LEVELS TRENDS AND FATE OF CYCLIC VOLATILE METHYL SILOXANES IN THE ENVIRONMENT: AN OVERVIEW

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Introduction

Volatile methyl siloxanes (VMS) are high-volume chemicals that have Si-O-Si bonds with both aliphatic, cyclic structures and methyl moieties. Organosilicon compounds produced commercially have both aliphatic and cyclic structures. The annual production of the cyclic volatile methyl siloxanes(cVMS), D4, D5, and D6 in the United States in 2006were in the range of 45 000–225 000, 22 500–45 000, and 450–4 500 tons respectively.[1]In general, D4 is widely used as an off-site intermediate in the production of polydimethylsiloxanes (PDMS). D5 and D6are used in personal care productsincluding fragrances, hair care products, deodorants, antiperspirants, nail polishes, lotions, and skin cleansers. The wide usage and release of these compounds has resulted in widespread environmental exposure. cVMShave been detected in biogas, air, water, soil, biosolids, sediment, and biota samples. Consequently, these compounds may pose a risk to the environment.
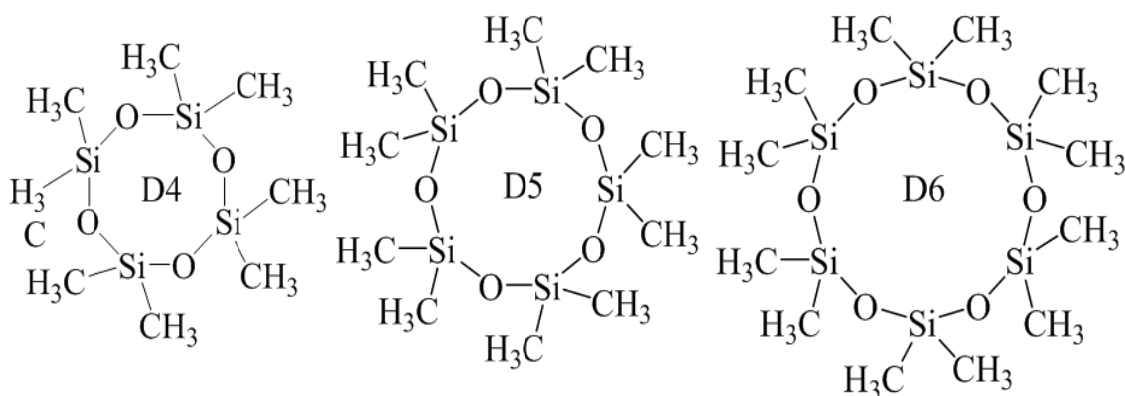

Figure 1. Molecular structures of D4, D5, and D6

Recently Wang et al.[2] provided an extensive overview on recent advances in the environmental occurrence, fate and toxicity of cVMS in the environment. In this presentation, we attempt to provide a summary of the physical-chemical properties, methods for determination in environmental matrices, environmental concentrations, and fate of these three most widely used cVMS.

Physical–chemical properties

In order to understand the fate and behavior of these compounds, it is essential to understand their physical-chemical properties. cVMS are hydrophobic compounds with a very low water solubility(56, 17, and 5 $\mu g\,L^{-1}$ for D4, D5, and D6 respectively)[3] and a relatively high vapor pressures (122, 25, and 2.2 Pa for D4, D5, and D6)[4], resulting in a preference for these compounds to partition into air from water. Log K_{OW} values (octanol/water partition coefficient) for D4, D5 and D6 vary from 4.5 to 7.0, 4.8 to 8.7, and 4.4 to 9.1 respectively[2], indicating these compounds favor partitioning into the lipid phase.
Environmental degradation of cVMS occurs mainly in the gas-phase. Under atmospheric conditions cVMS react with OH and NO_3 radicals and O_3, but reaction with OH radicals is by far the most dominant tropospheric removal process.The calculated atmospheric half-lives of these compounds were ~10 d for D4 and ~20 d for D5, assuming first-order kinetics and using a tropospheric concentration of OH radicals of 7.7×10^5 molecule cm^{-3} over a 24-h period.[5] In addition, an estimated atmospheric half-life of D6 of 1.6 d was observed using the

Jungerelationship from the GAPS dataset.[6]The half-lives of D4 and D5 are long enough so that they can undergo long-range atmospheric transport (LRAT) and be distributed both regionally and globally.[5,7]

