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Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment

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HIGHLIGHTS

- A critical assessment of the current state of knowledge of toxicity, fate, and environmental levels of cVMS is presented.
- An overview of the use, physico-chemical properties, methods of detection, of the three most widely used cVMS is reported.
- Knowledge gaps and recommendations for future research on cVMS have been identified.

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ABSTRACT

The fate and behavior of cyclic volatile methylsiloxanes (cVMS) octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) in the environment were reviewed. We evaluated their usage data and patterns, physico-chemical properties, toxicology, partitioning and degradation, methods of detection, and concentrations. The use of cVMS as an intermediate in the formation of silicone polymers, personal care and household products has resulted in their widespread environmental exposure; they have been detected in biogas, air, water, soil, biosolid, sediment, and biota samples. Modeled and experimental results suggest that cVMS may be subject to long-range atmospheric transport, but have low potential to contaminate the Arctic. For D4 and D5, there was no evidence of trophic biomagnification in aquatic food webs, while some aquatic organisms demonstrated a high degree of bioconcentration and bioaccumulation. High concentrations of cVMS observed in indoor air and biosolids resulted from point sources. Concentrations of cVMS in water, sediment, and soil were all below their no-observed-effect-concentrations.

1. Introduction

Organosilicon compounds have a backbone of alternating silicon (Si) and oxygen (O) atoms, with each silicon atom bearing one or several hydrocarbon groups, such as methyl, ethyl or phenyl. Three organosilicon classes, volatile methylsiloxane, polydimethylsiloxane, and polyethermethylsiloxane, have noteworthy environmental loadings. Cyclic volatile methylsiloxanes (cVMS) are a subgroup of volatile methylsiloxanes that favor partitioning into the atmosphere due to their high vapor pressures, low water solubilities, and high Henry's Law constants. cVMS consist of repeating units of $[Me_2SiO]_n$, and the Si–O atoms are singly bonded forming a ring. Three widely used cVMS are octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) (Fig. 1).

Starting in the 1940s, cVMS were produced commercially for use as specialty materials for consumer and industrial products (Hunter et al., 1946; Patnode and Wilcock, 1946; Chandra, 1997). The main uses of cVMS are as an intermediate for the production of other chemicals (silicone polymers), in personal care products (e.g. cosmetic, skin- and hair-care products), in household products, in industrial/institutional cleaning, and construction.

As a result of their widespread use, dispersion and accumulation in aquatic sediments, the US. EPA signed a testing consent order with six industrial manufacturers of D4 in the 1980s (Kent et al., 1996). A comprehensive aquatic toxicity and environmental fate testing program of D4 was sponsored by the Silicones Environmental Health and Safety Council of North America (SEHSC) supported by the silicone industry in the 1990s (Kent et al., 1994; Fackler et al., 1995; Hobson, 1995; Hobson and Silberhorn, 1995; Mueller et al., 1995; Potts and Guy, 1995; Sousa et al., 1995; Hamelink et al., 1996; Varaprath et al., 1996). Based on these results, in 1994 the US EPA concluded that D4 represents a low risk to aquatic species (Walker and Smock, 1995).

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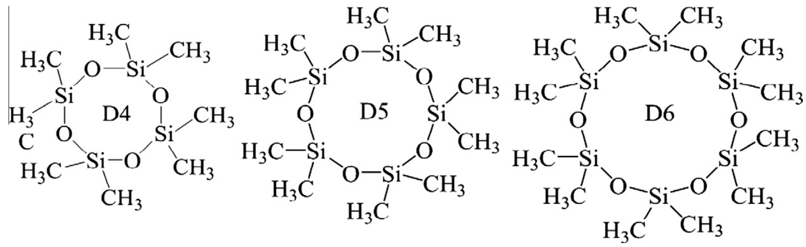

Fig. 1. Molecular structures of D4, D5, and D6.

Recently, several regulatory jurisdictions have prioritized a number of cVMS, including D4, D5, and D6 based on concerns regarding their persistence and bioaccumulation potential in the environment. Consequently, there have been extensive reviews assessing the environmental risks of cVMS as potential priority pollutants in Europe (Brooke et al., 2009a,b,c) and Canada (Environment Canada and Health Canada, 2008a,b,c).

Several countries that have been systematically screening the environment for potentially hazardous substances have identified cVMS (Lassen et al., 2005; Kaj et al., 2005a,b). The Nordic screening project has collected samples of biota, sediment, biosolids, soil, and water in Denmark, the Faroe Islands, Finland, Iceland, Norway, and Sweden since 2004 (Kaj et al., 2005a,b). This project reported the widespread distribution of cVMS in the Nordic environment, except for in soils, although, the observed concentrations were not of immediate concern.

