YATES, K., DAVIES, I., WEBSTER, L., POLLARD, P., LAWTON, L. and MOFFAT, C. 2007. Passive sampling: partition coefficients for a silicone rubber reference phase. *Journal of environmental monitoring* [online], 9(10), pages 1116-1121. Available from: https://doi.org/10.1039/B706716J

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

YATES, K., DAVIES, I., WEBSTER, L., POLLARD, P., LAWTON, L. and MOFFAT, C.

2007

Passive sampling: Partition coefficients for a silicone rubber reference phase

Kyari Yates[1, 2], Ian Davies[1], Lynda Webster[1], Pat Pollard[2], Linda Lawton[2] and Colin Moffat[1, 2]

1 Fisheries Research Services Marine Laboratory, 375 Victoria Road, Aberdeen, AB11 9DB, UK

2 School of Life Sciences, Robert Gordon University, Aberdeen, UK

Abstract

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

Introduction

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

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

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

where $K_{s,w}$ is the sampler-water partition coefficient, C_S and C_W is the concentration in the sampler and water respectively. The sampling rate is calculated from equation 2 [1]:

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

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

$$k_e = -\frac{\ln\left(N^t / N^0\right)}{t} \qquad (3)$$

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

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

Materials and methods

Materials

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

Loading of Compounds on silicone rubber

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

Partition coefficient determination

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

Deuterated PAH internal standards (D_8-naphthalene, D_{10}-biphenyl, D_{10}-anthracene, D_8-dibenzothiophene, D_{10}-pyrene and D_{12}-benzo[*a*]pyrene) were added to the methanol-water mixtures in the 1 l bottles and transferred into separation funnels. These were liquid-liquid extracted in separating funnels using 2 × 60 ml dichloromethane and the extracts dried over anhydrous sodium sulphate. The extracts were rotary evaporated to ~ 2 ml and 2 × 25 ml 2-methylpentane added followed by concentration, first by rotary evaporation, then by nitrogen blow down to 1 ml and split into 2 parts: 1 fraction was analysed by gas chromatography-mass selective detection (GC-MS) for PAHs and the other by gas chromatography-electron capture detection (GC-ECD) for CBs. The silicon rubber sheets were Soxhlet extracted using a 2-methylpentane: acetone (3:1 $^{v}/_{v}$) mixture for 6 h and the same suite of deuterated PAH internal standards added, then exchanged into 2-methylpentane by the addition of 2 × 25 ml of 2-methylpentane. The extract was concentrated by rotary evaporation followed by nitrogen blow down to 1 ml which was then split into 2 fractions by weight for PAHs and CBs. An aliquot of the PAH fraction was fractionated by isocratic, normal phase high performance liquid chromatography using a Genesis silica column and eluted with 2-methylpentane into aliphatic and aromatic fractions. The aliphatic fraction was discarded and the aromatic fraction collected and concentrated before analysis for PAHs. Similarly an aliquot of the CB fraction was fractionated as above and the eluate from the first 6 min (predetermined using a solution of CBs) collected and 2, 4-dichlorobenzyl alkyl ethers internal standard added, then concentrated before analysis for CBs. Recoveries calculated on the basis of the sum of the amounts determined in the methanol-water mixtures and amounts in the sheets relative to the amount loaded onto the sheets were 86 ± 20 % for the CBs and 101 ± 16 % for PAHs.

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

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

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

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

Chromatographic Analysis

The concentrations and composition of the PAHs were determined by gas chromatography mass selective detection (GC-MS) using an HP6890 Series Gas Chromatograph interfaced with an HP5973 MSD fitted with a cool on-column injector as described by Webster *et al.* [20]. Briefly, a non-polar HP5 (30 m × 0.25 mm id, 0.25 µm film thickness; Agilent Technologies, Stockport, England) column was used for the analyses with helium as the carrier gas, controlled using the constant flow mode at 0.7 ml min^{-1}. Injections were made at 50 °C and the oven temperature held constant for 3 min. Thereafter, the temperature was raised at 20 °C min^{-1} up to 100 °C, followed by a slower ramp of 4 °C min^{-1} up to a final temperature of 270 °C. The MSD was set for selective ion monitoring (SIM) with a dwell time of 50 ms. A total of 30 ions plus the six internal standard ions were measured over the analysis period, thus incorporating 2- to 6- ring, parent and branched PAHs.

