

Critical Review

Application of multimedia models for understanding the environmental behavior of volatile methylsiloxanes: Fate, transport, and bioaccumulation

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Abstract

Multimedia fate and transport models (MFTMs) describe how chemicals behave in the environment based on their inherent properties and the characteristics of receiving systems. We critically review the use of MFTMs for understanding the behavior of volatile methylsiloxanes (VMS). MFTMs have been used to predict the fate of VMS in wastewater treatment, rivers, lakes, marine systems, and the atmosphere, and to assess bioaccumulation and trophic transfers. More widely, they have been used to assess the overall persistence, long-range transport potential (LRTP), and the propensity for atmosphere–surface exchange. The application of MFTMs for VMS requires particularly careful selection of model inputs because the properties of VMS differ from those of most organic compounds. For example, although *n*-octanol/water partition coefficient (K_{OW}) values are high, air:water partition coefficient (K_{AW}) values are also high and *n*-octanol/air partition coefficient (K_{OA}) values are relatively low. In addition, organic carbon/water partition coefficient (K_{OC}) values are substantially lower than expectations based on K_{OW} . This means that most empirical relationships between K_{OC} and K_{OW} are not appropriate. Good agreement between modeled and measured concentrations in air, sediment, and biota indicates that our understanding of environmental fate is reasonable. VMS compounds are “fliers” that principally partition to the atmosphere, implying high LRTP, although they have low redeposition potential. They are degraded in air (half-lives 3–10 days) and, thus, have low overall persistence. In water, exposure can be limited by hydrolysis, volatilization, and partitioning to sediments (where degradation half-lives are likely to be high). In food webs, they are influenced by metabolism in biota, which tends to drive trophic dilution (i.e., trophic magnification factors are often but not always <1). Key remaining uncertainties include the following: (i) the strength and direction of the temperature dependence for K_{OC} ; (ii) the fate of atmospheric reaction products; and (iii) the magnitude of emissions to wastewater. *Integr Environ Assess Manag* 2022;18:599–621. © 2021 The Authors. Integrated Environmental Assessment and Management published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Environmental fate, Long-range transport potential, Multimedia fate and transport models, Persistence, Volatile methylsiloxane

INTRODUCTION

Volatile methylsiloxanes (VMS) are a class of low-molecular-weight organo-silicone compounds with an unusual set of physico-chemical properties. Specifically, they are all highly volatile but also very hydrophobic and

lipophilic. They are also resistant to microbially mediated biodegradation. This means that they have the potential for environmental longevity, for long-range transport in the atmosphere, and for accumulation in biota. This potential has triggered concerns about whether some VMS compounds should be classed as persistent organic pollutants (POPs). They have, therefore, been subjected to considerable regulatory scrutiny over approximately the last 15 years. For example, comprehensive risk assessment reports were produced for the three most commonly used cyclic VMS compounds (cVMS): octamethylcyclotetrasiloxane (D4, CAS 556-67-2), decamethylcyclopentasiloxane (D5, CAS 541-02-6), and dodecamethylcyclohexasiloxane (D6, CAS 540-97-6) in the United Kingdom in 2010 by the Environment Agency (Brooke et al., 2009a, 2009b, 2009c). Reviews have also

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been conducted in Canada (Environment Canada and Health Canada, 2008a, 2008b, 2008c; Giesy et al., 2011) and in Australia under the National Industrial Chemicals Notification and Assessment Scheme (NICNAS, 2018). More recently, they have been subjected to use restrictions by the European Chemicals Agency (2019).

Multimedia fate and transport models (MFTMs: e.g., Mackay, 2001; MacLeod et al., 2010) have played a key role in developing an understanding of the behavior of VMS in the environment and in assessing whether they should be classified as persistent and bioaccumulative or as POPs. MFTMs describe how chemicals are likely to behave in environmental systems based on their inherent properties (e.g., aqueous solubility, saturation vapor pressure, and affinity for organic matter), their emissions, and the characteristics of the system to which they are emitted (e.g., relative and absolute dimensions of different compartments, temperature, suspended matter dynamics, and flow rates for water and air). They can predict chemical concentrations in different media (which can be used to assess ecotoxicological risk and as an input to bioaccumulation models), estimate overall persistence, and act as a framework for interpreting measured data on chemical exposure. For example, they can be used to fill the spatial and temporal gaps that often exist between measurements and they can be used a priori to inform the design of experiments and monitoring campaigns (hence, acting as extended hypotheses). Since they are deliberately abstract, they are easy to run and computationally inexpensive, which makes them a cost-effective complement to environmental monitoring projects. However, this ease of use can also be a disadvantage (e.g., resulting in erroneous conclusions) if care is not taken to ensure that all the parameters are appropriate and if their outputs are not interpreted within their domain of applicability and with an understanding of the principal sources of uncertainty.

In this paper, we critically review the use of MFTMs for understanding the behavior of VMS in different environmental systems and their persistence, long-range transport potential (LRTP), and bioaccumulation potential. This provides some important illustrations of both the utility of MFTMs and some of the pitfalls that may be associated with their use for VMS. We should point out that other reviews on aspects of VMS occurrence and behavior in the environment have been produced (Bridges & Solomon, 2016; Wang, Norwood, et al., 2013). Our intention here is not to reproduce or supplant these. Rather, we focus on the role that modeling has played in understanding VMS fate and behavior in environmental systems, in addition to highlighting some of the existing uncertainties in model parameterization and interpretation. We also focus explicitly on fate, behavior, and trophic transfer and do not consider toxicity or associated toxicological or ecotoxicological risks. For context, VMS compounds have relatively low documented toxicities, with very few effects reported below their limits of aqueous solubility in water or sediment (Mackay, Powell, et al., 2015). In addition, our understanding is that VMS

compounds are not listed in maximum contaminant levels for drinking water quality in the United States or equivalent limits elsewhere. Although we refer to the behavior of VMS compounds in general, most of the examples used consider the three most widely used cVMS, that is D4, D5, and D6.

VMS IN THE ENVIRONMENT

VMS compounds have been in commercial use for several decades and are used as intermediates in the manufacture of silicone polymers and as ingredients in a range of cosmetics and personal care products such as skin creams, deodorants, and hair care products (Capela et al., 2016; Chandra & Allen, 1997; Dudzina et al., 2014; Horii & Kannan, 2008; Wang, Norwood, et al., 2013).

The principal physico-chemical properties of low-molecular-weight VMS compounds are shown in Table 1, as presented by Kim et al. (2018). These values are largely derived from studies conducted or sponsored by industry (e.g., S. Xu & Kropscott, 2012, 2014). However, other independent property data for some VMS compounds (predominantly for D5) have been reported elsewhere, some of which are consistent with the data shown in Table 1, some of which are not. Examples of a range of values for some key properties of D5 from various sources are shown in Table 2. Some of these are discussed in more detail below.

All the VMS compounds have a combination of partitioning properties that are very different from those of most other organic compounds. Certain major partition coefficients of VMS have been measured using three-phase equilibrium methods (S. Xu & Kropscott, 2012, 2014). The logarithms of the air–water partition coefficients ($\log K_{AW}$) for these compounds are all greater than 2.4 at 25 °C, except for D3. These values are greater than those of *n*-alkanes with similar molecular weights (e.g., 1.82 for *n*-hexane and 2.08 for *n*-octane: Jönsson et al., 1982) and much greater than those of polychlorinated biphenyls (PCBs) (e.g., final adjusted values of –2.02 for PCB-3 and –2.75 for PCB-194: N. Li et al., 2003). There is also an increase in $\log K_{AW}$ (and in $\log K_{OW}$ or the logarithm of the octanol–water partition coefficient) with increasing molar mass. Values of $\log K_{OW}$ for VMS range from 4.38 for D3 to 9.41 for L5 (Table 1). These values are greater than those of *n*-alkanes of equivalent molecular weight (e.g., 3.39 for *n*-pentane: Hansch et al., 1995 and 5.18 for *n*-octane: Miller et al., 1985) but are similar to those for PCBs (e.g., 4.49 for PCB-3 and 7.67 for PCB-194: N. Li et al., 2003). Such high values for K_{OW} suggest that the most hydrophobic VMS compounds (e.g., L4, L5, D5, and D6) could behave like POPs (e.g., they might be expected to show bioaccumulation and biomagnification in food webs). However, there are several other properties of VMS that challenge this expectation. For example, the affinity of VMS compounds for organic carbon in the natural environment (as described by the organic carbon to water partition coefficient, K_{OC}) has been found to be consistently lower than expectations (Kozerski et al., 2014) based on general relationships between K_{OC} and K_{OW} (Gerstl & Mingelgrin, 1984; Karickhoff,

TABLE 1 Physico-chemical properties of eight linear and cyclic volatile methylsiloxanes (modified from Kim et al., 2018)

Chemical name	L2	L3	L4	L5	D3	D4	D5	D6
Molecular mass (g mol ⁻¹)	162.4	236.5	310.7	384.8	222.5	296.6	370.8	444.9
Vapor pressure (Pa at 25 °C)	5500	535	58.1	6	671	140	33.2	6
Water solubility (mg L ⁻¹)	0.93	0.0345	0.00674	7.04E-5	1.56	0.056	0.017	0.0053
Melting point (°C)	-68.2	-86	-76	-80	64.5	17.5	-38	-68
Partition coefficients with enthalpy of phase change (ΔU)								
Log K_{AW} (at 25 °C)	2.5	3.1	3.5	4.0	0.4	2.7	3.2	3.0
ΔU_{AW} (kJ mol ⁻¹)	53	39.5	65.5	90	73.9	73.9	123.9	123.9
Log K_{OW} (at 25 °C)	5.2	6.8	8.1	9.4	4.4	7.0	8.1	8.9
ΔU_{OW} (kJ mol ⁻¹)	19.4	1	11.3	11.3	31.9	31.9	68.8	68.8
Log K_{OA} (at 25 °C)	2.7	3.7	4.7	5.5	4.0	4.2	4.9	5.9
ΔU_{OA} (kJ/mol)	-26.7	-40	-46.8	-39.9	-42.5	-42.5	-47.9	-58.5
Log K_{OC} (at 25 °C)	3.2	4.3	5.2	5.7	3.3	4.2	5.2	6.0
ΔU_{OC} (kJ mol ⁻¹)	19.4	1	11.3	11.3	31.9	31.9	68.8	68.8
Half-lives (HL , day) in air (A), water (W), soil (S), and sediment (Sed) with activation energy (E_a)								
HL_A (at 25 °C)	7.8	5.4	3.6	2.7	9.8	7.2	5.3	3.9
E_a (HL_A) (kJ mol ⁻¹)	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3
HL_W (at pH 7 and 25 °C)	4.8	13.7	30.3	41.5	0.03	3.9	70.4	401
E_a (HL_W) (kJ mol ⁻¹)	61.79	68.1	83.6	83.6	87.6	87.6	81.1	30.7
HL_S (at 25 °C)	7.9	4.5	7.6	16.5	0.53	5.3	12.6	401
E_a (HL_S) (kJ mol ⁻¹)	61.79	68.1	69.1	83.6	87.6	81.1	81.1	30.7
HL_{Sed} (at 25 °C)	98	365	420	912	3	365	3100	3100
E_a (HL_{Sed}) (kJ mol ⁻¹)	61.79	68.1	83.6	83.6	87.6	87.6	81.1	30.7

Note: Partition coefficients and half-lives are rounded to one decimal place to reflect the uncertainties in these estimates. Note that half-lives in soil and sediment are highly uncertain and may be longer in the field than those reported here.

