Dynamic Behaviors of Linear and Cyclic Volatile Methylsiloxanes in Global and Local Environments

Kim J[1], Mackay D[2], Whelan MJ[3]

[1]Toxicology and Environmental Research and Consulting, The Dow Chemical Company, Midland, MI, jaeshin.kim@dowcorning.com; [2]Chemistry Department, Trent University, Peterborough, ON, Canada; [3]Department of Geography, University of Leicester, Leicester LE1 7RH, United Kingdom

Introduction

Linear and cyclic volatile methylsiloxanes (VMSs) have a wide range of uses including as intermediates for the production of silicone polymers or as ingredients in personal care products[1-4]. They have an unusual combination of high hydrophobicity and elevated Henry's Law constants[5,6]. This implies that they partition from wastewater to both organic matter (biosolids) and air during wastewater treatment, with only a small fraction released to receiving waters via the effluent stream. It also means that they occupy a very different part of "chemical space" compared with carbon-based organic compounds which have been classified as persistent organic pollutants (POPs). Recently, regulatory concern has been raised about the environmental profile of some cyclic VMS compounds, regarding very persistent (vP) and very bioaccumulative (vB) criteria in REACH Annex XIII[7], in addition to consideration under the Stockholm Convention on Persistent Organic Pollutants due to their potential for long-range transport along with vPvB properties[8].

Based on previous environmental fate predictions with various emission scenarios[9,10], the majority of VMS compounds in water and sediment are the result of emission to water with insignificant contributions from emissions to air and soil. Concentration changes in different environmental media (in both the immediate vicinity of an emission and more widely) can be predicted, with appropriate caution, using dynamic (Level IV) multi-media fate and transport models (MFTMs).

Ideally, response times to emission change should be estimated using a comprehensive dynamic model describing all relevant uses, sources and environmental fate processes. In the case of VMS compounds, the two critical scales are (i) local aquatic environments close to emission points where bioaccumulation and food web transfers might be an issue (due to high hydrophobicity) and (ii) the global (hemispherical) environment in order to evaluate the potential for long-range transport (LRT) and deposition (due to high volatility). Thus, the specific objective of this work was to investigate systematically the inter-relationships between chemical properties and local environmental conditions (both of which can affect response times) and to provide guidance on strategic planning of future VMS monitoring programs.

Materials and methods

The Chemicals: Eight linear and cyclic volatile methylsiloxanes (VMSs) were selected for modelling: hexamethyldisiloxane (L2, CAS 107-46-0), octamethyltrisiloxane (L3, CAS 107-51-7), decamethyltetrasiloxane (L4, CAS 141-62-8), dodecamethylpentasiloxane (L5, CAS 141-63-9), hexamethylcyclotrisiloxane (D3, CAS 541-05-9), octamethylcyclotetrasiloxane (D4, CAS 556-67-2), decamethylcyclopentasiloxane (D5, CAS 541-02-6), and dodecamethylcyclohexasiloxane (D6, CAS 540-97-6).

Multimedia Models: Estimation of response times is needed in order to set expectations for the magnitude and timing of environmental concentration changes after VMS emission reductions are implemented. This information can help to identify the time scales required for monitoring and provide a framework for the interpretation of observed post-restriction concentration changes. Although VMS compounds have been in commercial use for decades, to date, no reliable response time data are available. Two models were selected: a dynamic version of the Quantitative Water Air Sediment Interactive model (QWASI)[11,12] and the Global-Scale Fate and Transport Model or GloboPOP[13]. These models were supplemented with outputs from the OECD P_{OV}

and LRTP Screening Tool (v2.2) to determine predicted overall persistence (P_{OV}), Characteristic Travel Distance (CTD) and atmospheric to surface media Transfer Efficiencies (TEs)[14,15].

Results and discussion

Dynamic Behaviors at the Global Scale: The P_{OV} from the OECD Screening Tool predicts that the P_{OV} of VMSs ranges from 9.8 to 120 days, the CTD ranges from 1,440 to 5,850 km and the TE ranges from 0.001 to 0.03%. The results indicate that persistence and atmospheric transport characteristics of VMS are significantly different from those of "well-established" POPs (P_{OV}: 210-48,000 days, CTD: 400-1,000,000 km, TE: 0.05-1,200%). Similarly, predictions of global behavior generated by GloboPOP suggest that the primary environmental compartment (i.e., that containing the highest fraction of total mass) for the eight VMSs is the atmosphere, in contrast to other POPs tested[16]. In fact, all the VMS materials are classified as "fliers" which do not readily deposit back to the Earth's surface. Most well-established POPs, instead, are classified as "hoppers" or "swimmers", moving to remote environments via the atmosphere in short "hops" as a consequence of their semi-volatile nature or via ocean currents in the case of more water-soluble compounds. A useful output from GloboPOP is Arctic Contamination Potential (ACP)[16] which is predicted to be very low for VMSs, supporting the suggestion of TE of a low likelihood of back deposition to surface environments in high latitudes, based on their partitioning properties. Values for the absolute ACP for VMSs assuming 10 and 20 years of emission ranged from 0.0006% to 0.0390% for eACP$_{10}$ and from 0.0006% to 0.0196% for eACP$_{20}$. After cessation of VMS emission, the mass predicted to be in surface media decreases exponentially with half-times (HTs, the time required for the concentration to fall to 50% of its initial value) of 0.1-4.5 years. HTs for L2, L3, D3 and D4 in Arctic surface media were 0.1-0.8 years whereas those for L4, L5, D5 and D6 were predicted to be between 1.4 and 4.5 years. GloboPOP predictions with the aforementioned emission scenario suggest that global concentrations of VMS will quickly reach a steady-state in all environmental compartments in all global zones under the assumption of constant emission. As expected, HTs in the Arctic are generally greater than those in N-temperate zone, mainly due to slower degradation rates at lower temperatures. HTs of VMSs in air (<0.1 years) were the shortest compared with the other compartments and HTs in sediment (up to 8.57 years) were the longest. HTs in sediment will depend on the assumptions made about the half-life in this compartment (which is uncertain) and will also depend on the depth assumed for the active sediment layer (i.e. sediment which is "available" to the system for resuspension and exposure to biota).

