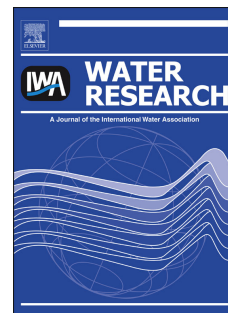


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**Dynamic multi-phase partitioning of  
decamethylcyclopentasiloxane (D5) in river water**

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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

66 Although D5 has a very high air : water partition coefficient ( $K_{AW}$ ), the potential for  
67 volatile losses from rivers may be tempered by interactions with dissolved, colloidal  
68 and suspended material. Estimating the partition coefficient for D5 between organic  
69 carbon and water ( $K_{OC}$ ) is, therefore, very important for understanding its  
70 environmental fate. David *et al.* (2000) observed significant reductions in the  
71 apparent  $K_{AW}$  of D5 measured in simulated waste water using equilibrium partitioning  
72 in closed headspace vials. They estimated an effective value of  $\log(K_{OC})$  of 4.38.  
73 More recently, Whelan *et al.* (2009) showed a clear inverse relationship between the  
74 rate of volatile loss of D5 and dissolved organic carbon concentration in open beakers  
75 containing mineral medium spiked with Aldrich humic acid (AHA). By fitting a  
76 simple dynamic partitioning model to the data, Whelan *et al.* (2009) estimated a mean  
77 effective  $\log(K_{OC})$  of 5.28 [ $\log(\text{L kg}^{-1})$ ]. This is very similar to a mean value of  $\log$   
78 ( $K_{OC}$ ) of 5.17 [ $\log(\text{L kg}^{-1})$ ] reported by Durham (2007), obtained from OECD 106  
79 batch equilibrium studies on three different soils. It is also similar to the molecular  
80 connectivity index estimate of 5.05 implemented in the KOCWIN software (Sabljic,  
81 1987; Meylan *et al.*, 1992). However, it is much lower than the value of  $K_{OC}$  which  
82 might be expected from single parameter linear free energy relationships (LFERs)  
83 between  $K_{OC}$  and  $K_{OW}$  (e.g. Karickhoff, 1981). Applying Karickhoff's relationship  
84 ( $K_{OC} = 0.41 \cdot K_{OW}$ ) yields a  $\log(K_{OC})$  value of 7.66, based on a  $\log(K_{OW})$  of 8.05, (i.e.  
85 the most recent industry-derived measured value: Xu and Kozerski, 2007) although  
86 the LFER recommended in EU Technical Guidance (Sabljic *et al.*, 1995; TGD, 2003)  
87 for "predominantly hydrophobic" substances yields a  $\log(K_{OC})$  value of 6.6 (Brooke *et*  
88 *al.*, 2008).  
89

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

99

## 100 **Materials and Methods**

101

### 102 Experimental

103 The experimental system was similar to that described by Whelan et al. (2009).  
104 Briefly, the concentration of  $^{14}\text{C}$ -labelled D5 was measured at different time intervals  
105 in open beakers (volume 0.4 L). Each beaker initially contained 300 mL of liquid.  
106 Six treatments were established, each with three replicates: (1) Millipore water,  
107 stirred; (2) Millipore water, static (unstirred). (3) River water filtered through a 0.45  
108  $\mu\text{m}$  filter, stirred; (4) River water filtered through a 0.45  $\mu\text{m}$  filter, static; (5) River  
109 water filtered through a 125  $\mu\text{m}$  filter, stirred and (6) River water filtered through a  
110 125  $\mu\text{m}$  filter, static. In those treatments which were stirred, identical glass-coated  
111 magnetic stirrer bars were used with a multiplace magnetic stirrer in a fume cupboard.  
112 The stirring rate was set at 150 rpm. River water was collected from the River Nene  
113 (Ditchford, Northamptonshire, UK) approximately 100 meters downstream of the  
114 Broadholme WWTP (which serves approximately 188,000 population equivalents).

