water mixtures in the 1 l bottles and transferred into separation funnels. These were  
21 liquid-liquid extracted in separating funnels using 2 × 60 ml dichloromethane and the  
22 extracts dried over anhydrous sodium sulphate. The extracts were rotary evaporated to ~  
23 2 ml and 2 × 25 ml 2-methylpentane added followed by concentration, first by rotary  
24 evaporation, then by nitrogen blow down to 1 ml and split into 2 parts: 1 fraction was  
25 analysed by gas chromatography-mass selective detection (GC-MS) for PAHs and the  
26 other by gas chromatography-electron capture detection (GC-ECD) for CBs. The silicon  
27 rubber sheets were Soxhlet extracted using a 2-methylpentane: acetone (3:1 <sup>v/v</sup>) mixture  
28 for 6 h and the same suite of deuterated PAH internal standards added, then exchanged  
29 into 2-methylpentane by the addition of 2 × 25 ml of 2-methylpentane. The extract was  
30 concentrated by rotary evaporation followed by nitrogen blow down to 1 ml which was  
31 then split into 2 fractions by weight for PAHs and CBs. An aliquot of the PAH fraction

1 was fractionated by isocratic, normal phase high performance liquid chromatography  
2 using a Genesis silica column and eluted with 2-methylpentane into aliphatic and  
3 aromatic fractions. The aliphatic fraction was discarded and the aromatic fraction  
4 collected and concentrated before analysis for PAHs. Similarly an aliquot of the CB  
5 fraction was fractionated as above and the eluate from the first 6 min (predetermined  
6 using a solution of CBs) collected and 2, 4-dichlorobenzyl alkyl ethers internal standard  
7 added, then concentrated before analysis for CBs. Recoveries calculated on the basis of  
8 the sum of the amounts determined in the methanol-water mixtures and amounts in the  
9 sheets relative to the amount loaded onto the sheets were  $86 \pm 20 \%$  for the CBs and  $101$   
10  $\pm 16 \%$  for PAHs.

11  
12 Confirmatory data were obtained using silicone rubber sheeting (Vizo, Technirub,  
13 Netherlands) for which partition coefficients had been independently determined<sup>17</sup>. Vizo  
14 and Altec sheeting were equilibrated together by loading them with the test compounds,  
15 in triplicate, in amber glass bottles as previously described. As the two materials were  
16 equilibrated in the same methanol-water phase, measurements of the concentrations in the  
17 methanol-water phase were not necessary since:

18 
$$\left( \frac{C_{sr}}{K_{sr,w}} \right)_1 = \left( \frac{C_{sr}}{K_{sr,w}} \right)_2 = C_w \quad (4)$$

19 Implying 
$$(K_{sr,w})_2 = \left( \frac{(C_{sr})_2}{(C_{sr})_1} \right) \cdot (K_{sr,w})_1 \quad (5)$$

20 where the subscripts sr- denotes silicone rubber, w-water and 1, 2 refer to Vizo, and Altec  
21 sheeting respectively.

22

### 23 **Chromatographic Analysis**

24

25 The concentrations and composition of the PAHs were determined by gas  
26 chromatography mass selective detection (GC-MS) using an HP6890 Series Gas  
27 Chromatograph interfaced with an HP5973 MSD fitted with a cool on-column injector as  
28 described by Webster *et al.*<sup>20</sup>. Briefly, a non-polar HP5 (30 m  $\times$  0.25 mm id, 0.25  $\mu$ m  
29 film thickness; Agilent Technologies, Stockport, England) column was used for the

1 analyses with helium as the carrier gas, controlled using the constant flow mode at 0.7 ml  
2 min<sup>-1</sup>. Injections were made at 50 °C and the oven temperature held constant for 3 min.  
3 Thereafter, the temperature was raised at 20 °C min<sup>-1</sup> up to 100 °C, followed by a slower  
4 ramp of 4 °C min<sup>-1</sup> up to a final temperature of 270 °C. The MSD was set for selective ion  
5 monitoring (SIM) with a dwell time of 50 ms. A total of 30 ions plus the six internal  
6 standard ions were measured over the analysis period, thus incorporating 2- to 6- ring,  
7 parent and branched PAHs.

