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

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ABSTRACT

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

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

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

1. Introduction

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

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

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

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

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

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

2. Methods

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

2.1 Preparation of LDPE samplers

LDPE (Fischer Scientific UK Ltd., with experimentally obtained estimates of density 0.94 g cm⁻³ and thickness 38 µm) was cut (12 cm × 5 cm; sampling area 120 cm²; volume 2.28 × 10⁻⁴ L; mass 0.21 g) and washed in *n*-hexane with gentle shaking (24 h). Sheets were dried (60°C, 3 h) to remove *n*-hexane, washed (2 x methanol; 24 h), dried and stored in sealed glass jars (1 L) submerged under methanol. This removed cVMS contamination and gave fabrication blanks < instrumental LoD. Sheets were spiked with three types of PRCs (i) ¹³C-D4/¹³C-D5, (ii) MT/TK and (iii) acenaphthene-d₁₀, fluorene-d₁₀, phenanthrene-d₁₀, pyrene-d₁₀ and benz(a)anthracene-d₁₂. Three solutions (methanol/water, 50/50 v/v) containing ¹³C-D4/¹³C-D5 (~ 90 µg L⁻¹), MT/TK (~ 85 µg L⁻¹) and d-PAHs (all ~ 100 µg L⁻¹) were prepared. Batches of twenty membranes were placed in amber glass jars (1 L), filled with appropriate spiking solution (no HS), sealed and rotated (24 h). Membranes were removed, wiped and soaked (2 × 12 h) in water to remove methanol and stored in water. Procedures were conducted in the clean air cabinet. Samplers were prepared shortly before use to avoid losses of PRCs. Three spiked samplers of each type were analysed prior deployment to ensure there was an adequate loading of PRCs (mean (± s.d.) masses (ng) spiked membranes were 3,010 ± 450 (¹³C-D4), 4,740 ± 580 (¹³C-D5), 3,750 ± 500 (MT) and 3,800 ± 980 (TK)), and the variability (r.s.d. (%)) was similar for ¹³C-D4/¹³C-D5 and MT (15, 12, 13% respectively) but larger (26%) for TK. Loading of d-PAHs was a function of log *K*_{ow}. The high variability in the amounts found in the spiked LDPE membranes may be attributed to several factors: difficulties in achieving uniform loading conditions with batches of 20 of membranes per spiking jar, and in handling membranes with very high loadings of PRCs, particularly where the compounds are volatile. Earlier work showed it was important to remove methanol used in the spiking solution from the membranes prior to deployment. This was achieved by water washes and storing the spiked sheets in water.

2.2 *In-field calibration*

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

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

2.3 Theory of passive sampling

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

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

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

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

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

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

At equilibrium equation 1 simplifies to:

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

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

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

$$M_s(t) = M_s(0) \exp(-k_e t) \quad \text{equation 5}$$

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

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

$$M_s(t) = C_w R_s t \quad \text{equation 6}$$

where $M_s(t)$ is the mass in the sampler after exposure time t , R_s is the sampler uptake rate (L day⁻¹).

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

$$R_s = K_{sw} k_e V_s \quad \text{equation 7}$$

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

3. Results and discussion

3.1 In-field trial

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

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3.2 Concentration of cVMS in effluent

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

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

Concentration (ng L ⁻¹) ⁽¹⁾	n	Mean	Standard error of mean	Standard deviation	Coefficient of variation	Median	Minimum	Maximum
D4	16 ⁽²⁾	50	10	35	70	40	15 ⁽²⁾	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 ⁽³⁾	49

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

3.3 Uptake of D4 and offloading of ¹³C-D4

Sets of samplers (unspiked, spiked ¹³C-D4/¹³C-D5, spiked MT/TK) were analysed for uptake of D4. Uptake was exponential and scatter between the independent sets of membranes was similar to that between the replicate membranes (Fig. 1). Data were fitted using an exponential model (GenStat 15). There was a significant regression ($p < 0.001$) and 99% of the variation in siloxane concentration was accounted for. k_e was 0.576 day⁻¹, M_{eq} was 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 L⁻¹) (log $K_{sw} = 4.4$). This was low compared