Abbreviations: D3, hexamethylcyclotrisiloxane (541-05-9); D4, octamethylcyclotetrasiloxane (556-67-2); D5, decamethylcyclopentasiloxane (541-02-6); D6, dodecamethylcyclohexasiloxane (540-97-6); L2, hexamethyldisiloxane (107-46-0); L3, octamethyltrisiloxane (107-51-7); L4, decamethyltetrasiloxane (141-62-8); L5, dodecamethylpentasiloxane (141-63-9).

1981). Whelan et al. (2009) and (2010), for example, looked at the effect of organic carbon on water–atmosphere transfers of radiolabeled D5 in open vessels in the laboratory and used model descriptions of these systems to derive an effective value of K_{OC} . The values obtained from the two experiments were different. In the case of Whelan et al. (2009), commercial humic acid was used, which resulted in a mean effective log K_{OC} value of 5.28 for D5. This was similar to the log K_{OC} value of 5.17 derived by Kozerski et al. (2014) from OECD 106 batch equilibrium studies on three different soils. Whelan et al. (2010) used natural river water and derived a mean effective log K_{OC} value of 6.16. A similar indirect method was used by Panagopoulos et al. in water at different temperatures (Panagopoulos et al., 2015, 2016, 2017). Their baseline K_{OC} values derived were similar to those reported by Whelan et al. (2010) but approximately 1 order of magnitude larger than the values reported by Kozerski et al. (2014) and Whelan et al. (2009). Although the

discrepancies are not fully accounted for, it is likely that the determination of K_{OC} might be affected by the methods used (“direct” and “indirect”) and by the types of organic material used in each study. Different sources of organic matter are known to show different affinities for organic chemicals and to yield effective values for partition coefficients that can often vary by an order of magnitude (e.g., Niederer et al., 2007). For the values reported by Kozerski et al. (2014), it is possible that the presence of colloids (which are known to be particularly sorptive: [Gschwend & Wu, 1985]) in the supernatant of the centrifugation may have reduced the derived K_{OC} values, but this argument is not applicable to the indirect methods. In any case, the effective K_{OC} values of VMS materials were all at least two orders of magnitude lower than values that would be expected based on the measured respective values of log K_{OW} (i.e., using a Karickhoff-type relationship).

TABLE 2 Range of key physico-chemical properties for D5 derived from and used in different studies

Property	Value	References	Comment
Molecular mass (g mol ⁻¹)	370.8	-	Molecular formula: C ₁₀ H ₃₀ O ₅ Si ₅
Vapor pressure (Pa)	33.2	Flaningam (1986)	At 25 °C
	22.7	Epona Associates (2005)	At 25 °C
	20.4	Lei et al. (2010)	At 25 °C
Water solubility (mg L ⁻¹)	0.017	Varaprath et al. (1996)	At 23 °C; SD ±0.00072
Melting point (°C)	-38	Budavari et al. (1996)	At atmospheric pressure (101.3 kPa)
log K _{AW} (-)	3.16	S. Xu and Kropscott (2014)	Slow stirring/microextraction method at 25 °C; equivalent to a Henry's Law constant of 33 atm m ³ mol ⁻¹
ΔU _{AW} (kJ mol ⁻¹)	123.9	S. Xu and Kropscott (2014)	Based on three-phase equilibrium tests at two temperatures
log K _{OW} (-)	8.09	S. Xu and Kropscott (2014)	Slow stirring/microextraction method at 25 °C
ΔU _{OW} (kJ mol ⁻¹)	68.8	S. Xu and Kropscott (2014)	Based on three-phase equilibrium tests at two temperatures
	40	Xu (2009)	Internal report
	29	S. Xu and Kozerski (2007)	Poster presentation at SETAC Europe
log K _{OA} (-)	4.93	S. Xu and Kropscott (2014)	Slow stirring/microextraction method at 25 °C
ΔU _{OA} (kJ mol ⁻¹)	-47.9	S. Xu and Kropscott (2014)	Based on three-phase equilibrium tests at two temperatures
log K _{OC} (-)	5.17	Kozerski et al. (2014)	At 25 °C; a batch equilibrium method
	5.28	Whelan et al. (2009)	At 25 °C; derived by model fits to time series of radiolabeled D5 concentrations in open vessels with different concentrations of Aldrich humic acid
	6.16	Whelan et al. (2010)	At 25 °C; derived by model fits to time series of radiolabeled D5 concentrations in open vessels containing river water
	4.38	David et al. (2000)	Used the Equilibrium Partitioning in Closed Systems (EPICS) method at 25°C in pure water and wastewater with different concentrations of organic carbon
	6.01	Panagopoulos et al. (2015)	At 25 °C; K _{OC} and K _{DOC} (very similar values) derived by multimedia model calibration to data from purge and trap experiments
	6.36	Panagopoulos et al. (2016)	At 25 °C; K _{OC} and K _{DOC} (very similar values) derived by multimedia model calibration to data from purge and trap experiments
	6.11	Panagopoulos et al. (2017)	At 25 °C; K _{OC} and K _{DOC} (very similar values) derived by multimedia model calibration to data from purge and trap experiments
ΔU _{OC} (kJ mol ⁻¹)	68.8	S. Xu and Kropscott (2014)	Assumed to be equal to ΔU _{OW}
	-48	Panagopoulos et al. (2017)	Based on purge and trap measurements at four different temperatures
HL _A (day)	7.33	Kim and Xu (2017)	At 25 °C; k _{OH} 1.46 × 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹ at [OH] _{eq} = 7.5 × 10 ⁵ molecule cm ⁻³
	6.90	Atkinson (1991)	At 25 °C; k _{OH} 1.55 × 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹ at [OH] _{eq} = 7.5 × 10 ⁵ molecule cm ⁻³

(Continued)

TABLE 2 (Continued)

Property	Value	References	Comment
	4.11	Safron et al. (2015)	At 25 °C; k_{OH} 2.60×10^{-12} cm ³ molecule ⁻¹ s ⁻¹ at $[OH]_{eq} = 7.5 \times 10^5$ molecule cm ⁻³
	4.35	Xiao et al. (2015)	At 25 °C; k_{OH} 2.46×10^{-12} cm ³ molecule ⁻¹ s ⁻¹ at $[OH]_{eq} = 7.5 \times 10^5$ molecule cm ⁻³
	5.09	Alton and Browne (2020)	At 25 °C; K_{OH} 2.1×10^{-12} cm ³ molecule ⁻¹ s ⁻¹ at $[OH]_{eq} = 7.5 \times 10^5$ molecule cm ⁻³
E_a (HL_A) (kJ mol ⁻¹)	4.3	Safron et al. (2015)	Based on temperature-dependent tests at 40–80 °C
	27.7	Xiao et al. (2015)	Based on temperature-dependent tests at 40–90 °C
	6.8	Bernard et al. (2018)	For D4 (possible read-across to D5); based on temperature-dependent tests between –3 °C and 97 °C
HL_W (day)	70.4	Kozerski (2008), Bidleman (2008)	Experimental data at pH 7 and 25 °C
	74	Environment Canada and Health Canada (2008d)	Recalculation of Kozerski (2008) data
E_a (HL_W) (kJ mol ⁻¹)	81.1	Kozerski (2008), Bidleman (2008)	Based on temperature-dependent tests at pH 7
HL_S (day)	12.6	Xu (2007)	Measured half-lives in two different types of soils (a Michigan Londo soil and a Wahiwa soil) at three different humidities and at room temperature. The greatest half-life was selected as the best value for a conservative approach
E_a (HL_S) (kJ mol ⁻¹)	81.1	Kozerski (2008), Bidleman (2008)	Assumed to be equal to E_a (HL_W) due to hydrolysis in the dissolved phase
HL_{Sed} (day)	3100	S. Xu and Miller (2010)	At pH 8 and 24 °C; experimental data from D5 degradation in Lake Pepin sediment under anaerobic conditions
	23,000	Whelan and Breivik (2013)	Estimated from the hydrolysis rate constant at pH 8 and 25 °C assuming an organic carbon content of 0.04 g g ⁻¹
E_a (HL_{Sed}) (kJ mol ⁻¹)	81.1	Kozerski (2008), Bidleman (2008)	Assumed to be equal to E_a (HL_W) due to hydrolysis in the dissolved phase

Abbreviations: A, air; W, water; S, soil; Sed, sediment.

As a consequence of their high affinity for air with respect to water, VMS compounds have much lower octanol–air partition coefficients, K_{OA} , compared to *n*-alkanes and PCBs with similar hydrophobicities. Values of log K_{OA} for VMS range from 2.71 to 5.86 (Table 1). This compares to a range of log K_{OA} values for organic compounds with log $K_{OW} > 4$ from ~6 to ~12, increasing as log K_{OW} increases. Together with their high K_{AW} values, which reduce partitioning to water droplets in the atmosphere, the relatively low K_{OA} values imply that VMS compounds are much less likely to be transferred from the air to terrestrial systems (e.g., via sorption to vegetation and soils) and to aquatic systems (e.g., via depositing aerosols) compared with classical POP-like substances such as PCBs.