8  
9 The concentration and composition of CB congeners were determined by gas  
10 chromatography with electron capture detection (GC-ECD) using a Perkin Elmer Gas  
11 Chromatograph Clarus 500 auto system (Perkin Elmer, Beaconsfield, UK) fitted with a  
12 cool on-column injector. A non-polar HP 5 column (60 m × 0.25 mm id, 0.25 µm film  
13 thickness; Agilent Technologies, Stockport, England) was used for the analyses along  
14 with an uncoated pre-column (2.5 m × 0.53 mm id). The carrier gas was hydrogen (1–3  
15 ml min<sup>-1</sup>) and make-up gas was nitrogen (30 ± 5 ml min<sup>-1</sup>). The initial oven temperature  
16 was 80 °C and held for 1 min after which it was ramped at 3 °C min<sup>-1</sup> to a final  
17 temperature of 280 °C and held at this temperature for 12 min. The chromatograph was  
18 calibrated using a series of external standards and the two 2, 4-dichlorobenzyl alkyl  
19 ethers. The data were quantified using a Client Server Turbochrom data system (Perkin  
20 Elmer, Beaconsfield, UK).

## 21 22 **Octanol-water partition coefficients**

23  
24 Octanol-water partition coefficients were obtained from literature. Sangster<sup>21</sup> compiled  
25 log  $K_{ow}$  values reviewed from available literature and gave recommended values for some  
26 compounds which were adopted in this study. For compounds where no recommended  
27 value was given, average value of the log  $K_{ow}$  data presented was chosen and where only  
28 one value was given this was adopted.



## 1 Results

### 3 Co-solvent method

4  
5 Silicone rubber-water partition coefficients were calculated (Eq. 1) at each methanol  
6 percentage and log linear curves plotted for  $K_{sr,w}$  as a function of the methanol volume  
7 percent (Figure 1). The partition coefficients by the co-solvent method were estimated  
8 from the intercept of the regression lines at 100 % water (0 % methanol) thus eliminating  
9 the need to measure the partition coefficients directly in pure water. Addition of the  
10 cosolvent increases the hydrophobicity of the resulting solvent (water/co-solvent  
11 mixture), which increases solubility of the target compounds in the solvent mixture <sup>14, 16,</sup>  
12 <sup>22, 23</sup>. The solubility increases exponentially while the logarithm of partition coefficients  
13 will decrease linearly with increasing mole fraction of methanol. Linear regressions were  
14 good descriptors of the relationship between  $\log K_{sr,w}$  and percent methanol with the  
15 intercept representing  $\log K_{sr,w}$  at 0 % methanol. Log  $K_{sr,w}$  values, along with the 95 %  
16 confidence interval of the intercept of  $\log K_{sr,w}$  - methanol volume percentage are shown  
17 in Table 1.

18  
19 For the more hydrophobic compounds, the number of data points used in the regression  
20 analysis is often less than 7 due to problems in the accurate measurement of  
21 concentrations of HOCs at low percentages of methanol in water. Inclusion of some of  
22 these data of relatively high uncertainty would not have improved the quality of the  
23 regression analysis or the estimates of partition coefficients. At least five partition  
24 coefficients are recommended for the regression, because if fewer partition coefficients  
25 are used for extrapolation, the statistical errors in the estimate of the intercept ( $\log K_{sr,w}$ )  
26 will tend to be large <sup>15</sup>.

## 1 **Batch incubation of reference phases**

2

3 The cosolvent method can however be laborious and so an attempt was made to estimate  
4 the  $\log K_{sr,w}$  from a material of known partition coefficients. Therefore using data  
5 obtained from the cosolvent method for Vizo sheets <sup>17</sup>,  $\log K_{sr,w}$  values were predicted for  
6 the Altec sheets using Eq. 5. Results obtained by incubating the Vizo and Altec silicone  
7 rubbers are presented in Table 2 for those compounds for which partition coefficients for  
8 Vizo rubber were available.