Response Times of VMSs in Specific Aquatic Systems: The QWASI model was employed in order to make more detailed site-specific predictions about chemical response times in water-sediment systems. Half-times in water and sediment were illustrated in Figure 1. Concentrations in water and sediment are predicted to decrease at different rates because the rates of transport and degradation processes differ locally. The lowest HT in water (<1 day) was predicted for D3 for all the environmental systems considered, suggesting little dependence on system properties. In the environments with large surface area-to-volume ratios (including the three evaluative EU regulatory environments and Lake Pepin), the predicted response times were also short (HTs <5.4 days which is much shorter than the hydraulic retention times (HRTs) of these systems: 12-198 days). In the other systems, the HTs of all VMSs, except D3, ranged from 3 to ~300 days, depending on temperature. As temperature increased from 1 to 20 °C, the predicted HTs in water decreased by a factor between 1.5 and 6, depending on the combination of location and VMS compound. In general, the lower molecular weight VMS molecules tend to degrade faster than the larger ones, which is reflected in shorter predicted HTs in water. The dominant loss process for D3 in all systems was degradation (>89%), due to its short degradation half-life. Degradation also made significant contributions to losses of the other linear VMSs, as well as D4 and D5 – particularly as temperature increased and as water volume (and depth) increased. Higher water depths reduce the relative contribution of volatilization and increased volume is correlated with longer water residence times (*cet. par.*) which increases the relative contribution of degradation in water when degradation can take place uniformly in the whole water column (as is the case when it is driven by hydrolysis). Advection makes a

relatively minor contribution to the HT for most chemicals in most systems, except in Lake Pepin (HRT: 12 days) where the contribution of advection was as high as 60% for L2, L3, D4 and D5 at 1 °C when degradation was slow. The contribution of volatilization to HTs was important in the evaluative EU regulatory environments, which have high surface area-to-volume ratios (i.e., low depth) because the impact of volatilization on concentration (expressed as an effective first order term calculated from the two-film resistance mass transfer coefficient) is inversely proportional to depth.

Predicted HTs in sediment ranged from 1.7 days to 16 years depending on aquatic system (Figure 1). D3 and L2 are predicted to have the lowest sediment HTs for all the environmental systems considered: <23 and <73 days, respectively. For the other VMSs, HTs in sediment increased with the active sediment layer depth. HTs in Lake Pepin (<1 year) and Oslofjord (<1.5 years) were relatively low for all VMSs due to the assumed high resuspension and burial rates. Of the eight VMSs considered, L4, L5, D5 and D6 had high HTs in sediment – although these depended on location, temperature and active sediment layer depth. However, the effect of temperature on sediment HTs differed for the linear and cyclic materials. For the linears, HTs in sediment decreased with increasing temperature, presumably due to increasing degradation rate: the Ea (activation energy) for hydrolysis is relatively high compared with the ΔU_{OC} (enthalpy of phase change between organic carbon and water) for the linears. For the cyclics, on the other hand (particularly for D5 and D6), predicted HTs in sediment tended to increase with increasing temperature because baseline degradation rate constants for these materials are relatively low but sorption to solids is predicted to increase relatively steeply with temperature. In sediment, there are three principal removal processes: degradation, resuspension, and burial. The absolute contribution made by degradation is correlated with the active sediment layer depth and temperature. This is because the total amount degraded is determined by the degradation rate constant and the volume of the compartment. Losses via resuspension depend on the concentration sorbed to sediment solids which depends on K_{OC} and temperature. When degradation in sediment becomes less effective, the concentration in sediment increases and removal by resuspension or burial also increases. The removal of VMSs by resuspension was predicted to be greater than by burial in most environmental systems.

