# Monitoring and modelling of siloxanes in a sewage treatment plant in the UK

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## ABSTRACT

Monitoring of cyclic volatile methylsiloxanes (cVMS) carried out at Anglian Water's Broadholme sewage treatment plant (STP) is described. The method deployed used headspace gas chromatography/mass spectrometry (HS-GC/MS) and the addition of isotopically labelled cVMS to correct for partitioning in samples containing high levels of particulate and dissolved organic carbon. The method was capable of measuring cVMS in raw sewage samples, with recoveries of 80%, 85% and 71% respectively, for $D_4$, $D_5$ and $D_6$. The limit of quantification was 0.2 μg $L^{-1}$ for all three substances. Recoveries close to 100% were observed for all cVMS spiked into treated effluent (LOQ = 0.01 μg $L^{-1}$). Despite the volatile nature of cVMS and its ubiquitous presence in the ambient atmosphere, the methods deployed showed excellent recoveries, reproducibility and quantification limits. A distinct diurnal variation in cVMS concentration, probably linked with the use of personal care products was observed for raw sewage but not in treated sewage effluent. The estimated per capita consumption of $D_5$ (~2.7 mg cap$^{-1}$ d$^{-1}$) derived for the population served by this plant was significantly lower than that derived in the Environment Agency (UK) risk assessment (11.6 mg cap$^{-1}$ d$^{-1}$). The cVMS were highly removed during sewage treatment with efficiencies greater than 98%. The methods and findings of this pilot study can be used as the basis for future studies on the fate of cVMS substances in STPs.

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## 1. Introduction

Cyclic volatile methylsiloxane (cVMS) materials are encountered in a range of home and personal care products (Horii and Kannan, 2008), due to the beneficial properties they bestow. Benefits such as ease of spreading and the ability to carry and release active ingredients are directly related to the physico-chemical properties of cVMS including low surface tension, hydrophobicity and volatility (Allen et al., 1997). Volatility and hydrophobicity are also key influences in the environmental fate and behaviour of cVMS after use and emission to the environment (Brooke et al., 2009a,b,c).

Previously it has been suggested that the majority of the most widely used cVMS, decamethylcyclopentasiloxane ($D_5$) will be lost from "leave-on" personal care products to the atmosphere (Brooke et al., 2009b), where it is expected to be broken down via reaction with hydroxyl radicals. $D_5$ is not thought to be removed from the atmosphere through partitioning to surface media (McLachlan et al., 2010).

However, due to the widespread use of $D_5$ and other cVMS in a range of personal care products, not all emissions will be to the atmosphere. "Rinse-off" products are likely to result in emissions to wastewater, where adsorption and volatilisation play significant and competing roles in the removal of cVMS during sewage treatment. For example, although in surface waters it was shown that volatilisation will be an important loss mechanism for $D_5$, the rate of loss decreased with increasing dissolved organic carbon (DOC) concentration (Whelan et al., 2009). As $D_5$ has not been shown to be biodegradable in standard tests, this suggests that in sewage treatment plants (STPs) the estimated removal via sludge solids, air and final effluent will be mainly determined by the treatment type (e.g. secondary activated sludge, secondary biological filter or tertiary), hydraulic retention time and DOC and particulate organic carbon (POC) concentrations in the final effluent. The estimated removals calculated (using default settings) by the SimpleTreat model (Struijs, 1996) in sewage treatment plants for $D_5$ and the related materials $D_4$ and $D_6$ were 95.3%, 96.4% and 93.5%, respectively (Brooke et al., 2009a,b,c). These studies also estimated that the per capita emissions to wastewater were 0.4, 11.6 and 1.3 mg cap$^{-1}$ d$^{-1}$ for $D_4$, $D_5$ and $D_6$, respectively.

Although previous work has shown the presence of $D_4$, $D_5$ and $D_6$ in untreated sewage samples at various locations, few studies have also measured concentrations in final effluent samples (Brooke et al., 2009a,b,c) in the same plant and at the same time. In addition, few if any studies have measured cVMS concentrations

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(as well as flow) over 24 h in order to more accurately estimate the amounts entering and leaving STPs. Recently workers have shown that the use of grab samples can produce misleading data when assessing the fate of personal care product ingredients in sewage treatment plants (Ort et al., 2010). In addition, most reported studies do not adequately describe the necessary quality control of background cVMS levels that are required to measure these substances, even in STP samples.

A previous study highlighted the major uncertainties in estimating chemical emission rates for volatile chemicals used in personal care products and suggested that measured concentrations in waste water are needed to refine exposure assessments (Price et al., 2010). In addition, no previous estimates of cVMS materials in wastewater influent and effluent have been reported in the open literature. In order to address this, we attempted to accurately measure the concentrations of $D_4$, $D_5$ and $D_6$ in untreated and final effluent in order to estimate the per capita loading of cVMS to an STP and to determine the removal of cVMS during sewage treatment in order to support the environmental risk assessment.

Few published methods exist with which to carry out these aims and a previously reported method for the analysis in surface water was adapted (Sparham et al., 2008). This is a partition-based method (headspace) which has several advantages including high sample throughput, low limits of quantification and the potential to measure dissolved and total concentrations of siloxanes in the same sample. The challenge was to adapt this method to deal with samples that contain much higher levels of organic carbon as well as samples that contain low concentrations of cVMS and which could be influenced by volatile losses during sampling and contamination during sample processing. The present study describes the findings of the work carried out at Broadholme sewage treatment works.

