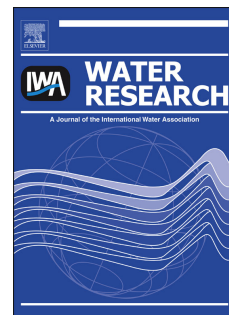


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**Dynamic multi-phase partitioning of
decamethylcyclopentasiloxane (D5) in river water**

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20

21 **Abstract**

22 The behaviour of decamethylcyclopentasiloxane (D5) in river water was evaluated by
23 measuring concentration changes in open beakers. Effective values for the partition
24 coefficient between organic carbon and water (K_{OC}) were derived by least-squares
25 optimisation of a dynamic model which accounted for partitioning between the sorbed
26 and dissolved phases of D5, and for losses via volatilisation and hydrolysis. Partial
27 mass transfer coefficients for volatilisation were derived from model fits to controls
28 containing deionised water. Effective values of $\log(K_{OC})$ were between 5.8 and 6.33
29 (mean 6.16). These figures are higher than some other experimentally-derived values
30 but much lower than those estimated from the octanol : water partition coefficient
31 using single-parameter linear free energy relationships (LFERs). A poly-parameter
32 LFER gave a predicted $\log(K_{OC})$ of 5.5. Differences in partitioning are believed to be
33 due to the nature of the organic matter present. The new value for effective K_{OC} was
34 employed in a simple model of D5 behaviour in rivers to ascertain the extent to which
35 a higher affinity for organic carbon would depress volatility. The results suggest that
36 despite the revised K_{OC} value, volatilisation of D5 remains a significant removal
37 mechanism in surface waters.

38

39

40 **Key Words:** Decamethylcyclopentasiloxane, D5, volatilisation, river water, K_{OC}

41

42 **Introduction**

43

44 Cyclic volatile methyl siloxanes (cVMS) possess an unusual combination of physico-
45 chemical properties, including both hydrophobicity and volatility. Recently, concerns
46 have been raised about their environmental profile (Brooke et al., 2008) because they
47 have relatively high bioconcentration factors, implying some potential for
48 bioaccumulation and because they partition to the atmosphere where they can
49 potentially be transported over long distances (e.g. Whelan et al., 2004; Wania, 2006).
50 One of the most widely used cVMS materials is decamethylcyclopentasiloxane (D5)
51 which has a range of commercial applications including acting as a carrier ingredient
52 in some personal care products (e.g. Horii and Kannan, 2008). Key properties for D5
53 are summarised in Table 1. Most D5 which is used in cosmetic products is likely to
54 be volatilised (Brooke et al., 2008), although some will be sorbed to sewage sludge
55 during waste water treatment, and subsequently applied to agricultural land. There
56 will also be an emission to surface waters in treated effluent. In the atmosphere, D5 is
57 expected to break down to silanols by reacting with hydroxyl radicals and is not
58 expected to partition significantly from the atmosphere to surface media (Wania,
59 2006), although silanols may be removed from the atmosphere by wet deposition (e.g.
60 Whelan et al., 2004). In water, D5 is not biodegradable but does undergo acid- and
61 base-catalysed hydrolysis. Estimated hydrolysis half lives derived from experiments
62 conducted by Dow Corning (cited by Brooke et al., 2008) range from 9 days at pH 8
63 and 25 °C to 449 days at pH 7 and 9 °C. D5 does not appear to be toxic to pelagic
64 organisms at the limit of aqueous solubility (e.g. Hobson et al., 1997).

65

Although D5 has a very high air : water partition coefficient (K_{AW}), the potential for volatile losses from rivers may be tempered by interactions with dissolved, colloidal and suspended material. Estimating the partition coefficient for D5 between organic carbon and water (K_{OC}) is, therefore, very important for understanding its environmental fate. David *et al.* (2000) observed significant reductions in the apparent K_{AW} of D5 measured in simulated waste water using equilibrium partitioning in closed headspace vials. They estimated an effective value of $\log(K_{OC})$ of 4.38. More recently, Whelan *et al.* (2009) showed a clear inverse relationship between the rate of volatile loss of D5 and dissolved organic carbon concentration in open beakers containing mineral medium spiked with Aldrich humic acid (AHA). By fitting a simple dynamic partitioning model to the data, Whelan *et al.* (2009) estimated a mean effective $\log(K_{OC})$ of 5.28 [$\log(L\ kg^{-1})$]. This is very similar to a mean value of $\log(K_{OC})$ of 5.17 [$\log(L\ kg^{-1})$] reported by Durham (2007), obtained from OECD 106 batch equilibrium studies on three different soils. It is also similar to the molecular connectivity index estimate of 5.05 implemented in the KOCWIN software (Sabljic, 1987; Meylan *et al.*, 1992). However, it is much lower than the value of K_{OC} which might be expected from single parameter linear free energy relationships (LFERs) between K_{OC} and K_{OW} (e.g. Karickhoff, 1981). Applying Karickhoff's relationship ($K_{OC} = 0.41 \cdot K_{OW}$) yields a $\log(K_{OC})$ value of 7.66, based on a $\log(K_{OW})$ of 8.05, (i.e. the most recent industry-derived measured value: Xu and Kozerski, 2007) although the LFER recommended in EU Technical Guidance (Sabljic *et al.*, 1995; TGD, 2003) for "predominantly hydrophobic" substances yields a $\log(K_{OC})$ value of 6.6 (Brooke *et al.*, 2008).