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

120

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

129

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

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

157

### 158 Model

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

164



$$165 \quad M_T = M_S + M_L + M_H + M_N \quad (1)$$

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

$$176 \quad \frac{dC_H}{dt} = k_{hyd} \cdot C_L \quad (2)$$

177

178 where  $k_{hyd}$  is a first order kinetic rate constant ( $\text{h}^{-1}$ ),  $t$  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- $\alpha,\omega$ -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

$$188 \quad \frac{dC_T}{dt} = -k_{vol} \cdot C_L \quad (3)$$

189

190 where  $C_T$  is the overall concentration of radiolabelled material and  $k_{vol}$  ( $\text{h}^{-1}$ ) 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  $k_T$  ( $\text{m h}^{-1}$ ) 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

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

218

## 219 **Results and Discussion**

220

221 The mean measured concentrations of total organic carbon in the 0.45  $\mu\text{m}$ - and 125  
222  $\mu\text{m}$ - filtered river water were 1.3 and 5.1  $\text{mg C L}^{-1}$ , respectively. Mean measured and  
223 best-fit estimates of the  $^{14}\text{C}$  remaining in beakers over time are shown in Figure 1 for  
224 stirred treatments and in Figure 2 for static treatments. In each case (stirred or static),  
225 there is a clear difference between treatments, with significant reductions in the  
226 apparent loss rate in both river water treatments compared with the respective controls  
227 (deionised water). In all cases, within-treatment variability was generally low. The  
228 mean coefficient of variability (ratio of measured standard deviation to measured  
229 mean  $^{14}\text{C}$  concentration for triplicate samples at each sampling point in each  
230 treatment, averaged by treatment) ranged between 6.1 and 13.5 % in the stirred  
231 treatments and between 2.1 and 6.7 % in the static treatments. As expected, loss rates  
232 were slower in the static treatments, confirming that volatilisation was the  
233 predominant loss mechanism. The lowest rate for both the stirred and non stirred  
234 treatments was observed for the 125  $\mu\text{m}$ -filtered river water, which had the highest  
235 organic carbon concentration (5.1  $\text{mg C L}^{-1}$  i.e. almost four times higher than in the  
236 0.45  $\mu\text{m}$  filtered water). For the 0.45  $\mu\text{m}$  filtered treatments, the increase in apparent  
237 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  $\mu\text{m}$  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  $\mu\text{m}$  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  $\mu\text{m}$  filtered static treatment and the highest for the 0.45  $\mu\text{m}$   
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  $^{14}\text{C}$   
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

263 ordinary differential equations, it is difficult to obtain confidence intervals using  
264 standard statistics without linearization. Instead, the sensitivity of  $K_{OC}$  to the  
265 measured TOC concentration was evaluated by re-optimising the model fits to the  
266 observed radioactivity data (Figures 1 and 2) using 95% confidence limits for the  
267 TOC concentration during fitting (rather than the mean TOC). The coefficient of  
268 variation for repeat TOC measurements on the same river water was typically in the  
269 range 3 - 6.5%. A conservative value of 6.5% was assumed here. The ranges in  
270 resulting values for fitted log ( $K_{OC}$ ) are shown in Table 2. Note that using the upper  
271 and lower 95% confidence limits for TOC results in a reduction and increase,  
272 respectively, in the derived  $K_{OC}$  relative to using the mean. However, the results  
273 suggest that the derived value of  $K_{OC}$  is relatively insensitive to minor measurement  
274 errors in TOC concentration, typically changing by only about 0.03 log units.  
275 Uncertainty arising from inter-replicate variability in measured  $^{14}\text{C}$  concentration was  
276 expressed as 95% confidence intervals for the derived  $K_{OC}$  value in each treatment  
277 (Table 2). These were calculated (using the t-distribution) from standard error  
278 estimates of  $K_{OC}$ , obtained from three different model fits on the data from individual  
279 replicates (rather than fitting on the mean values) in each treatment (Whelan *et al.*,  
280 2009).

