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Chemical fate, latitudinal distribution and long-range transport of cyclic volatile methylsiloxanes in the global environment: A modeling assessment

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ABSTRACT

Cyclic volatile methylsiloxanes (cVMS) such as octamethycyclotetrasiloxane (D4), decamethycyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) are widely used as intermediates in the synthesis of high-molecular weight silicone polymers or as ingredients in the formulation of personal care products. The global environmental fate, latitudinal distribution, and long range transport of those cVMS were analyzed by two multimedia chemical fate models using the best available physicochemical properties as inputs and known persistent organic pollutants (POPs) and highly persistent volatile organic chemicals ("fliers") as reference. The global transport and accumulation characteristics of cVMS differ from those of typical POPs in three significant ways. First, a large fraction of the released cVMS tends to become airborne and is removed from the global environment by degradation in air, whereas known POPs have a tendency to be distributed and persistent in all media. Secondly, although cVMS can travel a substantial distance in the atmosphere, they have little potential for deposition to surface media in remote regions. This contrasts with a deposition potential of known POPs that exceeds that of cVMS by 4–5 orders of magnitude. Thirdly, cVMS have short global residence times with the majority of the global mass removed within 3 months of the end of release. Global residence times of POPs on the other hand are in years. The persistent fliers resemble the cVMS with respect to the first two attributes, but their global residence times are more like those of the POPs.

1. Introduction

Cyclic volatile methylsiloxanes (cVMS) such as octamethycyclotetrasiloxane (D4), decamethycyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) are hydrophobic silicone fluids. They are used either as precursors in the synthesis of high-molecular-weight silicone polymers or as major ingredients in formulating personal care products (Allen et al., 1997; Hobson et al., 1997). They have unique partitioning properties which combine high volatility, reflected in high air/water partition coefficients (K_{AW}) and low octanol/air partition coefficients (K_{OA}), with medium to high sorption coefficients to organic matter from water (K_{OC}).

Once released to the environment, cVMS undergo degradation, transport and redistribution processes (Mueller et al., 1995). Major degradation processes include demethylation of airborne cVMS by hydroxyl radicals in air (Atkinson, 1991) and hydrolysis of cVMS in water (Kozerski and Durham, 2009), soil (Xu and Chandra, 1999) and sediment (Xu et al., 2010). Based on the global average OH radical concentrations, demethylation half-lives of cVMS are 1–2 weeks, which is long enough for inter-continental atmospheric transport. The measured half-lives of cVMS in soil, water and sediments are highly variable from a few hours for D4 in water (Kozerski and Durham, 2009) or air-dry soil (Xu and Chandra, 1999) to ~10 years for D5 in sediment with high organic matter content (Xu et al., 2010).

Long persistence and large potential for long range transport (LRTP) are two hazard indicators used in identifying persistent organic pollutants (POPs) (UNEP, 2001). Although single medium thresholds of half-lives are used in the current regulatory process to screen chemicals for POP-like behavior, persistence and transport of a chemical depend on many factors in addition to the longevity in interconnected environmental media, such as the mode of release and partitioning (Fenner et al., 2005). Therefore, multimedia environmental models are valuable tools for providing more accurate and comprehensive assessment of the real environmental hazard associated with chemicals (Klasmeier et al., 2006).

Several multimedia modeling studies including one or more organosilicon compounds have been published for different purposes. Muir and Howard (2006) and Howard and Muir (2010) have

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conducted a screening of a large numbers of chemicals in search for possible new POP candidates. Wania (2006) and Brown and Wania (2008) reported model screening assessments of LRTP of numerous chemicals including cVMS compounds. Gouin (2010) assessed high persistence and LRTP associated with chemicals including one siloxane (D5). In addition, multimedia chemical fate models have been used to understand monitoring data for cVMS in air (McLachlan et al., 2010; Genualdi et al., 2011) and in the aquatic environment (Whelan and Breivik, 2012). Finally, some specific models were also developed to predict the atmospheric fate of cVMS and their degradation products (Whelan et al., 2004) or to estimate the effects of atmospheric aerosols on the fate of airborne cVMS (Navea et al., 2011). However, many of those studies, especially the early ones, are based on the physicochemical parameters estimated by the quantitative structure property relationships implemented in version 3.12 of the property estimation software EPISuite. As has been discussed in several conference presentations (Xu et al. 2007, 2010; Xu and Kozerski, 2011), measured partition coefficients (K_{AW}, K_{OW} and K_{OC}), and half-lives in air, water and soil deviate considerably from the estimates provided by EPISuite V 3.12.

The objectives of this study were twofold: First, to estimate the global environmental fate, latitudinal distribution, and LRTP of cVMS using multimedia chemical fate models and the best measured physicochemical properties currently available, and secondly to compare the environmental behaviors of cVMS with those of prominent POPs and highly persistent volatile organic chemicals.