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

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

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

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

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

3.5 Uptake of D5 and offloading of ^{13}C -D5

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

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

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

3.6 Uptake and offloading of MT and TK

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

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

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

3.7 Offloading of d-PAHs

Uptake and offloading of PAHs by LDPE is understood (Adams et al., 2007; Allan et al., 2009; Booij et al., 2003; Booij and Smedes, 2010; Lohmann, 2012). Offloading of d-PAHs was used to link with data from other workers to set the cVMS results in context. Offloading rate constants were estimated by non-linear regression with the lower asymptote constrained to zero (Figures S9-S13). For less hydrophobic PAHs offloading rates were rapid, but that of benz(a)anthracene-d₁₂ was slower. Calculated (equation 7) sampling rates (Table 2) are based on the measured offloading rate constants and $V_s = 2.28 \times 10^{-4}$ L.

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

D5 and MT (2.1, 0.32, and 0.29 L day⁻¹ respectively) were low compared with those of the more non-polar PAHs, indicating membrane control, possibly due to very low diffusion coefficients in LDPE for cVMS. This was consistent with predictions of diffusion coefficients in LDPE based on molecular surface area. The predicted solvent accessible surface areas were high for the cVMS compared with equivalent PCBs and PAHs (see supplementary material), and the corresponding log diffusion coefficients (extrapolated from the relationship based on PAHs and PCBs) were small (D4 = -14.10, D5 = -15.94, D6 = -17.00, MT = -15.41, and TK = -16.60 measured as log m² s⁻¹ at 20°C) (Rusina, Smedes and Klanova, 2010).

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

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

⁽¹⁾Values for non-deuterated compound from Chemspider (www.chemspider.com);

⁽²⁾Calculated from log $K_{sw} = 0.972 \log K_{ow} - 0.13$ at water temperature of 13°C (from Booi et al., 2003);

⁽³⁾Average values of non-deuterated compounds from Hale et al., 2010; ⁽⁴⁾Values

for non-deuterated compound from Fernandez et al., 2009; ⁽⁵⁾Values for non-deuterated

compound from Adams et al., 2007; ⁽⁶⁾Values of K_{sw} had units of L L⁻¹.

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

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

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

3.8 Measurement of cVMS in water with LDPE samplers

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

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

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

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

4 Conclusions

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

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

estimates of key physico-chemical properties. However, the ability to measure cVMS at pg L⁻¹ is possible and these data would contribute to fate modelling and risk assessments.

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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 ⁻¹	296.6	370.8
Boiling point, °C	175	211
Melting point, °C	17	-44
Density, g cm ⁻³ at 25°C	0.95	0.95
Vapour pressure, Pa at 25°C	132	33.2
Water solubility, µg L ⁻¹ at 23°C	56	17
Henry's law constant, Pa m ³ mol ⁻¹ at 25°C	1,241,0000	3,342,000
Molar volume, cm ³ mol ⁻¹	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.

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Methods

Chemicals and glassware

D4, D5, MT and TK (> 98% purity) were from Sigma–Aldrich (Gillingham, UK). ^{13}C -D4 and ^{13}C -D5 (> 99% purity), used as internal standards and PRCs were from Moravek Biochemicals (Brea, California, USA). Deuterated PAHs (2 mg mL⁻¹ in acetone, > 99% purity) used as PRCs (acenaphthene-d₁₀, fluorene-d₁₀, phenanthrene-d₁₀, pyrene-d₁₀ and benz(a)anthracene-d₁₂) and internal standard (anthracene-d₁₀) were from Q_{mx} Laboratories (Thaxted, Essex, UK). HPLC grade *n*-hexane and methanol (Fischer Scientific UK Ltd. (Loughborough, UK)) and distilled-in-glass grade acetone (Rathburn Chemicals Ltd. (Walkerburn, UK)) from these sources had background concentrations of cVMS < limit of detection (LoD). Ultrapure water was from a Purite (Thame, UK) system. Other chemicals were from Fischer Scientific UK Ltd. or Sigma–Aldrich. Headspace (HS) glass vials (20 mL), butyl/PTFE septa (20 mm) and crimp caps were from Varian Inc. (Oxford, UK). Glassware was cleaned in detergent, rinsed three times with water, dried, rinsed again in either acetone or methanol, dried and stored in a clean air cabinet.