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One potential problem with extrapolating the observed behaviour and derived K_{OC} value reported by Whelan et al. (2009) to the natural environment is that this experiment was performed using a synthetic medium with AHA. AHA is a natural humic acid probably derived from coal (Latch and McNeil, 2006; Malcolm and MacCarthy, 1986) and differs in quality (and hence sorptive behaviour) from DOC derived from soils, from aqueous environments and from that found in domestic waste water (Malcolm and MacCarthy, 1986). In this paper, we examine the relative importance of phase partitioning in natural river water using a combination of laboratory experiment and mathematical modelling.

Materials and Methods

Experimental

The experimental system was similar to that described by Whelan et al. (2009). Briefly, the concentration of ^{14}C -labelled D5 was measured at different time intervals in open beakers (volume 0.4 L). Each beaker initially contained 300 mL of liquid. Six treatments were established, each with three replicates: (1) Millipore water, stirred; (2) Millipore water, static (unstirred). (3) River water filtered through a 0.45 μm filter, stirred; (4) River water filtered through a 0.45 μm filter, static; (5) River water filtered through a 125 μm filter, stirred and (6) River water filtered through a 125 μm filter, static. In those treatments which were stirred, identical glass-coated magnetic stirrer bars were used with a multiplace magnetic stirrer in a fume cupboard. The stirring rate was set at 150 rpm. River water was collected from the River Nene (Ditchford, Northamptonshire, UK) approximately 100 meters downstream of the Broadholme WWTP (which serves approximately 188,000 population equivalents).

At this point, the Nene has a mean annual discharge of approximately $4 \text{ m}^3 \text{ s}^{-1}$ (more than a third of which is derived from treated waste water) and is considered to be eutrophic (e.g. Balbi, 2000). It has also been significantly modified for navigation, principally via the construction of a series of locks. Further details are described in Balbi (2000), Williams *et al.* (2003), Jobling *et al.* (2006) and Sparham *et al.* (2008).

Radiolabelled D5 used in the experiment was kindly donated by Dow Corning. The material had a specific activity of $120.5 \text{ } \mu\text{Ci mg}^{-1}$. This was used to prepare a dosing solution by dissolving $10 \mu\text{L}$ in 1 mL of acetonitrile. The concentration of the dosing solution was $1.584 \text{ mCi mL}^{-1}$ ($13.145 \text{ mg mL}^{-1}$). Radiochemical purity was estimated to be $\sim 97\%$. As a suitable method for purification was not available at the time the experiments were conducted, and because of the volatile nature of the test substance, no purification was attempted. The impurities were accounted for in the model and are not believed to affect the interpretation of the data.

The dosing solution ($7 \mu\text{L}$) was added to the liquid in each beaker using a positive displacement pipette just under the surface. All treatments were at room temperature prior to test item addition. The experiment was conducted in the artificial light of the laboratory. Although this may have resulted in some algal growth, with associated addition of photosynthetic organic carbon to the system, no such growth was visible and it is assumed here that photosynthesis was negligible. Samples were collected from each beaker at 0, 2, 4, 6, 24, 48 and 72 h after dosing (t_0). At each sampling event, triplicate 5 mL aliquots were withdrawn (mid vessel) and were counted with 10 mL of Starscint (Perkin Elmer Life Sciences) in a Beckman-Coulter LS6000TA scintillation counter. Temperature was observed to be constant throughout the

experiment at 25 °C. The average pH at t_0 was 8.01 ± 0.01 and did not change significantly over the course of the experiment. At the conclusion of the study, the contents of each beaker were discarded and the beakers were rinsed with 10 mL of THF followed by 10 mL of acetonitrile. Residual radioactivity in rinse solvents was determined for 5 mL of solvent in 10 mL Starscint. Residual radioactivity associated with the glass beaker and stirrer bar at the end of the experiment was always $< 1\%$ of the ^{14}C present at t_0 and there was no evidence of any settling out of solid residues during the experiment. It was not possible to determine the extent of any association of ^{14}C with the beaker walls or stirrer bar during the course of the experiment because no provision was made for sacrificial analysis. However, this association is assumed to be minimal. Organic carbon concentration was measured using a Shimadzu TOC-V total organic carbon (TOC) analyzer. No characterisation of the organic matter was attempted. The nature of the organic matter present will reflect its multiple sources which include dissolved and particulate losses from soils in the catchment, autochthonous carbon from in-channel photosynthesis and sewage effluent. Treated effluent accounts for approximately 30% of mean river discharge at the sampling station.

