Chemosphere 195 (2018) 325–335

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Predicted persistence and response times of linear and cyclic volatile methylsiloxanes in global and local environments

Jaeshin Kim [a], [*], Donald Mackay [b], Michael John Whelan [c]

[a] Toxicology and Environmental Research and Consulting, The Dow Chemical Company, Midland, MI, USA
[b] Department of Chemistry, Trent University, Peterborough, ON, Canada
[c] School of Geography, Geology and the Environment, University of Leicester, Leicester LE1 7RH, United Kingdom

HIGHLIGHTS

- Response times of eight volatile methylsiloxanes (VMSs) in environmental systems.
- Quick response times in all media except sediment by GloboPOP and QWASI.
- Short response times in shallow water bodies due to degradation and volatilization.
- Response times in sediment are dependent on degradation and resuspension rates.

ARTICLE INFO

Article history:
Received 11 October 2017
Received in revised form
8 December 2017
Accepted 11 December 2017
Available online 12 December 2017

Handling Editor: I. Cousins

Keywords:
Volatile methylsiloxanes (VMS)
Environmental multimedia fate and transport models
Response times

ABSTRACT

We investigated the response times of eight volatile methylsiloxanes (VMSs) in environmental systems at different scales from local to global, with a particular focus on overall loss rates after cessation of emissions. In part, this is driven by proposals to restrict the use of some of these compounds in certain products in Europe. The GloboPOP model estimated low absolute Arctic Contamination Potentials for all VMSs and rapid response times in all media except sediment. 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.

1. Introduction

Volatile methylsiloxanes (VMSs) have a wide range of uses including as intermediates for the production of silicone polymers and as ingredients in personal care products (Chandra and Allen, 1997; Horii and Kannan, 2008; Wang et al., 2013b; Dudzina et al., 2014). They have an unusual combination of high hydrophobicity and high Henry's Law constant (Whelan et al., 2010; Xu et al., 2014). 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 organic compounds which have been classified as persistent organic pollutants (POPs).

VMSs have been detected in all environmental media (Alaee et al., 2013; Wang et al., 2013b; Rücker and Kümmerer, 2014): air

---

[*] Corresponding author.
E-mail address: jaeshin.kim@dowcorning.com (J. Kim).

https://doi.org/10.1016/j.chemosphere.2017.12.071

(McLachlan et al., 2010; Genualdi et al., 2011; Buser et al., 2013; Yucuis et al., 2013; Gallego et al., 2017), soils (Xu, 1999; Xu and Chandra, 1999; Wang et al., 2013a), aquatic systems (Warner et al., 2010; Krogseth et al., 2014; Capela et al., 2017), and aquatic organisms (Kierkegaard et al., 2013; Krogseth et al., 2014; Wang et al., 2017). Although few studies have monitored VMS concentrations in the same system over several years, there is increasing evidence that environmental concentrations of VMSs appear to be relatively stable, suggesting that many systems may be under approximately steady-state conditions in which system losses approximately equal emissions (Schøyen et al., 2016). This is also corroborated by reasonable agreement between steady-state model predictions and monitoring data (Whelan and Breivik, 2013).

Recently, regulatory concern has been raised about the environmental profile of some VMS compounds. For example, the Member State Committee (MSC) of the European Chemicals Agency (ECHA) (2015) has suggested that octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) should be classified as very persistent (vP) and very bioaccumulative (vB) against the vPvB criteria in REACH Annex XIII (the half-lives of D4 and D5 in sediment are >180 days, and they have bioconcentration factors >5000 L kg^{-1}). In addition, the Council of the European Union has proposed D4 for listing in Annex A, B and/or C of the Stockholm Convention on Persistent Organic Pollutants due to its potential for long-range environmental transport as well as its vPvB properties (European Commission, 2016). Since concerns have been raised about persistence and bioaccumulation in the aquatic environment, the Committee for Risk Assessment (RAC) and Committee for Socio-economic Analysis (SEAC) (2016) have proposed a restriction in the use of D4 and D5 in “wash-off” personal care products (PCPs), mainly to reduce their release to wastewater treatment plants (WWTPs) and subsequent exposure to aquatic systems. This proposed restriction will reduce the emission of D4 and D5 by an estimated 78% and 97%, respectively. Associated decreases in water and sediment concentrations are expected to be proportionate, although the time taken to achieve new steady state concentrations is currently unknown.

