

1 **Measurement of cyclic volatile methylsiloxanes in the aquatic environment**  
2 **using low-density polyethylene passive sampling devices using an in-field**  
3 **calibration study – challenges and guidance**

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14 **ABSTRACT**

15 Cyclic volatile methylsiloxanes (cVMS) are used in personal care products and are  
16 hydrophobic, volatile and persistent. Their environmental water concentrations are low and  
17 are difficult to detect using conventional sampling methods. This study shows the potential of  
18 passive sampling for cVMS. We used low-density polyethylene (LDPE) samplers and in-field  
19 calibration methods for octamethylcyclotetrasiloxane (D4) and  
20 decamethylcyclopentasiloxane (D5). <sup>13</sup>C-D4 and <sup>13</sup>C-D5, methyltris(trimethylsiloxy)silane  
21 (MT), tetrakis(trimethylsiloxy)silane (TK), and five deuterated polycyclic aromatic

22 hydrocarbons (PAHs) were used as performance reference compounds (PRCs). Samplers  
23 were calibrated (7-days) using effluent at a treatment plant, with uptake of cVMS and losses  
24 of the PRCs measured at 12 time-points. Concentrations of D4 (53 ng L<sup>-1</sup>) and D5 (1,838 ng  
25 L<sup>-1</sup>) were stable in the effluent. Uptake of D4 and loss of <sup>13</sup>C-D4 were isotropic and  
26 equilibrium was approached by 7-days. Two estimates of sampler uptake rate ( $R_s$ ) were 2.1 L  
27 day<sup>-1</sup> and 2.5 L day<sup>-1</sup>. The estimated log LDPE/water partition coefficient was 4.4. The  
28 uptake of D5 was slower ( $R_s = 0.32$  L day<sup>-1</sup>) and equilibrium was not reached. Offloading of  
29 <sup>13</sup>C-D5, MT and TK were slow, and isotropic behaviour was not demonstrated for D5.  
30 Offloading of PAHs followed the predicted pattern for LDPE. Uptake of cVMS appeared to  
31 be under membrane control, due to low diffusion coefficients in LDPE. Samplers can monitor  
32 time-weighted average concentrations of D4 for less than a week, and D5 for longer periods.  
33 LDPE samplers allow cVMS to be determined at lower concentrations than by spot sampling  
34 methods.

35 *Keywords:* Cyclic volatile methyl siloxanes (cVMS); Octamethylcyclotetrasiloxane (D4);  
36 Decamethylcyclopentasiloxane (D5); Low-density polyethylene passive samplers; Water;  
37 Calibration

## 38 **1. Introduction**

39 Cyclic volatile methyl siloxanes (cVMS) are used in personal care products and can  
40 persist and bioaccumulate. Two cVMS, octamethylcyclotetrasiloxane (D4) and  
41 decamethylcyclopentasiloxane (D5) (Fig. S1) are of environmental concern (Brooke et al.,  
42 2009a; 2009b). They are emerging contaminants and monitoring is needed for risk  
43 assessments and to validate fate models. D4 and D5 are both hydrophobic and volatile (Table  
44 S1) (Brooke et al., 2009a; 2009b). Reported partition coefficients vary: D4 log  $K_{ow} = 4.45$ -7.0  
45 and D5 log  $K_{ow} = 4.76$ -8.03 (Brooke et al., 2009a; Wang et al., 2013a). Recently, Xu and

46 Kropscott (2012) estimated log  $K_{ow}$  values of D4 = 6.98 and D5 = 8.07. cVMS are not stable  
47 in water and may hydrolyse to silanols by ring cleavage or demethylation (Wang et al.,  
48 2013a). Models indicate concentrations of cVMS in water will be low and challenging to  
49 analyse (Zhang et al., 2011; Sanchís et al., 2013; Xu, Shi and Cai, 2013; van Egmond et al.,  
50 2013).

51 Improvements in control of background contamination has lowered analytical  
52 detection limits for cVMS (Kierkegaard et al., 2011; Sparham et al., 2011; Companioni-  
53 Damas et al., 2012, Wang et al., 2013b). Monitoring cVMS in water by headspace-gas  
54 chromatography/mass spectrometry (HS-GC/MS) (Sparham et al., 2008) gave a limit of  
55 quantification (LoQ) of 10 ng L<sup>-1</sup> for D5. With HS-solid phase micro-extraction–GC/MS  
56 (Companioni-Damas et al., 2012) LoQs of 19, 19 and 18 ng L<sup>-1</sup> were reported for D4, D5 and  
57 dodecamethylcyclhexasiloxane (D6), respectively. Concentrations of D5 < 10-29 ng L<sup>-1</sup>  
58 (River Great Ouse, UK) and < 19-58.5 ng L<sup>-1</sup> (Rivers Lobregat and Besos, Spain) were  
59 reported. GC/MS/MS gave LoQs of 2.7-7.5 ng L<sup>-1</sup> (Sanchís et al., 2013). As the concentration  
60 of cVMS in pristine waters is close to LoQ, this is challenging when using low volume spot  
61 sampling. Passive sampling may overcome this problem.

62 Passive samplers give time-weighted average (TWA) concentrations of pollutants  
63 over the deployment time until equilibrium is reached and can also lower analytical detection  
64 limits (Huckins, Petty and Booij, 2006; Greenwood, Mills and Vrana, 2007). A range of  
65 devices is available: Chemcatcher<sup>®</sup>, POCIS and SPMD (Greenwood, Mills and Vrana, 2007;  
66 Allan et al, 2009) and single-phase systems (silicone rubber (Booij, Smedes and van Weerlee,  
67 2002; Allan et al, 2009) and low-density polyethylene (LDPE) (Booij, Smedes and van  
68 Weerlee, 2002; Allan et al, 2009)). Single-phase are attractive as these can be made in any  
69 size (Adams et al., 2007; Lohmann, 2012). Performance reference compounds (PRCs) (e.g.  
70 labelled analogues of the pollutants) can be used, to provide an *in situ* calibration if uptake

71 and offloading are isotropic (Booij, Smedes and van Weerlee, 2002; Huckins, Petty and  
72 Booij, 2006; Booij and Smedes, 2010). Before use, calibration experiments are needed to  
73 measure the sampler/water partition coefficient ( $K_{sw}$ ) and the uptake rate ( $R_s$ ), expressed as L  
74 day<sup>-1</sup>.  $R_s$  can be determined using batch or flow-through laboratory systems (Greenwood,  
75 Mills and Vrana, 2007) and more recently using in-field calibration (Harman, Reid and  
76 Thomas, 2011; Li et al., 2010). The latter is useful where it is difficult to maintain a constant  
77 concentration of an analyte over extended periods. Typically for in-field calibrations,  
78 deployments at waste water treatment plants (WWTP) are used (Mazzella et al., 2010;  
79 Harman, Reid and Thomas, 2011; Jacquet et al., 2012).

80 Passive samplers have been used to monitor siloxanes in air (Cheng et al., 2011), but  
81 to our knowledge have not been used to measure these chemicals in water. We used LDPE as  
82 a sampler as it is low-cost, easy to handle and easy to remove cVMS residues (unlike silicone  
83 rubber which may generate cVMS). We describe an in-field calibration for D4 and D5 and  
84 assessed <sup>13</sup>C-labelled analogues and methyltris(trimethylsiloxy)silane (MT),  
85 tetrakis(trimethylsiloxy)silane (TK) (Fig. S1) as PRCs. Deuterated PAHs (d-PAHs) were also  
86 used as PRCs to provide a comparison with the offloading rates of cVMS that have similar  
87 log  $K_{ow}$  values, but differ in other properties (Table S1). This method was chosen, as flow-  
88 through laboratory calibration tanks proved problematic in maintaining constant  
89 concentrations of cVMS.

## 90 **2. Methods**

91 Chemicals, glassware, analytical standards and methods used to measure the cVMS  
92 and d-PAHs are described in the supplementary material.

93

### 94 *2.1 Preparation of LDPE samplers*

95 LDPE (Fischer Scientific UK Ltd., with experimentally obtained estimates of density  
96  $0.94 \text{ g cm}^{-3}$  and thickness  $38 \text{ }\mu\text{m}$ ) was cut ( $12 \text{ cm} \times 5 \text{ cm}$ ; sampling area  $120 \text{ cm}^2$ ; volume  
97  $2.28 \times 10^{-4} \text{ L}$ ; mass  $0.21 \text{ g}$ ) and washed in *n*-hexane with gentle shaking (24 h). Sheets were  
98 dried ( $60^\circ\text{C}$ , 3 h) to remove *n*-hexane, washed (2 x methanol; 24 h), dried and stored in sealed  
99 glass jars (1 L) submerged under methanol. This removed cVMS contamination and gave  
100 fabrication blanks < instrumental LoD. Sheets were spiked with three types of PRCs (i)  $^{13}\text{C}$ -  
101  $\text{D}_4/^{13}\text{C}\text{-D}_5$ , (ii) MT/TK and (iii) acenaphthene- $\text{d}_{10}$ , fluorene- $\text{d}_{10}$ , phenanthrene- $\text{d}_{10}$ , pyrene- $\text{d}_{10}$   
102 and benz(a)anthracene- $\text{d}_{12}$ . Three solutions (methanol/water, 50/50 v/v) containing  $^{13}\text{C}$ -  
103  $\text{D}_4/^{13}\text{C}\text{-D}_5$  ( $\sim 90 \text{ }\mu\text{g L}^{-1}$ ), MT/TK ( $\sim 85 \text{ }\mu\text{g L}^{-1}$ ) and d-PAHs (all  $\sim 100 \text{ }\mu\text{g L}^{-1}$ ) were prepared.  
104 Batches of twenty membranes were placed in amber glass jars (1 L), filled with appropriate  
105 spiking solution (no HS), sealed and rotated (24 h). Membranes were removed, wiped and  
106 soaked ( $2 \times 12 \text{ h}$ ) in water to remove methanol and stored in water. Procedures were  
107 conducted in the clean air cabinet. Samplers were prepared shortly before use to avoid losses  
108 of PRCs. Three spiked samplers of each type were analysed prior deployment to ensure there  
109 was an adequate loading of PRCs (mean ( $\pm$  s.d.) masses (ng) spiked membranes were  $3,010 \pm$   
110  $450$  ( $^{13}\text{C}\text{-D}_4$ ),  $4,740 \pm 580$  ( $^{13}\text{C}\text{-D}_5$ ),  $3,750 \pm 500$  (MT) and  $3,800 \pm 980$  (TK)), and the  
111 variability (r.s.d. (%)) was similar for  $^{13}\text{C}\text{-D}_4/^{13}\text{C}\text{-D}_5$  and MT (15, 12, 13% respectively) but  
112 larger (26%) for TK. Loading of d-PAHs was a function of  $\log K_{ow}$ . The high variability in  
113 the amounts found in the spiked LDPE membranes may be attributed to several factors:  
114 difficulties in achieving uniform loading conditions with batches of 20 of membranes per  
115 spiking jar, and in handling membranes with very high loadings of PRCs, particularly where  
116 the compounds are volatile. Earlier work showed it was important to remove methanol used  
117 in the spiking solution from the membranes prior to deployment. This was achieved by water  
118 washes and storing the spiked sheets in water.

119

## 120 2.2 *In-field calibration*

121 The trial was conducted at Budds Farm WWTP (latitude 50°50'38.76"N and longitude  
122 0°59'39.19"W), Havant, UK. It treats water from a population c. 400,000 (inflow 2,400 L s<sup>-1</sup>)  
123 with flows from industry and stormwater. Previously stable concentrations of D4/D5 in water  
124 samples were found at this site, and hence it was deemed suitable for the calibration study.  
125 Samplers were deployed (6-13<sup>th</sup> March, 2012) in the effluent channel (~ 4 m depth of water)  
126 (Fig. S2). Average water flow = 1,140 ± 12 (s.e. of mean) L s<sup>-1</sup> (n = 769) and average  
127 turbidity = 20.1 (formazin units). Membranes were supported on a pre-washed (as for  
128 glassware)) stainless mesh plate (49.5 × 11.5 cm; Fig. S3). Six plates were linked to make  
129 the rig. Two rigs (due to depth restrictions) were used; located next to each other in the  
130 channel. Membranes were removed from jars, quickly wiped and (to reduce losses of PRCs  
131 by volatilisation and/or absorption of cVMS from air) fixed to the mesh with metal clips. The  
132 whole operation took less than 5 min for rig. Each plate held eight (Fig. S4) membranes (2  
133 off: unspiked, spiked <sup>13</sup>C-D4/<sup>13</sup>C-D5, spiked MT/TK, spiked d-PAHs); total 96 membranes.  
134 Rigs were submerged (~ 1 m below surface), being secured by weights and ropes. Unspiked  
135 field blank membranes (n = 6) were exposed to air at the site and handled as the experimental  
136 samplers. Twenty-four membranes (8 per set of membranes used for monitoring the cVMS  
137 only) were used to estimate the masses of <sup>13</sup>C-D4/<sup>13</sup>C-D5, and MT/TK that had been spiked,  
138 and 8 unspiked membranes to act as laboratory blanks. Membranes on one plate were  
139 removed at 20, 40 min and 1, 1.5, 2, 3, 5, 6, 22, 46, 70, and 167 h. Water (13.2-15.2°C) and  
140 air (5.4-10.5°C) temperatures were recorded. Membranes at the top were removed first and  
141 then others consecutively ensuring only samplers being removed were exposed to the  
142 atmosphere. Samplers were rinsed twice with water, dried with a paper tissue, and transferred  
143 immediately to vials containing *n*-hexane (6 mL), submerged totally in solvent and kept at  
144 4°C.