Conclusions

VMSs are predicted to be distributed predominantly in air where they react with OH radicals, leading to short response times. After cessation of emissions VMSs concentrations in the environment are expected to decrease rapidly from current levels. Response times in specific water and sediment systems were evaluated using a dynamic QWASI model. Response times were sensitive to both physico-chemical properties and environmental characteristics. Degradation was predicted to play the most important role in determining response times in water and sediment. In the case of the lowest molecular weight VMSs such as L2 and D3, response times were essentially independent of environmental characteristics due to fast hydrolysis in water and sediment. However, response times for the other VMSs are system-specific. They are relatively short in shallow water bodies but increase with depth due to the diminishing role of volatilization on concentration change as volume to surface area ratio increases. In sediment, degradation and resuspension rates also contribute most to the response times. The estimated response times for local environments are useful for planning future monitoring programs.

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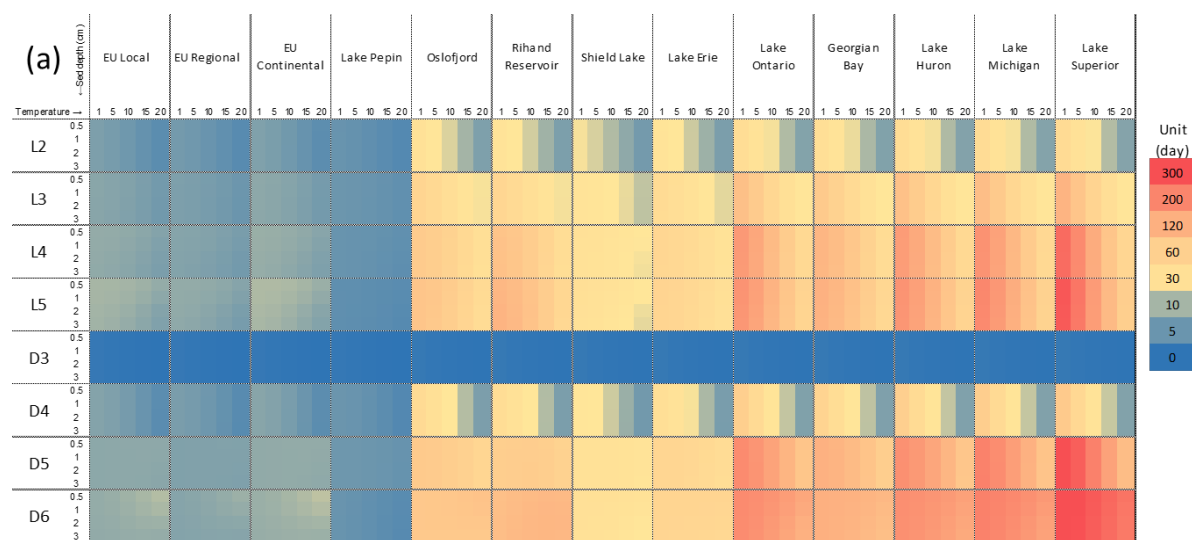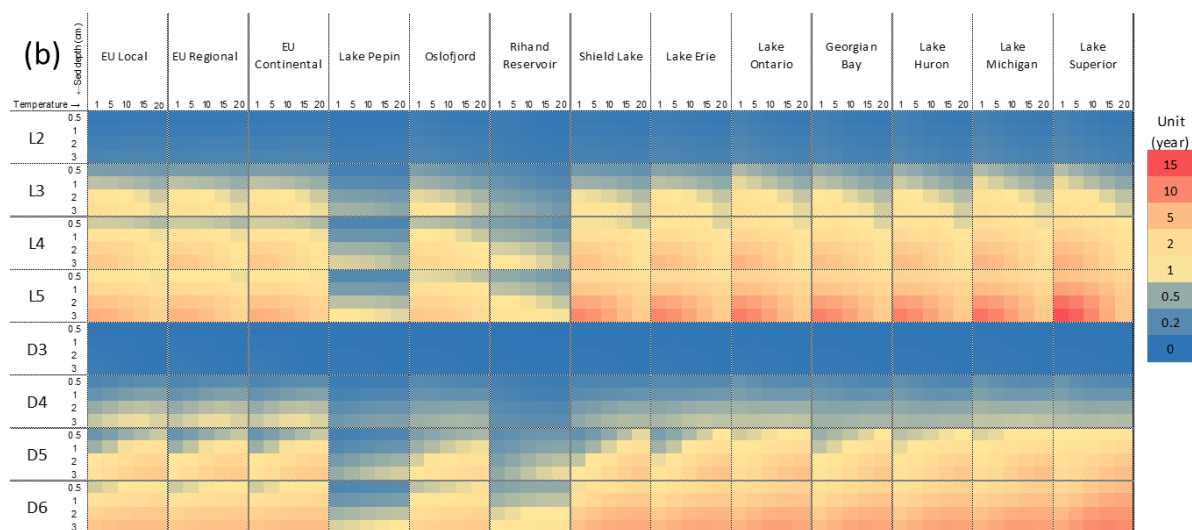
Figure 1. Half-times of the eight linear and cyclic VMSs in (a) water and (b) sediment in 13 different aquatic environments.