This review summarized the use and consumption, physico-chemical properties, toxicity, fate, methods of detection, environmental concentrations, and global distributions of the three most widely used cVMS, D4, D5, and D6. The goal of this review was to provide a comprehensive assessment of the current state of knowledge concerning the environmental risk of cVMS. Knowledge gaps and recommendations for future research were also identified.

2. Use and consumption

cVMS belong to a group of substances used in a number of industrial applications, cosmetics and personal care products (Graiver et al., 2003; Dewil et al., 2006). D4 has been used primarily as an off-site intermediate for the production of silicone polymers. However, the majority of cVMS used currently in personal care products have been identified as D5 and D6, including fragrances, hair care products, deodorants, antiperspirants, nail polishes, lotions, and skin cleansers. (Horii and Kannan, 2008; Wang et al., 2009; Gouin et al., 2012). Horii and Kannan (2008) reported that D4, D5, and D6 concentrations varied widely in cosmetics and personal care products purchased from Japan and America in 2006, ranging up to 9380, 81800, and 43100 $\mu g\ g^{-1}$ wet weight (ww), respectively. Wang et al. (2009) reported concentration ranges up to 11000, 683000, and 97700 $\mu g\ g^{-1}$ ww for D4, D5, and D6, respectively, in cosmetic products and a variety of baby products from several regions of Canada in 2007 and 2008. It is evident from both studies that the concentrations of these cVMS in cosmetics and personal care products are very high, implying that these products could be an important source of cVMS to the environment (Gouin et al., 2012; Montemayor et al., 2012).

In 2009, the global silicone market of silicone sold as fluids, elastomers, and resins was valued at approximately $11.5 billion USD (Will et al., 2010). Europe, North America, and China each account for about one quarter of the world consumption market. In 2008 and 2009, China was the largest manufacturer and consumer of polysiloxane in the world, with an output and consumption of 195000 and 375000 tons in 2008, and 270000 and 430000 tons in 2009, respectively (CRCSI, 2010).

In the United States, D4, D5, and D6 are high volume commercial chemicals. In 2006, the production volumes were in the range of 45000–225000, 22500–45000, and 450–4500 tons, for D4, D5, and D6 respectively (US EPA, 2006). In the European Union, the total amount of cVMS used is confidential, but approximately 9500, 19000, and 2000 tons of D4, D5, and D6, respectively, were used as an intermediate for the production of silicone polymers and personal care products in 2004 (Brooke et al., 2009a,b,c). In 2006, the total quantity of annual import volumes to Canada were 1000–10000 tons for D4 and D5, and 100–1000 tons for D6 (Environment Canada and Health Canada, 2008b,c,a) (Fig. 2).

3. Physico-chemical properties

3.1. Water solubility and vapor pressure

cVMS possess a rather unusual combination of physico-chemical properties, including both hydrophobicity and volatility. The water solubilities of cVMS in distilled water are very low (56, 17, and 5 $\mu g\ L^{-1}$ for D4, D5, and D6) (Varaprath et al., 1996), and the vapor pressures of cVMS are relatively high (122, 25, and 2.2 Pa for D4, D5, and D6) (Flaningam, 1986; Lei et al., 2010).

3.2. Octanol/water partitioning coefficient

The octanol/water partition coefficient (K_{OW}) is an important physico-chemical property, used for predicting the environmental uptake of individual organic compounds by aquatic biota through water and sediment. The $\log K_{OW}$ of D4, D5, and D6 were determined to be 4.45, 5.20, and 5.86, respectively, using a high performance liquid chromatography retention time method (Bruggeman et al., 1984). In addition, the $\log K_{OW}$ values for ^{14}C-labeled D5 and D6 were determined to be 4.76 (Sible, 2006) and 4.36 (Miller,

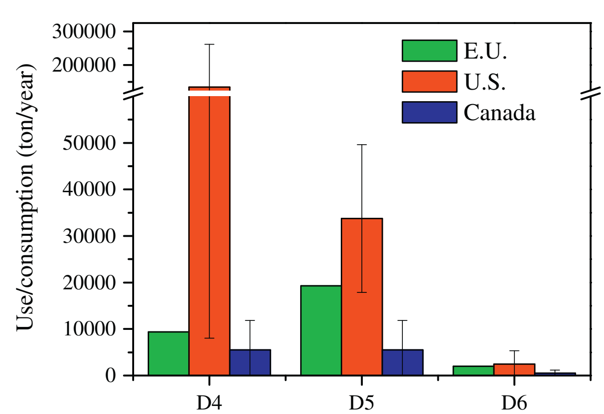

Fig. 2. Use/consumption of cVMS in the European Union (2004), the United States (2006), and Canada (2006).