Model

The behaviour of D5 in the experimental system was described using a dynamic mathematical model of partitioning and degradation. The model is based on that described in detail by Whelan et al. (2009) and was solved numerically. Only a brief description is included here. The total mass of radiolabel in the system (M_T) at any point in time is

$$M_T = M_S + M_L + M_H + M_N \quad (1)$$

166

167 where M_S is the mass of radiolabelled D5 in the sorbed phase, M_L is the mass of
 168 radiolabelled D5 in the dissolved phase, M_H is the mass of any hydrolysis products
 169 generated and M_N is the mass of radiolabelled contaminant (initially 3%). The
 170 radiolabelled contaminant was assumed to be non-volatile based on observations of
 171 residual radioactivity in a number of pilot trials which was approximately consistent
 172 with the level of radiochemical impurity.

173

174 Hydrolysis was described using

175

$$\frac{dC_H}{dt} = k_{hyd} \cdot C_L \quad (2)$$

177

178 where k_{hyd} is a first order kinetic rate constant (h^{-1}), t is time (h), C_L is the
 179 concentration of radiolabelled D5 in the dissolved phase and C_H is the concentration
 180 of radiolabelled non-volatile hydrolysis products (e.g. dimethylsiloxane- α,ω -diols i.e.
 181 $\text{HO}(\text{Me}_2\text{SiO})_n\text{H}$ [$n = 1 - 5$]). A value for k_{hyd} was assumed *a priori* based on a half
 182 life of 9 d (valid for pH 8 and 25 °C - derived from unpublished experimental data
 183 generated by Dow Corning and cited by Brooke *et al.*, 2008).

184

185 The only loss of radioactivity from the system was assumed to be via volatilisation
 186 which was described using:

187

$$\frac{dC_T}{dt} = -k_{vol} \cdot C_L \quad (3)$$

189

190 where C_T is the overall concentration of radiolabelled material and k_{vol} (h^{-1}) is the rate
191 constant for volatilisation i.e.

192

$$193 \quad k_{vol} = \frac{k_T}{z} \quad (4)$$

194

195 where z is the water depth (m) and k_T (m h^{-1}) is the overall water-air mass transfer
196 coefficient which was estimated by least-squares optimisation of the model on
197 measured concentration data from the controls (deionised water). Note that because
198 the K_{AW} for D5 is so high, k_T will be approximately equal to the water-side partial
199 mass transfer coefficient in the two-film resistance model of Evaporation (Liss and
200 Slater, 1974). The relative magnitude of diffusive resistance on the air side of the film
201 will be negligible. Depth changes over the course of the experiment due to
202 evaporation of water (rate $\sim 0.2 \text{ mm h}^{-1}$) and sample collection were accounted for in
203 the model via temporal adjustment of k_{vol} and the concentration of organic carbon
204 (C_{OC}) in each beaker. Equilibrium partitioning of D5 between organic carbon and
205 dissolved phases was assumed, i.e.

206

$$207 \quad C_L = \left(\frac{M_T - M_N - M_H}{V_L \cdot (1 + C_{OC} \cdot K_{OC})} \right) \quad (5)$$

208

209 where V_L is the volume of the liquid phase (which changes over the course of the
210 experiment). After derivation of k_{vol} (via optimisation on the control data), the only
211 unknown is K_{OC} , which can be derived by least-squares optimisation of the model on
212 the treatment data, given a measured value of C_{OC} . Note that, strictly speaking, the

K_{OC} values derived from the 0.45 μm -filtered treatments refer, operationally, to dissolved organic carbon (DOC) : water partitioning (i.e. they are effectively values of K_{DOC}). Whilst we recognise that there may be important systematic differences between K_{OC} and K_{DOC} for many chemicals (e.g. Burkhard, 2000), the limited scope of our experimental design does not allow these differences to be distinguished for D5.

Results and Discussion

The mean measured concentrations of total organic carbon in the 0.45 μm - and 125 μm - filtered river water were 1.3 and 5.1 mg C L^{-1} , respectively. Mean measured and best-fit estimates of the ^{14}C remaining in beakers over time are shown in Figure 1 for stirred treatments and in Figure 2 for static treatments. In each case (stirred or static), there is a clear difference between treatments, with significant reductions in the apparent loss rate in both river water treatments compared with the respective controls (deionised water). In all cases, within-treatment variability was generally low. The mean coefficient of variability (ratio of measured standard deviation to measured mean ^{14}C concentration for triplicate samples at each sampling point in each treatment, averaged by treatment) ranged between 6.1 and 13.5 % in the stirred treatments and between 2.1 and 6.7 % in the static treatments. As expected, loss rates were slower in the static treatments, confirming that volatilisation was the predominant loss mechanism. The lowest rate for both the stirred and non stirred treatments was observed for the 125 μm -filtered river water, which had the highest organic carbon concentration (5.1 mg C L^{-1} i.e. almost four times higher than in the 0.45 μm filtered water). For the 0.45 μm filtered treatments, the increase in apparent half life compared with the respective control was similar in both the stirred and

238 unstirred systems (at about 2.6 times). However, there was a much greater difference
239 in the behaviour of the two river water treatments in the stirred system than in the
240 static system. For the 125 μm filtered river water, the apparent half life in the stirred
241 system was about 8.3 times that in the control, whereas in the unstirred system the
242 apparent half life was only about 3.3 times greater than in the control.

