Effect of Aldrich humic acid on water–atmosphere transfer of decamethylcyclopentasiloxane

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ABSTRACT

The behaviour of the cyclic volatile methyl siloxane (cVMS) decamethylcyclopentasiloxane (D5) in surface waters is explored using a combination of laboratory experimentation and mathematical modelling. In the laboratory experiment, changes were observed in the concentration of radiolabelled D5 in open stirred beakers containing mineral medium with different concentrations of added Aldrich humic acid over 120 h. Although D5 is very volatile, its strong affinity for dissolved organic carbon (DOC) reduced the rate of water to air transfer significantly. The data were well described using a simple partitioning model which accounted for hydrolysis and for depth and DOC changes resulting from sampling and evaporation, although there was some evidence for the formation of a hypothetical bound residue with increasing time. The model was used to derive effective values for the partition coefficient between DOC and water [log(K_{DOC})]. These values were relatively consistent across five treatments and varied between 5.04 and 5.40 log(L kg^{-1}), with no systematic treatment bias. These values are significantly higher than previously published experimental estimates of K_{OC} for D5 but more than two orders of magnitude lower than some K_{OC} estimates based on the octanol:water partition coefficient (K_{OW}). The data confirm that volatilisation will be an important loss mechanism from surface waters for D5, although the rate of loss will decrease with increasing DOC concentration.

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1. Introduction

Cyclic volatile methyl siloxanes (cVMS) are used in a range of applications including personal care products. They possess a rather unusual combination of physico-chemical properties, including both hydrophobicity and volatility, which bestow a number of benefits to such products. However, concerns have been raised recently regarding their behaviour in the natural environment after their release. Due to their great hydrophobicity, cVMS are generally not toxic at the limit of water solubility (e.g. Hobson et al., 1997) but are not biodegradable, although they do undergo hydrolysis. In addition, they have high bioconcentration factors implying some potential for bioaccumulation in aquatic organisms, although air breathing organisms will rapidly eliminate them via the lungs (Brooke et al., 2008). Furthermore, they have the potential for long range transport in the atmosphere, although they are known to break down relatively quickly by reacting with OH radicals to form OH-substituted silanols. This is by far the dominant loss mechanism for siloxanes in the atmosphere (Atkinson, 1991). Silanols, in turn are likely to be progressively removed from

the atmosphere by wet and dry deposition as they become increasingly OH-substituted (Hobson et al., 1997; Whelan et al., 2004).

One of the most widely used cVMS materials in personal care products is decamethylcyclopentasiloxane (D5: $C_{10}H_{30}Si_5O_5$). Salient properties of D5 are shown in Table 1. There is some uncertainty about the exact values of the principal partition coefficients. The value of the log octanol:water partition coefficient, log(K_{OW}), is currently estimated to be about 8.05 (Xu and Kozerski, 2007) which is considerably higher than the previously reported value of 5.2 (Bruggeman et al., 1984). Xu and Kozerski (2007) also report a measured value for the log octanol:air partition coefficient, log(K_{OA}), of approximately 5.04 which suggests that the log air:water partition coefficient, log(K_{AW}), has a value of 3.01 (by difference). In comparison, the expected value of log(K_{AW}) based on the ratio of saturation vapour pressure and aqueous solubility is approximately 2.43 (Table 1). Only one measured estimate of the organic carbon:water partition coefficient (K_{OC}) has been previously reported in the primary literature. David et al. (2000) derived a value for log(K_{OC}) of 4.38 using an equilibrium partitioning approach in headspace vials containing either raw waste water or a synthetic solution consisting of KCl, Aldrich humic acid and resuspended sludge solids. Whilst this value is consistent with a value of log(K_{OW}) of 5.2, it appears to be rather low compared with the revised log(K_{OW}) estimate of 8.05.

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Table 1
Current estimates of salient properties of D5. Temperature-dependent parameters were determined at 20 °C.

Molar mass[a] (g mol^{-1})	Aqueous solubility[a] (g m^{-3})	Vapour pressure[a] (Pa)	log(K_{OW})[b]	log(K_{OA}) [b]	log(K_{AW})[b]
371	0.017	30.4	8.05	5.04	3.01

[a] From Mazzoni (1997).
[b] From Xu and Kozerski (2007).

Accurate determination of partition coefficients is essential for reliable prediction of chemical behaviour in the environment. The partition coefficients for D5 imply that a significant fraction of any emission to the waste water stream will be removed in waste water treatment via a combination of volatilisation and sorption to sludge solids. D5 discharged to fresh surface waters will have four main fate pathways: (1) volatilisation; (2) hydrolysis; (3) sorption to colloidal or suspended organic fractions in the water column and on the bed and banks of the receiving water body and (4) advection to lower river reaches and eventually into estuarine and marine systems. The results of measured hydrolysis experiments conducted by Dow Corning (cited by Brooke et al. (2008)) suggest that hydrolysis is expected to be relatively slow in freshwaters at environmentally realistic temperature and neutral pH. At pH 7 and 9 °C D5 is estimated to have a half life of approximately 449 d. At higher and lower pH values, the half life is expected to be significantly lower. For example at pH 8 and 25 °C the hydrolysis half life is expected to be 9 d, although at pH 8 and 9 °C it is 64 d. Given these relatively slow hydrolysis rates and given the propensity of D5 to partition from water to air, it is reasonable to expect volatilisation to make a significant contribution to losses from water. However, the affinity of D5 for dissolved and particulate carbon is likely to influence this contribution. David et al. (2000), for example, report significant reductions in the apparent K_{AW} of D5 measured in simulated waste water using equilibrium partitioning in closed headspace vials. In this paper, we attempt to ascertain the importance of volatilisation as a loss mechanism and the role of dissolved organic carbon concentration in reducing the air–water flux. We also derive an estimate for the effective partition coefficient between dissolved organic carbon (DOC) and water.