As for K_{AW} , both K_{OW} and K_{OC} for VMS compounds are likely to change with temperature. This relationship can be defined via an exponential relationship with the sensitivity of the partition coefficient to temperature defined by the enthalpy of phase change (ΔU_{OW} or ΔU_{OC} , respectively). S. Xu and Kropscott (2014) reported positive values of ΔU_{OW} for

all VMS compounds (see Table 1), suggesting an increase in hydrophobicity with increasing temperature. In the absence of specific measurements, values for ΔU_{OC} are often assumed to be equal to ΔU_{OW} in environmental models (Whelan & Breivik, 2013). However, data from experiments conducted by Panagopoulos et al. (2017), in which K_{OC} was indirectly measured at four different temperatures, suggest that K_{OC} decreases with increasing temperature, with estimated values of ΔU_{OC} ranging from –79.2 to –45.8 kJ mol⁻¹ for L4, L5, D4, D5, and D6. These values contrast with those of S. Xu and Kropscott (2014) in both magnitude and direction. In both cases, there is uncertainty. For Panagopoulos et al. (2017), the regression equations from which ΔU_{OC} values were derived were all statistically significant, but the R^2 values were variable, ranging between 0.46 (for D4) and 0.73 (for L4). For S. Xu and Kropscott (2014), partition coefficients were determined for only two temperatures—albeit for K_{OW} , K_{OA} , and K_{AW} simultaneously. These uncertainties have important implications for the predicted environmental behavior of VMS,

particularly in dynamic models, which account for seasonal variations in behavior (Krogseth, Whelan, et al., 2017; Panagopoulos Abrahamsson et al., 2020). An increase in K_{OC} with temperature implies that VMS compounds will be less hydrophobic at low temperatures (e.g., in high latitudes). This would make them less persistent because degradation of VMS in surface media predominantly takes place in the freely dissolved aqueous phase by hydrolysis and is negligible in the sorbed phase. In contrast, if K_{OC} decreases with increasing temperature, as suggested by Panagopoulos Abrahamsson et al. (2020), then persistence will be higher at low temperatures. Krogseth, Whelan, et al. (2017) and Panagopoulos Abrahamsson et al. (2020) suggest that measured concentrations of VMS compounds in sediment sampled from several locations in the Arctic are consistent with higher values of K_{OC} , which supports their hypothesis that ΔU_{OC} values for VMS are negative. This is an important uncertainty that requires additional research.

In the atmosphere, VMS compounds react with OH radicals to form siloxanols, which are much more water-soluble and less volatile, and which progressively hydrolyze in water to dimethylsilanediol (DMSD) (Whelan et al., 2004). They have also been shown to react with chlorine (Alton & Browne, 2020; Atkinson et al., 1995). Although these oxidation products are usually dispersed as individual molecules, they can be found in condensed forms such as secondary organic aerosols (Janecek et al., 2019; Milani et al., 2021). However, most VMS compounds are likely to act antagonistically with other volatile organic compounds (VOCs) overall. For example, empirical data from chamber experiments with four VMS compounds (Carter et al., 1992) suggest that they can strongly inhibit tropospheric ozone formation by decreasing OH radical concentrations and, thus, slow down the rate of NO oxidation and O₃ formation from the reaction of VOCs. The average estimated atmospheric half-lives of VMS compounds (when exposed to hydroxyl radicals in the gas phase at globally averaged concentrations) range from 2.66 to 9.82 days (Table 1) based on measured reaction rates in atmospheric chambers (Atkinson, 1991; Kim & Xu, 2017). The reaction rate is generally proportional to the number of methyl groups, but the linear VMS compounds also tend to be more reactive in the atmosphere compared with the cyclic compounds (Kim & Xu, 2017). Although these half-lives are longer than those for some hydrocarbons (e.g., most long-chain alkanes have half-lives of less than 1 day) and exceed the Stockholm Convention criterion for LRTP (atmospheric half-life of 2 days: Annex D of Stockholm Convention on Persistent Organic Pollutants, 2009), they are short enough to limit atmospheric accumulation and further limit any potential for redeposition to surface media, particularly in remote regions (Göktaş & MacLeod, 2016). For example, McLachlan et al. (2010) reported measured concentrations of D5 in air samples from rural Sweden in the range 0.3–9 ng m⁻³. Similarly, Krogseth et al. (2013) reported mean air concentrations of D5 and D6 of 0.73 ± 0.31 and 0.23 ± 0.17 ng m⁻³, respectively, in late summer and 2.94 ± 0.46 and

0.45 ± 0.18 ng m⁻³, respectively, in winter at the Zeppelin observatory on Svalbard in the high Arctic. These concentrations are markedly lower than the maximum mean monthly concentrations in temperate zone urban air (>400 ng m⁻³; Janecek et al., 2017).

The main degradation pathway for VMS in water is hydrolysis, with half-lives ranging from <0.1 days for D3 to 401 days for D6 at pH 7 and 25 °C. The hydrolysis half-life increases with increasing number of siloxanes, although the half-life of the linear compounds is less sensitive to the number of siloxane bonds than the cyclic oligomers, ranging from 4.8 days for L2 to 42 days for L5 (Table 1). In aquatic sediments, the main degradation mechanism is also hydrolysis in the aqueous phase. This means that the actual half-life in the sediment will be a function of partitioning between the sediment solid phase and the porewater, as well as the hydrolysis rate constant. Given the high K_{OC} values of most VMS compounds, a high fraction of the total mass of VMS in sediment will be in the sorbed phase. This means that long half-lives can be expected for VMS in the sediment compartment because most material will not be subjected to hydrolysis (which occurs only in the freely dissolved phase). For example, Whelan (2013) suggested that degradation half-lives for D5 and D6 in sediment could be of the order of several decades. Half-lives for VMS in the water column should also be adjusted for the fraction of the compound in the dissolved phase, which will be a function of the dissolved and particulate organic carbon concentration and K_{OC} . The hydrolysis half-lives for VMS compounds tend to decrease with increasing temperature and with increasing or decreasing pH away from pH 7. The Arrhenius activation energy for hydrolysis in water and sediment is relatively high (i.e., ranging from 31 to 88 kJ mol⁻¹), suggesting that the degradation rate constant is quite temperature-sensitive. D6 has the lowest activation energy (i.e., 31 kJ mol⁻¹) and degradation of this compound is, consequently, least sensitive to temperature. As an illustration of environmentally relevant values, calculated half-lives in sediment for D4, D5, and D6 at 9 °C and pH 8 (the mean annual values for Lake Ontario) are approximately 3, 66, and 340 days, respectively (Whelan, 2013). The predicted degradation half-life in sediment also increases with the number of siloxane bonds, ranging from 3 to 3100 days (Table 1), although Whelan (2013) suggested that the calculated degradation half-life in sediment rich in organic matter at 9 °C and pH 8 could be as long as 485 years for D5. It should be noted that the half-lives of D4 and D5 in Table 1 were measured using Lake Pepin sediment under anaerobic conditions at pH 8 and 24 °C (S. Xu & Miller, 2009, 2010). The half-life of D6 in sediment in Table 1 was assumed to be the same as that for D5 because the value is too large to affect model results. For other siloxanes, their half-lives in sediment were assumed to be ten times the half-lives measured in soil at a relative humidity of 100% (Kim et al., 2018). However, half-lives for these materials could be longer. If rates of degradation in sediment are so low, then burial is likely to be the most important loss mechanism.

Significant VMS contamination of soil will usually be restricted to cases where sewage sludge (biosolids) are applied. Kaj et al. (2005) reported mean concentrations of D4, D5, and D6 ($n = 54$) in Swedish biosolid samples of 0.39, 9.5, and $1.3 \mu\text{g g dw}^{-1}$, respectively. These values are approximately consistent with reported concentrations of D4, D5, and D6 in biosolid-amended Canadian soils in the ranges of <0.008 – 0.017 , <0.007 – 0.221 , and <0.009 – $0.711 \mu\text{g g dw}^{-1}$, respectively (Wang, Norwood, et al., 2013). For example, assuming a sludge application rate of $5 \text{ tons dw ha}^{-1}$, a soil bulk density of 1500 kg m^{-3} , and a mixing depth of 0.2 m (European Chemicals Bureau, 2003), a concentration of D5 in biosolids of $9.5 \mu\text{g g dw}^{-1}$ would result in a concentration in soil of $0.015 \mu\text{g g dw}^{-1}$, although biosolid application rates are sometimes higher than this in practice (e.g., Schowanek et al., 2004). Levels in other soils, which do not receive these emissions, are likely to be negligible (and certainly below current analytical detection limits—e.g., an LOD of $0.036 \mu\text{g g dw}^{-1}$ for D5 in biosolids: Wang, Alaei, et al., 2013). VMS compounds in soil will be subject to degradation as well as volatilization. Leaching losses are likely to be very low due to the very high affinity of VMS compounds for the soil solid phase, although there is some potential for leaching of colloid-associated VMS if there is significant translocation of particulates. This can be particularly significant in soils with preferential flow pathways (e.g., in soil macropores: de Jonge et al., 2004). There may also be some potential for losses from soil surfaces if overland flow mobilizes particle-associated VMS (see Kay et al., 2005 for a description of this process for veterinary antibiotics). However, thus far, there is no empirical evidence of such losses for VMS. Direct

degradation of VMS in soils has been observed experimentally (S. Xu, 1999; S. Xu & Chandra, 1999). This is believed to be principally due to the catalytic activity of clay minerals in soil. D4 and D5 were observed to hydrolyze to siloxanediols and DMSD at different rates depending on the mineral type, temperature, and soil moisture content. However, the soils used in these experiments were much drier than those usually observed in field soils, which means that loss rates may have been higher than those that occur in practice. The half-lives shown in Table 1 are, therefore, highly uncertain and should be used with caution.