243

244 The model was able to describe changes in radioactivity in the experimental system
245 well, particularly in the case of the stirred treatments (Figure 1). Deviation of model
246 fit from the experimental data is expressed as the Root Mean Square Error (RMSE).
247 For the control, the RMSE of the fits was 1.30 for the stirred system and 5.95 % for
248 the static system. The RMSE values obtained for the river water treatments are shown
249 in Table 1. In the static treatments (Figure 2) the predicted temporal pattern did not
250 match the observed data for some points (e.g. at 24 hours in the case of the control
251 and, in the case of the 0.45 μm filtered treatment, in the initial stages of the
252 experiment and at 72 hours) but overall the match was still reasonable.

253 Derived values for $\log(K_{OC})$, shown in Table 2, were between 5.8 and 6.33 and were
254 relatively consistent (mean 6.16; standard deviation 0.25). There was no apparent
255 relationship between the value of K_{OC} obtained and the treatment. The lowest value
256 was derived for the 125 μm filtered static treatment and the highest for the 0.45 μm
257 filtered stirred case.

258

259 Two of the main sources of uncertainty in the derived values of K_{OC} are uncertainty in
260 the measured concentration of TOC and uncertainty in the concentration of ^{14}C
261 remaining (characterised by the variability in the replicate measurements made in
262 each treatment). Since the model is implemented as a numerical solution to series of

ordinary differential equations, it is difficult to obtain confidence intervals using standard statistics without linearization. Instead, the sensitivity of K_{OC} to the measured TOC concentration was evaluated by re-optimising the model fits to the observed radioactivity data (Figures 1 and 2) using 95% confidence limits for the TOC concentration during fitting (rather than the mean TOC). The coefficient of variation for repeat TOC measurements on the same river water was typically in the range 3 - 6.5%. A conservative value of 6.5% was assumed here. The ranges in resulting values for fitted log (K_{OC}) are shown in Table 2. Note that using the upper and lower 95% confidence limits for TOC results in a reduction and increase, respectively, in the derived K_{OC} relative to using the mean. However, the results suggest that the derived value of K_{OC} is relatively insensitive to minor measurement errors in TOC concentration, typically changing by only about 0.03 log units. Uncertainty arising from inter-replicate variability in measured ^{14}C concentration was expressed as 95% confidence intervals for the derived K_{OC} value in each treatment (Table 2). These were calculated (using the t-distribution) from standard error estimates of K_{OC} , obtained from three different model fits on the data from individual replicates (rather than fitting on the mean values) in each treatment (Whelan *et al.*, 2009).

In analogous experiments in which changes in radiolabelled D5 concentrations were measured in an AHA-amended mineral medium (Whelan *et al.*, 2009) the model was also able to describe concentration changes very well in the initial period of the experiment. However, the rate of volatile loss appeared to decrease asymptotically in all treatments, with an apparent relationship between the asymptote and the organic carbon concentration in the treatment. Whelan *et al.* (2009) invoked a bound-residue

hypothesis to explain this phenomenon, based on a hypothetical slowly reversible absorption of D5 to internal sites within colloids consisting of complex AHA macromolecules. In the data described here, such a consistent asymptotic deviation in loss rate from first order kinetics was not apparent. This could be due to the shorter time over which this experiment was conducted (72 hours compared with 120 hours in the case of the AHA experiment). However, it could also be due to the nature of the organic matter present in the respective systems. This would also provide a reasonable explanation for differences in the apparent K_{OC} values observed in the two experiments. Different types of organic matter are known to exhibit different sorptive properties and to give different effective values for relevant partition coefficients (e.g. Gauthier et al., 1987; Raber et al., 1998; Tanaka et al., 2005; Niederer et al., 2007). For example, significant correlations have been established between increasing K_{OC} and decreasing polarity index and a reduced number of acidic functional groups (Tanaka et al., 2005). Partition coefficients can range over more than one order of magnitude using organic matter of different origins (Gauthier et al., 1987; Tanaka et al., 2005). Terrestrial humic materials often have higher sorption coefficients compared to organic acids taken from aquatic systems. Similarly, values of K_{OC} derived for AHA are often, although not always, reported to be higher than those for natural dissolved organic matter (e.g. Raber et al., 1998). However, in the case of cVMS materials, the type of molecular interactions which take place are known to differ from many organic chemicals, which is why they possess such unusual combinations of partitioning properties. The molecular interactions involved in D5 sorption to organic matter were explored using an Abraham-type poly parameter LFER. Such relationships account separately for the contribution of different

molecular interactions to the free energy of molecular transfer between two phases
(Abraham, 1993). They often take the general form for K_{OC} :