Preparation of standard solutions

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

598 Internal standards, ^{13}C -D4 (95.6 ng L⁻¹) and ^{13}C -D5 (95.8 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}C -D4, ^{13}C -D5) were prepared in *n*-hexane (0-1,200 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 ~ 10 ng L⁻¹). MT and TK were quantified against an external calibration (LoQ:
607 MT and TK ~ 5 ng L⁻¹). Mass spectral ions are shown in Table S2.

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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 µL) was added to crimped GC vial (2 mL) containing *n*-hexane
614 (900 µL). 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 µm film (HP-5 MS, Agilent)
617 column, using a temperature of 65°C (2 min) then 10°C min⁻¹ to 250°C (2 min). Splitless
618 injection (2 µL; at 250°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 ng mL⁻¹ for D4, D5, MT, TK, ^{13}C -D4 and ^{13}C -D5 respectively
620 (response 2-3 times greater than background in ten fabrication blanks).

LDPE membranes spiked with deuterated PAHs were extracted as above, with anthracene-d₁₀ (200 ng mL⁻¹) added as a standard. PAHs were analysed using a 430 model GC fitted with a VF-5ms capillary column (30 m long x 0.25 mm internal diameter, 0.25 µm film thickness) with a CP 8400 auto-sampler and interfaced to a 210-IT MS (Varian Inc.). Samples (1 µL) were injected (pressure pulse injection at 45 psi for 1 min) in splitless mode (split value open after 2 min, split ratio 1:50) with the injector maintained at 275°C. Helium flow rate was 1 mL min⁻¹. The oven temperature programme was: initial temperature 60°C (1 min) then to 150°C (300°C min⁻¹) then to 186°C (6°C min⁻¹) then to 280°C (4°C min⁻¹), hold for 20 min. The MS was operated in the scan mode with parent ions used for identification and quantification of the compounds. The concentrations of the d-PAHs were quantified from nine-point external calibration curves (10-2,000 ng mL⁻¹ in *n*-hexane).

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Table S2. Molecular ion, quantification and confirmation ions used for the GC/MS analysis of the cVMS and labelled standards in water samples and *n*-hexane extracts obtained from the 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
¹³ C-D4 (used as internal standard and PRC)		300	285	210, 135
¹³ C-D5 (used as internal standard and PRC)		375	355	270, 75

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

Time (h)	D4 (ng L ⁻¹)	D5 (ng L ⁻¹)	MT (ng L ⁻¹)	TK (ng L ⁻¹)
0	28	1,478	49	0*
1.87	42	1,754	68	21
1.87	47	1,834	68	7
3.08	69	2,297	80	6
3.08	75	2,272	91	30
5.17	54	1,352	65	49
5.17	36	1,320	55	20
6.25	152	3,562	39	0*
6.25	102	2,209	43	0*
22.17	19	1,665	43	26
22.17	2.2	1,223	34	8
46.33	24	757	37	25
46.33	65	1,226	30	22
70.23	34	1,425	19	20
70.23	15	1,348	32	9
166.8	36	3,089	59	7
166.8	38	2,439	54	9