281

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

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

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

314

$$315 \quad \log K_{OC} = e.E + s.S + a.A + b.B + v.V + c \quad (6)$$

316

317 where  $c$  is a constant,  $e$ ,  $s$ ,  $a$ ,  $b$  and  $v$  are matrix-specific parameters, which depend on  
318 the difference in chemical properties between organic carbon and water (Nguyen et  
319 al., 2005) and where  $E$ ,  $S$ ,  $A$ ,  $B$  and  $V$  are so-called solute descriptors, which quantify  
320 the capacity for specific intermolecular interactions. Specifically, they refer to excess  
321 molar refraction ( $E$ ), dipole-dipole interaction ( $S$ ), hydrogen-bond acidity ( $A$ ),  
322 hydrogen-bond basicity ( $B$ ) and characteristic volume ( $V$ ). Matrix descriptors for  $K_{OC}$   
323 have been derived empirically by Nguyen et al. (2005) using 356 measured  $K_{OC}$   
324 values for 75 chemicals in a range of soils and sediments. Nguyen et al. (2005) also  
325 report regression parameters for  $K_{OW}$ . Solute descriptors have been determined  
326 independently for siloxanes, including D5, by Ahmed et al. (2007) using a range of  
327 techniques, including gas chromatography and liquid-liquid partitioning. The above  
328 parameters, together with derived values of  $\log(K_{OC})$  and  $\log(K_{OW})$  for D5 are shown  
329 in Table 3. The derived values for  $\log(K_{OC})$  and  $\log(K_{OW})$  were 5.5 and 7.75,  
330 respectively. They suggest that the ppLFER is a reasonable predictor of  $\log(K_{OC})$   
331 compared with the measured values reported by Durham (2007) and Whelan et al.  
332 (2009). However, this value is somewhat lower than the values of  $K_{OC}$  derived from  
333 the experiments reported in this paper. There is also a discrepancy between the  
334 ppLFER-derived value of  $\log(K_{OW})$  and the observed value of 8.05 reported by Xu  
335 and Kozerski (2007). Without an independent measurement of  $K_{OW}$  it is not possible  
336 to comment further on the validity of this estimate. The solute descriptors shown in

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

346

347

#### 348 **Implications for Environmental Behaviour**

349

350 The implications of different effective values of  $K_{OC}$  derived from different  
351 experiments for the fate of D5 in river water were explored using an extension of the  
352 model described above. The model was solved to yield changes in D5 concentration  
353 for time-of-travel (i.e. the quotient of river distance and velocity) in a 2 m deep river  
354 over 96 hours. This corresponds to a distance of 138 km, based on a mean solute  
355 velocity of  $0.4 \text{ ms}^{-1}$ , which is representative of river lengths in the UK. Three  
356 different TOC concentrations (1, 5 and  $10 \text{ mg C L}^{-1}$ ) were considered with two values  
357 of  $\log(K_{OC})$ : 5.28 (after Whelan et al., 2009) and 6.16 (the mean value derived here).  
358 The range of TOC concentrations is typical of the range reported in British rivers (e.g.  
359 Worrall et al., 2004). Equilibrium partitioning between the freely dissolved and  
360 sorbed (suspended solid, colloidal and dissolved organic carbon fractions) phases was  
361 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<sup>-1</sup>, 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<sup>-1</sup>,  
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<sup>-1</sup>, 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

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

399  
400

## 401 **Conclusions**

402

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

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

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

419

420

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422

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427

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- 537
- 538



1

2 **Table 1.** Key properties for D5. Partition coefficients refer to <sup>1</sup>octanol : water;  
 3 <sup>2</sup>octanol : air; <sup>3</sup>air : water. <sup>4</sup>Cited in Brooke et al. (2008). <sup>5</sup>Based on an experimentally  
 4 derived rate constant of  $1.55 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (at 24°C) and an average  
 5 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 <sup>-1</sup>	Mazzoni, 1997
Aqueous solubility at 20 °C	0.017 g m <sup>-3</sup>	Mazzoni, 1997
Vapour pressure at 20 °C	30.4 Pa	Mazzoni, 1997
log ( $K_{OW}$ ) <sup>1</sup>	8.05	Xu and Kozerski (2007) <sup>4</sup>
log ( $K_{OA}$ ) <sup>2</sup>	5.04	Xu and Kozerski (2007) <sup>4</sup>
log ( $K_{AW}$ ) <sup>3</sup>	3.01	Xu and Kozerski (2007) <sup>4</sup>
Atmospheric half life	10.4 days	Atkinson (1991) <sup>5</sup>

7

8 **Table 2** Treatment, initial organic carbon concentration, initial value of  $k_{vol}$  (i.e.  $k_{vol}$  at  
 9  $t_0$ ) and estimated values of  $\log(K_{OC})$  at 25 °C. Values in round parentheses show the  
 10 95% confidence limits for measured organic carbon concentration and the resulting  
 11 range of  $\log(K_{OC})$  estimates. Bold values in square parentheses show the 95%  
 12 confidence intervals for  $\log(K_{OC})$ , arising from uncertainty in measured inter-replicate  
 13  $^{14}\text{C}$  concentrations in each treatment.  
 14