$$\log K_{OC} = e.E + s.S + a.A + b.B + v.V + c \quad (6)$$

where c is a constant, e , s , a , b and v are matrix-specific parameters, which depend on the difference in chemical properties between organic carbon and water (Nguyen et al., 2005) and where E , S , A , B and V are so-called solute descriptors, which quantify the capacity for specific intermolecular interactions. Specifically, they refer to excess molar refraction (E), dipole-dipole interaction (S), hydrogen-bond acidity (A), hydrogen-bond basicity (B) and characteristic volume (V). Matrix descriptors for K_{OC} have been derived empirically by Nguyen et al. (2005) using 356 measured K_{OC} values for 75 chemicals in a range of soils and sediments. Nguyen et al. (2005) also report regression parameters for K_{OW} . Solute descriptors have been determined independently for siloxanes, including D5, by Ahmed et al. (2007) using a range of techniques, including gas chromatography and liquid-liquid partitioning. The above parameters, together with derived values of $\log(K_{OC})$ and $\log(K_{OW})$ for D5 are shown in Table 3. The derived values for $\log(K_{OC})$ and $\log(K_{OW})$ were 5.5 and 7.75, respectively. They suggest that the ppLFER is a reasonable predictor of $\log(K_{OC})$ compared with the measured values reported by Durham (2007) and Whelan et al. (2009). However, this value is somewhat lower than the values of K_{OC} derived from the experiments reported in this paper. There is also a discrepancy between the ppLFER-derived value of $\log(K_{OW})$ and the observed value of 8.05 reported by Xu and Kozerski (2007). Without an independent measurement of K_{OW} it is not possible to comment further on the validity of this estimate. The solute descriptors shown in

Table 3 (Ahmed et al., 2007) suggest that D5 has negative excess molar refraction (E) and near zero polarizability (S) but relatively high characteristic volume (V) and hydrogen bond basicity (B). These features might explain the lower apparent affinity of D5 for AHA compared with the organic matter in water collected from the River Nene, which has mixed origins and which has a relatively high fraction of treated waste water effluent, if phase descriptors for AHA and river water organic matter were to be determined. In any case, additional empirical work is needed to understand differences in partitioning behaviour for D5 and other cVMS materials, with different types of organic matter in the natural environment.

Implications for Environmental Behaviour

The implications of different effective values of K_{OC} derived from different experiments for the fate of D5 in river water were explored using an extension of the model described above. The model was solved to yield changes in D5 concentration for time-of-travel (i.e. the quotient of river distance and velocity) in a 2 m deep river over 96 hours. This corresponds to a distance of 138 km, based on a mean solute velocity of 0.4 ms^{-1} , which is representative of river lengths in the UK. Three different TOC concentrations (1, 5 and 10 mg C L^{-1}) were considered with two values of $\log(K_{OC})$: 5.28 (after Whelan et al., 2009) and 6.16 (the mean value derived here). The range of TOC concentrations is typical of the range reported in British rivers (e.g. Worrall et al., 2004). Equilibrium partitioning between the freely dissolved and sorbed (suspended solid, colloidal and dissolved organic carbon fractions) phases was assumed. No D5 exchanges between the bed and banks of the river and the water

362 column were considered. This is reasonable if the system is in steady state, such that
 363 the bed material is in equilibrium with the water column (Schwarzenbach et al.,
 364 2003). Whilst rivers clearly experience transient conditions during storm events,
 365 under normal and low flows the steady state assumption is a valid one for chemicals
 366 discharged continuously via waste water (Whelan *et al.*, 1999; Facchi *et al.*, 2007).
 367 Values for the partial mass transfer coefficients in the two-film resistance model for
 368 volatilisation (e.g. Mackay, 2001) were set at 0.05 and 5 m h⁻¹, respectively, for the
 369 water (k_W) and air (k_A) sides, as recommended in EU Technical Guidance (TGD,
 370 2003). Again, it should be noted that for such a high value of K_{AW} , the value of k_A has
 371 no influence on the rate of volatilisation. A hydrolysis half life of 64 d was assumed
 372 for dissolved phase D5 (representing pH 8 and 9 °C). Over the four-day time-of-
 373 travel considered here, hydrolysis was always a relatively unimportant contributor to
 374 D5 losses (< 4%), even in the absence of organic carbon.
 375
 376 Changes in the predicted concentration of D5 in river water with time-of-travel are
 377 shown in Figure 3. With no organic carbon in the water, the loss of D5 is relatively
 378 rapid with a dissipation half life of 27.7 h. However, with increasing TOC
 379 concentrations, the rate of volatile loss decreases, particularly if a high value is
 380 assumed for K_{OC} . The effective half lives for the high K_{OC} scenario were factors of
 381 2.07, 4.38 and 5.79 higher than for the low K_{OC} scenario for 1, 5 and 10 mg C L⁻¹,
 382 respectively, given an equivalent TOC concentration. Volatilisation was predicted to
 383 reduce D5 concentrations by 63, 25 and 13%, respectively for TOC concentrations of
 384 1, 5 and 10 mg C L⁻¹, in the high K_{OC} scenario over a four day time-of-travel.
 385 However, it should be noted that in real rivers concentration changes are likely to be
 386 influenced by river discharge and depth variations (spatial and temporal) and by