EMISSIONS

Predicted environmental concentrations of contaminants are directly and proportionally related to emission rates in MFTMs, which use linear equations (and first-order kinetics for reactions). For example, if the emission rate is doubled with all other factors remaining the same, the predicted steady-state concentrations in each compartment also double. It is, therefore, important to estimate emission rates as accurately as possible to minimize uncertainties in predicted environmental concentrations, although some model outcomes without a mass term (e.g., persistence and the fraction of the total mass in each compartment) are independent of emission rates.

Emissions of VMS to the environment can take place at any point in the product life cycle including (1) during their manufacture; (2) their use in the synthesis of other chemicals (e.g., polymers) and products; (3) in the formulation of personal care products; (4) during their use in leave-on or wash-off personal care products, either by volatilization to the atmosphere or via

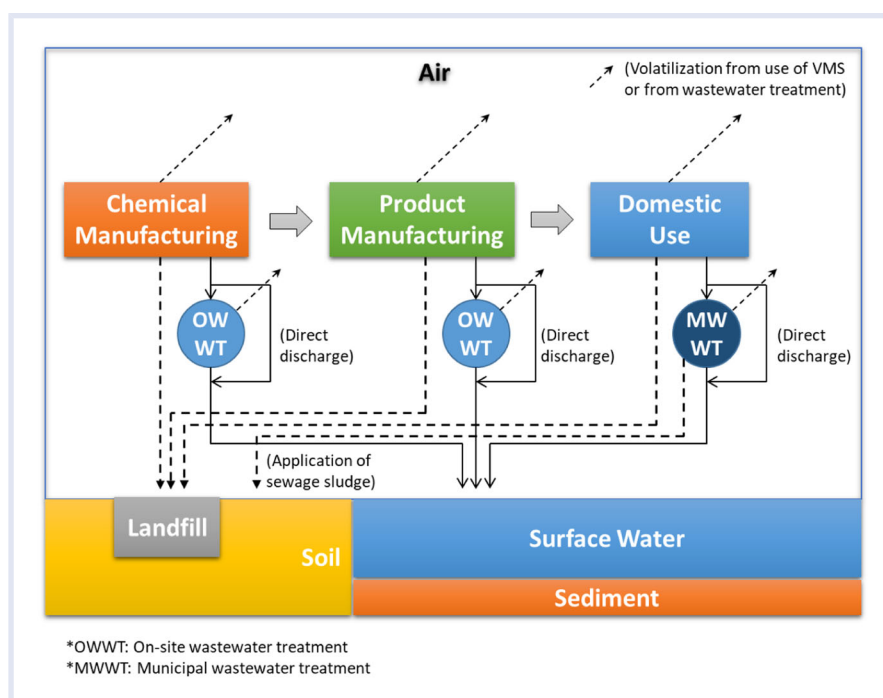


FIGURE 1 Schematic illustration of the three main stages of product life cycle and possible emission pathways to air, soil, surface water, and landfill. Dashed lines indicate emissions to air; thin solid lines show fluxes in the aqueous phase; and thick lines show solid-phase emissions to landfill and soil. MWWT, municipal wastewater treatment; OWWT, on-site wastewater treatment

wash-off of residues to the wastewater stream; and (5) in their post-use (waste) phase (e.g., in landfill gas or landfill leachate). This is illustrated schematically in Figure 1.

Factory emissions occur at a limited number of locations (so-called point-sources) and can be regulated via controls, such as containment and treatment, during processing. However, chemical use in personal care products can result in widespread (diffuse) emissions to the atmosphere and to the wastewater stream. Diffuse emissions can, in principle, be predicted based on breakdowns of production volumes, sales, use patterns (e.g., for different products), and wastewater treatment efficiency (Brooke et al., 2009a, 2009b, 2009c). However, since there are many different producers of VMS and many different downstream users, some of these data can be difficult to obtain and are often highly uncertain. Per capita emissions to water can also be calculated based on monitored concentrations and flows at municipal wastewater treatment plant (MWWTP) influents to yield the flux (i.e., the product of concentration and flow rate), which is then divided by the population served by the plant. However, it is important that these calculations take into account the, now well-known, diurnal (and sometimes weekly) patterns in both wastewater flow and contaminant concentrations (e.g., Whelan et al., 1999) and, ideally, stagger influent and effluent sample collection by the hydraulic retention time of the plant (e.g., Holt et al., 1995). Such monitoring exercises can also be used to estimate MWWTP removal efficiency and, hence, improve the estimate for environmental emission. For example, van Egmond et al. (2013) reported monitoring data for D5 in the influent and effluent of a MWWTP in the UK and from these data, estimated a per capita use of $2.7 \text{ mg cap}^{-1} \text{ day}^{-1}$ and a removal efficiency from the wastewater stream of $>98\%$. In wastewater treatment, VMS are partitioned significantly from wastewater to the air (particularly during the aerobic secondary treatment phase) and to sewage sludge (aka “biosolids”), with a relatively small fraction remaining in the effluent stream released to surface water.

Sewage sludge can be dried and combusted, subjected to anaerobic digestion (to produce methane), disposed of to landfill, or (most commonly) applied to soil. The application of sludge to soil is often considered to be beneficial to agriculture because it has a high nutrient content and can also enhance soil organic matter levels (Smith et al., 1997). However, it can also result in soil exposure to sludge-associated pollutants (Butler et al., 2012; Harrison et al., 2006), including VMS (Wang, Norwood, et al., 2013). Approximately half of the VMS that are removed from the wastewater stream during sewage treatment are expected to be sorbed to sludge (Hughes et al., 2012; Kim et al., 2013; Mackay, Cowan-Ellsberry, et al., 2015). Sludge can, therefore, have high concentrations of VMS and can represent a major vector for VMS transfer to soils. According to Bianchini et al. (2016), the average annual per capita European biosolids production rate is $22.5 \text{ kg cap}^{-1} \text{ year}^{-1}$. This is equivalent to an environmental D5 emission of $0.59 \text{ mg cap}^{-1} \text{ day}^{-1}$ to land, assuming that this sludge has a

D5 concentration of $9.5 \mu\text{g g}^{-1}$ (Kaj et al., 2005), which is approximately consistent with (although slightly lower than) expectations based on the estimate of per capita emission in wastewater made by van Egmond et al. (2013).

If the monitoring data are representative of the region of interest, then the per capita data can be scaled up to estimate regional emissions, although it should be noted that some uncontrolled emissions can also take place at combined sewer overflows in wet weather (Krogseth, Whelan, et al., 2017; Phillips et al., 2012). Furthermore, if MWWTPs are not present, then, wastewater can be emitted to surface waters directly, without treatment (Whelan et al., 2007). This results in much higher levels of in-stream exposure because MWWTPs remove a high fraction of VMS (and other organic pollutants) from the aqueous phase via degradation, volatilization, and sorption to sludge (van Egmond et al., 2013; Wang, Norwood, et al., 2013). Attempts have also been made to estimate VMS emissions to the atmosphere by monitoring air concentrations close to a wastewater treatment plant (Q. Li et al., 2020; Shoeib et al., 2016), using a simplified Gaussian dispersion model.

Estimation of the emission mode (i.e., the fraction of total chemical emission to each environmental compartment) is just as important as estimation of the total emission rate in MFTMs because chemical transfers between compartments are regulated by physical processes (such as interphase diffusion), which can limit the development of equilibrium concentration ratios. The emission mode is related to both the physico-chemical properties of the compound under consideration and the pattern of chemical use and disposal.

The emission rate is assumed to be constant (i.e., time-independent) for steady-state models but can be time-variable for dynamic models. If the emission rate is subject to significant changes due to shifts in consumer use or regulatory restrictions, dynamic models can be used to predict changes in chemical fate and transport (and associated exposure) over time (Kim et al., 2018). MFTMs require emissions estimates for all compartments. However, since the half-lives for VMS in the atmosphere are relatively short and since it is widely believed that atmospheric emissions will not result in significant back-deposition, exposure in surface waters is not likely to be sensitive to total emission. Instead, emission estimations for MFTMs have mainly focused on the aqueous pathway (i.e., via WWTPs). For VMS, emission rates via MWWTPs vary geographically, depending on consumer use. Table 3 shows some estimated emission estimates for VMS compounds. Some model applications for D4, D5, and D6 exposure in Europe before recent EU restrictions in use (e.g., Whelan and Breivik [2013 for the Inner Oslofjord] and Price et al. [2010 for two UK river catchments] have assumed emission estimates made by Brooke et al. [2009a, 2009b, 2009c]). These, in turn, were based on a combination of tonnage data supplied by VMS manufacturers, the estimated fractions used in personal care products, and an estimate of the amount of material in these products that is eventually washed off to the wastewater stream (see Table 3). Some products such as

TABLE 3 Examples of per capita emission estimates for different VMS compounds to the wastewater stream

Chemical name	Per capita emission (mg cap ⁻¹ day ⁻¹)	Method	Location	References
D4	0.4	Estimated from tonnage, fraction used in personal care products, and fraction to wastewater (10%)	UK	Brooke et al. (2009c)
D5	11.6			Brooke et al. (2009a)
D6	1.3			Brooke et al. (2009b)
D5	2.7	Measured concentrations in MWWTP influent and measured wastewater flow over 24 h	UK	van Egmond et al. (2013)
D4	0.007	Measured concentrations in MWWTP influent (two samples) and estimated per capita wastewater flow based on literature	Svalbard, Norway	Panagopoulos Abrahamsson et al. (2020)
D5	0.027			
D6	0.006			
D4	0.07–1.7	Measured concentrations in 11 Canadian MWWTP influents and estimated per capita wastewater flow for Canada (251 L cap ⁻¹ day ⁻¹)	Canada	Wang, Steer et al. (2013)
D5	1.9–33.9			
D6	0.38–6.8			
D4	0.69	Measured concentrations in 1 MWWTP influent in Beijing and estimated per capita wastewater flow for Beijing (238 L cap ⁻¹ day ⁻¹)	China	L. Xu et al. (2013)
D5	0.78			
D6	0.52			
D4	0.15	Measured concentrations in 9 Japanese MWWTP influents and estimated per capita wastewater flow for Japan (314 L cap ⁻¹ day ⁻¹)	Japan	Horii et al. (2019)
D5	2.8			
D6	0.31			

Abbreviations: MWWTP, municipal wastewater treatment plant; VMS, volatile methylsiloxanes.

