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Concentrations of cyclic volatile methylsiloxanes in biosolid amended soil, influent, effluent, receiving water, and sediment of wastewater treatment plants in Canada

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HIGHLIGHTS

- Removal efficiencies of D4, D5, and D6 are above 90% in wastewater treatment plants in summer.
- D5 concentrations in effluent have an influence on those in receiving water.
- Potential risks of cVMS to aquatic, sediment-dwelling, and terrestrial organisms are low from the reported concentrations.

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ABSTRACT

A comprehensive surveillance program was conducted to determine the occurrence of three cyclic volatile methylsiloxanes (cVMS) octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) in environmental compartments impacted by wastewater effluent discharges. Eleven wastewater treatment plants (WWTPs), representative of those found in Southern Ontario and Southern Quebec, Canada, were investigated to determine levels of cVMS in their influents and effluents. In addition, receiving water and sediment impacted by WWTP effluents, and biosolid-amended soil from agricultural fields were also analyzed for a preliminary evaluation of the environmental exposure of cVMS in media impacted by wastewater effluent and solids. A newly-developed large volume injection (septumless head adapter and cooled injection system) gas chromatography – mass spectrometry method was used to avoid contamination originating from instrumental analysis. Concentrations of D4, D5, and D6 in influents to the 11 WWTPs were in the range 0.282–6.69 μg L^{-1}, 7.75–135 μg L^{-1}, and 1.53–26.9 μg L^{-1}, respectively. In general, wastewater treatment showed cVMS removal rates of greater than 92%, regardless of treatment type. The D4, D5, and D6 concentration ranges in effluent were <0.009–0.045 μg L^{-1}, <0.027–1.56 μg L^{-1}, and <0.022–0.093 μg L^{-1}, respectively. The concentrations in receiving water influenced by effluent, were lower compared to those in effluent in most cases, with the ranges <0.009–0.023 μg L^{-1}, <0.027–1.48 μg L^{-1}, and <0.022–0.151 μg L^{-1} for D4, D5, and D6, respectively. Sediment concentrations ranged from <0.003–0.049 μg g^{-1} dw, 0.011–5.84 μg g^{-1} dw, and 0.004–0.371 μg g^{-1} dw for D4, D5, and D6, respectively. The concentrations in biosolid-amended soil, having values of <0.008–0.017 μg g^{-1} dw, <0.007–0.221 μg g^{-1} dw, and <0.009–0.711 μg g^{-1} dw for D4, D5, and D6, respectively, were lower than those in sediment impacted by wastewater effluent in most cases. In comparison with the no-observed-effected concentrations (NOEC) and IC50 (concentration that causes 50% inhibition of the response) values, the potential risks to aquatic, sediment-dwelling, and terrestrial organisms from these reported concentrations are low.

1. Introduction

Cyclic volatile methylsiloxanes (cVMS) octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2), decamethylcyclopentasiloxane (D5; CAS No. 541-02-6), and dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6) were assessed under the Canadian Chemicals Management Plan (CMP). The purpose of the CMP is to manage chemicals that present risks to human health or the environment. In November 2008, the final screening assessment reports concluded that D4 and D5 were not a concern for human health but that they were harmful to the environment (Environment Canada and Health Canada,

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2008a,c). No concerns were identified for D6 based on the available information on its potential to cause harm to human health and aquatic organisms (Environment Canada and Health Canada, 2008b). The D4 chronic no-observed-effected concentration (NOEC) for 93-d fish (rainbow trout) early life-stage was 4.4 $\mu g\ L^{-1}$ (Sousa et al., 1995). The D5 NOEC would be expected less than or equal to its maximum solubility of 17 $\mu g\ L^{-1}$ in water (Giesy et al., 2011). The D4 NOEC to midges was 44 $\mu g\ g^{-1}$ in a prolonged sediment toxicity study (Krueger et al., 2008). The D5 NOEC for sediment-dwelling midges was 69 $\mu g\ g^{-1}$ (Springborn Smithers Laboratories, 2003). Recently, a toxicity study of D5 was reported on some terrestrial organisms (Velicogna et al., 2012). The IC50 (concentration that causes 50% inhibition of the response) values of the most sensitive terrestrial animal (springtail) and plant (barley) were 767 $\mu g\ g^{-1}$ dw and 209 $\mu g\ g^{-1}$ dw, respectively.

cVMS possess an unusual combination of physico-chemical properties. They have both very high hydrophobicity and volatility. Their $\log K_{OW}$ and $\log K_{AW}$ for D4, D5, and D6 were 6.98, 8.07, and 8.87, and 2.69, 3.13, and 3.01, respectively (Xu and Kropscott, 2012). This means that they readily partition to the atmosphere and sediment and soil with high organic matter in a multi-media environment (Brooke et al., 2009a–c). Wastewater treatment plants (WWTPs) are important point sources to the surrounding aquatic environment (Wang et al., 2012b). However, systematic information on health effects to aquatic organisms and contaminant levels in point sources including WWTPs and agricultural land to which biosolid had been applied were generally lacking. Environment Canada (EC) identified several key areas for further research to provide additional perspectives on the inherent properties and risks due to their presence in the aquatic, sediment, and soil compartments. Specifically, EC identified a data gap for environmental concentrations of cVMS in and around Canadian wastewater effluent release points.