changes in turbulence (which will affect gas exchange), as well as by various emissions from waste water treatment plants along the length of the river. It should also be noted that K_{OC} is likely to be temperature dependent. Unpublished data from Dow Corning suggest that there is a positive relationship between K_{OW} and temperature (positive enthalpy of phase change). It is expected, therefore, that the effective environmental K_{OC} value will, in fact, be lower than that implied by the experimental data reported here since, except for the tropics, river water temperatures are likely to be lower than 25 °C. Additional empirical work is needed to verify the river predictions reported here, which should include a study to measure changes in concentration in the same mass of water with time of travel (e.g. employing dye tracing) similar to that described by Whelan *et al.* (2007) for Linear Alkylbenzene Sulphonate.

Conclusions

- A simple model was used to describe observed changes in the concentration of radiolabelled decamethylcyclopentasiloxane (D5) in open beakers containing deionised and river water.
- Values for the effective log partition coefficient between organic carbon and water [$\log(K_{OC})$] were estimated, via model optimisation, to range between 5.8 and 6.33, with an average value of 6.12 $\log(\text{L kg}^{-1})$.
- The model was extrapolated to predict D5 behaviour in an idealised river reach under steady state conditions with different concentrations of TOC and assuming different values of K_{OC} . The results suggest that although the rate of

volatilisation is retarded by higher values of K_{OG} , water-air transfer is still likely to make a significant (>50%) contribution to concentration changes of D5 over typical solute travel times in relatively shallow river reaches with low, but realistic, TOC concentrations.

- Additional work is required to quantify the affinity of D5 for natural organic matter of different origins and to develop a mechanistic understanding of any differences observed.

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427

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- 538

1

2 **Table 1.** Key properties for D5. Partition coefficients refer to ¹octanol : water;3 ²octanol : air; ³air : water. ⁴Cited in Brooke et al. (2008). ⁵Based on an experimentally4 derived rate constant of $1.55 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (at 24°C) and an average5 atmospheric hydroxyl radical concentration of $5 \times 10^5 \text{ molecule cm}^{-3}$.

6

Property	Value	Source
CAS Number	541-02-6	Mazzoni, 1997
Molar mass	371 g mol ⁻¹	Mazzoni, 1997
Aqueous solubility at 20 °C	0.017 g m ⁻³	Mazzoni, 1997
Vapour pressure at 20 °C	30.4 Pa	Mazzoni, 1997
log (<i>K</i> _{OW}) ¹	8.05	Xu and Kozerski (2007) ⁴
log (<i>K</i> _{OA}) ²	5.04	Xu and Kozerski (2007) ⁴
log (<i>K</i> _{AW}) ³	3.01	Xu and Kozerski (2007) ⁴
Atmospheric half life	10.4 days	Atkinson (1991) ⁵

7

Table 2 Treatment, initial organic carbon concentration, initial value of k_{vol} (i.e. k_{vol} at t_0) and estimated values of $\log(K_{OC})$ at 25 °C. Values in round parentheses show the 95% confidence limits for measured organic carbon concentration and the resulting range of $\log(K_{OC})$ estimates. Bold values in square parentheses show the 95% confidence intervals for $\log(K_{OC})$, arising from uncertainty in measured inter-replicate ^{14}C concentrations in each treatment.

Treatment	OC content (mg C L ⁻¹)	Initial k_{vol} (h ⁻¹)	Best fit log (K_{OC})	RMSE (% loss)
¹⁴ C-labelled D5 in 125 µm filtered river water. Stirred.	5.1 (4.78, 5.42)	0.188	6.22 [0.07] (6.19, 6.25)	8.41
¹⁴ C-labelled D5 in 0.45 µm filtered river water. Stirred.	1.3 (1.22, 1.38)	0.188	6.33 [0.20] (6.30, 6.36)	3.47
¹⁴ C-labelled D5 in 125 µm filtered river water. Unstirred.	5.1 (4.78, 5.42)	0.067	5.80 [0.04] (5.78, 5.84)	1.76
¹⁴ C-labelled D5 in 0.45 µm filtered river water. Unstirred.	1.3 (1.22, 1.38)	0.067	6.30 [0.15] (6.27, 6.33)	3.66

16

17 **Table 3** Matrix parameters for $\log(K_{OC})$ and $\log(K_{OW})$ [Nguyen et al., 2005], solute
 18 descriptors for D5 [Ahmed et al., 2007] and derived values of $\log(K_{OC})$ and $\log$
 19 (K_{OW}). See text for explanation of terms. *Derived using all collected data rather than
 20 using averages.