LoQ = limit of quantification

Statistical analysis of concentrations of cVMS found in spot water samples

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

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

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

Fig. S1. Chemical structure of (a) octamethylcyclotetrasiloxane (D4) molecular weight: 296.6 g mol⁻¹, molecular formula: C₈H₂₄O₄Si₄ (b) decamethylcyclopentasiloxane (D5), molecular weight: 370.8 g mol⁻¹, molecular formula: C₁₁H₃₄O₅Si₅ (c) methyltris(trimethylsiloxy)silane (MT) molecular weight: 310.7 g mol⁻¹, molecular formula: C₁₀H₃₀O₃Si₄ and (d) tetrakis(trimethylsiloxy)silane (TK), molecular weight: 384.8 g mol⁻¹, molecular formula: C₁₂H₃₆O₄Si₅.

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Fig. S2. The effluent channel at Budds Farm waste water treatment plant used for deploying the passive samplers. Ropes indicate where the rigs deployed and secured to railings.

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

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}C -D4 and ^{13}C -D5, (2) MT and TK and (3) acenaphthene- d_{10} , fluorene- d_{10} , phenanthrene- d_{10} , pyrene- d_{10} and benz(a)anthracene- d_{12}) membranes.

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.

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

Fig. S7. Fitted values (standard exponential function in the non-linear regression routine of GenStat 15) for offloading of ¹³C-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.

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

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Fig. S9. Observed data for offloading (corrected for fabrication and field blanks) of acenaphthene- d_{10} from LDPE membranes over a deployment period of one week. The line was fitted using the standard simple exponential function in the non-linear regression routine of GenStat 15.

Fig. S10. Observed data for offloading (corrected for fabrication and field blanks) of fluorene-d₁₀ from LDPE membranes over a deployment period of one week. The line was fitted using the standard simple exponential function in the non-linear regression routine of GenStat 15.

Fig. S11. Observed data for offloading (corrected for fabrication and field blanks) of phenanthrene- d_{10} from LDPE membranes over a deployment period of one week. The line was fitted using the standard simple exponential function in the non-linear regression routine of GenStat 15.

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

Fig. S13. Observed data for offloading (corrected for fabrication and field blanks) of benz(a)anthracene-d₁₂ from LDPE membranes over a deployment period of one week. The line was fitted using the standard simple exponential function in the non-linear regression routine of GenStat 15.

Prediction of diffusion coefficients of cVMS in LDPE

Log diffusion coefficient (D , m² s⁻¹) in LDPE can be predicted from total surface area (TSA) of a molecule, and the relationship is similar for PAHs and PCBs (Rusina, Smedes and Klanova, 2010). TSA values are not readily available in the literature for cVMS, but solvent accessible surface areas (SASA) are available as predictions in Chemspider (www.chemspider.com) for PAHs, PCBs and cVMS. For the PAHs used as PRCs in this study and a representative subset of PCBs drawn from the range presented in Rusina, Smedes

and Klanova (2010) were used to determine the relationship between TSA and SASA (Table S3 and Figure S14). A significant ($p < 0.001$) linear regression (Genstat 15) of TSA on SASA accounted for 95% of the variation in TSA, with a slope of 0.75, and an intercept that was not significantly ($p = 0.855$) different from zero. On the basis of this analysis, a linear regression (Genstat 15) of $\log D$ in LDPE on SASA for the representative PAHs and PCBs was used to predict the $\log D$ in LDPE for some cVMS of interest. The equation ($\log D_{LDPE} = -9.82 - 0.01 \text{ SASA}$) was significant ($p < 0.001$). The values of SASA for the cVMS fell outside the range of the PAHs and PCBs and so the predicted values of $\log D$ for the cVMS were extrapolations, and the confidence intervals were wider than for the set of predictors (Figure S15).

Fig. S14. Plot of the relationship between solvent accessible surface area (SASA) and total surface area (TSA) for PAHs and PCBs. Key: PAHs = open circles, PCBs = closed circles. SASA values from Chemspider and TSA data from Rusina, Smedes and Klanova (2010).

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

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

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

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