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The atmospheric lifetimes and concentrations of cyclic methylsiloxanes octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) and the influence of heterogeneous uptake

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ABSTRACT

The environmental fate of the cyclic methylsiloxanes (cVMS), octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5), is important because of the potential for long range transport. Previous studies of environmental loss pathways for D_4 and D_5 focused on gas phase oxidation, establishing OH as the main gas phase reactant, with OH kinetics consistent with atmospheric lifetimes of approximately 7 days (D_5) and 11 days (D_4) at an OH concentration of 10^6 molec cm^{-3}. In this work, we assess the sensitivity of atmospheric lifetime to other factors using an atmospheric compartment model. D_4 and D_5 were modeled using an compartment model to simulate emission, decay, and atmospheric transport across a range of three levels of population density corresponding to urban, transition, and rural areas of a developed mid-latitude location. The model was used to examine sensitivities of lifetime and concentration of D_4 and D_5 to spatial variation in OH, variation in the time-of-day for cVMS emissions, and to relative humidity dependent heterogeneous uptake and/or reactions on mineral dusts. cVMS lifetime was found to be insensitive to urban OH concentrations because of limited residence time, and somewhat sensitive to enhanced OH levels in the transition area between the urban and rural compartments. Realistic aerosol loadings and heterogeneous kinetics consistent with recent laboratory results (uptake coefficients of 1.2×10^{-5} and 1.6×10^{-5} for D_4 and D_5, respectively) were calculated to reduce the cVMS lifetime by ~3% under dry conditions but have negligible effects at RH values above 50%. The heterogeneous kinetics were based on experimental observations of uptake to mineral aerosol surfaces at cVMS loadings well above ambient levels. The compartment model, after tuning of residence times and ceiling heights to reproduce benzene observations, predicted D_5 at 6, 28, and 50 ng m^{-3} in areas with low, medium, and high population densities, respectively. Corresponding D_4 concentration predictions were 5, 20, and 33 ng m^{-3}. These values were compared with available measurements.

1. Introduction

Cyclic volatile methyl siloxanes (cVMS) such as octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) are low viscosity silicone fluids with low water solubility (Kochetkov et al., 2001; Mazzoni et al., 1997; Varaprath et al., 1996) and relatively high vapor pressure (Flaningam, 1986). These compounds are released into the environment from different anthropogenic sources including industrial releases associated with the manufacture of higher molecular weight silicone polymers and from the use of products which contain cVMS (Hobson et al., 1997) such as some deodorants, hair and skin care products, and cleaning products. D_4 and D_5 are a subset of a larger class of linear and cyclic siloxanes (Mazzoni et al., 1997). The cVMS compound class as a whole has a molecular weight range from 222 to 445 g mol^{-1}, while the compounds of interest for this work have molecular weights of 297 g mol^{-1} (D_4) and 371 g mol^{-1} (D_5).

Measured and estimated values of ecologically relevant properties for cVMS compounds are extensively documented (Brooke et al., 2009a,b; Mazzoni et al., 1997). Both Allen et al. (1997) and Mueller et al. (1995) report that more than 90% of cVMS released to the environment is released directly to air, or quickly partitions

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from water or soil to the atmospheric; volatilization rates from river water have recently been refined (Whelan et al., 2010). Wania (2006) classifies D_4 and D_5 as "flyer" chemicals which achieve long range transport in the atmospheric as opposed to less volatile and/or more soluble compounds, but fail to deposit from the remote atmosphere to the surface media. Because of this strong tendency to partition to air, reactions of D_4 and D_5 in the atmosphere are critical to their overall environmental fate. Oxidation by OH leads to atmospheric half lives of 6–21 days for cVMS (D_3 to D_6). This overall picture of cVMS (strong partitioning to the atmosphere and decay predominantly by OH) is supported by a recent combined modeling and measurement study for D_5 (McLachlan et al., 2010, referred to in this work as M10).

Heterogeneous removal of D_4 and D_5 on mineral dust aerosols has recently been demonstrated (Navea et al., 2009b,c) but the atmospheric implication of these experiments has not yet been quantified. These works are referred to herein as N09b and N09c, respectively. Although the current work does not consider the environmental fate in soil, water and sediment, this remains an important topic of research, especially for releases made directly to such media. For example, a calculation using the EQC (Equilibrium Criterion) model (Mackay et al., 1996) predicts that D_5 released to water will predominantly partition to underwater sediments, resulting in a overall lifetime about 10 times that of the release to air only (Kaj et al., 2005a, herein referred to as K05a). Recent measurements on volatilization from rivers indicate strong partitioning to dissolved organic matter that can hinder volatilization (Whelan et al., 2010). In soils, *in situ* degradation by hydrolysis is thought to compete with volatilization rates dependent on RH and soil composition (Xu, 1999; Xu and Chandra, 1999).

As exemplified by recent national and international regulations such as the Stockholm Convention on POPs (persistent organic pollutants) and the European Registration, Evaluation, Authorization and Restriction of Chemical substances (REACH), there is an increased interest in understanding and managing chemicals with potential environmental persistence (UNEP, 2001). Screening of chemicals for their degree of PBT characteristics (persistence, bioaccumulation, and toxicity) and potential for long range transport is becoming more widespread (Brown and Wania, 2008; Howard and Muir, 2010).