## 2. Methods

### 2.1. Solvents, standards and materials

Octamethylcyclotetrasiloxane ($D_4$), decamethylcyclopentasiloxane ($D_5$) and dodecamethylhexacyclosiloxane ($D_6$) were purchased from Sigma–Aldrich (>98% purity, Gillingham, UK). The internal standards used in the study were $^{13}C_4$-octamethylcyclotetrasiloxane, $^{13}C_5$-decamethylcyclopentasiloxane and $^{13}C_6$-dodecamethylcyclohexasiloxane ($^{13}C_4$–$D_4$, $^{13}C_5$–$D_5$ and $^{13}C_6$–$D_6$), synthesised by Moravek Biochemicals (>99% pure, Brea, CA, USA). Solvents were high pressure liquid chromatography grade and purchased from Rathburn Chemicals (Walkerburn, UK). Ultrapure water was obtained from a Milli Q Plus® system (Millipore, Watford, UK). Filters for dissolved organic carbon (DOC) determination were obtained from Millipore (MF-Millipore, cellulose, 0.45 μm).

### 2.2. STP sampling

Cyclic volatile methylsiloxanes (cVMS) were measured at Broadholme sewage treatment plant (Ditchford Lane, Wellingborough, UK, SP 940 688). Broadholme STP treats predominately domestic waste (industrial input < 15% of organic load) and serves an estimated population of 179,841. Samples were taken on the 22/23 March 2010 and the 07/08 of July 2010.

Autosamplers (Xian 1000, Bühler) were set up to collect degritted raw sewage and final effluent. The autosamplers contained 8 × 1 L glass tubes and samples were collected every 1½ h (~500 mL shot, two shots per tube, 1.5 h apart, a total of 16 aliquots over 22.5 h). Sampling tubes were cleaned using laboratory detergent, Ultrapure water, methanol and finally Ultrapure water. Samples were thoroughly mixed in the sampling tube and

prepared in the field by transfer to headspace vials, spiked with internal standard and crimped as described in Sparham et al. (2008). Additional grab samples were taken on 07/08 of July using a stainless steel vessel and transferred to 1 L glass bottles (methanol rinsed, Ultrapure water rinse and a final rinse with site water) at sites depicted in Fig. 1.

### 2.3. Sample preparation

Raw sewage samples were typically diluted one in 20 before analysis by headspace-gas chromatography/mass spectrometry (HS-GC/MS). Dilutions were carried out in the laboratory by taking 10 mL aliquots from a continuously stirred influent sample and diluting to 200 mL with Ultrapure water in a volumetric flask. Manipulation of raw sewage samples (and appropriate blanks) was always carried out within a fume cupboard in a controlled laboratory, due to the hazardous nature of the samples. Effluent samples were prepared in the field to avoid losses due to volatilisation, as described in Sparham et al. (2008). Briefly, the internal standards ($^{13}C_4$–$D_5$, $^{13}C_5$–$D_5$ and $^{13}C_6$–$D_6$) were added to all calibration solutions, field blanks and effluent samples to give a final concentration of 96 ng L$^{-1}$. All spiking was carried out using microlitre syringes with the needle inserted well below the liquid surface (15 μL in 15 mL of sample or diluted sample). After the addition of the standards, the vials were immediately capped in preparation for analysis. Blanks of Ultrapure water were analysed alongside samples in the field. All critical standard preparation was carried out in a clean air cabinet (Bigneat, Waterlooville, UK).

### 2.4. Method validation

Raw sewage was spiked with cVMS in the following manner. A 100 mL aliquot of the stirred raw sewage was spiked at levels in the range 1–32 μg L$^{-1}$ of $D_4$, $D_5$ and $D_6$. After stirring for 60 min, headspace samples were prepared as described earlier. High level spiked raw sewage samples were diluted 10–100 mL in Ultrapure water using a volumetric flask, before adding 1.5 mL of the diluted sample to 13.5 mL of Ultrapure water in a headspace vial for analysis. Effluent was spiked with cVMS directly in headspace vials (typically at levels of 0.640 μg L$^{-1}$ of $D_4$, $D_5$ and $D_6$ carried out in the clean air cabinet). The stability of raw sewage and effluent samples was addressed prior to sampling and the stability of effluent was also assessed during field work.

Verification of the stability of samples in the collection tubes, as collected using the Xian 1000 autosampler, was addressed in the following manner. Sample tubes containing effluent (0.221 μg L$^{-1}$) and raw sewage (11.6 μg L$^{-1}$) were placed in the clean air cabinet and left for 168 h at ambient temperature. The samples were analysed for $D_5$ initially and at selected time points. In tube stability in the field was assessed for an effluent, analysed immediately after collection in the auto-sampler containing 0.004, 0.34 and 0.08 μg L$^{-1}$ $D_4$, $D_5$ and $D_6$, respectively with repeat analysis after 26 h in situ (device packed with ice).

### 2.5. HS-GC/MS analysis

Briefly, samples were analysed as follows (full details of the method can be found in Sparham et al. (2008): HS-GC/MS analysis of cVMS was performed on an Agilent Technologies (Stockport, UK) 6890/5975 GC/MS system fitted with a Gerstel MPS2 autosampler, enabling 1 mL injections of the headspace at 80 °C. Helium carrier gas (Technical grade, Air Products, Crewe, UK) was used at a flow of 1 mL min$^{-1}$ through a DB-Wax column (30 m × 0.25 mm internal diameter, 0.5 μm film thickness). The MS was operated in electron ionisation (EI) mode and single ion monitoring (SIM) with ions $m/z$ 73, 267 and 355 monitored for $D_5$, ions $m/z$ 133, 207 and 281 mon-