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

15

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

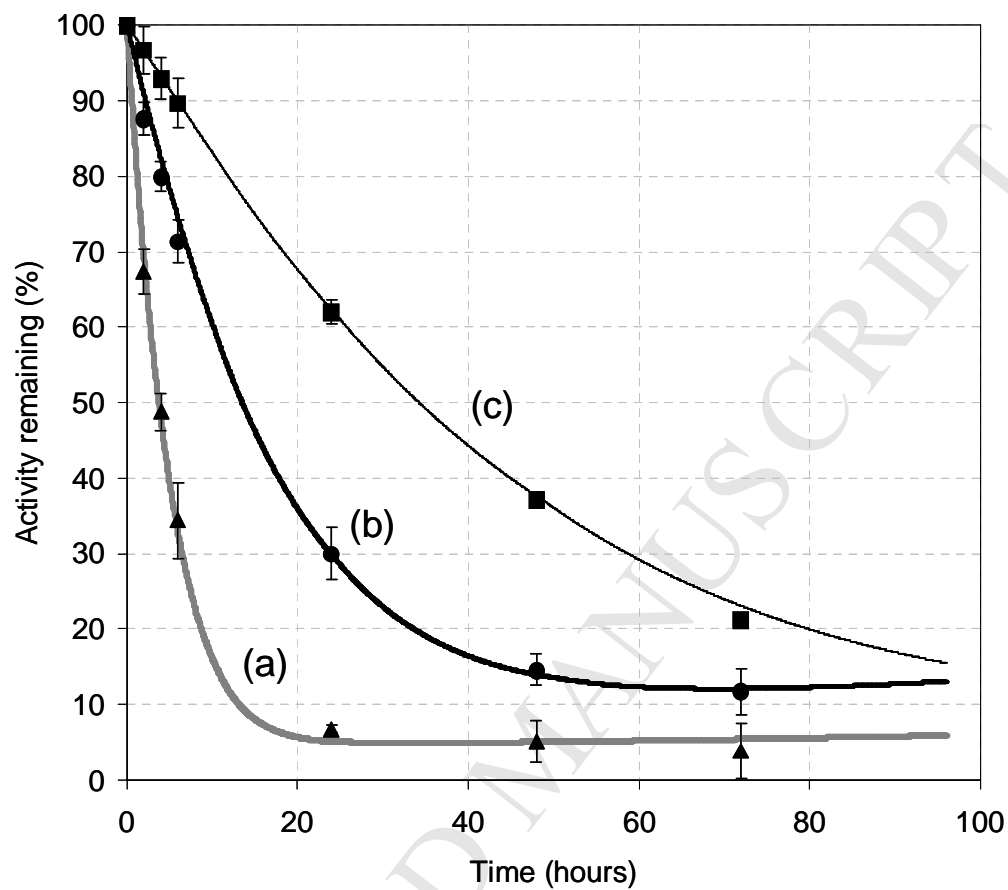
	<i>e</i> or <i>E</i>	<i>s</i> or <i>S</i>	<i>a</i> or <i>A</i>	<i>b</i> or <i>B</i>	<i>v</i> or <i>V</i>	<i>c</i>	Derived Value
Matrix descriptor [ $\log(K_{OC})$ ]*	1.08	0.83	0.28	1.85	2.55	0.12	5.5
Matrix descriptor [ $\log(K_{OW})$ ]	0.78	1.17	0.14	2.85	3.25	0.47	7.75
Solute descriptor	-0.698	-0.083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

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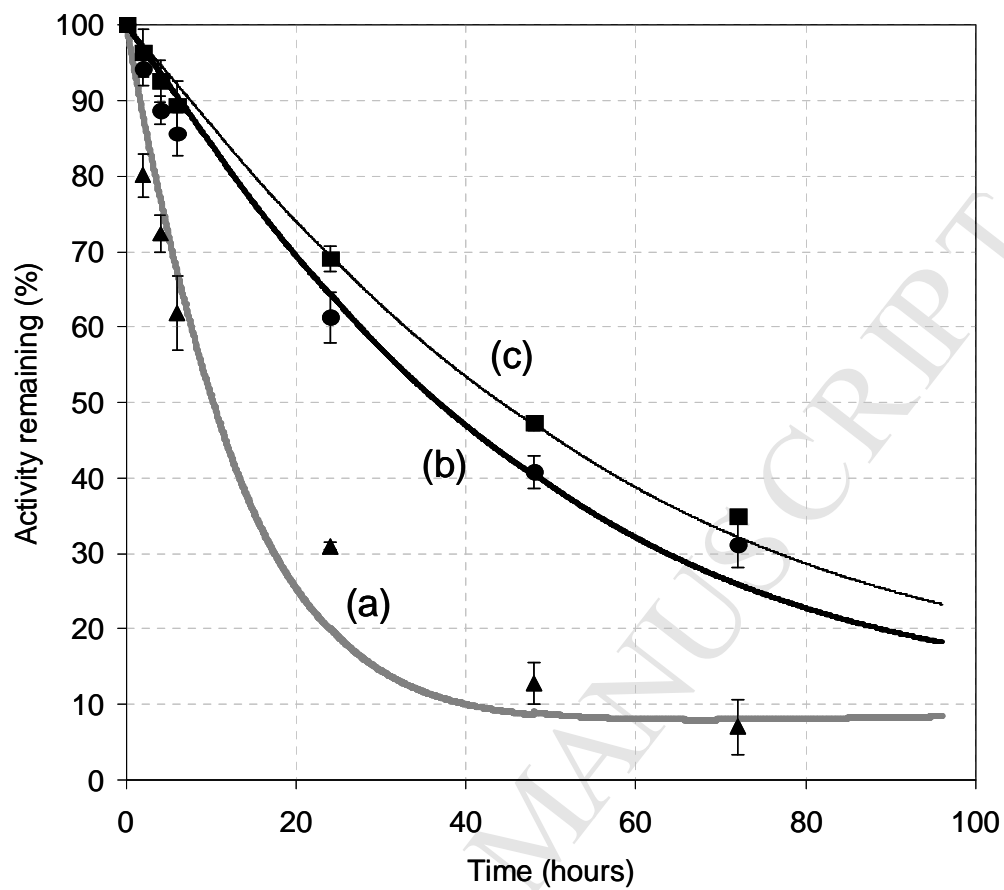