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

Octanol-water partition coefficients

Octanol-water partition coefficients were obtained from literature. Sangster [21] compiled $\log K_{ow}$ values reviewed from available literature and gave recommended values for some compounds which were adopted in this study. For compounds where no recommended value was given, average value of the $\log K_{ow}$ data presented was chosen and where only one value was given this was adopted.

Results

Co-solvent method

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

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

Batch incubation of reference phases

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

Discussion

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

Combining both classes of compounds also yields a linear relationship (Table 4) but the decrease in the quality of the regression indicates systematic differences in the relationship between $\log K_{sr,w}$ and $\log K_{ow}$ for different classes of compound. (*c.f.* Vrana *et al.* [29]). The measured partition coefficients were on average, 0.70 units less than the octanol-water partition coefficients for the CBs and 0.18 units for the PAHs. The regressions of $\log K_{POM}$ of CBs and PAHs with $\log K_{ow}$ have been reported [3] not to differ significantly which allow for pooling of both classes of compounds while in our study the regressions differed significantly (F-test; $p < 0.001$). The observed differences in the regressions may be due to structural differences between PAHs and CBs. Differences have been shown [1, 15, 30] between $\log K_{OC}$ (organic carbon normalised partition coefficients) -$\log K_{ow}$ regression lines for PAHs and CBs which have been attributed to differences in molecular structure between the two classes of compounds. Similarly, caution has been suggested with regards to estimation of bioconcentration factors (BCF) from log BCF-$\log K_{ow}$ correlations (which are essentially partitioning models between biological membranes and water) for different classes of compounds [31, 32] due to uncertainties in the measurement of both BCF's and $\log K_{ow}$ (especially at $\log K_{ow} > 6$) .

SPMD-water partition coefficients (reviewed from literature) are available in Huckins *et al.* [23], and the average $\log K_{spmd,w} - \log K_{ow}$ values from the various data was described by a quadratic fit with deviations from linearity observed from $\log K_{ow} > 5$ possibly due to solute-triolein incompatibility. This was not the case in the good linear relationships found in this study over a $\log K_{ow}$ range of 3 – 8, suggesting that such complications do not occur with silicone rubber and that equilibrium partitioning between the silicone rubber and aqueous phases is almost entirely a function of the hydrophobicity of the target contaminants. The need to determine partition coefficients for both the lipid and the membrane as is the case for SPMDs is eliminated as only a single partition coefficient is sufficient to describe partitioning in the silicone rubber sampler.

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

(PAHs) times the errors from the predicted values (Table 3) from the log $K_{sr,w}$ - log K_{ow} regressions.

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

Conclusions

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

References

1. K. Booij, J. H. Hoedemaker, and J. F. Bakker, *Environ. Sci. Technol.*, 2003, **37**, 4213-4220

2. K. Booij, F. Smedes, and E. M. van Werlee, *Chemosphere*, 2002, **46**, 1157-1161

3. M. T. O. Jonker, and A. A. Koelmans, *Environ. Sci. Technol.*, 2001, **35**, 3742-3748

4. G. Cornelissen, H. Rigterink, D. E. M. ten Hulscher, B. A. Vrind, and P. C. M. van Noort, *Environ. Toxicol. Chem.*, 2001, **20**, 706–711

5. P. Mayer, W.H.J. Vaes, and J.L.M Hermens, *Anal. Chem.*, 2000, **72**, 459-464

6. T. P. Rusina, F. Smedes, J. Klanova, K. Booij, and I. Holoubek, *Chemosphere*, 2007, DOI: 10.1016/j.chemosphere.2007.01.025

7. L. Wennrich, B. Vrana, P. Popp, and W. Lorenz, *J. Environ. Monit.*, 2003, **5**, 813-822

8. J. N. Huckins, M. W. Tubergen, and G. K. Manuweera, *Chemosphere*, 1990, **20**, 533-552

9. J. N. Huckins, G. K. Manuweera, J. D. Petty, D. Mackay, and J. A. Lebo, *Environ. Sci. Technol.*, 1993, **27**, 2489-2496

