Volatile Methyl siloxanes in the Environment: Emerging Challenges Assessing Sources, Bioaccumulation, and Environmental Fate

Michael McLachlan, Stockholm University and Todd Gouin, Unilever

Cyclic volatile methyl siloxanes (cVMS) are present in a wide range of consumer and personal care products. Recently, several regulatory jurisdictions have expressed concern regarding their persistence and bioaccumulation in the environment. Consequently, a number of cVMS are currently under review for priority pollutant classification in North America and Europe. The motivation for this session was to explore recent developments regarding the environmental fate and bioaccumulation of cVMS, with a goal of advancing our understanding of the processes that influence their emissions, distribution, levels in the environment, and potential risk.

This session was included under the Emerging Pollutants theme at the SETAC Europe meeting in Seville, and although cVMS have only recently been identified as “emerging” pollutants, the regulatory assessment is proceeding quickly. The rapid speed at which the assessment is occurring, however, could prove problematic, since it is being conducted on the basis of very few field data. Given the unusual properties of cVMS, i.e. highly volatile and highly hydrophobic, there are no similar precedents on which to base decisions, which implies that this is a potentially risky strategy. Thus, there is an urgent need for good independent science to inform the assessment process, in particular science based on field observations. Presentations covered a wide range of topics, such as methodologies for trace analysis, field measurements, laboratory experiments addressing key processes, and environmental fate modeling.

Session Highlights

As an ‘emerging’ pollutant, the paucity of analytical methods suitable for the environmental trace analysis of cVMS is a major hindrance in the study of these compounds. Blank problems are the major concern due to cVMS use in personal care products and their presence in chemicals, solvents, and in silicon parts/lubricants in laboratory equipment and instrumentation. A major breakthrough was achieved in 2010, with the first report of a successful inter-laboratory comparison for the analysis of cVMS at trace levels. Liver from Atlantic cod was analysed, and the three participating labs (Dow Corning, Evonik, Norwegian Institute for Air Research) obtained similar results. Furthermore, they reported method detection limits in the low ng/g wet weight range (Warner et al. 2010). Additionally, two new analytical methods were also reported: A method for decamethylcyclopentasiloxane (D5) in air was developed based on sampling with Isolute ENV+, which was shown to be robust, reproducible, and had a limit of quantification of 0.3 ng/m³ (Kierkegaard et al. 2010a), and the same sorbent was also used in a purge and trap method to analyse cVMS in biota. This method offered several advantages over the existing cold solvent extraction method, including cleaner extracts and somewhat lower limits of quantification (Kierkegaard et al. 2010b).

Concerns relating to the persistence and long range transport potential of cVMS was also presented, specifically, the atmospheric fate of D5 was assessed in a combined measurement and modeling study. The concentrations in air were measured every 24 hr over a 5-month period at a rural site in Sweden. The measured values were then compared with concentrations predicted by a hemispheric scale atmospheric circulation and fate model driven by emission estimates derived from consumer product use. Excellent
agreement was obtained, indicating that there is a good understanding of emissions and fate of D5 in air. The work showed that D5 is clearly subject to long-range atmospheric transport, but that only a very small portion of it is deposited to surfaces in remote regions. It is eliminated from the atmosphere via reaction with OH radicals at a rate that varies strongly with latitude and season, but reflects an average atmospheric half life of ~10 days (McLachlan et al. 2010).

This relatively rapid degradation of D5 combined with the low rate of deposition to terrestrial and aquatic ecosystems means that emissions of D5 to air are considered to be relatively unproblematic. Some 90% of D5 is estimated to be emitted to air, while 10% is released to water. Of this 10%, about 95% is estimated to be removed in wastewater treatment plants (WWTPs). Nevertheless, it is the discharge via WWTP effluent (just ~0.5% of emissions!) that is the major regulatory concern.

Concerns regarding the amount being discharged to the aquatic environment reflect a number of significant activities focused on assessing the bioaccumulation potential of cVMS in aquatic organisms, and in particular fish. During the SETAC meeting the first data on D5 levels in fish sampled distant from point sources were reported. Each of the cVMS were shown to be present at mid- ng/g lipid levels in herring sampled at ten stations along the Swedish coast of the Baltic Sea and the Skagerrak, as well as in blue mussels and seven other fish species from one of these stations (Kierkegaard et al. 2010). These chemicals were also measured in livers from Atlantic cod and sculpin sampled in three fjords in Spitzbergen, whereby a relationship between the measured concentrations and the proximity to municipal WWTP discharges was observed (Warner et al. 2010).

In an effort to quantitatively evaluate bioaccumulation of cVMS in the field, trophic magnification factors were determined in a food web in Lake Pepin, a lake in the Mississippi River downstream of the metropolis Minneapolis/Saint Paul. D4 and D5 were analyzed to excellent quality standards in 2 benthic invertebrates and 15 species of fish. The trophic magnification factors were 0.31 and 0.18, for D4 and D5, indicating that the lipid-normalized concentrations of these chemicals tended to decrease as they moved up the food chain (Woodburn et al. 2010).

Two other studies took a different approach to quantifying bioaccumulation, one that was necessitated by the very low concentrations of cVMS in water. The underlying premise was that bioaccumulation is the fraction of the chemical present in the aquatic environment that is transferred to fish. Since sediment is the major reservoir of D5 in the aquatic environment, this transfer was estimated using the ratio of the D5 concentrations in fish and sediment. To provide a basis of comparison, the same ratio was calculated for PCB180. Measurements were conducted for lugworms and flounder in the Humber estuary and perch in six Swedish lakes. The ratio for D5 was similar to or greater than the ratio for PCB180, indicating that the bioaccumulation of D5 was similar to or greater than PCB180 (Kierkegaard and McLachlan 2010c; van Egmond et al. 2010a).

One important factor governing the losses of cVMS from the aquatic environment, and that also strongly influences its overall environmental persistence, is the partitioning of cVMS between sediment and water. There is growing evidence that the partition coefficients are considerably lower than one would expect from the high octanol/water partition coefficients of these chemicals (van Egmond et al. 2010b). However, it is recognized that there are, to
date, no field studies on the persistence of cVMS in soils or sediments, which is an area that warrants future research.

The session was thus successful at providing a forum for discussing issues surrounding the persistence, bioaccumulation, and toxicity of cVMS. Information that is critical for supporting current regulatory activities.

References


Authors’ contact information: michael.mclachlan@itm.su.se; todd.gouin@unilever.com