The PBT characteristics of D_4 and D_5 are extensively reported in risk assessment reports (Brooke et al., 2009a,b). EPA's voluntary PBT screening program (Tunkel, 2006) places both D_4 and D_5 in intermediate persistence and bioaccumulation categories and in high aquatic toxicity concern categories. cVMS compounds are not targeted for elimination or restriction under the Stockholm convention or under the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR).

Increased understanding of the environmental fate of D_4 and D_5 remains desirable within the industrial, scientific, and regulatory communities. Periodic review or screening of D_4 and D_5 with respect to environmental fate is anticipated. As high production volume chemicals (USEPA), the concentrations and fate of cVMS may be important indicators of the environmental loadings of a wider range of personal care, fragrance, and consumer product components. Human exposure to D_4 and D_5 is not a focus of this work, as human exposure is likely dominated by product use and indoor concentrations, and insensitive to changes in lifetime which are the subject of the current study.

Chamber studies have examined the kinetics of cVMS oxidation by O_3, as well as OH, and NO_3 radicals. Abe et al. (1981) observed stability of D_4 under irradiation, but did see degradation in the presence of photolyzed O_3, with a rate enhancement in the presence of water vapor, suggestive of D_4 consumption by OH attack. Subsequent work determined kinetic parameters and established OH oxidation as dominant relative to O_3 and NO_3 reactions (Atkinson, 1991, 2000; Karl et al., 2001; Sommerlade et al., 1993). Assuming an OH number density of 10^6 molec cm^{-3}, the lifetimes of D_4 and D_5 are 11.5 days and 7.5 days, respectively.

Partition coefficients of cVMS between air and water are documented (Brooke et al., 2009a,b). Partitioning between air and aerosol species has been studied for cVMS and for reaction products of D_5 such as 1-hydroxynonamethylcyclopentasiloxane, D_4TOH (Latimer et al., 1998). D_5 partitioned weakly to the aerosols, indicating that equilibrium partitioning of cVMS to aerosols is unlikely to remove significant quantities, although there is uncertainty in the extrapolation of the partition coefficients to atmospheric concentration ratios of dust and cVMS. Affinity for aerosols was much stronger for the more polar oxidation product D_4TOH. In a related study in the same environmental chamber (Chandramouli and Kamens, 2001), mixtures of D_5, mineral dust aerosols, and irradiated NO_x (to yield O_3 and OH) showed minimal D_5 in the particle phase. However, one experiment exhibited an unexpected rapid decay of D_5, possibly attributable to heterogeneous reactions.

In recent studies carried out in our laboratory, significant loss of gas-phase cVMS was observed in the presence of reactive mineral dust aerosol under dry conditions (N09b). Elevated RH was observed to inhibit the cVMS heterogeneous uptake. In addition, no gas-phase products were detected in these experiments, suggesting that cVMS and cVMS reaction products remained in the condensed phase after initial uptake by the aerosol phase. We hypothesize that reactive surface sites on the aerosols eventually become saturated with cVMS, and that the lack of volatile products is due to a surface reaction, such as polymerization of cVMS, on the mineral dust. Heterogeneous polymerization of siloxanes has been previously observed on clays through a ring-opening mechanism mediated by the dust surface (Bi et al., 2007). One challenge with interpretation of the laboratory uptake experiments is that they were conducted at high concentrations of both reactive dusts ($\sim 10^5$ times ambient loadings) and cVMS ($\sim 10^8$ times ambient loadings). Hydrolysis or other reactions may be atmospherically relevant but difficult to detect through the experiments performed to date. Additional heterogeneous loss pathways and changes in kinetic parameters under atmospheric conditions cannot be ruled out. Build up of products in the higher concentration experiments may hinder further reaction progress, although this requires further experimental confirmation.

Environmental compartment and 3D chemical transport models are routinely used to study the fate and long range transport of POPs (Chandramouli and Kamens, 2001; McLachlan et al., 2010; Wania, 2003; Whelan et al., 2004). Two studies have developed compartmental models specifically to study cVMS (Mueller et al., 1995; Whelan et al., 2004). Mueller et al. used a 6 compartment model with two atmospheric compartments (continental US and Atlantic ocean) and modeled partitioning and reaction with OH, with compartment residence times tuned to match observed acetylene concentrations. Modeled atmospheric cVMS concentrations were less than 10 ng m^{-3}. Whelan et al. used a one box (no transport) model for the continental U.S. with height of 6 km, also assuming OH concentration of 5×10^5 molec cm^{-3}, and modeled the reaction, partitioning, dry deposition, and wet deposition of cVMS and its more hygroscopic reaction products. Despite the ability to partition to clouds, Whelan et al. showed preferential partitioning of siloxanes and mono-substituted OH silanols to the gas phase. M10 employed a hemispheric chemical transport model with country-specific D_5 emissions and model-predicted OH concentrations for a model-measurement comparison for daily D_5 measurements at a rural Swedish site. The modeled D_5 concentrations were less than 15 ng m^{-3} in winter and less than 4 ng m^{-3} in summer. Measured D_5 concentrations by M10 were typically lower than the modeled concentrations.