10. P. Mayer, J. Tolls, J. L. P. Hermens, and D. Mackay, *Environ. Sci. Technol.*, 2003, **37**, 187A-191A

11. J. N. Huckins, J. D. Petty, and K. Booij, *Monitors of Organic Chemicals in the Environment: Semipermeable membrane devices*, Springer Science+Business Media, New York, 2006, pp 183- 186

12. R. Doong, and S. Chang, *Anal. Chem.*, 2000, **72**, 3647 – 3652

13. T. W. Jabusch, and D. L. Swackhamer, *Chemosphere*, 2005, **60**, 1270-1278

14. A. Li, A. W. Andren, S. H. Yalkowsky, *Environ. Toxicol. Chem.*, 1996, **15**, 2233–2239

15. M. T. O. Jonker, and F. Smedes, *Environ. Sci. Technol.*, 2000, **34**, 1620-1626

16. W. J. M. Hegeman, C. H. van Der Weijden, and J. P. Gustav Loch, *Environ. Sci. Technol.*, 1995, **29**, 363-371

17. F. Smedes, In *Comprehensive Analytical Chemistry*, ed. R. Greenwood, G. Mills, B. Vrana, Elsevier, Oxford, UK, 1st edn., 2007, vol. 48, ch. 22, pp. 407-448

18. A. Li, and A. W. Andren, *Environ. Sci. Technol.*, 1994, **28**, 47-52

19. P. R. Brookes and A. G. Livingston, *J. Memb. Sci.*, 1995, **104**, 119-137

20. L. Webster, L. Phillips, M. Russell, E. Dalgarno, and C. Moffat, *J. Environ. Monit.*, 2005, **12**, 1378-1387

21. Sansgter, J. [online] Sansgter Research Laboratories, CNC/CODATA; http://logkow.cisti.nrc.ca/logkow/index.jsp Accessed 03 September, 2005

22. R. C. Chawla, K. F. Doura, and D. McKay, Proceedings of the 2001 Conference on Environmental Research, Kansas State, University, Manhattan, KS, 2001

23. F. C. Spurlock, and J. W. Biggar, *Environ. Sci. Technol.*, 1994, **28**, 1003-1009

24. W. M. Meylan, and P. H. Howard, *Chemosphere*, 2005, **61**, 640-644

25. C. T. Chiou, *Environ. Sci. Technol.*, 1985, **19**, 57-62

26. US EPA, EPI SUITE™ (Estimation Programs Interface) [online] http://www.epa.gov/oppt/exposure/docs/episuite.htm Accessed 12 June 2005

27. D. W. Hawker, and D. W. Connell, *Environ. Sci. Technol.*, 1988, **22**, 382-387

28. D. Mackay, W. Y. Shiu, and K. C. Ma, Illustrated Handbook of Physical Chemical Properties and Environmental Fate of Organic Chemicals, Lewis Publishers, London, UK, 1992, vol. 1, pp 327-668