Determination of cVMS in environmental matrices

Gas Chromatography coupled to mass spectrometry is the method of choice for the determination of cVMS in environmental matrices. There are several sources of cVMS in the gas chromatography system itself including traps for the carrier gas, inlet septa and GC columns which need to be addressed. To avoid background contamination excess gas traps are removed. Wang et al.[8] have described the use of a septumless inlet system to avoid contamination from silicon based septa and Sparham et al.[9] recommended the use of non silicon based columns such as those that are Carbowax based. Several methods have been used for the determination of cVMS in atmospheric samples with the main challenge being the relatively wide range of possible concentrations in these types of samples. Concentrations can vary from being relatively high in biogas samples, to low in atmospheric samples from pristine areas such as the Arctic. Several techniques including direct measurements, active and passive samplers using gas impinges and sorption to solid phases have been employed in the determination of cVMS in atmospheric samples. Wang et al.[8] described a method based on membrane assisted solvent extraction for determination of cVMS in water samples. Sparham et al.[10] described a liquid solid extraction method for the determination of cVMS in sediment and soil. Warner et al.[11] described extraction of biota samples in a fume hood within a clean room facility while Kierkegaard et al.[12] designed a closed purge and trap system to analyze biota.

Environmental Levels

A summary of the levels of cVMS in the atmosphere is provided in Figure 2.[2] Figure 2 shows that biogas has by far the highest concentration of cVMS. These high concentrations have even been shown to create major problems for turbines used in electrical cogeneration plants where special scrubbers prior to burning of biogas have been installed. The concentration of cVMS in air was highest in biogas and ranged between 100 and 10 000 $\mu g\ m^{-3}$, followed by air near point sources such as WWTP, which ranged between 0.1 and 30 $\mu g\ m^{-3}$ and outdoor air which was <1 $\mu g\ m^{-3}$.

Concentration of cVMSin water is directly influenced by point sources

Figure 2. Box-and-whisker plot summarizing concentrations of cVMS in biogas, point source air, and outdoor air.Adapted from Wang et al.[3]

mainly municipal wastewater treatment plants as they receive their influents from both PDMS manufacturing plants and households. cVMS concentrations in influent WWTPs in samples collected in Canada in 2010 ranged between 9.6 and 170$\mu g\ L^{-1}$ and between 0.004 and 1.7 $\mu g\ L^{-1}$ for effluent samples indicating a removal efficiency of >98% for most WWTP. The concentrations of cVMS in receiving waters were< 2 $\mu g\ L^{-1}$. The concentration in biosolidsranged between 0.1−100 $\mu g\ g^{-1}$dw compared to sediment and soil, which were generally less than 1 μg g-1dw. cVMS in fish and mammals from aquatic environments were <0.1 $\mu g\ g^{-1}$ww, with the exception of fish collected close to some point/diffuse sources.[2]

Environmental Fate

cVMS have been detected in several environmental matrices and have been identified as a class of compounds with significant long-range atmospheric transport (LRAT) potential.[7,13] Once released into air, based on high
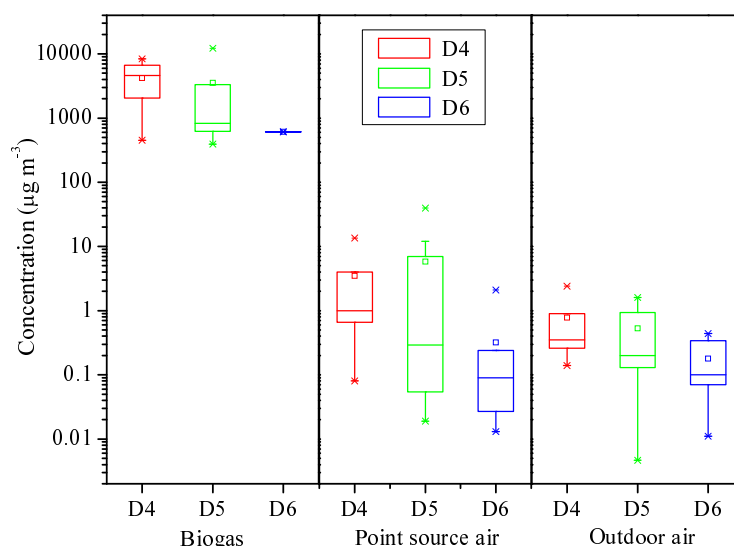
vapor pressures and Henry's Law constants, these compounds should remain in the atmosphere (>99.9%). Atmospheric degradation is the main removal mechanism; however, cVMS have long half-lives in air, indicating that they will remain in the atmosphere for a significant amount of time. On the other hand, cVMS released into water will partition between the atmosphere and sediment due to their high vapor pressures and Henry's law constants. As such, relatively high removal efficiencies were observed in most WWTPs. Hydrolysis in fresh water is relatively slow and does not play an important role, however it is a significant factor in marine environments. Another point source for cVMS is through amendment of biosolids to agricultural soil. Volatilization is the main mechanism for loss of cVMS and accounted for 89%, 71% and 32% of the loss of D4, D5, and D6 from amended soils respectively.[14] The biodegradation rate for cVMS under both aerobic and anaerobic conditions was found to be very slow.[15,16]

Acknowledgements

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