9

## 10 **Discussion**

11

12 In the absence of direct measurements, estimates of partition coefficients for passive  
13 samplers are often obtained from  $\log K_{ow}$  values. The measured Altec silicone rubber-  
14 water partition coefficients were plotted against corresponding  $\log K_{ow}$  values and good  
15 linear relationships were found (Figure 2a & b, Table 4). This confirms that partitioning  
16 into the silicone rubber is strongly determined by compound hydrophobicity, as has been  
17 reported for other materials, such as POM <sup>3</sup> and PDMS fibres <sup>5</sup>. No significant  
18 differences were found (F-test;  $p > 0.05$ ) between the  $\log K_{sr,w}$  -  $\log K_{ow}$  relations  
19 depending on the source of the  $\log K_{ow}$  data for either the PAHs or CBs. The regressions  
20 using different sources of  $\log K_{ow}$  differ in their intercepts for PAHs while the slope did  
21 not differ significantly (slope =  $0.97 \pm 0.11$ ; slope =  $1.13 \pm 0.19$ , Table 4) when the  
22 intercepts are ignored. Deviations from linearity could arise from some uncertainty in  
23 available  $K_{ow}$  values <sup>13, 24</sup> and other factors, such as possible transport resistance of  
24 silicone rubber to large molecules (large  $K_{ows}$ ), as had been observed for various tissues  
25 and membranes <sup>25</sup>.

26

27 Combining both classes of compounds also yields a linear relationship (Table 4) but the  
28 decrease in the quality of the regression indicates systematic differences in the  
29 relationship between  $\log K_{sr,w}$  and  $\log K_{ow}$  for different classes of compound. (*c.f.* Vrana

1 *et al.*<sup>29</sup>). The measured partition coefficients were on average, 0.70 units less than the  
2 octanol-water partition coefficients for the CBs and 0.18 units for the PAHs. The  
3 regressions of  $\log K_{POM}$  of CBs and PAHs with  $\log K_{ow}$  have been reported<sup>3</sup> not to differ  
4 significantly which allow for pooling of both classes of compounds while in our study the  
5 regressions differed significantly (F-test;  $p < 0.001$ ). The observed differences in the  
6 regressions may be due to structural differences between PAHs and CBs. Differences  
7 have been shown<sup>1, 15, 30</sup> between  $\log K_{oc}$  (organic carbon normalised partition  
8 coefficients) - $\log K_{ow}$  regression lines for PAHs and CBs which have been attributed to  
9 differences in molecular structure between the two classes of compounds. Similarly,  
10 caution has been suggested with regards to estimation of bioconcentration factors (BCF)  
11 from  $\log BCF$ - $\log K_{ow}$  correlations (which are essentially partitioning models between  
12 biological membranes and water) for different classes of compounds<sup>31, 32</sup> due to  
13 uncertainties in the measurement of both BCF's and  $\log K_{ow}$  (especially at  $\log K_{ow} > 6$  ).  
14  
15 SPMD-water partition coefficients (reviewed from literature) are available in Huckins *et*  
16 *al.*<sup>23</sup>, and the average  $\log K_{spmd,w} - \log K_{ow}$  values from the various data was described by  
17 a quadratic fit with deviations from linearity observed from  $\log K_{ow} > 5$  possibly due to  
18 solute-triolein incompatibility. This was not the case in the good linear relationships  
19 found in this study over a  $\log K_{ow}$  range of 3 – 8, suggesting that such complications do  
20 not occur with silicone rubber and that equilibrium partitioning between the silicone  
21 rubber and aqueous phases is almost entirely a function of the hydrophobicity of the  
22 target contaminants. The need to determine partition coefficients for both the lipid and  
23 the membrane as is the case for SPMDs is eliminated as only a single partition coefficient  
24 is sufficient to describe partitioning in the silicone rubber sampler.

25  
26 In view of the uncertainties inherent in the measurements of partition coefficients by  
27 either the co-solvent or batch incubation method, it is suggested that use can be made of  
28 the linear regressions between  $\log K_{sr,w}$  and  $\log K_{ow}$  to obtain estimates of  $\log K_{sr,w}$ . The  
29 standard errors in the experimental data in Table 1 are on average 2.35 (CBs) and 1.69