29. B. Vrana, P. Popp, A. Paschke, and G. Schűűrmann, *Anal. Chem.*, 2001, **73**, 5191-5200

30. K. Booij, H. M. Sleiderink, and F. Smedes, *Environ. Toxicol. Chem.*, 1998, **17**, 1236–1245

31. D. Mackay, *Environ. Sci. Technol.*, 1982, **16**, 274-278

32. M. G. Barron, *Environ. Sci. Technol.*, 1990, **24**, 1612-1618

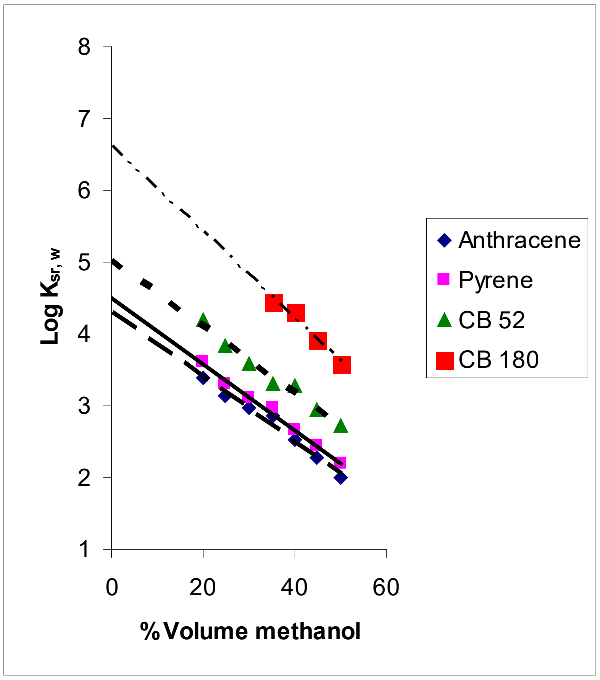

Figure 1: Silicone rubber-water partition coefficients as a function of volume percentage methanol for anthracene (diamonds), pyrene (squares), CB 52 (triangle) and CB 180 (large squares). Only four points were used for the regression of CB 180, as it was not detected in 20-30 % volume methanol. Linear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

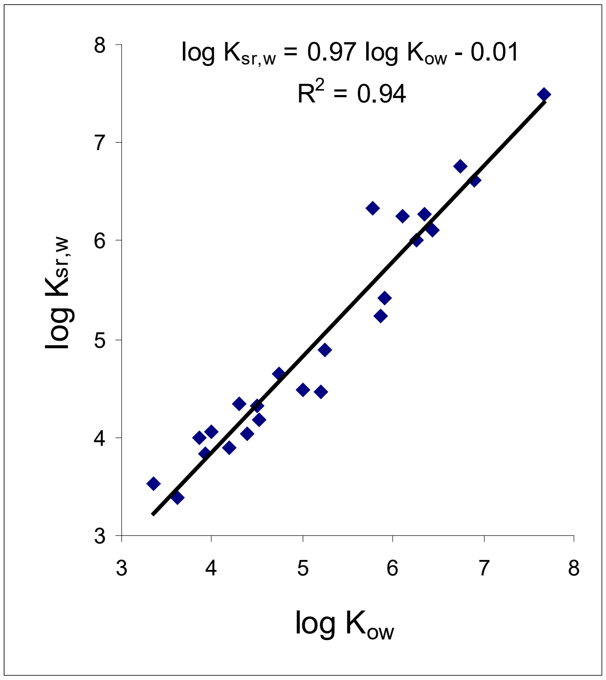

Figure 2a: Correlation of log $K_{sr,w}$ with log K_{ow} for 24 PAH compounds. Log $K_{sr,w}$'s are mean values of duplicate measurements and log K_{ow} are from Sansgter [21]

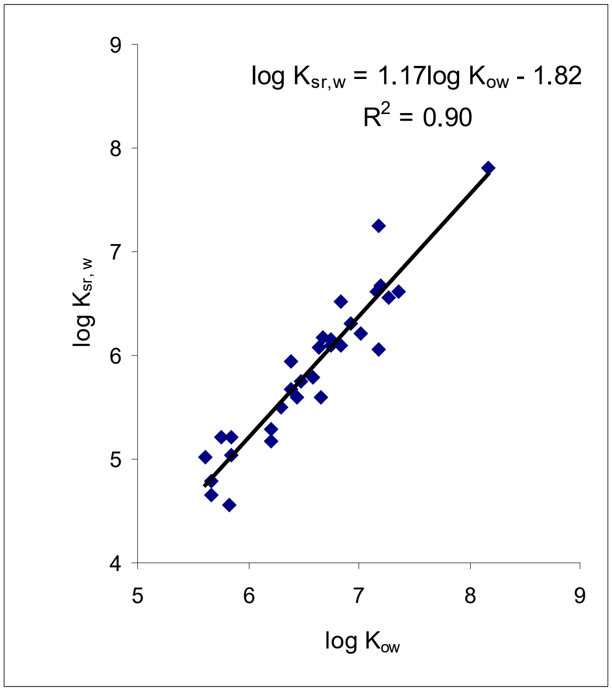

Figure 2b: Correlation of log $K_{sr,w}$ with log K_{ow} CBs. Log $K_{sr,w}$ are mean values of duplicate measurements and log K_{ow} are from Hawker and Connell [27]