145 Water samples were aliquoted (15 mL) into a HS vial, spiked with  $^{13}\text{C}$ -labelled  
 146 internal standards in the field, sealed and kept at  $4^\circ\text{C}$ . A water sample was taken on  
 147 deployment and then duplicates at 2, 3, 5, 6, 22, 46, 70, 167 h. On each occasion a field blank  
 148 containing distilled water was opened while sampling took place. Concentration of cVMS in  
 149 the field blank was subtracted from the corresponding effluent water sample. The method  
 150 provided total concentrations of the cVMS due to similar partitioning behaviour of internal  
 151 standards to any particulate matter/dissolved organic carbon.

152

### 153 *2.3 Theory of passive sampling*

154 Uptake of pollutants by passive samplers has been described (Huckins, Petty and  
 155 Booij, 2006; Greenwood, Mills and Vrana, 2007). Uptake and offloading of a chemical can  
 156 be described by equations 1 and 2 respectively.

$$157 \quad C_s(t) = C_w K_{sw} (1 - \exp[-k_e t]) \quad \text{equation 1}$$

158 (Conditions:  $C_s(0) = 0$ ;  $C_w$  is constant)

$$159 \quad C_s(t) = C_s(0) \exp(-k_e t) \quad \text{equation 2}$$

160 (Conditions:  $C_s(0) \neq 0$ ;  $C_w = 0$ )

161 where  $C_s(t)$  and  $C_w$  are the concentrations of an analyte in the sampler and water respectively  
 162 after an exposure time  $t$ ,  $C_s(0)$  is the concentration in the sampler at zero time,  $K_{sw}$  is the  
 163 sampler water partition coefficient ( $\text{L L}^{-1}$ ), and  $k_e$  is the first order rate constant. Equation 1  
 164 is used for modelling the uptake of an analyte, and equation 2 for the offloading of a PRC.

165 At equilibrium equation 1 simplifies to:

$$166 \quad C_s = C_w K_{sw} \quad \text{equation 3}$$

167 Equations 1 and 2 can be expressed in terms of the mass accumulated in the sampler:

$$168 \quad M_s(t) = M_{eq} (1 - \exp[-k_e t]) \quad \text{equation 4}$$

169  $M_s(t) = M_s(0) \exp(-k_e t)$  equation 5

170 where  $M_s(t)$  is the mass accumulated in the sampler after time  $t$ , and  $M_{eq}$  is the mass in the  
171 sampler at equilibrium.

172 Over the period between the start of exposure and the half-time to equilibrium ( $t_{(0.5)}$ )  
173 uptake is approximately linear (integrative mode) and equation 1 simplifies to:

174  $M_s(t) = C_w R_s t$  equation 6

175 where  $M_s(t)$  is the mass in the sampler after exposure time  $t$ ,  $R_s$  is the sampler uptake rate (L  
176 day<sup>-1</sup>).

177  $R_s$  can be calculated from equation 6 using the slope ( $M_s(t)/t$ ) of the regression of the  
178 mass in the sampler on time (over the linear portion of the uptake data) and the concentration  
179 ( $C_w$ ) in the water and from the offloading of a PRC as:

180  $R_s = K_{sw} k_e V_s$  equation 7

181 where  $V_s$  is volume of sampler. The latter method depends on knowing  $K_{sw}$  and assumes  
182 isotropic kinetics.

### 183 **3. Results and discussion**

#### 184 *3.1 In-field trial*

185 Water temperature and flow varied slightly since there was no precipitation.  
186 Turbulence was high so there was minimal biofouling of the samplers (Fig. S5). The trial  
187 involved sampling water and LDPE membranes at a range of times. Of the 96 samplers  
188 deployed, only two (unspiked and spiked <sup>13</sup>C-D4/<sup>13</sup>C-D5) at 3 h were lost. Several samplers  
189 were removed at the beginning to detect any lag-phase.

190

#### 191 *3.2 Concentration of cVMS in effluent*



192 Concentrations of D4, D5, MT and TK in water varied over time (Table 1). For all  
 193 compounds the high s.d. values were due to a few samples that constituted only a small part  
 194 of the total exposure time (Table S3). There are few published data on concentrations of  
 195 cVMS in effluents. Van Egmond et al. (2013) found D4 below 20 ng L<sup>-1</sup> (LoQ) and D5 ~ 350  
 196 ng L<sup>-1</sup>, with little variation over a day. Wang et al. (2013c) reported D4 = < 9-45 ng L<sup>-1</sup> and  
 197 D5 = < 27-1,500 ng L<sup>-1</sup>; Xu et al. (2013) reported D4 = 250-550 ng L<sup>-1</sup> and D5 = 780-1,000  
 198 ng L<sup>-1</sup>; Bletsou et al. (2013) reported D5 = 1,790 ng L<sup>-1</sup> and Sanchís et al. (2013) found D4 =  
 199 LoQ-476 ng L<sup>-1</sup> and D5 = 42-3,587 ng L<sup>-1</sup>. Concentrations (Table 1) at Budds Farm are  
 200 consistent with these. There are no reported occurrences of MT, though it is used in  
 201 cosmetics (NICNAS Report, 2013). However, unexpectedly high concentrations of MT were  
 202 found in the influent (> 30 µg L<sup>-1</sup>) and effluent (96-2,218 ng L<sup>-1</sup>) of another local WWTP  
 203 with a cosmetics factory within its catchment (unreported observation, 2010). At Budds  
 204 Farm, the concentration of MT was 50 ng L<sup>-1</sup>, similar to that of D4. No measurable  
 205 concentrations of TK have been reported; one report (Environment Canada, 2011) predicted  
 206 concentrations in surface waters < 1 ng L<sup>-1</sup>. Here, TK was 15 ng L<sup>-1</sup>, slightly above LoQ.

207 **Table 1.** Descriptive statistics for the concentrations of cVMS found in the effluent from  
 208 Budds Farm over the field deployment period (0-167 h).

209

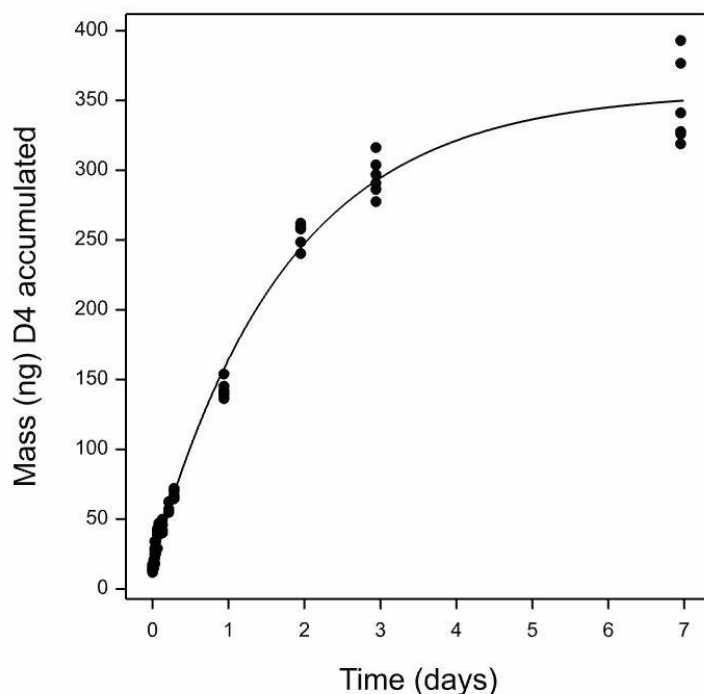
Concentration (ng L <sup>-1</sup> ) <sup>(1)</sup>	n	Mean	Standard error of mean	Standard deviation	Coefficient of variation	Median	Minimum	Maximum
D4	16 <sup>(2)</sup>	50	10	35	70	40	15 <sup>(2)</sup>	152
D5	17	1,840	180	730	40	1,670	757	3,562
MT	17	50	5	20	40	50	19	91
TK	17	15	3	13	90	10	0 <sup>(3)</sup>	49

210 <sup>(1)</sup>All concentrations based on calibrations corrected for corresponding field water blanks.  
211 Concentrations in nine blanks ranged from D4 (LoQ-32 ng L<sup>-1</sup>), D5 (10-188 ng L<sup>-1</sup>), MT (LoQ-40 ng  
212 L<sup>-1</sup>) and TK (LoQ-44 ng L<sup>-1</sup>). <sup>(2)</sup>One measurement of D4 at 22 h was an outlier and removed.  
213 <sup>(3)</sup>Concentration below LoQ.

214

### 215 3.3 Uptake of D4 and offloading of <sup>13</sup>C-D4

216 Sets of samplers (unspiked, spiked <sup>13</sup>C-D4/<sup>13</sup>C-D5, spiked MT/TK) were analysed for  
217 uptake of D4. Uptake was exponential and scatter between the independent sets of  
218 membranes was similar to that between the replicate membranes (Fig. 1). Data were fitted  
219 using an exponential model (GenStat 15). There was a significant regression ( $p < 0.001$ ) and  
220 99% of the variation in siloxane concentration was accounted for.  $k_e$  was 0.576 day<sup>-1</sup>,  $M_{eq}$  was  
221 356 ng and  $t_{(0.5)}$  was 1.6 days. From equation 3, using  $M_{eq}$ ,  $V_s$  and  $C_w$ , the  $K_{sw} = 2.6 \times 10^4$  (L  
222 L<sup>-1</sup>) ( $\log K_{sw} = 4.4$ ). This was low compared



223

224

225

226 **Fig. 1.** Uptake of D4 into LDPE membranes over a deployment period of one week.  
227 Replicate points represent the three independent sets of membranes (unspiked, spiked  $^{13}\text{C}$ -  
228 D4/ $^{13}\text{C}$ -D5 and MT/TK) exposed concurrently. The values were adjusted for the blank levels  
229 (mean = 14, s.d. = 2.9, s.e. of mean = 0.54 ng per sheet, n = 30) based on the six field control  
230 membranes and the 24 fabrication control membranes.

231

232 with some published (Brooke et al., 2009b; Wang et al., 2013a) values of the log  $K_{ow}$  (= 4.45-  
233 7.0).  $K_{ow}$ , is not purely a measure of hydrophobicity and is determined by a number of  
234 properties (e.g. hydrogen bonding properties, molar volume and polarizability). Compounds  
235 of similar  $K_{ow}$  may have different solvation properties. For non-polar compounds there is a  
236 relationship between log  $K_{sw}$  and log  $K_{ow}$ , but there a consistent difference of 0.5 log units  
237 between the log  $K_{sw}$  values of PCBs and PAHs of similar log  $K_{ow}$ , and is influenced by  
238 polarity (Smedes et al., 2009). Here the cVMSs may have a lower  $K_{sw}$  than PAHs and PCBs  
239 of similar  $K_{ow}$ , and the latter may not be a reliable predictor of  $K_{sw}$  for these compounds.

240 Since samplers behave integratively to  $t_{(0.5)}$ , data to 1.6 days were analysed using a  
241 linear regression of mass accumulated/time. Regression was significant ( $p < 0.001$ ,  $r^2 = 98\%$ )  
242 and slope was 122 ng day $^{-1}$ . Average concentration in the water was  $60 \pm 10$  (s.e.) ng L $^{-1}$  (n =  
243 12) over the linear range (up to 46 h) of sampling. Using equation 6,  $R_s$  was  $2.1 \pm 0.4$  (s.e.) L  
244 day $^{-1}$ , based on the standard propagation of errors method.

