Chemosphere 93 (2013) 741–748

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Determination of cyclic volatile methylsiloxanes in water, sediment, soil, biota, and biosolid using large-volume injection–gas chromatography–mass spectrometry

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HIGHLIGHTS

- A series of methods to determine D4, D5, and D6 in water, sediment, soil, biota, and biosolid were developed.
- Sealed extraction system were used to avoid volatilization and contamination by indoor/laboratory air.
- Large volume injection enhanced detection limits for cVMS in environmental samples.
- cVMS were stable for 3 weeks in WWTP influent and effluent stored at 4 °C and in sediment stored at −20 °C.

ARTICLE INFO

Article history:
Available online 1 December 2012

Keywords:
Siloxanes
Large-volume injection
Water
Sediment
Soil
Biota

ABSTRACT

Several methods were developed to detect the cyclic volatile methylsiloxanes (cVMSs) including octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) in water, sediment, soil, biota, and biosolid samples. Analytical techniques employed to optimize measurement of this compound class in various matrices included membrane-assisted solvent extraction in water, liquid–solid extraction for sediment, soil, biota, and biosolid samples. A subsequent analysis of the extract was conducted by large-volume injection–gas chromatography–mass spectrometry (LVI–GC–MS). These methods employed no evaporative techniques to avoid potential losses and contamination of the volatile siloxanes. To compensate for the inability to improve detection limits by concentrating final sample extract volumes we used a LVI–GC–MS. Contamination during analysis was minimized by using a septumless GC configuration to avoid cVMS's associated with septum bleed. These methods performed well achieving good linearity, low limits of detection, good precision, recovery, and a wide dynamic range. In addition, stability of cVMS in water and sediment was assessed under various storage conditions. D4 and D5 in Type-I (Milli-Q) water stored at 4 °C were stable within 29 d; however, significant depletion of D6 (60–70%) occurred only after 3 d. Whereas cVMS in sewage influent and effluent were stable at 4 °C within 21 d. cVMS in sediment sealed in amber glass jars at −20 °C and in pentane extracts in vials at −15 °C were stable during 1 month under both storage conditions.

1. Introduction

Cyclic volatile methylsiloxanes (cVMSs) including octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) were investigated due to their reported volume of usage, persistence, and potential to bioaccumulate (Muir and Howard, 2006; Howard and Muir, 2010; Kierkegaard et al., 2011). cVMS substances are widely used as ingredients for cosmetic and personal care products including antiperspirant, baby products, shampoo, nail polishes, etc. (Hoh and Mastovska, 2008; Wang et al., 2009; Gouin et al., 2012).

Analytical determination in the laboratory of these compounds was complicated by the ubiquitous nature of cVMS; hampering the accurate measurement in the environment (Varaprath et al., 2006). Indoor and outdoor air, solvent, caps, silicone-based GC injection septa, GC glass-liners containing silanized glass-wool, the use of personal care products by laboratory technicians, and even GC columns were known to be sources of cVMS contamination (Varaprath et al., 2006; Horii and Kannan, 2008; Wang et al.,

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http://dx.doi.org/10.1016/j.chemosphere.2012.10.044

2009). Laboratory air was identified as one of the sources of contamination in the extraction of water samples (Sparham et al., 2008) and ostensibly for other matrices as well. To avoid or minimize the contamination from air, particular measures were taken to minimize exposure during preparation and processing of samples. Kierkegaard and McLachlan (2010) used a clean air cabinet under a laminar flow with charcoal and particle filtered air to prepare and process air samples. Sparham et al. (2011) also processed the sediment samples in a clean air cabinet with a carbon filtration system. Warner et al. (2010) extracted their sediment and biota samples in a fume hood within a clean room facility while Kierkegaard et al. (2010) designed a closed purge and trap system to analyze biota.

In addition to contamination arising from the extraction procedure, other sources also originated from instrumental analysis. The main source of cVMS in the analytical instrument was from the inlet septum made of silicone rubber (Horii and Kannan, 2008). At high temperatures, the septum will release cVMS substances that interfere with the final quantitative analysis. To avoid or reduce the contamination during instrumental analysis, a new atmospheric pressure chemical ionization-tandem mass spectrometry (APCI-MS/MS) method was developed to directly analyze cVMS in gaseous matrices without extraction or prior chromatographic separation (Badjagbo et al., 2009a). This new method prevented contamination from GC system components and had been successfully applied to the analysis of siloxanes in air and biogas in realistic environmental matrices (Badjagbo et al., 2009b). However, this method was not easily adapted to trace analysis of samples from remote locations due to the specialized instrumentation and relative high detection limits (4–6 $\mu g\ m^{-3}$).

Recently, several studies developed the analytical methods of cVMS in water (Sparham et al., 2008), sediment (Sparham et al., 2011), and biota (Kierkegaard et al., 2010) samples. Sparham et al. (2008) reported the headspace method for D5 in water samples. The static headspace method can be used for clean water samples not samples such as influent and effluent with high organic matters since cVMS have high organic carbon–water partition coefficients ($\log K_{OC} > 4$) (Wang et al., 2012a). Sparham et al. (2011) also reported liquid–solid extraction and accelerated solvent extraction methods for D4 and D5 in sediment samples. Kierkegaard et al. (2010) developed a very good purge and trap method to analyze cVMS in biota samples, but this method needs a special designed extraction apparatus and very long purge time (24–72 h) using high purity nitrogen.