deodorants and sunscreens are designed to be “left on” the body for several hours. This means that VMS have an opportunity to volatilize to the air before being washed off during showering (Gouin et al., 2013; Montemayor et al., 2013). Other products, such as shampoos, conditioners, and shaving products, are likely to be washed off immediately and make a bigger contribution to the wastewater load (Franco & van Egmond, 2020). Monitoring data presented by van Egmond et al. (2013) suggested that the Brooke et al. (2009a) estimate load estimates for D5 to wastewater (11.6 mg cap⁻¹ day⁻¹) may be overestimated by as much as a factor of 4. Their estimate (2.7 mg cap⁻¹ day⁻¹) was similar to an independent estimate of 2.8 mg cap⁻¹ day⁻¹ for D5 emission in Japan, based on composite sampling of nine MWWTPs (Horii et al., 2019) and assuming a Japanese domestic water-use rate of 314 L cap⁻¹ day⁻¹ Ueda (Ueda & Benouahi, 2009). In an MFTM application to Storvannet, a small lake in Arctic Norway, Krogseth, Whelan, et al. (2017) scaled D4, D5, and D6 loads accordingly and still overestimated measured cVMS concentrations in untreated wastewater. This appears to confirm that the Brooke et al. (2009a, 2009b, 2009c) estimates may not be universally applicable for the whole of Europe. This is also supported by Panagopoulos Abrahamsson et al. (2020), who reported concentration ranges for D4, D5, and D6 in untreated wastewater sampled from Longyearbyen,

Svalbard (albeit from only two samples, which did not account for temporal variability), of approximately 30–50, 75–240, and 25–45 ng L⁻¹, respectively (i.e., approximately 2–3 orders of magnitude lower than the ranges reported by Wang, Steer, et al., 2013). However, it should be noted that Longyearbyen is not a typical European town, given its small population, very remote location, high numbers of tourists in summer, and large student population. VMS emissions could, therefore, vary seasonally much more than in towns of the same size in temperate latitudes. Conversely, Whelan (2013) doubled the Brooke et al. estimates for assumed emissions in North America, on the basis of a Silicones Environmental, Health and Safety Council (SEHSC) of North America survey, which suggested that VMS use in personal care products is likely to be much higher there than in Europe. This is approximately consistent with the fact that van Egmond et al. (2013) reported much lower D5 concentrations in a UK MWWTP influent (6–36 µg L⁻¹) compared with those reported by Wang, Steer, et al. (2013) for 11 Canadian WWTP influents (7.75–135 µg L⁻¹). That said, van Egmond et al. (2013) reported a range of D6 concentrations (3–24 µg L⁻¹) that was similar to that reported by Wang, Steer, et al. (2013) for Canada (1.5–26.9 µg L⁻¹), suggesting that higher usage in North America may not be universal for all VMS compounds. Daily emission estimates derived from the Wang et al. concentration data are shown

in Table 3, using a residential Canadian water-use estimate for 2011 of 251 L cap⁻¹ day⁻¹ (Government of Canada, 2017). Elsewhere in the world, emission estimates also vary considerably. Whilst use rates of D4, D5, and D6 in Japan appear to be similar to those in Europe (Horii et al., 2019), use rates in China appear to be different, with slightly higher emission rates of D4 and D6 and much lower rates for D5 (e.g., from measured influent concentrations reported by L. Xu et al., 2013 and per capita water-use data reported for Beijing in Zhang & Brown, 2005).

MFTMS FOR UNDERSTANDING VMS BEHAVIOR

Once VMS compounds are released to the environment, their transport and fate are subject to natural physical, chemical, and biological processes. As a result, they can be present in some or all environmental media. MFTMs can be used to predict the multimedia distribution of VMS (i.e., the expected concentrations in different environmental compartments) based on a combination of chemical-specific properties, parameters describing the characteristics of the receiving environment (dimensions, temperature, and advective flow rates in and out), and emission rates. This can form the basis of a risk assessment, where predicted exposures are compared to (eco)toxicological effect thresholds. MFTMs can also act as a framework for understanding field measurements and for targeting monitoring in the compartments in which the chemical is most likely to be present at measurable levels (e.g., via the “realistic presence” concept of Woodfine & Mackay, 2001), hence potentially reducing sampling and analytical costs. In the case of VMS in surface waters, the compartment of interest is often the sediment because of the relatively high affinity of VMS for sediment solids and because measured concentrations in the water column are often less than analytical limits of detection. For VMS, typical reported limits of detection in water range from <1 ng L⁻¹ (e.g., Yaman et al., 2020 for L3, L4, and L5) to ca. 10 ng L⁻¹ (Sparham et al., 2008). Interpretive frameworks are needed because field data can be influenced by (systematic and random) spatial and temporal variabilities in concentrations in the matrices of interest and in environmental properties such as temperature and flow rates, which frustrate interpretation (Kim et al., 2016). Interpretation challenges can be further complicated by choices of sampling time and/or location, particularly in the case of time-varying emissions (Facchi et al., 2007; Whelan, 2013), and by deficiencies in analytical methods. For VMS compounds, in particular, this can include a high potential for sample contamination (e.g., from indoor air) and the occurrence of high blank concentrations (artifacts), which can lead to high limits of detection and limits of quantification (Sparham et al., 2008). That said, it is important to stress that monitoring data remain essential in understanding chemical exposure and distribution and for validating model predictions in specific environmental systems. VMS compounds have been monitored in several specific compartments in a range of environments (Alaee et al., 2013; Rucker & Kümmerer, 2014; Wang, Norwood,

et al., 2013). For example, measured concentration data have been published based on sampling in urban air (Buser et al., 2013; Gallego et al., 2017; Genualdi et al., 2011; McLachlan et al., 2010; Yucuis et al., 2013); in air in rural or remote areas (e.g., Genualdi et al., 2011; Krogseth et al., 2013; McLachlan et al., 2010); in soils (Wang, Alaee, et al., 2013; S. Xu, 1999; S. Xu & Chandra, 1999); in aquatic systems (Capela et al., 2017; Krogseth et al., 2014; Warner et al., 2010); and in aquatic organisms (Kierkegaard et al., 2013; Krogseth et al., 2014; Wang et al., 2017).

Good agreement between model predictions of concentrations and fluxes of chemicals in environmental media and appropriate measurements can give us confidence that our understanding is sound. In contrast, poor agreement can highlight gaps in our understanding or problems with parameterization (epistemic and aleatory uncertainty, respectively: sensu Oberkampff et al., 2002). Models can be used to explore the implications of parameter uncertainties via scenario analyses (Kim et al., 2018; Krogseth, Whelan, et al., 2017). Provided that they can be shown to yield accurate representations of chemical behavior, MFTMs can be used to examine the effects of different emission scenarios on chemical fate and transport in receiving environmental media at different scales and in different contexts (Kim et al., 2018).

MFTMs vary in terms of the simplicity of their assumptions, the spatial scale considered, and the degree to which they discretize space and time. Many MFTMs used in a research context assume steady-state (no change in concentrations over time), but not thermodynamic, equilibrium between different phases (i.e., chemical transfers between phases can be limited by processes such as diffusion). These are often referred to as Level III models (Mackay, 2001) and are appropriate when emissions are approximately constant. They include regional evaluative models such as the Equilibrium Criterion (EQC) model (Mackay et al., 2006), the SimpleBox model (Schoorl et al., 2015), and system-specific models such as the QWASI (Quantitative Water Air Sediment Interaction) model (Guo et al., 2019; Kim et al., 2013; Mackay et al., 1983; Whelan, 2013). However, dynamic or “Level IV” models (which represent changes in concentrations over time) can be used to explore system responses to changes in emission or to seasonality in environmental properties (Whelan & Breivik, 2013).

The simplest MFTMs often represent receiving environments using single compartments (i.e., they ignore spatial variations in system properties and gradients in concentrations away from emission points). This is often adequate for many relatively persistent pollutants that are present in the environment for long periods and for which partitioning between media is more important than spatio-temporal variations within compartments (Wania & Mackay, 1999). Since some VMS compounds have relatively long half-lives in water under ambient conditions (e.g., 66 and 340 days, respectively, for D5 and D6 at 9 °C and pH 8), such assumptions hold, particularly for systems with long hydraulic residence times (large volume to inflow ratio).

The single-compartment steady-state nonequilibrium lake model QWASI has been applied to predict the behavior of VMS compounds in several lakes (e.g., Lakes Pepin and Ontario in North America: Kim et al., 2017; Mackay et al., 2014; Whelan, 2013 and Dian Lake in China: Guo et al., 2019) and semienclosed marine systems (e.g., Tokyo Bay: Whelan et al., 2019 and the Inner Oslofjord: Kim et al., 2017).

Some more complex models consider the environment as a continuously varying system, which can be described by gridded discretization, representing the solution space for the differential equations describing the spatio-temporal behavior of environmental properties and chemical fate and transport. Alternatively (and more commonly with MFTMs), the receiving environment can be divided into interconnected subcompartments that have different properties (dimensions, flows, and emissions) to represent spatial patterns in concentrations. For example, the Oslofjord POP model (Breivik et al., 2003, 2004) extended the QWASI model to include six interconnected compartments to describe chemical behavior in the Inner Oslofjord. This model was used by Whelan and Breivik (2013) to predict water column and sediment exposures of D4, D5, and D6 in the Inner Oslofjord, with reasonable agreement between modeled and measured concentrations in sediment, albeit with limited measured concentration data. A similar approach was used by Panagopoulos and MacLeod (2018) to represent VMS behavior in the Adventfjorden, Svalbard, in Arctic Norway. The need for spatial discretization (breaking up media-specific compartments into subcompartments) generally increases as the spatial domain considered increases in size. This is a consequence of increased overall advective residence time for a given in-system loss rate and a reduction in the likelihood that chemicals will completely mix (i.e., concentration gradients become important). At the local scale, it is usually not necessary, but for regional and hemispherical scales, the value of single-compartment models becomes more limited, except in general terms. It may also be useful to use spatially segregated models for river basins (see Warren et al., 2005) if predictions of concentration variations through the channel network are required (Price et al., 2010; Sakurai et al., 2019).