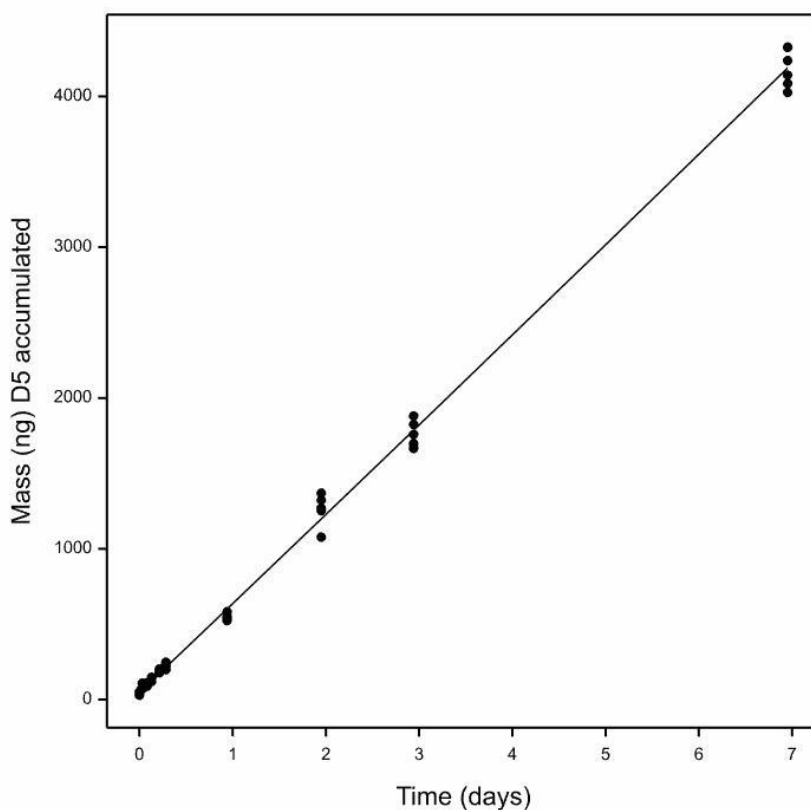
245  $^{13}\text{C}$ -D4 offloading data (Fig. S6) were fitted and there was a significant regression ( $p$   
246  $< 0.001$ ), with 75% of the variation in labelled siloxane concentration being accounted for.  
247 The offloading rate constant ( $k_e$ ) was 0.432 day $^{-1}$ , and the lower asymptote was not  
248 significantly different ( $t$ -test,  $p = 0.58$ ) from zero.  $R_s$  can be calculated (equation 7) from the  
249 independent offloading data and  $K_{sw}$ , providing kinetics were isotropic. The kinetics of  
250 uptake and offloading were found to be isotropic with a cross over point close to 50%,

251 justifying use of  $^{13}\text{C}$ -D4 as PRC (Fig. S7). Based on  $K_{sw}$  estimated from the uptake data  
252 (equation 4),  $R_s = 2.6 \text{ L day}^{-1}$ . This was similar to the independent estimate of  $2.1 \text{ L day}^{-1}$   
253 based on the uptake data (equation 6).

254

### 255 3.5 Uptake of D5 and offloading of $^{13}\text{C}$ -D5

256 Average concentration of D5 in water was  $1,840 \pm 180$  (s.e. of mean)  $\text{ng L}^{-1}$ . Uptake  
257 data for the three sets of samplers were analysed (Fig. 2). Uptake was linear over the  
258 deployment and equilibrium was not approached. It was not possible to estimate the  
259 equilibrium concentration because of insufficient curvature, and it was therefore not possible  
260 to estimate  $K_{sw}$ .



261

262 **Fig. 2.** Uptake of D5 into LDPE membranes over a deployment period of one week. The  
263 replicate points represent the three independent sets of membranes (unspiked, spiked with  
264  $^{13}\text{C-D4}/^{13}\text{C-D5}$  and MT/TK) exposed concurrently. The values were adjusted for blank levels  
265 (mean = 31, s.d. = 4.2, s.e. of mean = 0.76 ng per sheet, n = 30) based on the six field control  
266 membranes and the 24 fabrication control membranes.

267

268 Linear regression of mass of D5 in the sampler/time was effected; with a significant  
269 ( $p < 0.001$ ) regression that accounted for 99.8% of the total variation in mass of D5. The  
270 slope was  $600 \pm 2.88$  (s.e.)  $\text{ng day}^{-1}$  and gave (equation 6)  $R_s = 0.32 \pm 0.03$  (s.e.)  $\text{L day}^{-1}$   
271 (standard propagation of errors). It was not possible to obtain the offloading rate constant; the  
272 slope ( $34 \text{ ng day}^{-1}$  of a linear regression of offloading of  $^{13}\text{C-D5}$  was not significantly  
273 different from zero ( $t_{30} = 0.27$ ,  $p = 0.79$ )). The sampler would remain integrative for long  
274 periods ( $> 14$  days) and if the offloading of D5 and  $^{13}\text{C-D5}$  can be shown to be isotropic, the  
275 latter may used as a PRC.

276

### 277 3.6 Uptake and offloading of MT and TK

278 In view of the expense of using  $^{13}\text{C-D4}/^{13}\text{C-D5}$  as PRCs, offloading of MT and TK  
279 was investigated. MT (Companioni-Damas et al., 2012) and TK (Companioni-Damas et al.,  
280 2012; Bletsou et al., 2013; Xu et al., 2013) are used as internal standards for cVMS analyses.  
281 As these compounds appeared unexpectedly in the effluent, it was difficult to use them as  
282 reliable PRCs, which should be absent from the medium. MT (average  $50 \text{ ng L}^{-1}$ ) remained  
283 reasonably constant (Table 1). Two sets of membranes (unspiked, spiked  $^{13}\text{C-D4}/^{13}\text{C-D5}$ )  
284 were used to measure the uptake of MT (Fig. S8). Uptake was linear and equilibrium was not  
285 approached and it was not possible to estimate  $K_{sw}$  or  $k_e$ . A significant ( $p < 0.001$ ) linear  
286 regression of mass in the sampler upon time had an  $r^2_{\text{adjusted}}$  value of 98%, and the slope was

287 14.64.  $\pm$  0.288 (s.e.) ng day<sup>-1</sup>, giving  $R_s = 0.29 \pm 0.03$  (s.e.) L day<sup>-1</sup> (equation 6 and standard  
288 propagation of errors).  $R_s$  values for D5 and MT were similar.

289 Offloading data for MT showed scatter, probably due to inhomogeneity in spiking and  
290 evaporative losses during deployment. The slope (56 ng day<sup>-1</sup>) of a linear regression of the  
291 offloading data was not significantly different from zero ( $t_{27} = -1.33$ ,  $p = 0.194$ ). Uptake and  
292 offloading of TK were slow and their changes in mass were not detectable within the  
293 experimental error. The slope (31 ng day<sup>-1</sup>) of a linear regression of the offloading of TK was  
294 not significant from zero ( $t_{27} = -0.4$ ,  $p = 0.69$ ). In order to use LDPE for measuring TK, a  
295 larger sampling surface area and longer deployments are needed. TK could potentially be  
296 used as a PRC for D5 (or D6), but requires further validation. Findings are compatible with  
297  $\log K_{ow} = 6.52$ -9.84 for TK (Environment Canada, 2011).

298

### 299 3.7 Offloading of d-PAHs

300 Uptake and offloading of PAHs by LDPE is understood (Adams et al., 2007; Allan et  
301 al., 2009; Booij et al., 2003; Booij and Smedes, 2010; Lohmann, 2012). Offloading of d-  
302 PAHs was used to link with data from other workers to set the cVMS results in context.  
303 Offloading rate constants were estimated by non-linear regression with the lower asymptote  
304 constrained to zero (Figures S9-S13). For less hydrophobic PAHs offloading rates were rapid,  
305 but that of benz(a)anthracene-d<sub>12</sub> was slower. Calculated (equation 7) sampling rates (Table  
306 2) are based on the measured offloading rate constants and  $V_s = 2.28 \times 10^{-4}$  L.

307 Sampling rates (Table 2) of PAHs agree roughly with other studies (Booij et al.,  
308 2003). Samplers operate under aqueous boundary layer control for compounds  $\log K_{ow} > 4.4$ ,  
309 and the impact of water turbulence is high, making direct comparisons with published values  
310 difficult (Booij et al., 2003). The effluent channel was highly turbulent. The  $R_s$  values for D4,

311 D5 and MT (2.1, 0.32, and 0.29 L day<sup>-1</sup> respectively) were low compared with those of the  
 312 more non-polar PAHs, indicating membrane control, possibly due to very low diffusion  
 313 coefficients in LDPE for cVMS. This was consistent with predictions of diffusion  
 314 coefficients in LDPE based on molecular surface area. The predicted solvent accessible  
 315 surface areas were high for the cVMS compared with equivalent PCBs and PAHs (see  
 316 supplementary material), and the corresponding log diffusion coefficients (extrapolated from  
 317 the relationship based on PAHs and PCBs) were small (D4 = -14.10, D5 = -15.94, D6 = -  
 318 17.00, MT = -15.41, and TK = -16.60 measured as log m<sup>2</sup> s<sup>-1</sup> at 20°C) (Rusina, Smedes and  
 319 Klanova, 2010).

320

321 **Table 2.** Log *n*-octanol/water (log  $K_{ow}$ ) and log LDPE/water (log  $K_{sw}$ ) partition coefficients  
 322 of d-PAHs, and their corresponding calculated (equation 7) sampling rates ( $R_s$ ).

<b>Deuterated compound</b>	<b>Acenaphthene</b>	<b>Fluorene</b>	<b>Phenanthrene</b>	<b>Pyrene</b>	<b>Benz(a)anthracene</b>
log $K_{ow}$	3.92 <sup>(1)</sup>	4.18 <sup>(1)</sup>	4.5 <sup>(5)</sup>	5.0 <sup>(5)</sup>	5.91 <sup>(4)</sup>
log $K_{sw}$ <sup>(6)</sup>	3.68 <sup>(2)</sup>	3.93 <sup>(2)</sup>	4.15 <sup>(3)</sup>	4.99 <sup>(3)</sup>	5.5 <sup>(4)</sup>
$R_s$ (L day <sup>-1</sup> )	6.4	11.4	22.8	13.4	7.6

323 <sup>(1)</sup>Values for non-deuterated compound from Chemspider ([www.chemspider.com](http://www.chemspider.com));

324 <sup>(2)</sup>Calculated from log  $K_{sw} = 0.972 \log K_{ow} - 0.13$  at water temperature of 13°C (from Booiij et

325 al., 2003); <sup>(3)</sup>Average values of non-deuterated compounds from Hale et al., 2010; <sup>(4)</sup>Values

326 for non-deuterated compound from Fernandez et al., 2009; <sup>(5)</sup>Values for non-deuterated

327 compound from Adams et al., 2007; <sup>(6)</sup>Values of  $K_{sw}$  had units of L L<sup>-1</sup>.

328 Log  $K_{ow}$  when used to estimate log  $K_{sw}$  has a large impact on the calculated value of  
 329  $R_s$ . In our study, if a published estimate (Table S1) of log  $K_{ow}$  for D4 was used to calculate

330  $\log K_{sw}$ , and used with our measured offloading rate ( $k_e$ ), then  $R_s = 15.5 \text{ L day}^{-1}$ ; roughly a  
331 factor of six different from the measured values (2.1 and  $2.6 \text{ L day}^{-1}$ ). This further underlines  
332 the unreliability of using  $\log K_{ow}$  as a predictor of  $\log K_{sw}$  for the cVMS.

333 For PAHs, PCBs and chlorobenzenes the relationship between  $\log K_{ow}$  and  $R_s$  is not  
334 linear, and temperature dependent (Booij et al., 2003). For a change in  $\log K_{ow}$  between 3.5-  
335 5.0,  $R_s$  increases steeply, above this hydrophobicity has a less marked effect on sampling rate  
336 (Booij et al, 2003). In offloading experiments retention was high and changed very little with  
337 increasing hydrophobicity above  $\log K_{ow} = 5.5$  (Booij and Smedes, 2010). Very hydrophobic  
338 d-PAH PRCs would be expected to be retained on the LDPE over our deployment. The  $\log$   
339  $K_{sw}$  of D4 falls between those of phenanthrene and pyrene (Table 2), for which the  $R_s$  values  
340 are 22.8 and  $13.4 \text{ L day}^{-1}$  respectively. The two calculated values of  $R_s$  (2.1 and  $2.6 \text{ L day}^{-1}$ )  
341 for D4 are both much lower than those of these equivalent PAHs. These differences are  
342 consistent with a low diffusion coefficient of D4 in LDPE.