2. Modeling assessment

The LRTP of cVMS was estimated using the OECD P_{OV} and LRTP Screening Tool, version 2.1.2 (the OECD Tool) (Wegmann et al., 2009), which builds upon a spatially unresolved, three-compartment global box model. A detailed analysis of the fate and distribution of cVMS in the global environment was conducted using the GloboPOP model, which is a zonally-averaged multimedia environmental fate model in which the global environment is divided into 10 climate zones (Wania, 2003, 2006). Each climate zone has 9 compartments, namely stratosphere, middle/upper troposphere, lower/middle troposphere, atmospheric boundary layer, uncultivated soil, agricultural soil, freshwater, sea water, and freshwater sediments. Except for the emission scenario and chemical specific inputs, all simulations were conducted using default values of the corresponding models (Wania and Mackay, 2000; Wegmann et al., 2009).

Three cVMS (D4, D5 and D6) were evaluated together with three prominent POPs [Hexachlorobenzene (HCB), 2,4,4′-Trichlorobiphenyl (PCB 28), and 2,2′,3,4,4′,5,5′-Heptachlorobiphenyl (PCB 180)] and two highly persistent volatile organic chemicals called FC and Hypo-D5. FC is a fluorinated ester, $CF_3(CF_2)_7C(O)OCH_2F$, with a long half-life in air similar to those of POP substances, while Hypo-D5 is a hypothetical chemical with the same physicochemical properties as D5 except that its air half-life is assumed to be about 155 times that of D5 (Table S1).

The chemical-specific inputs for cVMS such as physicochemical properties (Table S1) were all obtained experimentally or were based on experimental data (see Table S1 for the data sources). In the original OECD Tool and GloboPOP models, K_{OC} values are calculated based on an empirical relationship between K_{OC} and K_{OW} ($K_{OC} = 0.35\ K_{OW}$) (Seth et al., 1999). Because recent studies demonstrated that this relationship is not applicable to siloxanes (Xu and Kozerski, 2011), measured log K_{OC} values for cVMS (Kozerski et al., 2009) were fed into the modified GloboPOP model which allowed direct inputs of the measured log K_{OC} values for the simulations presented here. In the OECD Tool the relationship between K_{OC} and K_{OW} was modified in such a way that the log K_{OC} values used in the simulations matched the measured log K_{OC} values.

All inputs for three reference POPs were taken from the literature. Details on the exact values and sources are provided as supplementary data (Table S1). The property data for FC are currently not available; the physicochemical data for this compound (Table S1) were generated using EPISuite (V4.0). The data in Table S1 refer to a standard temperature of 25 °C and a globally-averaged OH concentration in the troposphere over a 24-h period, 7.5×10^5 molecules cm^{-3} (Prinn et al., 1987). For specific regions, compound properties and degradation rates may be different due to regionally variable OH radical concentration in air and temperature. Furthermore, all physicochemical properties are subject to measurement errors. To assess the effect of such parameter variability on the uncertainty of the LRTP estimates made by the OECD Tool, Monte Carlo simulations were run with a dispersion factor (Wegmann et al., 2009) set to be 3 for half-lives in water, 5 for half-lives in soils, 2 for half-lives in air (which corresponded to a concentration of OH radicals ranging from 0.3 to about 2.5 times the global average) and 2 for all other parameters.

The OECD Tool calculations were done with default emission scenarios and no specific emission rates were needed. In simulations with the GloboPOP model, detailed emission data were required including an annual rate of global emission, its zonal distribution and seasonal patterns, and the mode of entry. The global emissions of cVMS originate mainly from three regions: North America (USA and Canada), Western Europe and East Asia (Japan, South Korea, and China), each accounting for one third of cVMS emission (Brook et al., 2009). For example, D5 in Western Europe accounts for roughly 1.56×10^7 kg $year^{-1}$ or one third of the total release in the three regions (Brook et al., 2009). The emission rate per capita in developing economies outside the three major emission regions was assumed to be one tenth of that in the developed economies of the above regions. The annual global emission rate used in the simulations was 4.8×10^7 kg $year^{-1}$ for D5. No total emission for D4 and D6 was needed for this study since all the calculated quantities were independent of the total emission rate. The zonal distribution of these emissions in Table S2 was estimated based on the above information in combination with the population distribution and zonal division of the GloboPOP model (Wania, 2003). Emissions were assumed to have no seasonal variation.

The mode of entry for the emissions in Table S1 was estimated based on the assumption that more than 90% of cVMS contained in personal care products vaporizes during application with the remainder entering the waste water stream (Mueller et al., 1995; Montemayor et al., 2012). A modeling assessment (Mueller et al., 1995) and experimental measurements (Parker et al., 1999) indicate that a large fraction of cVMS such as D5 in the waste water influent is removed in municipal waste water treatment processes: half by volatilization and half by partitioning into sewage sludge (Powell, 2008). Recent monitoring data from Environment Canada suggested that the removal efficiency of cVMS is as high as 98% for higher tier (e.g., secondary) waste water treatment processes, but could be as low as 90% in a lagoon in the winter time (Wang et al., 2012). This range leads to two possible estimations of the mode of entry given in Table S1.

3. Results and discussion

3.1. Potential for long-range transport

Characteristic travel distance (CTD) and transfer efficiency (TE) are two metrics frequently used to characterize the LRTP of chemicals. Whereas the former indicates to what extent a chemical may be transported in the atmosphere, the latter seeks to quantify the