21

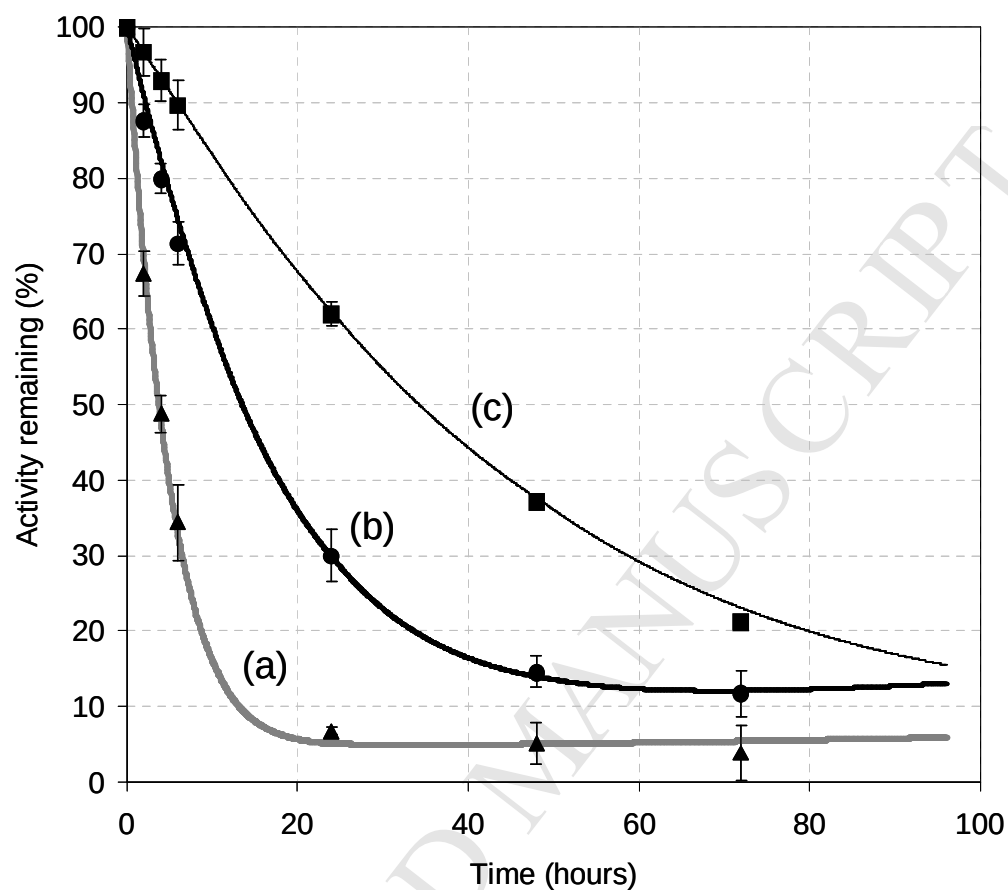
	<i>e</i> or <i>E</i>	<i>s</i> or <i>S</i>	<i>a</i> or <i>A</i>	<i>b</i> or <i>B</i>	<i>v</i> or <i>V</i>	<i>c</i>	Derived Value
Matrix descriptor [$\log(K_{OC})$]*	1.08	0.83	0.28	1.85	2.55	0.12	5.5
Matrix descriptor [$\log(K_{OW})$]	0.78	1.17	0.14	2.85	3.25	0.47	7.75
Solute descriptor	-0.698	-0.083	0	0.632	2.931	1	

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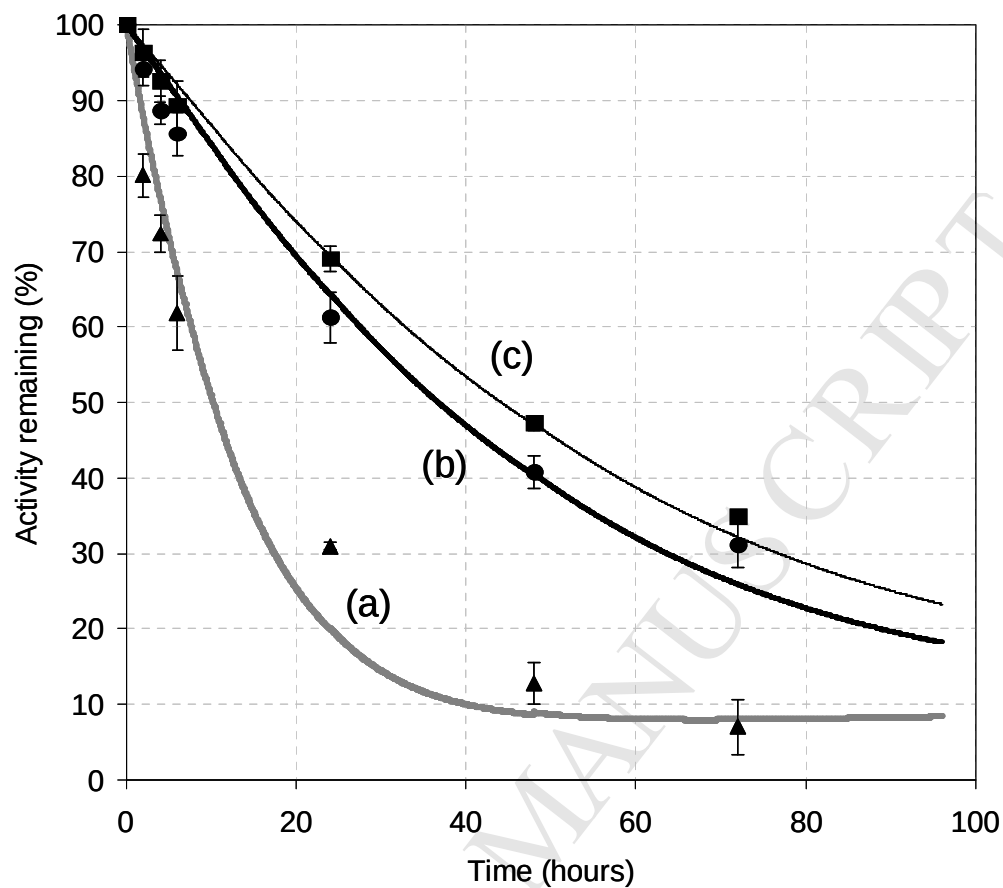