343

### 344 *3.8 Measurement of cVMS in water with LDPE samplers*

345 Single phase devices measure the free fraction of the chemical in water, so there are  
346 difficulties in comparing data with spot water samples (includes free, bound to particulate  
347 matter/dissolved organic material; often called total concentration). Due to the high volatility  
348 of cVMS, filtration of water was not possible. Data from HS-GC/MS is based on the total  
349 concentration. cVMS can bind to dissolved organic material. Van Egmond et al. (2013)  
350 calculated  $D5 = 73\%$  and  $D6 = 26\%$  were present in effluent as the free form and also  
351 recoveries of  $^{13}\text{C-D4} = 88\%$  and  $^{13}\text{C-D5} = 73\%$  were obtained. Using these labelled data,  $R_s$   
352 for D4 and D5 (corrected for the bound fraction) were  $2.4$  and  $0.44 \text{ L day}^{-1}$  respectively  
353 (compared with uncorrected estimates of 2.1 and  $0.32 \text{ L day}^{-1}$ ).



354 LDPE samplers provide concentrated analyte extracts. For example, over the 7-day  
355 trial, each sheet would sample the equivalent of ~ 5.9 L of water for D4 (where the device  
356 would be at equilibrium) and ~ 2.4 L of water for D5. Furthermore, exposed membranes can  
357 be extracted ~ 5-10 mL of *n*-hexane and several sheets can be combined for extraction.  
358 Hence, devices have potential for measuring cVMS in pristine environments that is not  
359 generally possible using conventional spot water sampling methods combined with HS  
360 analysis. The latter is limited by the volume (typically around 25 mL) of the HS vial that can  
361 be used in conjunction with automated analysers. Alternative higher volume techniques, such  
362 as solvent or solid-phase extraction, are not practical for these volatile compounds. The utility  
363 of passive samplers is governed the concentration of cVMS in laboratory and field blanks.  
364 We found cVMS (D4 = 14 ng and D5 = 31 ng per sheet) in exposed blank samplers at the  
365 site. Atmospheric concentrations of cVMS at such plants are high (D4 ~ 2,000 ng m<sup>-3</sup>; D5 ~  
366 5,550 ng m<sup>-3</sup>) (Cheng et al., 2011). Assuming no contamination of blank samplers (i.e. good  
367 laboratory control procedures and pristine sites) and using the LoQ of the analytical method,  
368 the LDPE samplers over a 7-day deployment should be able to measure D4 ~ 3 ng L<sup>-1</sup>  
369 (equilibrium measurement) and D5 < 2 ng L<sup>-1</sup> (TWA measurement). The use of the large  
370 volume on-column GC/MS procedure of Sparham et al. (2011) would typically provide LoQs  
371 ten-fold lower than those found for the method used in this study for the analysis of *n*-hexane  
372 extracts of LDPE samplers. Combined with low blank values found at pristine sites, this  
373 approach would a useful alternative to available spot water sampling techniques.

374

375

376 In-field calibration was more reliable than use of through flow tank systems for  
377 chemicals with similar log  $K_{ow}$  values (Rusina et al., 2010). In our laboratory it was difficult  
378 to maintain constant concentrations of cVMS over 14-days, despite using a separate loading

379 tank to supply the calibration tank, volatile and adsorptive losses were high, being  
380 exacerbated by the turbulent conditions used to simulate field conditions. In contrast, in the  
381 field where very large volumes of water are involved, the concentrations of the analytes are  
382 relatively constant.

## 383 **4 Conclusions**

384 To our knowledge, this is the first time passive samplers have been used to measure  
385 D4 and D5 in water. Our experiments show the potential for LPDE; as it is adaptable to  
386 different monitoring applications. cVMS are difficult to handle and measurement of  $\log K_{ow}$   
387 is problematic. LDPE samplers have provided data indicating that the solvation behaviour of  
388 cVMS may not follow that of compounds with similar  $\log K_{ow}$  (or  $\log K_{sw}$ ) but having very  
389 low volatility. The low  $R_s$  values compared with those of PCBs and PAHs of similar  
390 hydrophobicity could be due to their predicted low diffusion coefficients in LDPE. The  
391 behaviour of cVMS provide additions to the data-sets based on PAHs and PCBs, that form  
392 most of the literature on sampling of hydrophobic compounds.

393 Samplers can be used to monitoring D4 integratively over days and for equilibrium  
394 sampling over longer periods; use of PRCs is feasible. Samplers for D5 operated integratively  
395 over long periods, though the applicability of PRCs was not demonstrated. Samplers could be  
396 used for linear siloxanes (e.g. L4/L5) (Companioni-Damas et al., 2012). Higher volatilities of  
397 L2, L3 and D3 would cause losses from the membrane during handling and time to  
398 equilibrium would be short. In contrast, D6 reported in wastewater (Xu et al., 2013), should  
399 be measurable. Based on  $\log K_{ow} = 8.87$  (Xu and Kropscott, 2012) the time integrative period  
400 would be long and use of PRCs difficult. Further work is needed to explore applications of  
401 these samplers in monitoring these problematic compounds, and to provide more reliable

402 estimates of key physico-chemical properties. However, the ability to measure cVMS at  $\text{pg L}^{-1}$   
403 <sup>1</sup> is possible and these data would contribute to fate modelling and risk assessments.

404

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549 **Supplementary material**

550 **Measurement of cyclic volatile methylsiloxanes in the aquatic environment**  
551 **using low-density polyethylene passive sampling devices using an ‘in-field’**  
552 **calibration study – challenges and guidance**

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570 **Table S1.** Typical physico-chemical properties of D4 (Brooke et al., 2009b) and D5 (Brooke  
 571 et al., 2009a) relevant to their analysis and environmental fate.

Property	D4	D5
Molecular weight, g mol <sup>-1</sup>	296.6	370.8
Boiling point, °C	175	211
Melting point, °C	17	-44
Density, g cm <sup>-3</sup> at 25°C	0.95	0.95
Vapour pressure, Pa at 25°C	132	33.2
Water solubility, µg L <sup>-1</sup> at 23°C	56	17
Henry's law constant, Pa m <sup>3</sup> mol <sup>-1</sup> at 25°C	1,241,0000	3,342,000
Molar volume, cm <sup>3</sup> mol <sup>-1</sup>	310	384
log $K_{OW}$	6.49	8.03
log $K_{OA}$	4.22	5.17
log $K_{AW}$	2.69	3.13

572 Key:  $K_{OW}$  = *n*-octanol/water partition coefficient,  $K_{OA}$  = *n*-octanol/air partition coefficient,  $K_{AW}$  = air/water partition  
 573 coefficient.

574



## 575 **Methods**

576 Chemicals and glassware

577

578 D4, D5, MT and TK (> 98% purity) were from Sigma–Aldrich (Gillingham, UK).  
579  $^{13}\text{C}$ -D4 and  $^{13}\text{C}$ -D5 (> 99% purity), used as internal standards and PRCs were from Moravek  
580 Biochemicals (Brea, California, USA). Deuterated PAHs (2 mg mL<sup>-1</sup> in acetone, > 99%  
581 purity) used as PRCs (acenaphthene-d<sub>10</sub>, fluorene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, pyrene-d<sub>10</sub> and  
582 benz(a)anthracene-d<sub>12</sub>) and internal standard (anthracene-d<sub>10</sub>) were from Q<sub>mx</sub> Laboratories  
583 (Thaxted, Essex, UK). HPLC grade *n*-hexane and methanol (Fischer Scientific UK Ltd.  
584 (Loughborough, UK)) and distilled-in-glass grade acetone (Rathburn Chemicals Ltd.  
585 (Walkerburn, UK)) from these sources had background concentrations of cVMS < limit of  
586 detection (LoD). Ultrapure water was from a Purite (Thame, UK) system. Other chemicals  
587 were from Fischer Scientific UK Ltd. or Sigma–Aldrich. Headspace (HS) glass vials (20  
588 mL), butyl/PTFE septa (20 mm) and crimp caps were from Varian Inc. (Oxford, UK).  
589 Glassware was cleaned in detergent, rinsed three times with water, dried, rinsed again in  
590 either acetone or methanol, dried and stored in a clean air cabinet.

591 Preparation of standard solutions

592 To reduce contamination of the analytical laboratory, preparation was conducted in  
593 another room using a clean air cabinet (Bigneat Ltd., Waterloooville, UK). Standards, spiked  
594 water samples and spiked passive samplers were returned to the analytical laboratory and  
595 kept in a similar enclosure (Sparham et al., 2008). Standards (analysis of water) were  
596 prepared by spiking water with standard solutions in acetone. The calibration curve range was  
597 D4: 0-400 ng L<sup>-1</sup>, D5: 0-2,600 ng L<sup>-1</sup>, MT: 0-400 ng L<sup>-1</sup> and TK: 0-400 ng L<sup>-1</sup> in water.

598 Internal standards,  $^{13}\text{C-D4}$  ( $95.6 \text{ ng L}^{-1}$ ) and  $^{13}\text{C-D5}$  ( $95.8 \text{ ng L}^{-1}$ ) were added to all  
599 calibration solutions.

600 For analysis of extracts from LDPE samplers, external calibration standards (D4, D5,  
601 MT, TK,  $^{13}\text{C-D4}$ ,  $^{13}\text{C-D5}$ ) were prepared in *n*-hexane ( $0-1,200 \text{ ng mL}^{-1}$ ).

#### 602 *Analysis of cVMS in water*

603 A GC/MS (Agilent 7890A/5975) with automated HS attachment (CTC Analytics,  
604 Zwingen, Switzerland) was used. D4, D5, MT and TK in water were quantified by HS-  
605 GC/MS (Sparham et al., 2008). D4 and D5 were quantified against labelled standards (LoQ:  
606 D4 and D5  $\sim 10 \text{ ng L}^{-1}$ ). MT and TK were quantified against an external calibration (LoQ:  
607 MT and TK  $\sim 5 \text{ ng L}^{-1}$ ). Mass spectral ions are shown in Table S2.

608

#### 609 *Analysis of cVMS and deuterated PAH in extracts from LDPE membranes*

610 Each exposed sampler was immediately placed in a glass vial (20 mL) containing *n*-  
611 hexane (6 mL); this represented an extraction ratio of 4% (v/v). The membrane was totally  
612 submerged in the solvent. cVMS were extracted (24 h) using agitation. This extracted  $> 90\%$   
613 of the cVMS. An aliquot (100  $\mu\text{L}$ ) was added to crimped GC vial (2 mL) containing *n*-hexane  
614 (900  $\mu\text{L}$ ). For concentrations outside the calibration range, the extract was further diluted  
615 with *n*-hexane. Extracts were analysed using GC/MS (Agilent 6890N/5973) using ions in  
616 Table S2. cVMS were separated on a 30 m x 0.25 mm x 0.25  $\mu\text{m}$  film (HP-5 MS, Agilent)  
617 column, using a temperature of  $65^\circ\text{C}$  (2 min) then  $10^\circ\text{C min}^{-1}$  to  $250^\circ\text{C}$  (2 min). Splitless  
618 injection (2  $\mu\text{L}$ ; at  $250^\circ\text{C}$ ) was used (split valve shut for 30 s, 50:1 split ratio). LoQs were 2.5,  
619 0.7,  $< 0.1$ ,  $< 0.1$ , 0.2 and  $< 0.1 \text{ ng mL}^{-1}$  for D4, D5, MT, TK,  $^{13}\text{C-D4}$  and  $^{13}\text{C-D5}$  respectively  
620 (response 2-3 times greater than background in ten fabrication blanks).

621 LDPE membranes spiked with deuterated PAHs were extracted as above, with  
 622 anthracene-d<sub>10</sub> (200 ng mL<sup>-1</sup>) added as a standard. PAHs were analysed using a 430 model  
 623 GC fitted with a VF-5ms capillary column (30 m long x 0.25 mm internal diameter, 0.25 µm  
 624 film thickness) with a CP 8400 auto-sampler and interfaced to a 210-IT MS (Varian Inc.).  
 625 Samples (1 µL) were injected (pressure pulse injection at 45 psi for 1 min) in splitless mode  
 626 (split value open after 2 min, split ratio 1:50) with the injector maintained at 275°C. Helium  
 627 flow rate was 1 mL min<sup>-1</sup>. The oven temperature programme was: initial temperature 60°C (1  
 628 min) then to 150°C (300°C min<sup>-1</sup>) then to 186°C (6°C min<sup>-1</sup>) then to 280°C (4°C min<sup>-1</sup>), hold  
 629 for 20 min. The MS was operated in the scan mode with parent ions used for identification  
 630 and quantification of the compounds. The concentrations of the d-PAHs were quantified from  
 631 nine-point external calibration curves (10-2,000 ng mL<sup>-1</sup> in *n*-hexane).