Like physico-chemical properties, environmental characteristics also exert important influences on chemical fate. MFTMs require a description of the dimensions of the different environmental media considered (e.g., water depth and surface area, “active” sediment layer depth, soil depth, soil surface area, and tropospheric height), compartment properties (e.g., pH, dissolved and particulate organic carbon concentrations, sediment, and soil bulk densities), and rates for physical transfer (e.g., advective flows of water and particles into and out of the system of interest, organic carbon exchanges between the water column, and the sediment and partial mass transfer coefficients for diffusive transport between media). Some MFTMs use a hypothetical set of environmental parameters that are fixed for evaluative purposes so that the relative

behavior of different chemicals can be compared under the same conditions (e.g., EQC: Hughes et al., 2012; Mackay et al., 2006 and SimpleBox: Schoolt et al., 2015, which is used in the European Union System for the Evaluation of Substances: EUSES). Other MFTMs use environmental properties that are designed to represent specific real systems (e.g., a specific lake or region). In such cases, predicted concentrations can be compared with monitoring data, if available, provided that reasonable estimations of emissions can be made. Such comparisons constitute a form of validation for MFTMs, provided that the data set is independent (i.e., it was not used in any iterative parameter calibration process, although calibration is uncommon for most MFTM applications). For many chemicals, the spatial and temporal frequencies of samples are often low, which means that a formal rigorous validation is not always possible. For VMS, data for some compartments may be missing (e.g., concentrations in water are often below limits of detection: e.g., Whelan & Breivik, 2013), so comparisons between predictions and measured data are restricted (e.g., to concentrations in sediment). Confidence in model performance can be enhanced if predictions about the relative magnitude of exposure for several different compounds (including other non-VMS compounds) in the same system appear to be correct. More generally, our confidence in the ability of a model to capture the behavior of a chemical also relies on successful applications to different environmental systems, in different geographical locations (e.g., Whelan, 2013).

As the number of major and subcompartments increases, the number of environmental parameters also increases proportionally. This sometimes introduces additional uncertainty into model outputs (which result from a propagation of input uncertainties). Thus, it is always important to clearly understand the source and accuracy of environmental parameters (see Krogseth, Whelan, et al., 2017 for a good example) and the sensitivity of model outputs to all inputs (chemical- and environment-specific: Mackay et al., 2014; Panagopoulos & MacLeod, 2018; Whelan, 2013).

Different combinations of model parameters generate different model outcomes, and the sensitivity of key predictions (such as concentration or persistence) can differ for different compounds and receiving environments. It is important to use the best estimates for all the model parameters, but particularly so for those parameters to which the model is most sensitive. These parameters can be identified using sensitivity analyses (Whelan, 2013). The sensitivity of a predicted model output to an individual parameter depends on the values for the other parameters. For example, the predicted steady-state concentration of VMS in sediment is often sensitive to the K_{OC} value (i.e., a compound-specific property) but will also depend on (inter alia) the advective residence time of the water column and the sediment deposition rate (extrinsic system-specific factors). This results in different predicted concentrations, steady-state chemical distributions (e.g., between the water column and the sediment), and overall persistence in

different systems. Within a given system, the relatively high sensitivity of some model predictions to K_{OC} (e.g., concentration in sediment) means that uncertainties in K_{OC} (and its temperature dependence) become critically important (Krogseth, Whelan, et al., 2017; Panagopoulos Abrahamsson et al., 2020; Panagopoulos & MacLeod, 2018). It is also important to point out that there may be several different combinations of parameters that generate similar predicted outcomes for one or a few predicted variables (e.g., concentration in sediment), a phenomenon known as “equifinality.” This was illustrated by Whelan et al. (2019) using D4, D5, and D6 in a QWASI model of Tokyo Bay, as an example. Thus, considerable uncertainty can still remain even when there appears to be reasonable fidelity between predictions and measured data because the “right results” can be obtained for the “wrong reasons.” For example, the same concentration of VMS in sediment can be predicted with different baseline K_{OC} values, if different assumptions are made about the temperature dependence of K_{OC} (ΔU_{OC}) or about emissions.

The chemical mass balance in each compartment of an MFTM can be expressed as follows:

$$V \frac{dC}{dt} = E - k_R CV - CQ - \sum S_i, \quad (1)$$

where V is the medium volume (m^3), C is the chemical concentration, E is the emission rate ($g \text{ day}^{-1}$), k_R is a degradation rate constant (day^{-1}), Q is an advective outflow rate ($m^3 \text{ day}^{-1}$), and $\sum S_i$ ($g \text{ day}^{-1}$) is the sum of exchanges between compartments (e.g., volatilization, transfers from water to sediment via deposition or from sediment to water via resuspension, etc.), where i is an index representing an adjacent compartment with which chemical can be exchanged. For the steady-state condition, $dC/dt=0$. This leads to a set of linear equations that can be easily solved. For dynamic (time varying) conditions, Equation (1) can be solved by numerical integration.

Equivalent equations can be written and solved using fugacity concepts (Mackay, 2001) in which thermodynamic equilibrium between compartments is defined using equal fugacity rather than using concentration ratios and partition coefficients. However, these two different conceptual approaches yield identical outputs (Mackay, 2001). In either case, the basic equations can be extended depending on

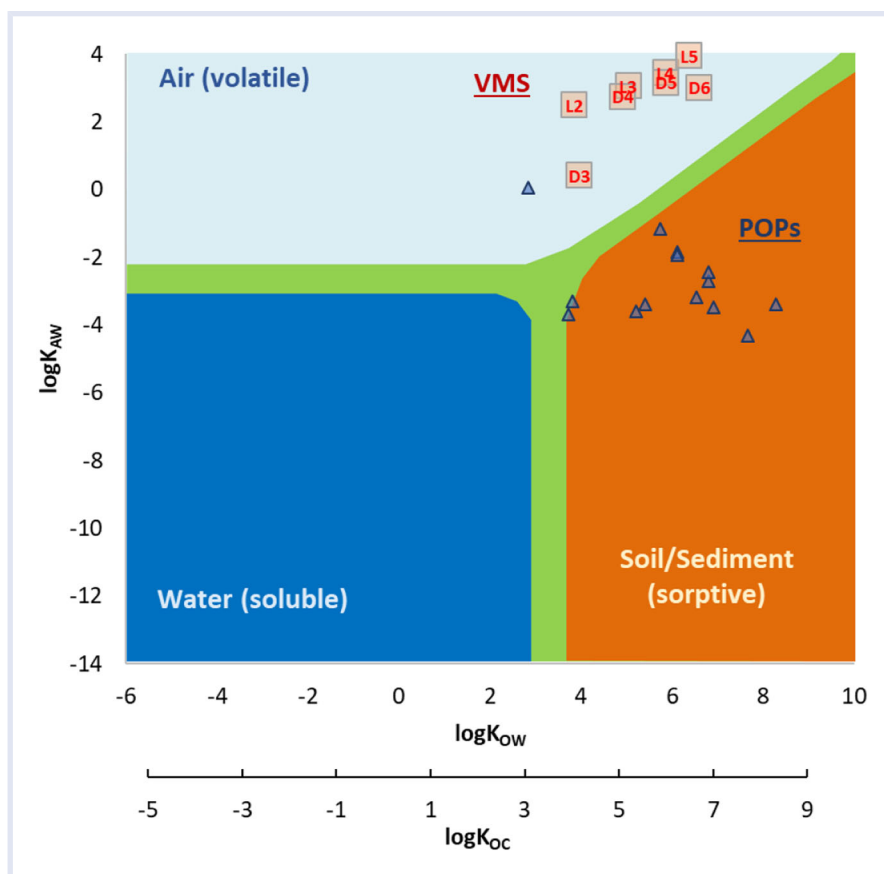


FIGURE 2 Chemical space diagram of primary environmental compartments with K_{AW} (representing volatility) and K_{OW} (representing hydrophobicity). VMS compounds are located in air as the primary compartment, whereas most POPs tend to partition to sediment/soil. Primary compartments are color-coded for 2/3 of the total mass distribution based on EQC Level I model predictions: air (light blue), water (dark blue), soil/sediment (brown), and multimedia (green). Square symbols indicate VMS species. Triangles indicate 14 POPs including γ -HCH (CASRN: 58-89-9), α -HCH (319-84-6), chlordane (5103-71-9), BDE-99 (60348-60-9), TCDD (1746-01-6), dieldrin (60-57-1), PCB-101 (37680-73-2), CCl_4 (56-23-5), PCB-180 (35065-29-3), endrin (72-20-8), heptachlor (76-44-8), hexachlorobenzene (118-74-1), dichlorodiphenyltrichloroethane (50-29-3), and 2,3,7,8-tetrachlorodibenzofuran (51207-31-9). EQC, Equilibrium Criterion; POPs, persistent organic pollutants; VMS, volatile methylsiloxanes

the number of environmental compartments and time dependence. For modeling of VMS fate and transport in different environmental media (i.e., air, soil, wastewater, water or sediment, and biota), the type of modeling approach adopted can be (and should be) tailored for the spatial scales considered (e.g., point, local, regional, and hemispherical or global).

MODEL APPLICATIONS

Chemical space plots

A useful application of MFTMs is the production of “chemical space diagrams.” These diagrams display model predictions (e.g., the fraction of chemical mass in different environmental compartments, the potential for long-range transport, or overall persistence) over a range of chemical properties, such as different combinations of fundamental partition coefficients, with different assumptions for mode of emission and chemical half-lives in different media (Fenner et al., 2005; Wania, 2003). This allows the behavior of chemicals with different properties to be compared. A simple example displaying the distribution of equilibrium chemical mass between different environmental compartments predicted by the EQC model (Hughes et al., 2012; Mackay, 2001) is shown in Figure 2 for a range of $\log K_{OW}$ values from -6 to 10 and a range of $\log K_{AW}$ from -14 to 4 . This illustrates that hydrophilic, nonvolatile compounds (i.e., $\log K_{OW} < 3$ and $\log K_{AW} < -3$) are expected to reside predominantly in the water compartment (the dark blue area) and that hydrophobic, nonvolatile compounds (with $\log K_{OW} > 4$ and $\log K_{OA} > 7$) are expected to reside predominantly in the sediment or soil compartments (the brown area). Volatile compounds (with $\log K_{AW} > -2$ and $\log K_{OA} < 7$) are expected to partition to the air compartment (the light blue area in Figure 2). The green area is for multimedia compounds that are widely distributed in different environmental media. Similar plots can be generated using Level III and IV models with different assumptions about chemical half-lives and modes of emission (see, e.g., Wania, 2003, 2006).