1 (PAHs) times the errors from the predicted values (Table 3) from the  $\log K_{sr,w}$ - $\log$   
2  $K_{ow}$  regressions.  
3  
4 The  $\log K_{sr,w}$  values obtained by incubation (referred to as estimated  $K_{sr,w}$ , Table 2)  
5 correlated well ( $r^2 = 0.93$ , PAHs and  $0.90$ , CBs) with the cosolvent method values (Table  
6 1), however, there was an observed increase in deviation of  $\log K_{sr,w}$  between the two  
7 methods with increasing  $\log K_{ow}$ . Uncertainties in the silicone rubber-water partition  
8 coefficients for the Vizo rubber will have added to overall uncertainties in the partition  
9 coefficients estimated by this method for the Altec rubber. It may be noted that a quick  
10 estimate of  $\log K_{sr,w}$  values can be obtained by, equilibrating the silicone rubber of known  
11 partition coefficient with an unknown rubber, for example to confirm the quality of a new  
12 batch of rubber.

## 14 **Conclusions**

15  
16 The co-solvent method offers a practical way to estimate partition coefficients for passive  
17 sampling materials, such as silicone rubber. The estimated partition coefficients showed  
18 strong linear relations with published values for  $\log K_{ow}$  confirming that partitioning into  
19 the silicone rubber is largely a function of compound hydrophobicity, and that absorption  
20 into the silicone rubber is the main mechanism governing retention of analytes in the  
21 polymer. It is suggested that best estimates of partition coefficients for silicone rubber  
22 may be obtained from regressions between  $\log K_{ow}$  and  $\log K_{sr,w}$ . The fitted values can be  
23 used to estimate sampling rates of passive samplers and in the determination of free  
24 dissolved concentrations of PAHs and CBs in water and sediment pore water. In cases  
25 where no silicone rubber-water partition coefficients are available, estimations can be  
26 made using the octanol-water partition coefficients, although measured values are always  
27 better. It is also possible to attempt to measure  $\log K_{sr,w}$  in pure water, with any  
28 agreement of the cosolvent values with water-only values greatly enhancing the

1 reliability of the final values, although there always will be some uncertainty with the  
2 individual methods.

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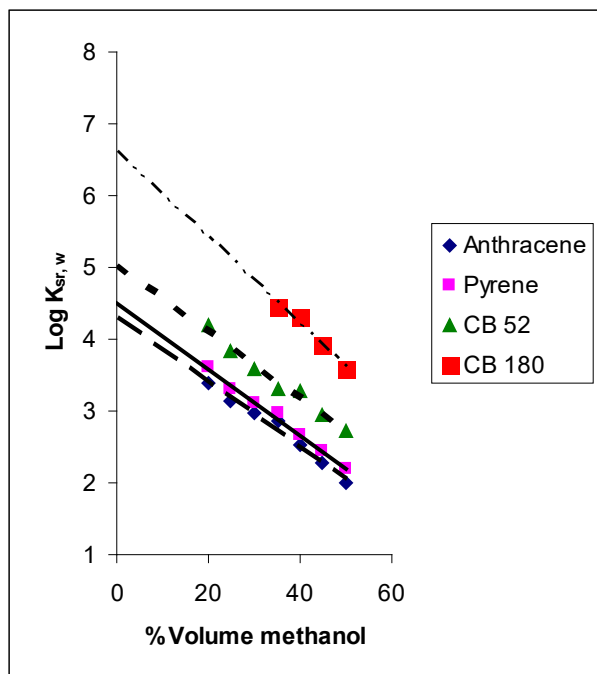
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2 Figure 1: Silicone rubber-water partition coefficients as a function of volume percentage  
 3 methanol for anthracene (diamonds), pyrene (squares), CB 52 (triangle) and CB 180  
 4 (large squares). Only four points were used for the regression of CB 180, as it was not  
 5 detected in 20-30 % volume methanol. Linear regression was used to obtain estimates of  
 6 intercept.