632

633 **Table S2.** Molecular ion, quantification and confirmation ions used for the GC/MS analysis  
 634 of the cVMS and labelled standards in water samples and *n*-hexane extracts obtained from the  
 635 LDPE samplers.

Compound	Abbreviation	Molecular ion ( <i>m/z</i> )	Quantification ion ( <i>m/z</i> )	Confirmation ions ( <i>m/z</i> )
Octamethylcyclotetrasiloxane	D4	296	281	207, 133
Decamethylcyclopentasiloxane	D5	370	355	267, 73
Methyltris(trimethylsiloxy)silane	MT	310	295	207, 73
Tetrakis(trimethylsiloxy)silane	TK	384	281	281, 147, 73
<sup>13</sup> C-D4 (used as internal standard and PRC)		300	285	210, 135
<sup>13</sup> C-D5 (used as internal standard and PRC)		375	355	270, 75

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638 **Table S3.** Concentration (ng L<sup>-1</sup>) of D4, D5, MT, and TK in water samples taken from the  
 639 effluent outlet of the Budds Farm waste water treatment plant at a series of times during the  
 640 exposure of LDPE membranes. Each concentration was adjusted for the field water blank  
 641 taken at each sampling time. \*Concentration below the LoQ value.

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660	660	660	660	660	660
643	Time (h)	D4 (ng L <sup>-1</sup> )	D5 (ng L <sup>-1</sup> )	MT (ng L <sup>-1</sup> )	TK (ng L <sup>-1</sup> )
644	0	28	1,478	49	0*
645	1.87	42	1,754	68	21
646	1.87	47	1,834	68	7
647	3.08	69	2,297	80	6
648	3.08	75	2,272	91	30
649	5.17	54	1,352	65	49
650	5.17	36	1,320	55	20
651	6.25	152	3,562	39	0*
652	6.25	102	2,209	43	0*
653	22.17	19	1,665	43	26
654	22.17	2.2	1,223	34	8
655	46.33	24	757	37	25
656	46.33	65	1,226	30	22
657	70.23	34	1,425	19	20
658	70.23	15	1,348	32	9
659	166.8	36	3,089	59	7
660	166.8	38	2,439	54	9

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 662 LoQ = limit of quantification  
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#### 664 **Statistical analysis of concentrations of cVMS found in spot water samples**

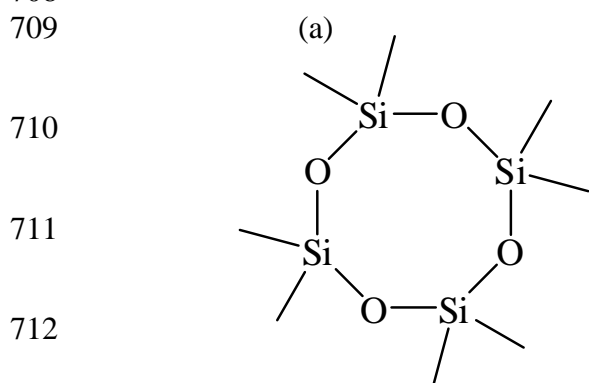
665 The smallest value (2.2 ng L<sup>-1</sup>) for D4 was associated with an abnormally large blank  
 666 control value, and was suspected to be an outlier. The values of D4 were log normally  
 667 distributed, and a two-sided outlier test (Barnett and Lewis, 1978) was performed on the  
 668 logged values. The smallest value (2.2 ng L<sup>-1</sup>) was highly likely ( $p < 0.01$ ) to be an outlier,  
 669 while the highest value (152 ng L<sup>-1</sup>) was marginally significant ( $p = 0.05$ ). The smallest value  
 670 was excluded on a combination of chemical and statistical grounds. The highest value was  
 671 retained, but its presence or absence had only a negligible impact on subsequent calculations  
 672 and conclusions.

673 For D4 there was a statistically significant ( $p = 0.017$ ) effect of time, but only the

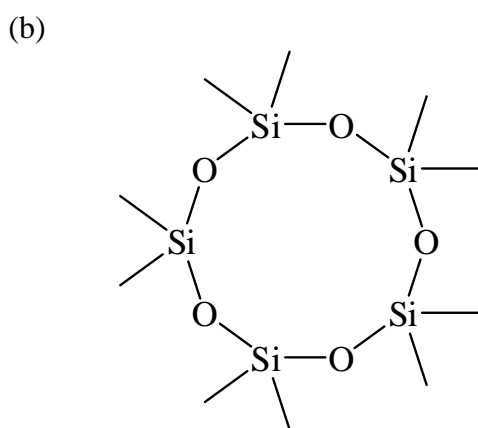
674 concentration at 6 h was statistically different from the rest, and there were no significant  
675 differences between any of the other concentrations (*post hoc* Tukey's test, 5% level of  
676 probability). For D5 there was also a significant ( $p = 0.015$ ) effect of time, but this was due to  
677 only a significant difference between the concentration at 6 h and those 46 and 117 h. None  
678 of the other concentrations were statistically significantly different from each other (*post hoc*  
679 Tukey's test, 5% level of probability). For MT there was a statistically significant ( $p < 0.001$ )  
680 effect of time, and most of the differences were between the concentrations in the three  
681 samples taken between 2 and 5 h (*post hoc* Tukey's test, 5% level of probability). There were  
682 no significant ( $p = 0.248$ ) differences between the concentrations of TK at any of the  
683 sampling times. The period in which significant differences were found represented only a  
684 very small proportion of the total exposure time, and in subsequent calculations of sampling  
685 rates ( $R_s$ ), the concentrations of the analytes in water were assumed to be approximately  
686 constant, and the mean values ( $C_w$ ) over time were used. There was a weak relationship  
687 between the concentrations of D4 and D5 in the effluent, where D4 was present at some 3%  
688 of the concentration of D5. A linear regression of D4 on D5 was significant ( $P = 0.003$ ), but  
689 there was a large scatter of the data ( $r^2_{\text{(adjusted)}} = 42\%$ ).

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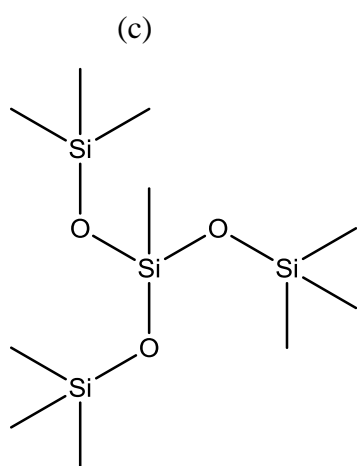
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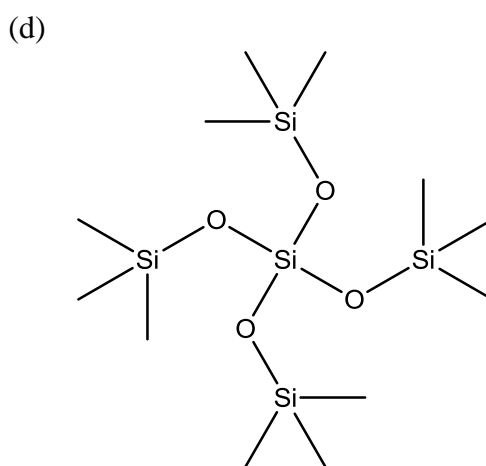
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718 **Fig. S1.** Chemical structure of (a) octamethylcyclotetrasiloxane (D4) molecular weight: 296.6  
719  $\text{g mol}^{-1}$ , molecular formula:  $\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4$  (b) decamethylcyclopentasiloxane (D5), molecular  
720 weight: 370.8  $\text{g mol}^{-1}$ , molecular formula:  $\text{C}_{11}\text{H}_{34}\text{O}_5\text{Si}_5$  (c) methyltris(trimethylsiloxy)silane  
721 (MT) molecular weight: 310.7  $\text{g mol}^{-1}$ , molecular formula:  $\text{C}_{10}\text{H}_{30}\text{O}_3\text{Si}_4$  and (d)  
722 tetrakis(trimethylsiloxy)silane (TK), molecular weight: 384.8  $\text{g mol}^{-1}$ , molecular formula:  
723  $\text{C}_{12}\text{H}_{36}\text{O}_4\text{Si}_5$ .

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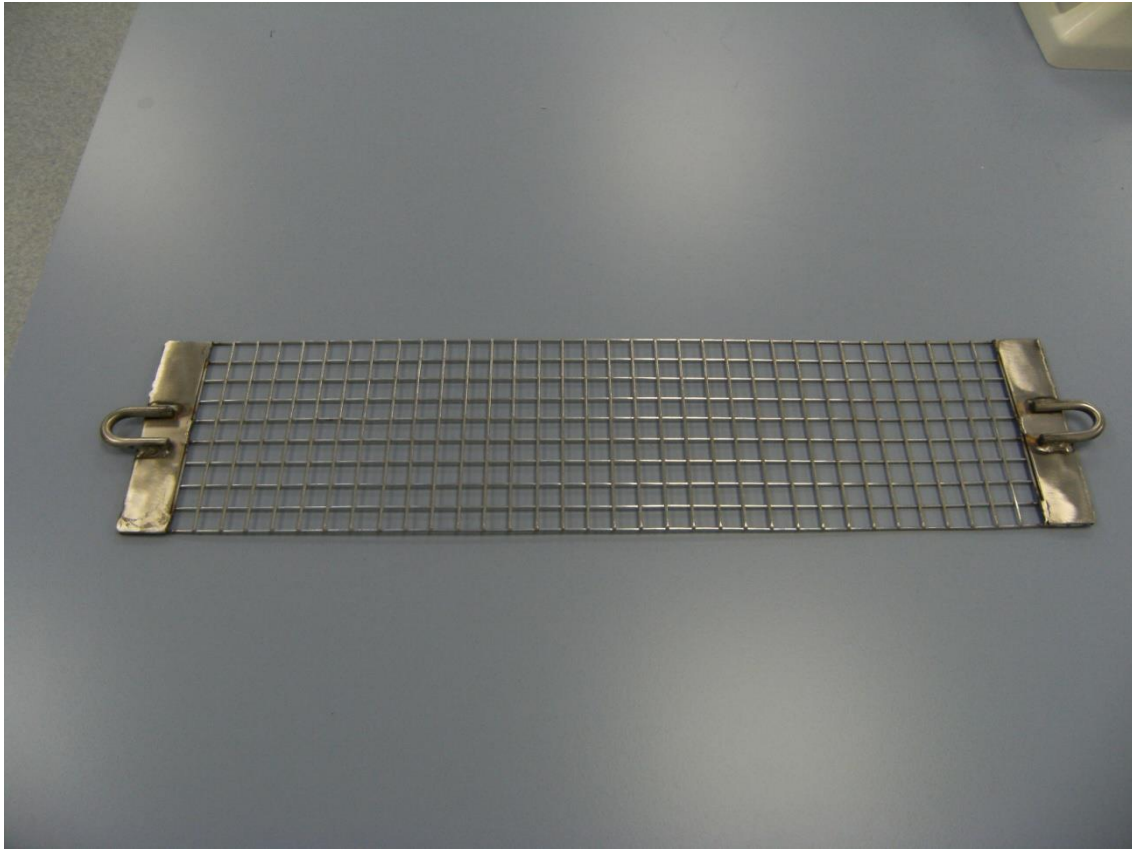
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738 **Fig. S2.** The effluent channel at Budds Farm waste water treatment plant used for deploying

739 the passive samplers. Ropes indicate where the rigs deployed and secured to railings.