2

3 **Figure 1** Changes in the activity remaining over time in stirred beakers spiked with
 4 ^{14}C -labelled D5. Symbols: measured mean $\pm$ 1 standard deviation; Lines: Best fit
 5 model. (a) Deionised water; (b) River water filtered through 0.45 μm ; (c) River water
 6 filtered through 125 μm .

7

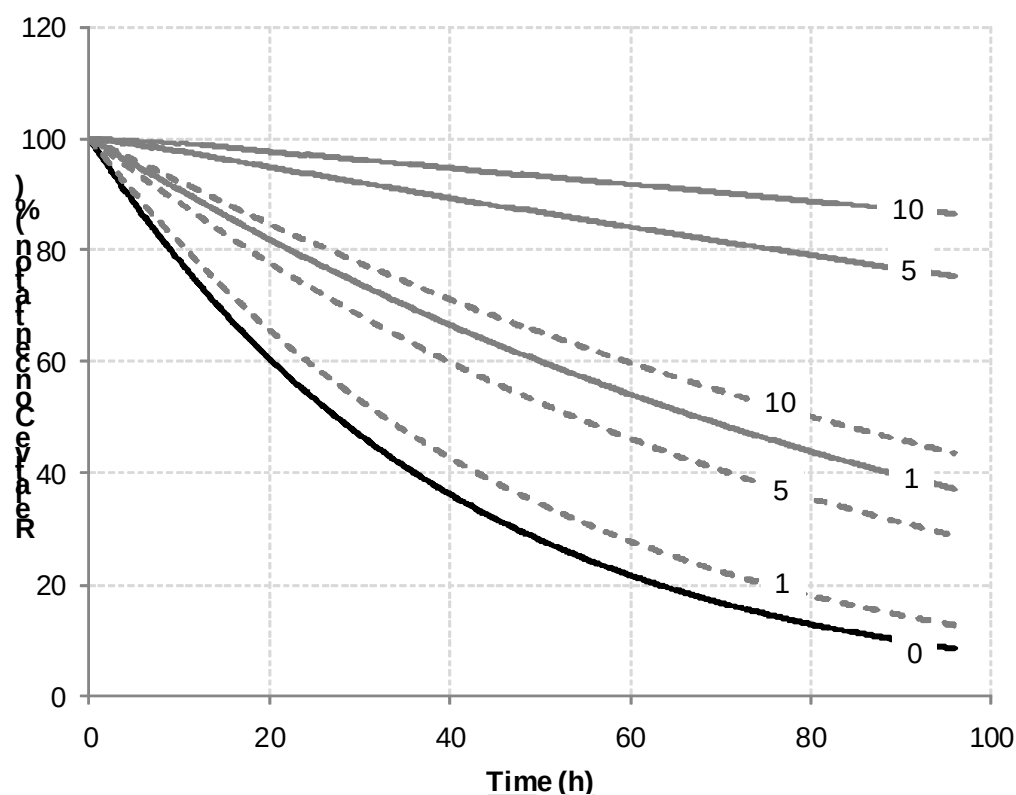
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10 **Figure 2** Changes in the activity remaining over time in static (unstirred) beakers
 11 spiked with ^{14}C -labelled D5. Symbols: measured mean $\pm$ 1 standard deviation; Lines:
 12 Best fit model. (a) Deionised water; (b) River water filtered through 0.45 μm ; (c)
 13 River water filtered through 125 μm .

14



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16

17 **Figure 3** Changes in the predicted concentration of D5 with time-of-travel in river
 18 water with different concentrations of organic carbon (0, 1, 5 and 10 mg C L⁻¹) and
 19 assuming different values for $\log(K_{OC})$. Solid Lines: $\log(K_{OC}) = 6.16$; Dashed Lines:
 20 $\log(K_{OC}) = 5.28$. Numbers show the concentration of TOC (mg C L⁻¹). In all cases
 21 the depth was 2 m.

22

23



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Dynamic multi-phase partitioning of decamethylcyclopentasiloxane (D5) in river water

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