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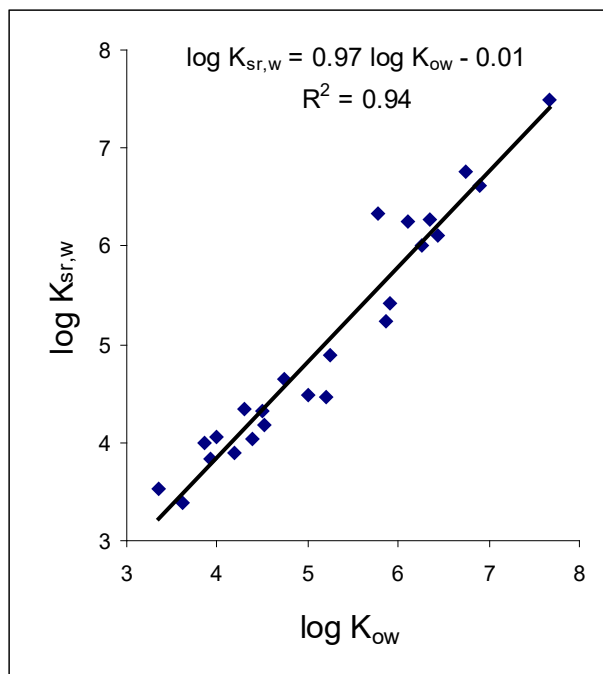
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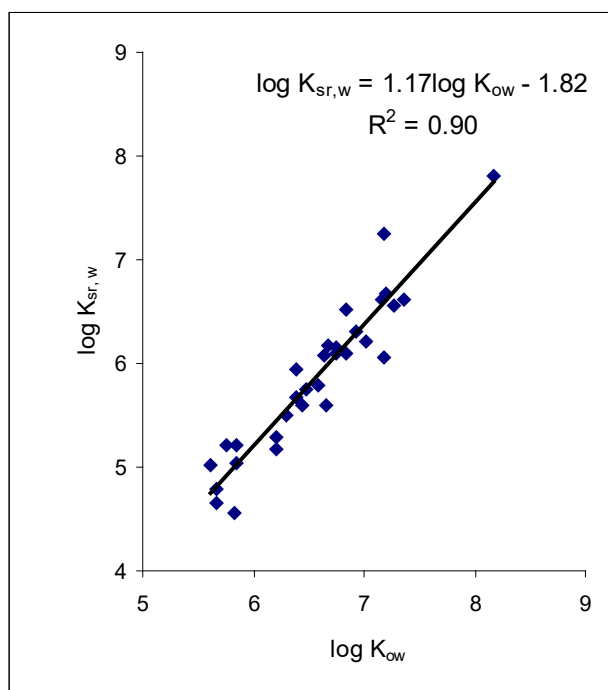
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2 **Figure 2a:** Correlation of  $\log K_{sr,w}$  with  $\log K_{ow}$  for 24 PAH compounds.  $\log K_{sr,w}$ 's are  
 3 mean values of duplicate measurements and  $\log K_{ow}$  are from Sansgter <sup>21</sup>

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6 **Figure 2b:** Correlation of  $\log K_{sr,w}$  with  $\log K_{ow}$  CBs.  $\log K_{sr,w}$  are mean values of  
 7 duplicate measurements and  $\log K_{ow}$  are from Hawker and Connell <sup>27</sup>

1 **Table 1:** Log Partition coefficients and 95 % confidence interval of estimate of intercept  
 2 from regression of test compounds