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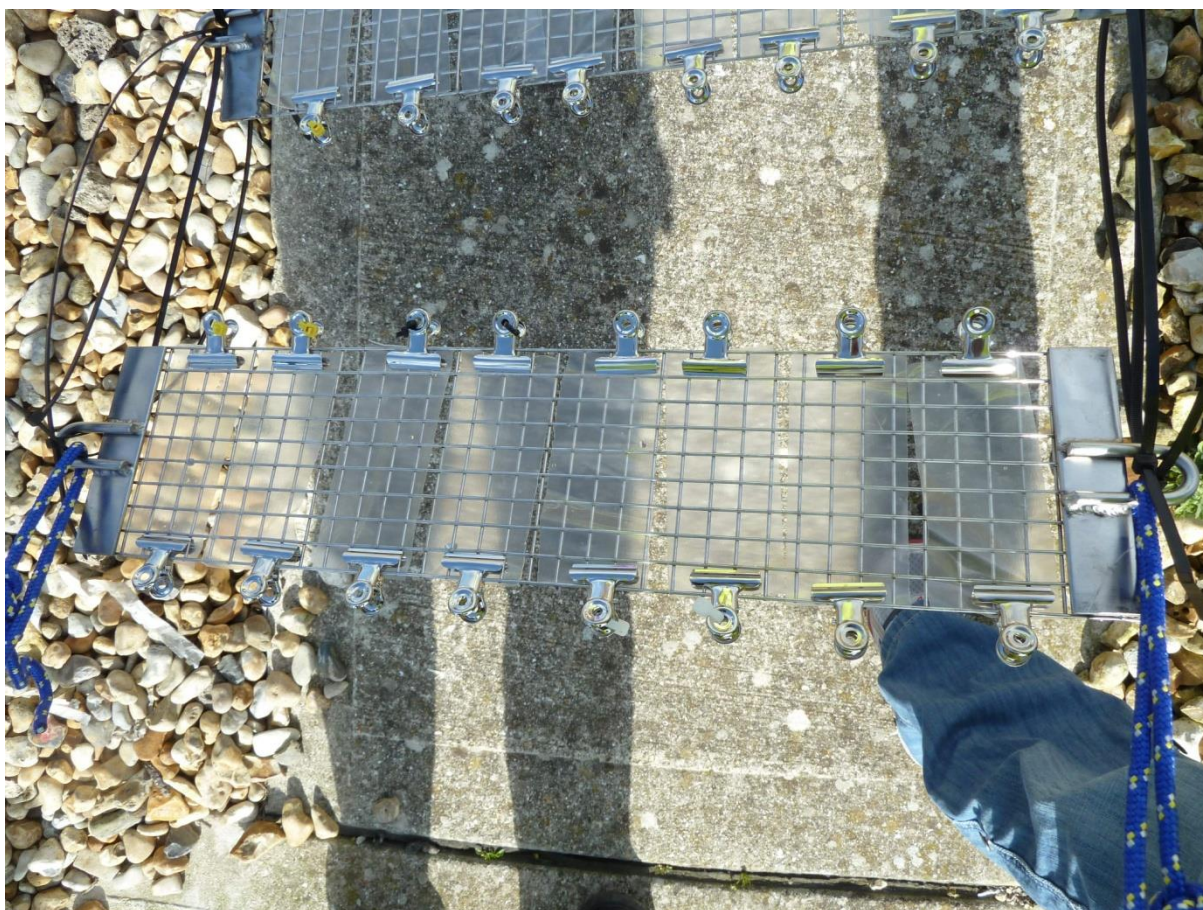
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**Fig. S3.** The stainless steel mesh plate used to hold the LDPE membranes during the ‘in-field’ calibration trial.





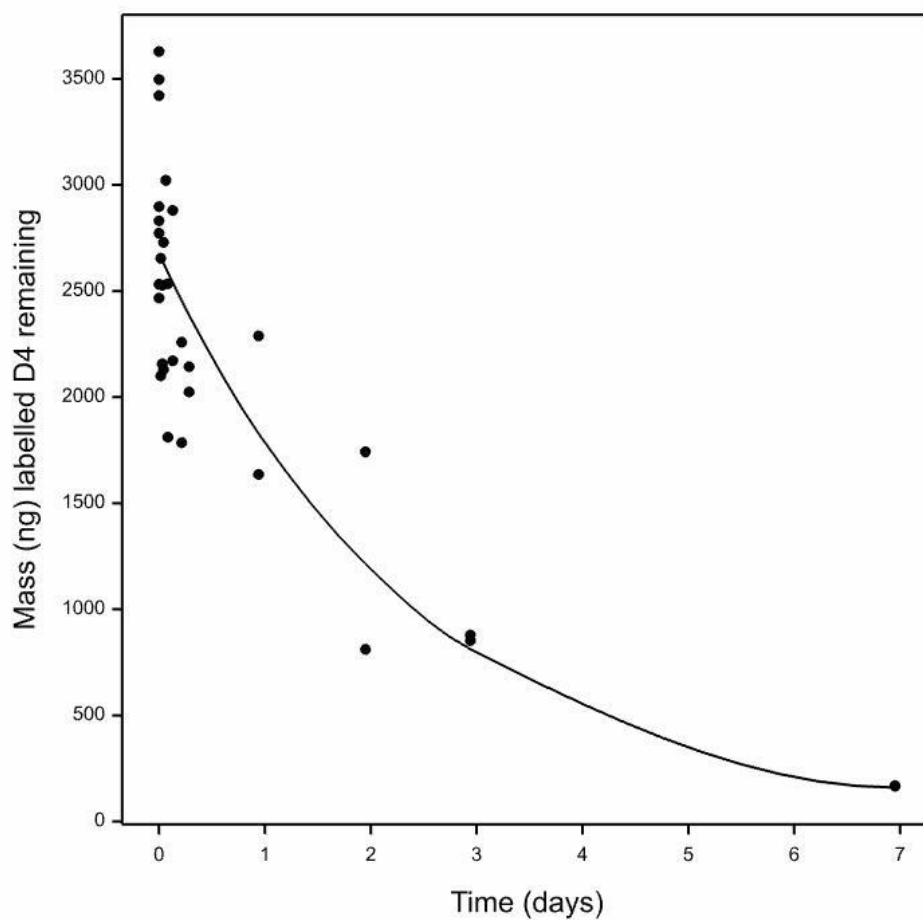
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**Fig. S4.** Set of LDPE membranes clipped to the stainless steel support mesh prior to deployment in the effluent channel. Metal clips with coloured tags were used to identify the four different (unspiked and three different types of PRCs (1)  $^{13}\text{C-D4}$  and  $^{13}\text{C-D5}$ , (2) MT and TK and (3) acenaphthene- $\text{d}_{10}$ , fluorene- $\text{d}_{10}$ , phenanthrene- $\text{d}_{10}$ , pyrene- $\text{d}_{10}$  and benz(a)anthracene- $\text{d}_{12}$ ) membranes.

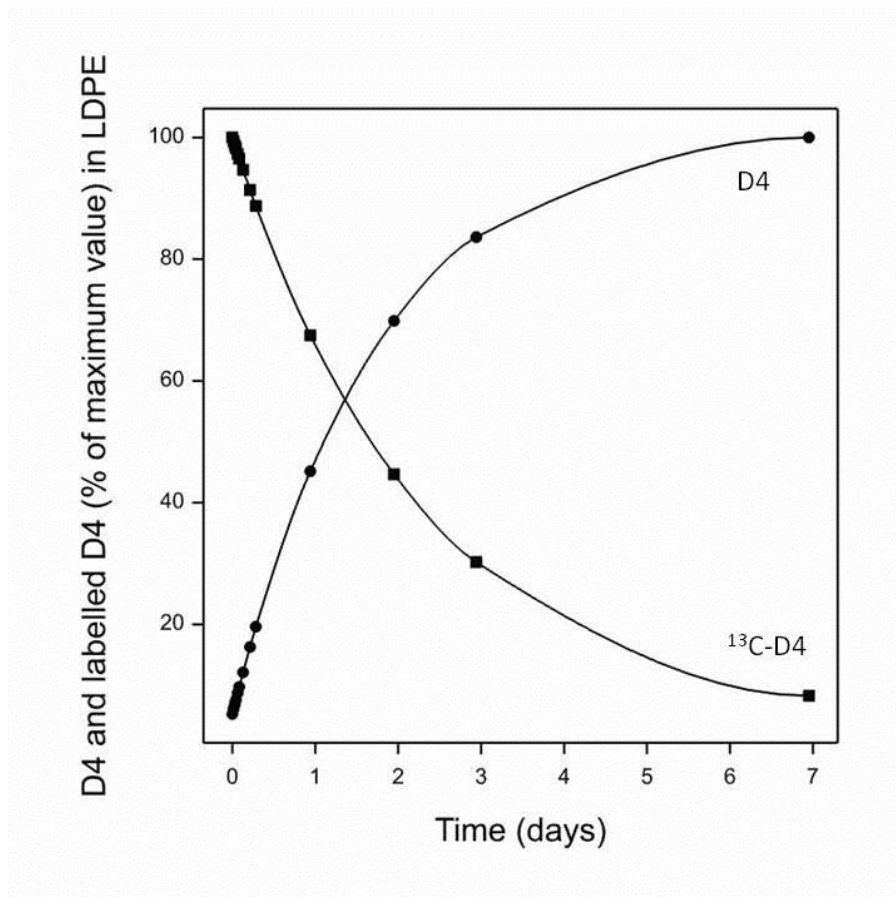


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**Fig. S5.** Set of LDPE membranes at the end of the field trial. Due to the highly turbulent conditions in the waste water effluent channel even after deployment for one week there was minimal biofouling of the surface the membranes.

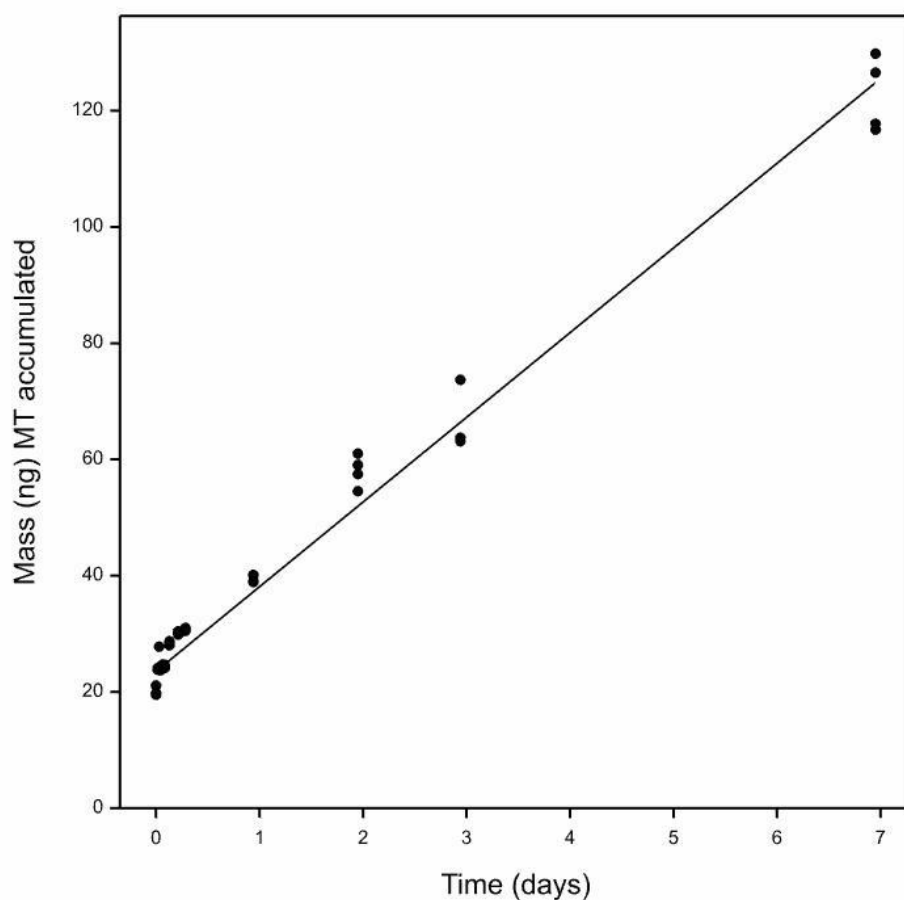


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814 **Fig. S6.** Observed data for offloading of  $^{13}\text{C}$ -D4 from LDPE membranes over a deployment  
815 period of one week. The line was fitted using the standard exponential function in the non-  
816 linear regression routine of GenStat 15.