2. Materials and methods

The rate of D5 volatilisation was estimated in a laboratory experiment in which the concentration of ^{14}C-labelled D5 was measured in stirred beakers at various intervals over time. Reconstituted water was prepared according to the method described in ASTM (2002). Total hardness (CaCO$_3$) was 145 mg L^{-1} using the titration method described in Eaton et al. (1995).

A concentrated stock of 1000 mg L^{-1} humic acid (Aldrich humic acid ex Sigma) was prepared in the ASTM water and filtered through deionised (Millipore) water-rinsed Whatman GF/C glass microfibre filters (pore size 1.2 μm). The filtrate was analysed for TOC/DOC using a Shimadzu TOC-V total organic carbon analyzer. The mean DOC concentration from three assays was 228.8 (SD = 2.7) mg L^{-1}.

[methyl-^{14}C]-D5 (69 mCi/mmol or 186.1 μCi mg^{-1}) was purchased from Moravek Biochemicals Inc., Brea, California, USA. A stock solution of [methyl-^{14}C]-D5 in acetonitrile was prepared and, by liquid scintillation counting, was shown to have an activity of approximately 96 μCi mL^{-1}. The radiochemical purity of [methyl-^{14}C]-D5 was checked by using a SpectraSystem HPLC (Thermo Separation Products, Hemel Hempstead) fitted with a Polymer C18 (250 × 4.6 mm, 5 μm particle size) HPLC column (YMC Polymer Labs Europe, Dinslaken, Germany) and using a 5–90% acetonitrile gradient method at a flow rate of 1 mL min^{-1}.

Radio-detection was performed using a Beta-RAM radiodetector (LabLogic Systems Ltd., Sheffield, UK) fitted with a 500 μL flow cell and with 100% post-column liquid scintillation mixing using Ultima-Flo M cocktail (Perkin Elmer Life Sciences) at 1 mL min^{-1}. The [methyl-^{14}C]-D5 was shown to be approximately 94.2% radiochemically pure by HPLC. As a suitable method for purification was not available at the time the experiments were conducted, and because of the volatile nature of the test substance, no purification was attempted. The impurities were accounted for in the model and are not believed to affect the interpretation of the data.

Aliquots of the humic acid stock filtrate (228 mg mL^{-1} DOC) were diluted with ASTM water to give solutions with the following nominal concentrations: 0.5, 1, 2.5, 5 and 10 mg C L^{-1}. Duran bottles (1 L) were filled to the brim (no headspace) with each humic acid solution together with a mineral medium control. A 3 μL aliquot of stock [methyl-^{14}C]D5 in acetonitrile (equivalent to approximately 600 000 dpm or 1.45 g of [methyl-^{14}C]-D5 was added to each bottle and the sample shaken thoroughly to mix. Aliquots (3 × 5 mL) were removed and mixed with 10 mL of Starscint (Perkin Elmer Life Sciences) for liquid scintillation counting in a Beckman-Coulter LS6000TA scintillation counter to determine the initial concentration of ^{14}C in each sample. The bottles were topped up to the brim with the appropriate humic acid solution or ASTM water, tightly capped and stored in the dark at ambient temperature (~20 °C) for approximately 21 h, after which a repeat assay for ^{14}C was conducted. Aliquots (300 mL) from each humic acid or ASTM water control solution were decanted into 400 mL glass beakers (n = 3 per treatment) and slowly stirred using magnetic glass followers. The height of 300 mL water in the beaker was measured and found to be 85 mm. Immediately after decanting (t_0) and after 1, 4, 7, 10, 24, 48 and 120 h, 3 × 5 mL aliquots of each solution were assayed for ^{14}C by liquid scintillation counting. The temperature of each solution was also recorded at each sampling point. Temperature was observed to be constant throughout the experiment at 25 °C. The average pH at t_0 was 8.24 with SD = 0.0147. After the final time point, the volume of water in each beaker was measured and, after correction for the 15 mL volumes withdrawn for ^{14}C assay, the rate of water evaporation was calculated.

3. Modelling

A numerical model was constructed to simulate the behaviour of D5 in the beaker system described above (see Fig 1). It is assumed that radioactivity can be lost from the water column only via volatilisation from the dissolved phase. Observations from preliminary experiments showed that only 0.5–1% of the ^{14}C present at t_0 was associated with the glass beaker and stirrer bar at the end of the experiment. Deposition of sorbed material to the walls of the (stirred) beaker was, therefore, assumed to be negligible over the course of the experiment (120 h). There was no evidence of any settling out of solid residues during the experiment.

At any point in time, the total mass of radiolabel in the system (M_T) is

$$M_T = M_S + M_L + M_H + M_N \tag{1}$$

where M_S is the mass of radiolabelled D5 in the sorbed phase, M_L is the mass of radiolabelled D5 in the dissolved phase, M_H is the mass