Therefore, it was necessary to develop simple, effective, and reliable methods to analyze siloxanes in environmental matrices. A series of methods to determine targeted D4, D5, and D6 in water, sediment, soil, biota, and biosolid were developed in this study. These methods all used the sealed extraction system to extract cVMS in sample matrices to avoid air contamination and volatilization. These methods employed the use of low solvent extraction volumes and no evaporation steps to avoid cVMS losses. Following evaluation of these methods, they were applied to determine the cVMS in industrial wastewater, influent, effluent, receiving water, and biosolid collected from or near wastewater treatment plants (WWTPs), in sediment collected near the WWTPs, biosolid amended soil, and biota.

2. Materials and methods

2.1. Chemicals

D4, D5, and D6 were purchased from Gelest (Purity: 98%, Morrisville, PA., USA). $^{13}C_4$–D4, $^{13}C_5$–D5, and $^{13}C_6$–D6 were acquired from Moravek (Purity: 98%, Brea, CA, USA), and were used as the internal standards (added prior to extraction) of non-labeled cVMS to calculate their concentrations in all samples. Deuterium-labeled naphthalene (naphthalene-D_8) was obtained from Sigma–Aldrich Supelco (Oakville, ON, Canada) and was used as the internal standard (added prior to analysis) of labeled cVMS to calculate their recoveries and to compensate for variations in injection proficiency and instrument response in all samples. Pesticide grade pentane and acetonitrile were purchased from Fisher (Nepean, ON, Canada). Pesticide grade methanol and hexane were purchased from Caledon Laboratories (Georgetown, ON, Canada).

2.2. Membrane-assisted solvent extraction of water samples

Membrane-assisted solvent extraction (Hauser and Popp, 2001; Hauser et al., 2002, 2004) technology (GERSTEL, Germany) was used to extract the cVMS in water. The polyethylene membrane was prewashed three times with both methanol and pentane. Since cVMS are highly volatile, the water samples were processed without filtration to avoid losses and contamination from extra handling and processing. To keep all concentrations within the linear range of the standard curve, 1:10 dilutions for effluent, 1:10 and 1:100 dilutions for influent, and 1:500, 1:1000, and 1:5000 dilutions for industrial wastewater were prepared. Each 100 mL of water sample was spiked with a mixture of $^{13}C_4$–D4, $^{13}C_5$–D5, and $^{13}C_6$–D6 (0.01 μg/sample). A stainless steel membrane holder and membrane were quickly inserted and held in the neck of the bottle. Pentane (0.5 mL) was added to the membrane as the extracting solvent followed by the addition of 1-μg naphthalene-D_8 in 10 μL of pentane. The bottle was immediately crimp capped with an aluminum seal fitted with a Teflon faced butyl rubber septum. Using a Brunswick incubator shaker, the water sample in the bottle was extracted at 28.5 °C for 60 min. The temperature was set below boiling point of pentane (35 °C) and the extraction time was referenced to the study by Hauser et al. (2002). After extraction, the pentane extract was removed and analyzed using a large-volume injection with gas chromatography−mass spectrometry (LVI−GC−MS).

2.3. Liquid–solid extraction of sediment, soil, biota, and biosolid samples

Liquid–solid extraction technology was used to extract cVMS in sediment, soil, biosolid, and biota samples. This method has been successfully used by Sparham et al. (2011) for the analysis of D4 and D5 in sediment. It was modified for the analysis of D4, D5, and D6 in our study that pentane was used as one of extraction solvents instead of hexane due to the need of large-volume injection. Triplicate aliquots of approximately 1.0 ± 0.2 g (wet weight sediment and soil) were measured gravimetrically in separate 50-mL glass centrifuge tubes for extraction. Concurrently from the main collection jars, a sub sample of each sediment sample was taken to calculate the dry weight. A mixture of 2-μg $^{13}C_4$–D4, $^{13}C_5$–D5, and $^{13}C_6$-D6 in a total volume of 50 μL methanol was added directly to the sample and vortexed lightly. After 20 min, acetonitrile (5 mL) and pentane (5 mL) were added to the sample and briefly vortexed. Tubes were placed on an orbital shaker for 60 min at 175 rpm followed by centrifugation at 1500 rpm for 10 min. Pentane (1.8-mL supernatant) was transferred to 2-mL GC vials. Prior to analysis, 1-μg naphthalene-D_8 in 10 μL of pentane was added to each vial as the performance standard. After the extraction, the sample was analyzed using LVI−GC−MS.

All biota extraction procedures were conducted at the National Laboratory for Environmental Testing's Ultra-Trace Laboratory (Class 10 000) in Burlington, ON. Due to high $\log K_{OA}$ values of 4.29, 4.94, and 5.86 for D4, D5, and D6 (Xu and Kropscott, 2012), cVMS in air can sorb to the extraction solvent. The cVMS concentrations in air of the ultra-trace lab (0.84 $\mu g\ m^{-3}$) were nearly