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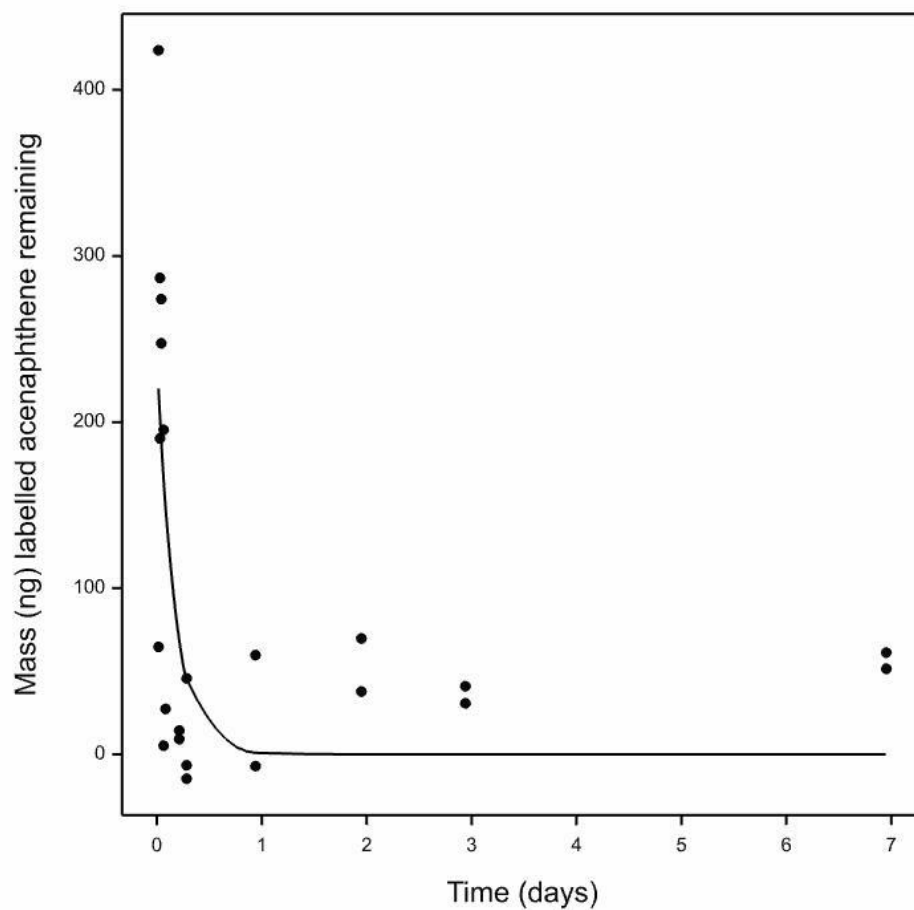
**Fig. S7.** Fitted values (standard exponential function in the non-linear regression routine of GenStat 15) for offloading of <sup>13</sup>C-D4 (filled squares) from, and uptake of D4 (filled circles) into LDPE membranes over the deployment period of one week. The values are displayed as the percentage of equilibrium, and starting masses in the sampler for uptake and offloading data respectively.



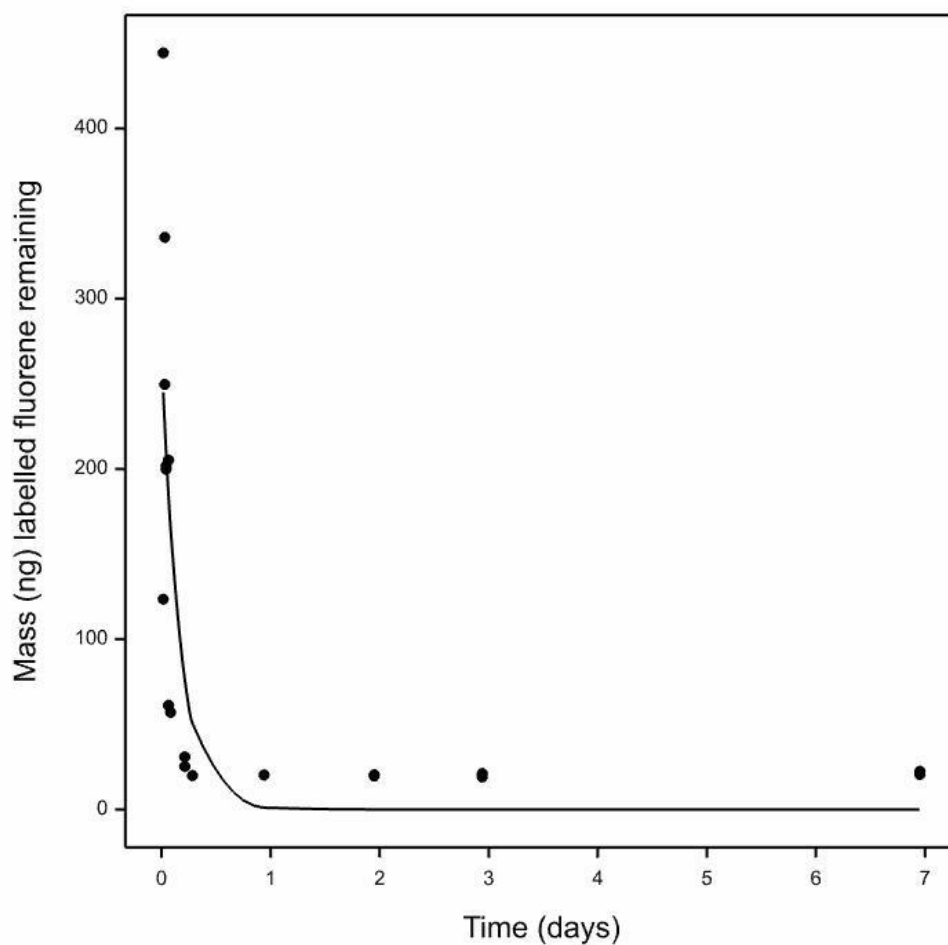
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828 **Fig. S8.** Observed data for uptake of MT into LDPE membranes over a deployment period of  
829 one week. The replicate points represent the three independent sets of membranes (unspiked,  
830 spiked with  $^{13}\text{C-D4}$  and  $^{13}\text{C-D5}$ , and spiked with MT and TK) exposed concurrently.

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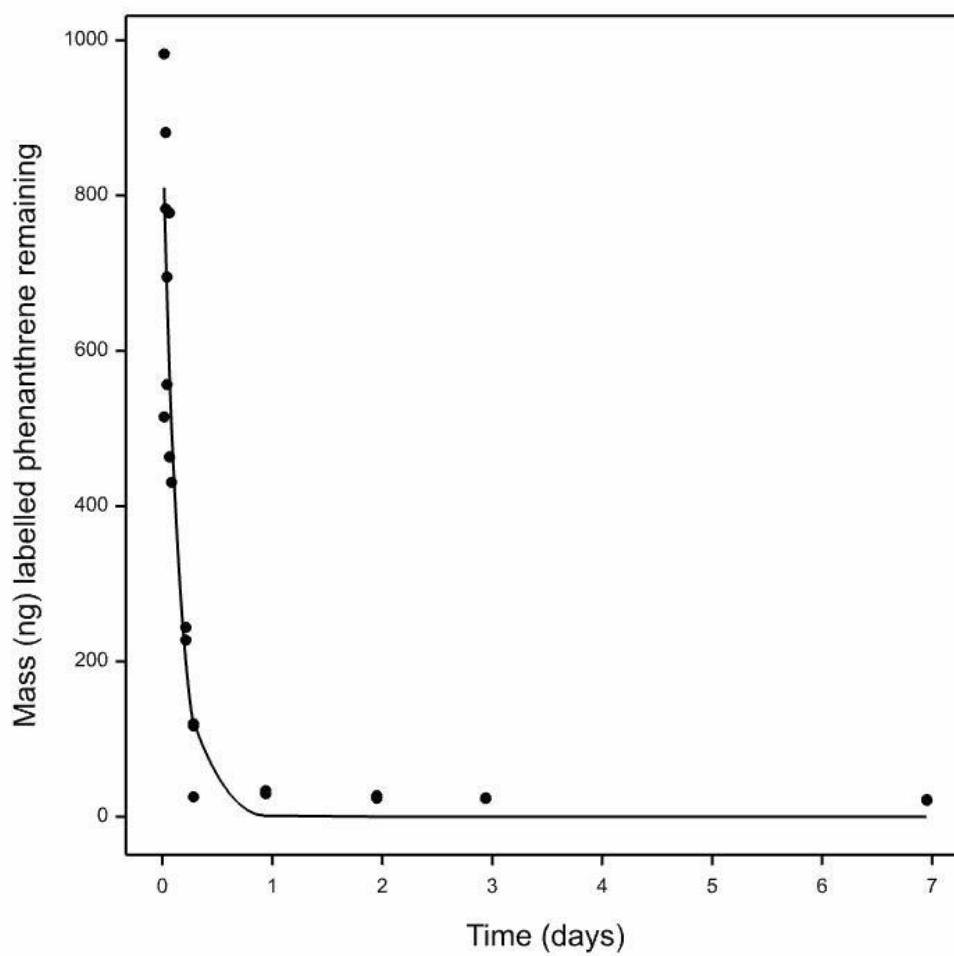
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855 **Fig. S9.** Observed data for offloading (corrected for fabrication and field blanks) of  
856 acenaphthene-d<sub>10</sub> from LDPE membranes over a deployment period of one week. The line  
857 was fitted using the standard simple exponential function in the non-linear regression routine  
858 of GenStat 15.  
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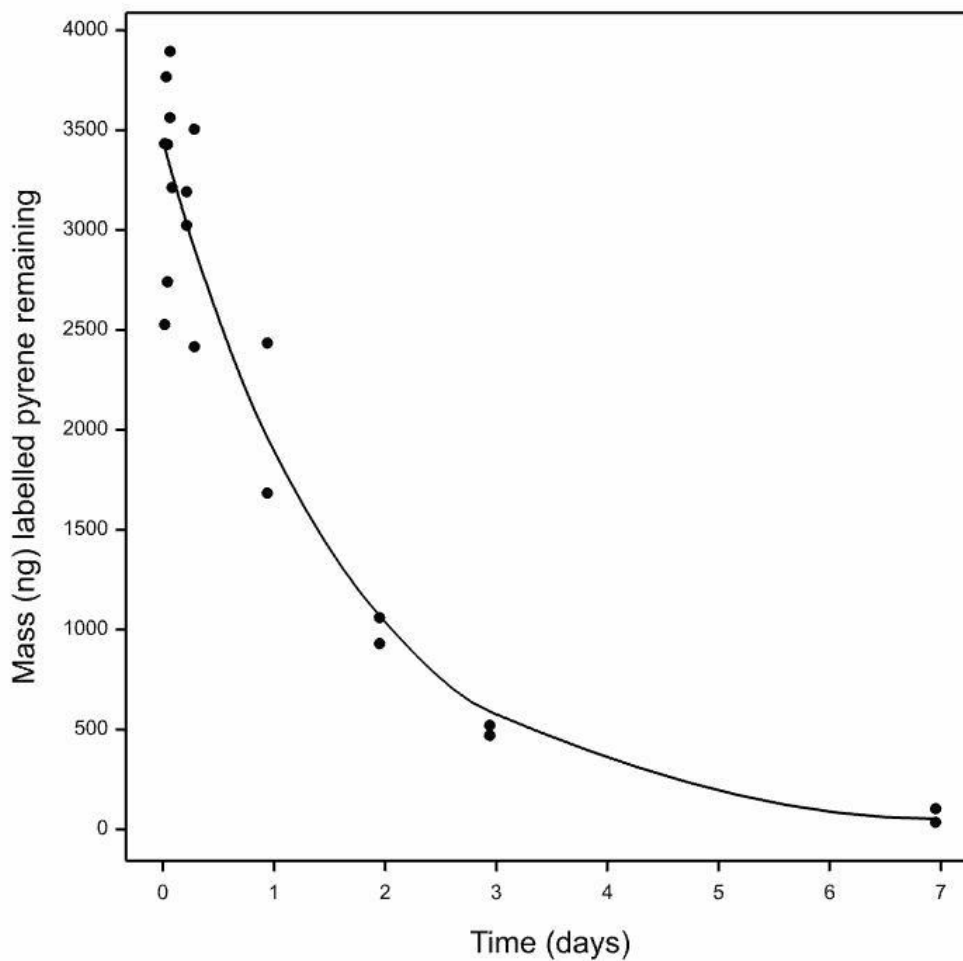
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861 **Fig. S10.** Observed data for offloading (corrected for fabrication and field blanks) of  
862 fluorene-d<sub>10</sub> from LDPE membranes over a deployment period of one week. The line was  
863 fitted using the standard simple exponential function in the non-linear regression routine of  
864 GenStat 15.  
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867 **Fig. S11.** Observed data for offloading (corrected for fabrication and field blanks) of  
868 phenanthrene- $d_{10}$  from LDPE membranes over a deployment period of one week. The line  
869 was fitted using the standard simple exponential function in the non-linear regression routine  
870 of GenStat 15.