cVMS are ubiquitous in many commercial products used in laboratories, personal care products (Horii and Kannan, 2008; Wang et al., 2009) and solvents (Wang et al., 2012a). cVMS are also present in laboratory air (Alaee et al., 2010). These sources can interfere with analytical determinations. Silicone-based GC injection septa and GC column are another main source of cVMS contamination during analysis (Varaprath et al., 2006; Horii and Kannan, 2008; Wang et al., 2009). Septa used in typical GC inlets are made of silicone. At high temperatures, the septa will release cVMS that interfere with the final quantitative analysis. The siloxane-based GC columns release cVMS with increasing GC oven temperature program (Horii and Kannan, 2008). Therefore, it is usual to have background concentrations of cVMS with most analyses. In this study, a Gerstel CIS4 inlet and septumless head adapter were used to avoid septum contamination. A large-volume injection technique using a septumless head adapter with cryogenic cooling was originally developed by Hauser et al. (2002). Modifications of this sample introduction technique resulted in minimal instrumental contamination while lowering D4, D5, and D6 detection limits.

The purpose of this study was to fill the knowledge gap by analyzing influent and effluent from several Canadian WWTPs as well as nearby ambient water and sediment. This study also included analysis of environmental exposure to cVMS from agricultural use of wastewater biosolids by analyzing biosolid-amended soil at several Canadian farms. The WWTPs were selected in Southern Ontario and Quebec, Canada, and they encompassed different wastewater treatment types including lagoon, secondary activated sludge, and chemically-assisted primary treatment. In addition, cVMS bound to biosolids may be incinerated, landfilled or applied to agricultural land as a soil amendment. To study cVMS contamination in biosolid-amended soil 11 farms with biosolid amended soils, including two experimental farms of Agriculture Canada and nine commercial farms, were selected for soil sampling. The extensive sampling program at WWTPs, coupled with the enhanced analytical techniques enabled us to better understand the fate of cVMS during wastewater treatment as well as in the receiving environment either as a component in effluent or biosolids.

2. Materials and methods

2.1. Chemical and reagents

D4, D5, and D6 were purchased from Gelest (Morrisville, PA, USA). $^{13}C_4$-D4, $^{13}C_5$-D5, and $^{13}C_6$-D6 were acquired from Moravek (Brea, CA, USA), and were used as the internal standards (added prior to extraction) of native 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) and methanol distilled in glass was purchased from Caledon Laboratories (Georgetown, ON, Canada).

2.2. Sampling

Eleven WWTPs in Southern Ontario and Southern Quebec were sampled between May and October 2010 (Table S1). Many previous studies of pharmaceuticals and personal care products in WWTPs reported concentrations of 24 h composite samples (Ort et al., 2010). However, very high background concentrations of cVMS were observed using an on-line automatic sampling instrument in our preliminary study, because the peristaltic pump required silicone tubing. Therefore, single time point (grab) sampling was used in this study. Aqueous samples (influent, effluent, and receiving water) and sediment impacted by wastewater discharges were collected concurrently at each plant. Duplicate trip and field blanks consisting of 100 mL of Milli-Q water sealed in glass bottles were included in each sampling event. Trip blank samples (used to evaluate bottle contamination) were sealed for the entire sampling trip and procedure. Field blanks samples (used to subtract possible diffusive contamination) were uncapped and exposed to the air for one sampling cycle in the sampling location and recapped after finishing the sampling procedure. Water and sediment samples were transferred into prewashed glass containers, and stored at 4 °C until extraction. Extractions were completed within 24 h of collection.

Aqueous samples were collected without headspace into 100 mL serum bottles and quickly crimp sealed with Teflon coated butyl septa and aluminum seals to avoid volatilization. The temperature of collected water was also recorded. In addition, triplicate water samples were collected at each site for total organic carbon (TOC) analysis using a 100 mL clear glass Boston round bottles and capped with Teflon lined polypropylene caps. Surface sediment samples were collected at the same location in the receiving water into 500 mL amber glass jars in triplicate and capped with Teflon coated lids. Receiving water was collected one meter below the surface of lakes using a Niskin water sampler. Where shallow streams and rivers (Sites 1, 6, 7, and 11) were sources of receiving water, the water was collected about 0.3 m below the surface of the water. Sediment samples were collected from the surface of the sediment bottom. In lakes, a Ponar was used to collect the sediment sample. In shallow rivers and streams, a stainless steel scoop was used to directly fill the amber glass jars. The collection sites were chosen as the closest accessible location to the effluent discharge points. In some cases, outflow pipes from treatment plants