Compounds	Log K <sub>ow</sub>	Log K <sub>sr,w</sub>	C.I. <sup>1</sup>	n <sup>2</sup>	Compounds	Log K <sub>ow</sub>	Log K <sub>sr,w</sub>	C.I. <sup>1</sup>	n <sup>2</sup>
Naphthalene	3.35	3.53	0.40	7	CB 28	5.67	4.79	0.33	7
Acenaphthylene	3.61	3.39	0.20	7	CB 31	5.67	4.66	0.30	7
Acenaphthene	3.92	3.84	0.35	7	CB 35	5.82	4.56	0.40	7
Fluorene	4.18	3.89	0.33	7	CB 44	5.75	5.21	0.32	7
2-Methylnaphthalene	4.00	4.06	0.48	7	CB 49	5.85	5.22	0.40	7
1-Methylnaphthalene	3.87	4.00	0.50	7	CB 52	5.84	5.04	0.29	7
C2-naphthalene	4.31	4.33	0.40	7	CB53	5.62	5.02	0.39	7
C3-naphthalene	4.73	4.64	0.41	7	CB 70	6.2	5.17	0.35	7
C4-naphthalene	5.17 <sup>a</sup>	5.17	0.44	7	CB 74	6.2	5.29	0.34	7
Phenanthrene	4.52	4.18	0.31	7	CB 97	6.29	5.49	0.32	7
Anthracene	4.50	4.31	0.28	7	CB 99	6.39	5.68	0.29	7
2-Methylphenanthrene	5.24	4.89	0.37	7	CB 101	6.38	5.93	0.31	6
3,6-Dimethylphenanthrene	5.25 <sup>a</sup>	5.15	0.25	7	CB 105	6.65	5.60	0.33	7
2,6,9-Trimethylphenanthrene	5.99 <sup>a</sup>	5.34	0.30	7	CB 110	6.48	5.74	0.32	6
Dibenzothiophene	4.38	4.04	0.31	7	CB 112	6.45	5.59	0.31	7
Fluoranthene	5.20	4.45	0.21	7	CB 118	6.74	6.16	0.33	6
Pyrene	5.00	4.49	0.17	7	CB 128	6.74	6.10	0.42	7
1-Methylfluoranthene	5.48 <sup>a</sup>	5.01	0.19	7	CB 132	6.58	5.79	0.29	7
2,7-Dimethylpyrene	6.03 <sup>a</sup>	6.30	0.27	7	CB 137	6.83	6.10	0.35	6
Benzo[ <i>c</i> ]phenanthrene	5.76 <sup>*</sup>	5.38	0.18	7	CB 138	6.83	6.52	0.31	6
Benz[ <i>a</i> ]anthracene	5.91	5.42	0.16	7	CB 149	6.67	6.17	0.40	6
Chrysene	5.86	5.23	0.15	7	CB 151	6.64	6.07	0.37	7
2-Methylchrysene	6.88 <sup>+</sup>	6.15	0.20	7	CB 153	6.92	6.30	0.25	4
Benzo[ <i>b</i> ]fluoranthene	5.78	6.33	0.09	7	CB 156	7.18	7.26	0.34	5
Benzo[ <i>k</i> ]fluoranthene	6.11	6.25	0.05	7	CB 157	7.18	6.06	0.38	6
Benzo[ <i>e</i> ]pyrene	6.44	6.12	0.06	7	CB 158	7.02	6.20	0.30	7
Benzo[ <i>a</i> ]pyrene	6.35	6.27	0.14	7	CB 170	7.27	6.56	0.82	4
Perylene	6.25	6.02	0.12	6	CB 180	7.36	6.61	0.67	4
7-Methylbenzo[ <i>a</i> ]pyrene	nf	6.97	0.18	6	CB 183	7.2	6.67	0.42	4
Indeno[ <i>1,2,3-cd</i> ]pyrene	7.66	7.48	0.17	7	CB 187	7.17	6.61	0.36	4
Benzo[ <i>ghi</i> ]perylene	6.90	6.63	0.14	6	CB 189	7.24	6.45	0.40	4
Dibenz[ <i>a,h</i> ]anthracene	6.75	6.76	0.23	6	CB 209	8.18	7.81	0.28	3
D <sub>12</sub> -Chrysene	5.80 <sup>b</sup>	5.15	0.15	7					
D <sub>12</sub> -Benzo[ <i>e</i> ]pyrene	6.29 <sup>c</sup>	6.29	0.14	7					

3 <sup>1</sup> C.I. = Confidence interval of the estimate of the regression intercept; <sup>2</sup> n = number of data points  
 4 making up plot; <sup>3</sup> log K<sub>ow</sub> of PAHs are from Sangster <sup>21</sup>, <sup>a</sup> from ref 1, <sup>b</sup> from ref 24, <sup>c</sup> adopted  
 5 the value of Benzo[*e*]pyrene and those of CBs from Hawker and Connell <sup>27</sup>, nf = no log K<sub>ow</sub>

- 1 value found, <sup>+</sup> value adopted from ([www.nature.nps.gov/hazardssafety/toxic/chrys\\_c1.pdf](http://www.nature.nps.gov/hazardssafety/toxic/chrys_c1.pdf)), \*
- 2 value for naphthacene is used. Log  $K_{sr, w}$  values are means of 2 replicates.
- 3

1 **Table 2:** Log partition coefficients obtained by equilibration of 2 different silicone  
 2 rubbers