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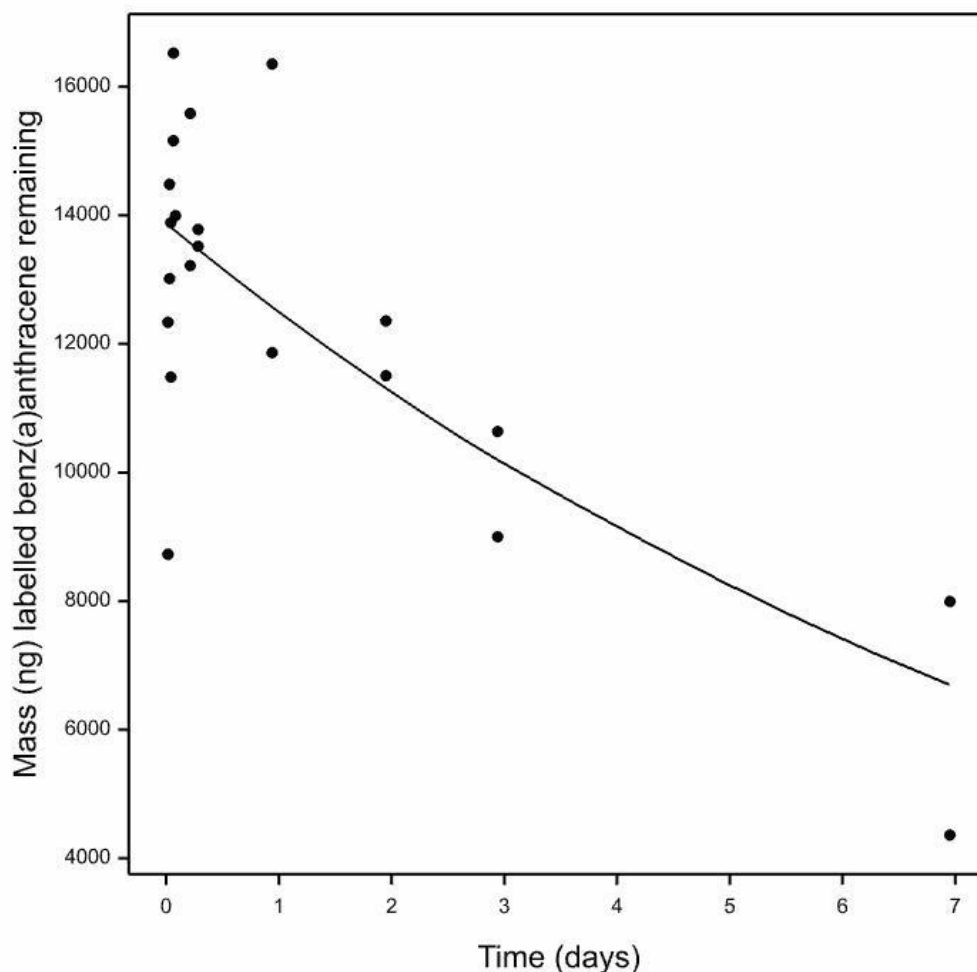
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875 **Fig. S12.** Observed data for offloading (corrected for fabrication and field blanks) of pyrene-  
876  $d_{10}$  from LDPE membranes over a deployment period of one week. The line was fitted using  
877 the standard simple exponential function in the non-linear regression routine of GenStat 15.

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881 **Fig. S13.** Observed data for offloading (corrected for fabrication and field blanks) of  
 882 benz(a)anthracene-d<sub>12</sub> from LDPE membranes over a deployment period of one week. The  
 883 line was fitted using the standard simple exponential function in the non-linear regression  
 884 routine of GenStat 15.  
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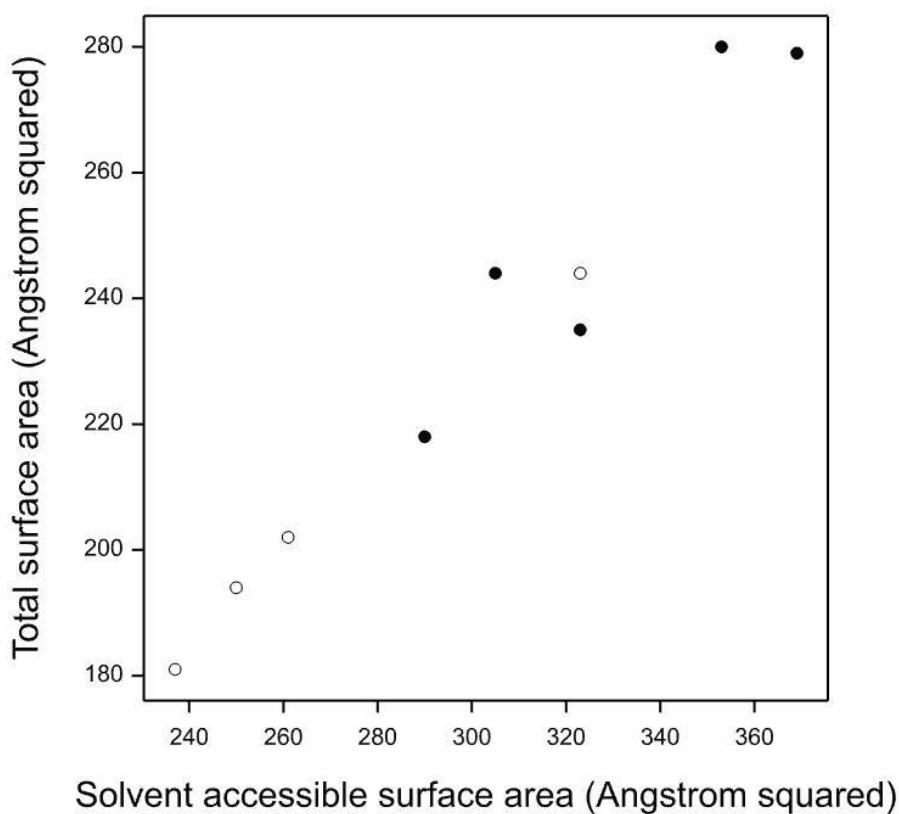
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### 887 **Prediction of diffusion coefficients of cVMS in LDPE**

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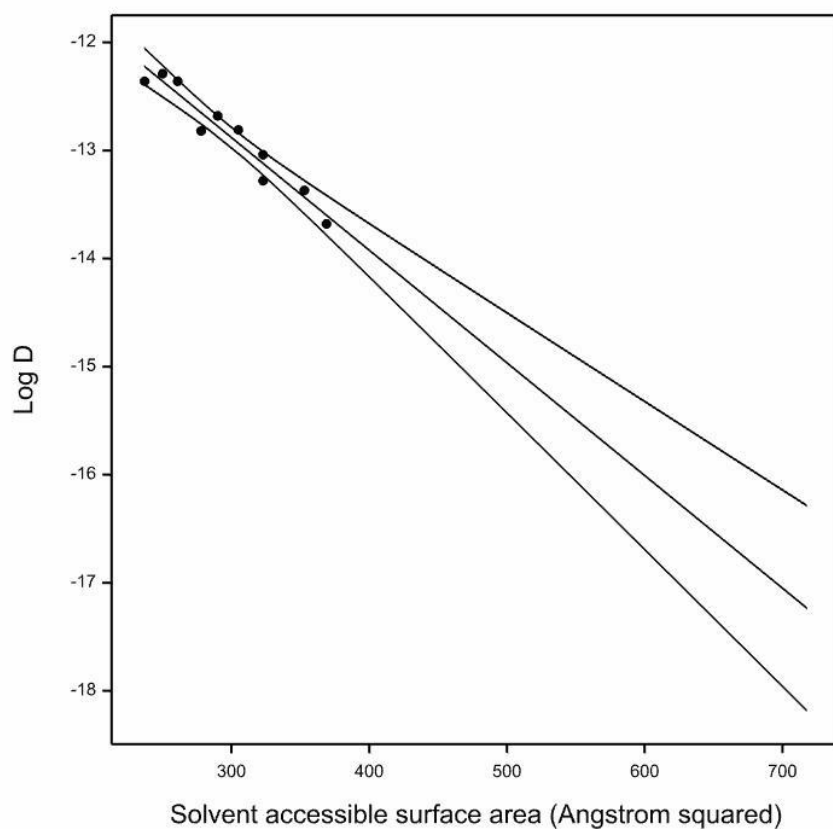
889 Log diffusion coefficient ( $D$ ,  $m^2 s^{-1}$ ) in LDPE can be predicted from total surface area (TSA)  
 890 of a molecule, and the relationship is similar for PAHs and PCBs (Rusina, Smedes and  
 891 Klanova, 2010). TSA values are not readily available in the literature for cVMS, but solvent  
 892 accessible surface areas (SASA) are available as predictions in Chemspider  
 893 ([www.chemspider.com](http://www.chemspider.com)) for PAHs, PCBs and cVMS. For the PAHs used as PRCs in this  
 894 study and a representative subset of PCBs drawn from the range presented in Rusina, Smedes

895 and Klanova (2010) were used to determine the relationship between TSA and SASA (Table  
896 S3 and Figure S14). A significant ( $p < 0.001$ ) linear regression (Genstat 15) of TSA on SASA  
897 accounted for 95% of the variation in TSA, with a slope of 0.75, and an intercept that was not  
898 significantly ( $p = 0.855$ ) different from zero. On the basis of this analysis, a linear regression  
899 (Genstat 15) of  $\log D$  in LDPE on SASA for the representative PAHs and PCBs was used to  
900 predict the  $\log D$  in LDPE for some cVMS of interest. The equation ( $\log D_{LDPE} = -9.82 -$   
901  $0.01 \text{ SASA}$ ) was significant ( $p < 0.001$ ). The values of SASA for the cVMS fell outside the  
902 range of the PAHs and PCBs and so the predicted values of  $\log D$  for the cVMS were  
903 extrapolations, and the confidence intervals were wider than for the set of predictors (Figure  
904 S15).  
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907 **Fig. S14.** Plot of the relationship between solvent accessible surface area (SASA) and total  
908 surface area (TSA) for PAHs and PCBs. Key: PAHs = open circles, PCBs = closed circles.  
909 SASA values from Chempider and TSA data from Rusina, Smedes and Klanova (2010).

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 913 **Fig. S15.** Regression of log diffusion coefficient ( $D$  in  $\text{m}^2 \text{s}^{-1}$  at  $20^\circ\text{C}$ ) in LDPE upon solvent  
 914 accessible surface area (SASA) for selected PAHs and PCBs (see Table S3) with fitted line  
 915 and 95% confidence limits (using Genstat 15). Log  $D$  in LDPE data taken from Rusina,  
 916 Smedes and Klanova (2010) and SASA data from Chemspider.

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928 **Table S3.** Physico-chemical properties of PCBs, non-deuterated PAHs and cVMS used to  
 929 predict the diffusion coefficient of the cVMS in LDPE.

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<b>Compound</b>	<b>MW</b>	<b>MV</b>	<b>TSA<sup>(1)</sup></b>	<b>SASA<sup>(2)</sup></b>	<b>Log <i>D</i><sup>(1)</sup></b>
PCB 18	258	191	218	290	-12.68
PCB 56	292	203	244	305	-12.81
PCB 104	326	214	235	323	-13.04
PCB 180	395	238	280	353	-13.37
PCB 204	426	250	279	369	-13.68
Acenaphthene	154	135	181	237	-12.36
Phenanthrene	178	158	198	261	-12.45
Fluorene	166	148	194	250	-12.29
Pyrene	202	160	213	278	-12.82
Benz(a)anthracene	228	192	244	323	-13.28
D4	296	310	<i>n/a</i>	482	-14.75*
D5	370	384	<i>n/a</i>	602	-15.98*
D6	445	458	<i>n/a</i>	718	-17.17*
MT	311	355	<i>n/a</i>	559	-15.54*
TK	385	430	<i>n/a</i>	678	-16.76*

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932 Key: MW = molecular weight ( $\text{g mol}^{-1}$ ), MV = molecular volume ( $\text{cm}^3 \text{mol}^{-1}$ ), TSA = total  
933 surface area ( $\text{Å}^2$ ), SASA = solvent accessible surface area ( $\text{Å}^2$ ),  $D$  = diffusion coefficient in  
934 LDPE at  $20^\circ\text{C}$  ( $\text{m}^2 \text{s}^{-1}$ ), \*predicted value using plot in Fig. S15,  $n/a$  = not available. <sup>(1)</sup>Data  
935 from Rusina, Smedes and Klanova (2010), <sup>(2)</sup>Data from Chemspider.

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937 cVMS have large molecular structures, comparatively large SASA and consequently low  
938 values of  $D$  (Table S3). These substances have less flexibility and hence will diffuse more  
939 slowly. This will reduce uptake rate and hence  $R_s$  (Rusina, Smedes and Klanova, 2010).

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