One important outcome from these plots is the revelation that, *cet. par.*, VMS compounds almost always occupy a very different region of chemical space to those chemicals that are accepted as being POPs. This is the case for several different endpoints including overall persistence (P_{OV}) and target-based metrics of LRTP, as a consequence of the unusual steady-state mass distribution of VMS (i.e., with a predominant presence in air). POPs (which include chemicals such as DDT, HCB, PCBs, dioxins, and some PBDEs) tend to occur in all media and, for some, predominantly in sediment and soil (see Figure 2), whereas VMS compounds are mainly found in the air. This is principally due to the much larger values of $\log K_{AW}$ for VMS compounds (often 3 log units higher than many POPs) for similar $\log K_{OW}$ values. This results in low P_{OV} values due to the relatively short atmospheric half-lives, even though degradation half-lives in water, soil, and sediment can be substantial.

Atmospheric behavior and LRTP

Since VMS compounds tend to volatilize from water and other media to the air, emissions to the atmosphere (direct and indirect) are likely to be high. A number of studies have, therefore, explored aspects of the atmospheric behavior of VMS compounds using MFTMs. These range from relatively simple single-box models used to examine the relative roles of reaction (principally with OH radicals: Atkinson, 1991; Kim & Xu, 2017) and partitioning (to aerosols and water droplets: Navea et al., 2009) in affecting VMS fate (Whelan et al., 2004) to comprehensive dynamic and spatially referenced descriptions (Janecek et al., 2017; McLachlan et al., 2010). Whelan et al. (2004) combined the known partitioning properties with atmospheric reaction rate constants, derived from measurements in experimental chambers, and predicted that most VMS compounds in the atmosphere should eventually be converted into DMSD. DMSD is much more water-soluble than VMS compounds and will be washed out of the atmosphere in precipitation. DMSD is believed to degrade in surface waters and soils to SiO_2 and water, although empirical evidence base for this is limited and additional research would be useful. Navea et al. (2011) developed a compartment model with three boxes in series to describe the transport of D4 and D5 in urban (source point), transition, and rural areas. The outputs from this model indicate that lifetimes of D4 and D5 are sensitive to OH radical levels in the transition area, but that the lifetime reduction of these compounds by aerosol-associated dry deposition was $< 3\%$.

LRTP is often characterized in MFTMs as the characteristic travel distance (CTD). This is the distance at which the atmospheric concentration is estimated to have dropped to $1/e$ (or 37%) of its initial concentration due to degradation in the air and removal by net deposition (Beyer et al., 2000). Most MFTM calculations suggest that VMS compounds emitted to the atmosphere will travel long distances, with CTDs ranging from 1440 to 5850 km (Figure 3A), as predicted by Kim et al. (2018) and S. Xu and Wania (2013) using the OECD P_{OV} and LRTP Screening Tool (Wegmann et al., 2009). Although there is little doubt that the atmospheric transport of VMS compounds will be substantial, Xu et al. (2019) suggest that these predicted CTDs may be overestimates of actual travel distances. They compared CTDs generated by the OECD tool with “empirical” CTDs (eCTDs) derived from measured concentration data at different latitudes and found that the eCTDs were lower than those predicted by the OECD tool. This suggests that the actual rates of atmospheric removal may be higher than those assumed in the model. Furthermore, the high volatility and relatively low K_{OA} for VMS compounds mean that a very low fraction of these compounds is expected to be deposited to surface media from the atmosphere (Kim et al., 2018; S. Xu & Wania, 2013). In other words, VMS compounds have low values for “target-oriented” metrics of LRTP such as the transfer efficiency (TE: Klasmeier et al., 2006; MacLeod & Mackay, 2004) and the Arctic Contamination Potential (ACP: Wania, 2003, 2006).

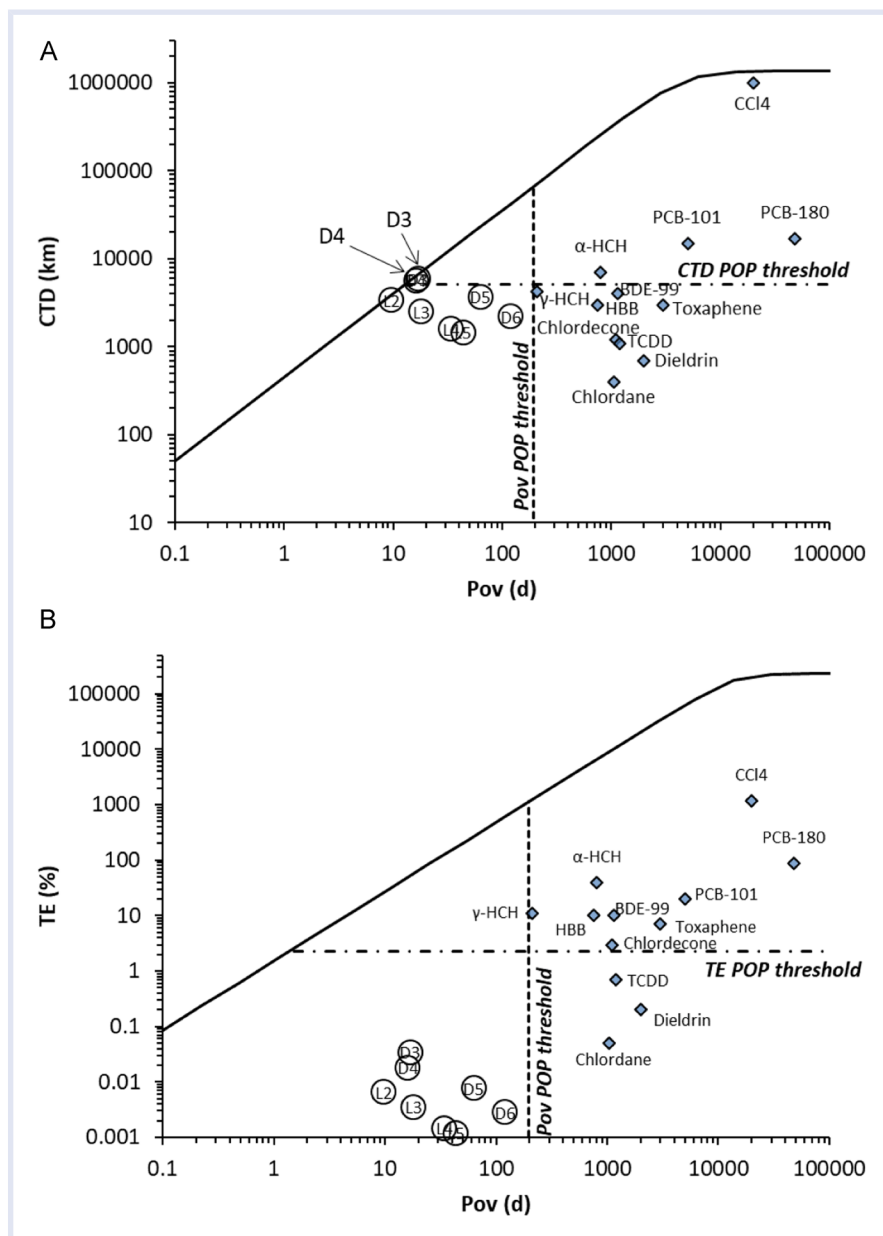


FIGURE 3 Plots of (A) predicted characteristic travel time (CTD) and (B) predicted transfer efficiency (TE) versus overall persistence (P_{OV}) from the OECD P_{OV} and LRTP Screening Tool (Wegmann et al., 2009) for volatile methylsiloxanes and benchmark chemicals of POPs using the default parameter values. Reference lines show the cutoff criteria for persistence and LRTP proposed by Klasmeier et al. (2006): (i) $P_{OV} > 195$ days, (ii) $CTD > 5096$ km, and (iii) $TE > 2.25\%$ (UNEP, 2012)

Target-oriented metrics are important because they allow compounds that have a high CTD but that do not transfer to surface environments in locations distant from their points of emission (Annex D 1(d)(iii) of the Stockholm Convention) to be distinguished from those chemicals that are likely to contaminate remote surface media. The range of predicted TE values for VMS from the OECD P_{OV} and LRTP Screening Tool is 0.001%–0.03% (median: 0.005%). This is illustrated in Figure 3B. Model outputs for selected POPs are also shown in Figure 3B. Values of TE for POPs are generally much higher than for VMS ranging from 0.005% to 1200%, with a median of 10%. The ACP is a target-oriented metric generated by the latitudinally zoned dynamic GloboPOP model (Wania &

Mackay, 1995, 2000). For a set of hypothetical chemical partition coefficient combinations and assumptions about degradation half-lives, Wania (2006) produced chemical space diagrams of the ACP. For constant emission over 10 years and with the combination of half-lives most representative of VMS (10 days in air and 0.1–1 year in surface media), VMS compounds are predicted to be in the lowest class of ACP 0%–0.25%. According to S. Xu and Wania (2013), VMS compounds have deposition potentials that are 4–5 orders of magnitude lower than those of most known POPs.

McLachlan et al. (2010) applied a spatially explicit dynamic model of atmospheric transport and reaction for the

northern hemisphere (the Danish Eulerian Hemispheric Model: DEHM) to explore the atmospheric transport of D5. Although this is not strictly an MFTM, because it represents a dynamic atmospheric reaction and transport processes in much more detail, its use here is worthy of mention because it is an excellent example of where model predictions can be used to explain variations in measured concentrations. They compared the predicted time series of atmospheric concentrations of D5 to measured concentrations of D5 in air samples collected at a remote site in Sweden (200 km west of Stockholm). The temporal pattern of predicted D5 concentrations agreed very well with the measured data, suggesting that the model was based on a good understanding of emissions and atmospheric behavior. Krogseth et al. (2013) also applied the DEHM and compared its predictions to measured concentrations of D3, D4, D5, and D6 at the Zeppelin Observatory on Svalbard in the high Arctic. Again, there was good agreement between predicted and measured concentrations, confirming relatively low (but detectable) concentrations in arctic air that were influenced by the seasonality of OH radical concentrations in the northern hemisphere.