2

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

7

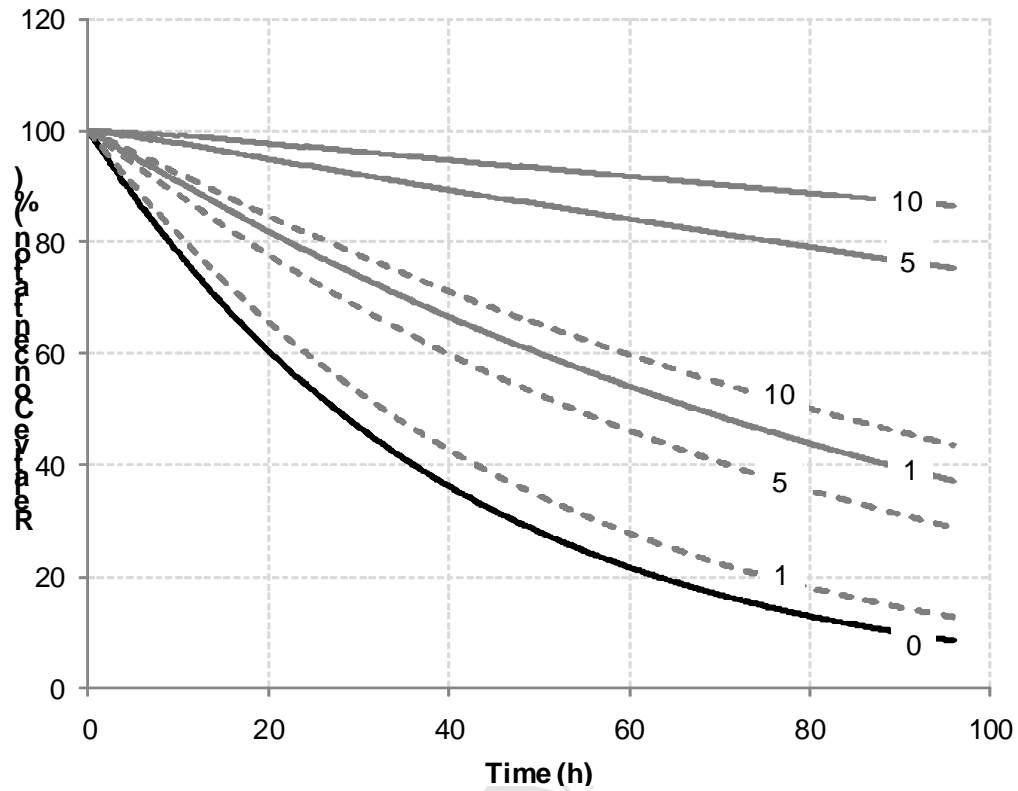
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10 **Figure 2** Changes in the activity remaining over time in static (unstirred) beakers  
11 spiked with  $^{14}\text{C}$ -labelled D5. Symbols: measured mean  $\pm$  1 standard deviation; Lines:  
12 Best fit model. (a) Deionised water; (b) River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

14



15

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<sup>-1</sup>) 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<sup>-1</sup>). In all cases  
 21 the depth was 2 m.

22

23