Compounds	ALTEC Measured <sup>1</sup>	VIZO <sup>2</sup>	ALTEC Estimated <sup>3</sup>	Compound	ALTEC Measured	VIZO	ALTEC Estimated
Phenanthrene	4.18	3.89	4.06	CB 28	4.79	5.22	5.36
Anthracene	4.31	4.00	4.18	CB 31	4.66	5.23	5.33
Fluoranthene	4.45	4.38	4.59	CB 44	5.21	5.56	5.71
Pyrene	4.49	4.44	4.66	CB 49	5.22	5.66	5.78
Benz[ <i>a</i> ]anthracene	5.42	5.06	5.29	CB 52	5.04	5.57	5.70
Chrysene	5.23	4.97	5.20	CB 101	5.93	6.03	6.13
Benzo[ <i>b</i> ]fluoranthene	6.33	5.51	5.71	CB 105	5.60	6.17	6.31
Benzo[ <i>k</i> ]fluoranthene	6.25	5.51	5.71	CB 118	6.16	6.20	6.30
Benzo[ <i>e</i> ]pyrene	6.12	5.45	5.65	CB 138	6.52	6.53	6.64
Benzo[ <i>a</i> ]pyrene	6.27	5.52	5.71	CB 153	6.30	6.45	6.54
Indeno[ <i>1,2,3-cd</i> ]pyrene	7.48	5.99	6.20	CB 156	7.26	6.58	6.65
Benzo[ <i>ghi</i> ]perylene	6.63	5.92	6.12	CB 170	6.56	6.90	6.98
Dibenz[ <i>a,h</i> ]anthracene	6.76	6.04	6.26	CB 180	6.61	6.84	6.90
D12-Chrysene	5.15	4.91	5.14	CB 187	6.61	6.77	6.84

3 <sup>1</sup>Experimentally measured in this study; <sup>2</sup>estimated using equation 4 and

4  $\log K_{sr,w}$  values for the Vizo rubber from ref 17

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1 **Table 3:** Selected estimated  $\log K_{sr,w}$  values from the  $K_{sr,w}$  -  $\log K_{ow}$  regressions

Compound	$\log K_{sr,w}$	S. E. <sup>a</sup>	$\log K_{ow}$
<b>PAHs</b>			
Acenaphthene	3.78	0.09	3.92
Fluorene	4.04	0.08	4.18
Phenanthrene	4.36	0.07	4.52
Fluoranthene	5.02	0.06	5.20
Chrysene	5.66	0.07	5.86
Benzo[ <i>a</i> ]pyrene	6.14	0.08	6.35
Benzo[ <i>g,h,i</i> ]perylene	6.67	0.11	6.90
Dibenz[ <i>a,h</i> ]anthracene	6.52	0.10	6.75
<b>CBs</b>			
CB 31	4.81	0.08	5.67
CB 52	5.01	0.07	5.84
CB 101	5.64	0.05	6.38
CB 110	5.76	0.05	6.48
CB 118	6.07	0.05	6.74
CB 105	5.96	0.05	6.65
CB 183	6.60	0.07	7.20
CB 170	6.69	0.07	7.27

2 <sup>a</sup>S.E. = Standard error of predicted value,  $\log K_{ow}$  of PAHs are from Sangster<sup>21</sup> and those of CBs  
 3 from Hawker and Connell<sup>27</sup>.

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5 **Table 4:** Summary of linear regression analysis of  $\log K_{sr,w}$  versus  $\log K_{ow}$

	$\log K_{ow}$	<i>Slope</i>	<i>Intercept</i>	$r^2$	$s^a$	$n^b$
PAHs	Ref 21	0.97	-0.01	0.94	0.29	24
	Ref 26	1.13	-0.79	0.94	0.38	17
<b>CBs</b>						
CBs	Ref 27	1.17	-1.82	0.9	0.25	31
	Ref 28	1.2	-1.98	0.91	0.28	15
<b>Pooled (PAHs &amp; CBs)</b>						
Pooled (PAHs & CBs)	Ref 21 & 27	0.87	0.30	0.89	0.35	55

6 <sup>a</sup> standard deviation of the fit; <sup>b</sup> sample size

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