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

Compounds	Log K_{ow}	Log $K_{sr,w}$	C.I.[1]	n[2]	Compounds	Log K_{ow}	Log $K_{sr,w}$	C.I.[1]	n[2]
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[a]	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[a]	5.15	0.25	7	CB 105	6.65	5.60	0.33	7
2,6,9-Trimethylphenanthrene	5.99[a]	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[a]	5.01	0.19	7	CB 132	6.58	5.79	0..29	7
2,7-Dimethylpyrene	6.03[a]	6.30	0.27	7	CB 137	6.83	6.10	0.35	6
Benzo[*c*]phenanthrene	5.76*	5.38	0.18	7	CB 138	6.83	6.52	0.31	6
Benz[*a*]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[+]	6.15	0..20	7	CB 153	6.92	6.30	0.25	4
Benzo[*b*]fluoranthene	5.78	6.33	0.09	7	CB 156	7.18	7.26	0.34	5
Benzo[*k*]fluoranthene	6.11	6.25	0.05	7	CB 157	7.18	6.06	0.38	6
Benzo[*e*]pyrene	6.44	6.12	0.06	7	CB 158	7.02	6.20	0.30	7
Benzo[*a*]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[*a*]pyrene	nf	6.97	0.18	6	CB 183	7.2	6.67	0.42	4
Indeno[*1,2,3-cd*]pyrene	7.66	7.48	0.17	7	CB 187	7.17	6.61	0.36	4
Benzo[*ghi*]perylene	6.90	6.63	0.14	6	CB 189	7.24	6.45	0.40	4
Dibenz[*a,h*]anthracene	6.75	6.76	0.23	6	CB 209	8.18	7.81	0.28	3
D_{12}-Chrysene	5.80[b]	5.15	0.15	7					
D_{12}-Benzo[*e*]pyrene	6.29[c]	6.29	0.14	7					

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

value found, [+] value adopted from (www.nature.nps.gov/hazardssafety/toxic/chrys_c1.pdf), [*] value for naphthacene is used. Log $K_{sr,\,w}$ values are means of 2 replicates.

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

Compounds	ALTEC Measured[1]	VIZO[2]	ALTEC Estimated[3]	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[*a*]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[*b*]fluoranthene	6.33	5.51	5.71	CB 105	5.60	6.17	6.31
Benzo[*k*]fluoranthene	6.25	5.51	5.71	CB 118	6.16	6.20	6.30
Benzo[*e*]pyrene	6.12	5.45	5.65	CB 138	6.52	6.53	6.64
Benzo[*a*]pyrene	6.27	5.52	5.71	CB 153	6.30	6.45	6.54
Indeno[*1,2,3-cd*]pyrene	7.48	5.99	6.20	CB 156	7.26	6.58	6.65
Benzo[*ghi*]perylene	6.63	5.92	6.12	CB 170	6.56	6.90	6.98
Dibenz[*a,h*]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

[1] Experimentally measured in this study; [2] estimated using equation 4 and $\log K_{sr,w}$ values for the Vizo rubber from ref 17

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.[a]**	**log K_{ow}**
PAHs			
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[*a*]pyrene	6.14	0.08	6.35
Benzo[*g,h,i*]perylene	6.67	0.11	6.90
Dibenz[*a,h*]anthracene	6.52	0.10	6.75
CBs			
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

[a]S.E. = Standard error of predicted value, log K_{ow} of PAHs are from Sangster [21] and those of CBs from Hawker and Connell [27].

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

	log K_{ow}	*Slope*	*Intercept*	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
CBs	Ref 27	1.17	-1.82	0.9	0.25	31
	Ref 28	1.2	-1.98	0.91	0.28	15
Pooled (PAHs & CBs)	Ref 21 & 27	0.87	0.30	0.89	0.35	55

[a] standard deviation of the fit; [b]sample size