Based on previous environmental fate predictions with various emission scenarios (Hughes et al., 2012; Kim et al., 2013), 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): e.g., Whelan et al. (2015); Kim et al. (2017); Krogseth et al. (2017a, 2017b). Furthermore, subsequent monitoring of key environmental systems would validate *a priori* predictions of VMS concentrations and environmental persistence. Although the utility of existing monitoring data for evaluating response times is limited, good matches between model predictions and observations can also suggest that model assumptions are (at least) not inconsistent with reality and, hence, lend some credibility to dynamic model predictions of response times.

Ideally, response times should be estimated using a comprehensive dynamic model describing all relevant uses, sources and environmental fate processes. This would include separate consideration of ‘leave on’ and ‘wash off’ products, evaporation during use, discharge to waste water, subsequent transport to treatment facilities and discharge to receiving waters followed by dilution, sedimentation, volatilization, hydrolysis and bioaccumulation in food webs. Atmospheric fate (including interactions with surface media, especially in potentially vulnerable cold climate ecosystems) would also be addressed at local and global scales. Since (regrettably) no such single validated model exists different models that address aspects of environmental fate and behavior processes at different scales need to be employed. 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). As a result, two models were selected: a dynamic version of the Quantitative Water Air Sediment Interactive model (QWASI) (Mackay et al., 1983, 2014) and the Global-Scale Fate and Transport Model or GloboPOP (Wania and Mackay, 1995). 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) (OECD, 2006; Wegmann et al., 2009). This model also compares P_{OV}, CTD and TE estimates with those of well-known POPs (OECD, 2006; Wegmann et al., 2009): i.e., the so-called “benchmarking approach”. A specific objective 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 monitoring programs.

2. Methods

2.1. The chemicals

Eight linear and cyclic volatile methylsiloxanes (VMSs) were selected for modeling: hexamethyldisiloxane (L2, CAS No. 107-46-0), octamethyltrisiloxane (L3, CAS No. 107-51-7), decamethyltetrasiloxane (L4, CAS No. 141-62-8), dodecamethylpentasiloxane (L5, CAS No. 141-63-9), hexamethylcyclotrisiloxane (D3, CAS No. 541-05-9), octamethylcyclotetrasiloxane (D4, CAS No. 556-67-2), decamethylcyclopentasiloxane (D5, CAS No. 541-02-6), and dodecamethylcyclohexasiloxane (D6, CAS No. 540-97-6). These compounds are all oligomers of polydimethylsiloxanes (PDMS) with relatively low molecular weights. As the number of siloxane bonds and methyl groups increases, the molecular weight increases (from 162 to 389 g mol^{-1} for the linear materials and from 222 to 445 g mol^{-1} for the cyclic compounds). In parallel, vapor pressure decreases markedly (from 5500 to 6 Pa for the linears and from 671 to 6 Pa for the cyclics) and hydrophobicity increases significantly (i.e. aqueous solubility decreases and the octanol-water partition coefficient, K_{OW}, increases). The physico-chemical properties and environmental half-lives (HL) of the VMS compounds examined here are shown in Table 1 (see more details in Table S1), along with parameters describing the temperature-dependence of partition coefficients and half-lives (enthalpies of phase change and activation energies, respectively). These values were used as required inputs of the models and were mostly based on direct measurement. Where a property had no measured data, its value was estimated via interpolation or extrapolation based on (statistically significant) empirical relationships between the property concerned and molecular weight. These values are shown in *italics* in Table 1.

VMSs have unique partitioning properties compared with organic compounds. The partition coefficients of many VMSs (Table 1) have been successfully measured using three-phase equilibrium methods (Xu and Kropscott, 2012, 2014). Air-water partition coefficients, $\log K_{AW}$, were greater than 2.4 at 25 °C for all the selected VMS except D3. The $\log K_{AW}$ values are much greater than those of comparable n-alkanes; e.g., −1.70 for n-pentane and −2.16 for n-octane (Jönsson et al., 1982) and those of