Predictions of VMS concentrations in air from more conventional MFTMs have also been compared with measured data. MacLeod et al. (2011) explored the fate of D5 using the fugacity-based global-scale Berkeley–Trent (BETR) model. This model links 288 regions in a $15^\circ \times 15^\circ$ grid, each containing seven environmental compartments. The modeled concentrations of D5 in air were generally in good agreement with the measured data reported by McLachlan et al. (2010). These results confirmed the strong dependence of the D5 concentration in air on spatial and temporal variations of OH radical concentrations. At steady state, the predicted distribution of total mass was predominantly in air (>75%), followed by soil. However, the predicted mass in soil is highly uncertain due to uncertainties about the degradation half-life in soil. A half-life of 2300 days was assumed here. Whilst this is much longer than the measured half-life of 5 days reported for D4 in soil by (S. Xu & Chandra, 1999), the measured data were obtained using soils with much lower moisture contents than those normally observed in humid zones.

Water and sediment

Since the fugacity capacity of air is about 2 orders of magnitude higher than the fugacity capacity of water for VMS compounds (due to the fact that K_{AW} values for VMS compounds are so high: Table 1), the fugacity gradient (which quantifies the direction and magnitude of thermodynamic disequilibrium: Mackay, 2001) is rarely in the direction from air to water (i.e., the fugacity in water is almost always greater than the fugacity in air). This means that there is a net movement of VMS compounds by diffusion from water to air in most situations. Furthermore, even when the fugacity in air is greater than the fugacity in water (e.g., when atmospheric concentrations are relatively high and aqueous concentrations are negligible), diffusion across the

air–water interface is limited by the (relatively low) partial mass transfer coefficient in water. This means that almost all surface-water exposure to VMS is likely to occur via wastewater emission (treated or untreated). It is important, therefore, to understand the fate of VMS along the wastewater pathway including in MWWTPs. This can be done by monitoring (van Egmond et al., 2013) in combination with the application of models that describe relevant wastewater treatment processes. Overall, the removal rates for cVMS compounds from the wastewater stream tend to be reasonably well described by the two main MFTMs describing the fate of organic pollutants in MWWTPs (i.e., SimpleTreat: Struijs, 2014 and the STP model: Clark et al., 1995). Early work by Parker et al. (1999) assessed the fate of two VMS compounds in a pilot-scale wastewater treatment plant. They reported removal rates of 86% for D4 and 96% for D5, principally due to volatilization and sorption to sludge solids. These high removal rates have since been confirmed by other monitoring campaigns. van Egmond et al. (2013) reported a loss rate for D5 of >98% at a large UK MWWTP, and a similar rate was reported by Wang, Steer, et al. (2013) for 11 MWWTPs in Canada, whilst L. Xu et al. (2013) estimated a wide range of treatment efficiencies for cVMS in MWWTPs up to 92.7%, depending on the types of primary and secondary treatment processes and time for aerobic/anaerobic digestion at an MWWTP in Beijing. According to van Egmond et al. (2013), the SimpleTreat model predicted a loss rate for D5 of 95% (i.e., slightly lower than they observed, which they attributed to a high default value assumed for the suspended solids concentration, which lowered the predicted dissolved fraction and, hence, losses via volatilization and hydrolysis). However, the STP model, with default parameters, predicts loss rates for D5 and D4 of 98% and 97%, respectively (Whelan & Breivik, 2013). Thus, the emission rates of VMS to surface water are likely to vary significantly, resulting in a wide range of environmental exposure in receiving systems.

A number of attempts have been made to describe the fate of cVMS compounds in surface waters using MFTMs. A popular tool for this purpose is the QWASI model (Mackay et al., 1983), which describes the most important processes affecting chemical behavior in lakes. In its basic form, QWASI is a Level III model (steady-state nonequilibrium) that uses single compartments for water and sediment. Whelan (2013) applied a modified version of the QWASI model to two contrasting lake systems in North America (Lake Ontario and Lake Pepin). This work showed that chemical behavior (persistence and the dominance of different loss processes) is dependent on a combination of multiple factors (chemical- and system-specific) depending on a location. For example, the overall persistence of VMS in Lake Pepin (Minnesota, USA, a shallow lake formed from a broadening of the Mississippi River downstream of the Twin Cities) was influenced by high rates of sediment burial and advection resulting from high water discharge (hence, relatively short residence times). Another modified QWASI model was used by Mackay et al. (2014) to explore aspects

of sensitivity and uncertainty of target end-points for D5 (together with PCB-180, as a comparison). Dynamic versions of the QWASI model have also been developed (Kim et al., 2017; Krogseth, Whelan, et al., 2017) and applied to predict the effects of changes to emissions of VMS on concentration response times in water and sediment (Kim et al., 2017, 2018). These studies have shown that concentrations of VMS in water and sediment are likely to approach new steady-state levels following shifts in emission much faster than those of legacy compounds. Krogseth, Whelan, et al. (2017) applied modified (steady-state and dynamic) versions of the QWASI model to explore the behavior of D4, D5, and D6 in an Arctic lake (i.e., Lake Storfjorden) receiving intermittent wastewater emissions. Since this lake has a relatively short hydraulic residence time (9 days in summer and 38 days in winter) and a low rate of sediment deposition, cVMS compounds were predicted to be removed predominantly by advection and volatilization. Guo et al. (2019) also used the QWASI model to predict the behavior of cVMS in Dian Lake, China. Predicted concentrations in the summer and winter compared well with measured data. A more sophisticated model was applied by Sakurai et al. (2019) to predict VMS concentrations in air, soil, and river (water and sediment) of the Tokyo Bay catchment using the georeferenced multimedia model (G-CIEMS Grid-Catchment Integrated Environmental Modeling System: Suzuki et al., 2004). The predicted concentrations were generally in good agreement with monitoring data published by Horii et al. (2017). In addition, the mass balance indicated that contributions of D5 and D6 were much more significant from direct MWWTP emissions to Tokyo Bay than from discharges to rivers.

Several studies have identified K_{OC} as the chemical-specific parameter with most influence on many model outputs (Krogseth, Whelan, et al., 2017; Mackay et al., 2014; Whelan, 2013). This is not unexpected, given the importance of hydrophobicity for interactions between the dissolved and sorbed phases in many important processes affecting VMS. Processes such as volatilization and hydrolysis can only take place in the dissolved phase and net deposition to sediment takes place in the sorbed phase. This work also highlights that uncertainties in the size and timing of emissions and in the magnitude and temperature dependence of K_{OC} constrain understanding of VMS fate processes in this system. It is, therefore, essential that the correct value of K_{OC} is used in any predictions of VMS behavior. It is also important for the uncertainties in the temperature dependence of K_{OC} to be resolved (see above). In most published model applications (Guo et al., 2019; Krogseth, Whelan, et al., 2017; Mackay et al., 2014; Sakurai et al., 2019; Whelan, 2013), a value for K_{OC} has been set directly. However, in some “off-the-shelf” models, K_{OC} is derived from K_{OW} using a Karickhoff-type relationship. Since, in the case of VMS compounds, such relationships are known to overestimate K_{OC} by approximately 2 orders of magnitude, they should not be used.

Uptake and behavior in organisms (including trophic transfer)

Hydrophobic organic compounds are often bio-accumulative (Kelly et al., 2007). Given their high K_{OW} values (Table 1), it is, therefore, unsurprising that the behavior of VMS compounds in aquatic food webs has received some attention over the last 10 years. Much of this research has used MFTMs to help interpret laboratory tests and field observations. There are several ways to determine the bio-accumulation potential of chemicals, including the bio-concentration factor (BCF), the bioaccumulation factor (BAF), the biomagnification factor (BMF), the trophic magnification factor (TMF) (Gobas et al., 2009; Mackay et al., 2013), and the biota-sediment accumulation factor (BSAF) (Tracey & Hansen, 1996). Many of these metrics are based on mathematical models ranging from simple relationships with K_{OW} , such as the BCF and BAF (e.g., in the EPI Suite™ BCFBAF model: US EPA, 2019), to more complex descriptions of organic chemical concentrations in food webs (e.g., AQUAWEB: Arnot & Gobas, 2004). The BCF is usually derived as the ratio of volumetric concentrations in the test animal (usually fish) and water, where exposure is via the water only, usually in a standardized laboratory study (Mackay et al., 2013). The BAF is similar to the BCF, except that the animal is exposed to the chemical via its food, soil, or sediment, rather than just the water. The BMF is usually defined as the lipid-normalized ratio of the chemical concentration in a predator to that in its diet (in the laboratory or in the field). The BSAF is the ratio of the lipid-normalized chemical concentration in an organism (usually a sediment-dweller) to the organic-carbon-normalized concentration in the sediment. All these metrics can be difficult to derive for VMS compounds due to low aqueous concentrations, possible losses in the experimental systems (e.g., due to hydrolysis and volatilization), and sorption to surfaces and organic matter (Mackay, Powell, et al., 2015). These factors can also frustrate attempts to determine the toxicity of these “super-hydrophobic” compounds. Mackay, Powell, et al. (2015) summarized the existing empirical data for D4, D5, and D6 for BCF (2450 L kg ww⁻¹ for D4; 1950–7060 L kg ww⁻¹ for D5; and 240–1160 L kg ww⁻¹ for D6), BMF (0.66 kg kg⁻¹ for D4 and 0.85 kg kg⁻¹ for D5), and aquatic toxicity (little or no toxic effects up to aqueous solubility limits in water and sediment). These are all lower than expectations, based on the high K_{OW} values for cVMS. Mackay, Powell, et al. (2015) used a chemical uptake model of laboratory tests to explore the potential reasons for this apparent mismatch. Their results suggest that low aqueous concentrations lengthen the time required to achieve a baseline narcotic critical body residue (CBR: i.e., the internal concentration above which adverse effects are observed) and hence to achieve a toxic effect. This is exacerbated by biotransformation in the test organisms (reducing the internal concentration of the toxicant). Biotransformation also reduces the BCF values derived.

The TMF essentially reflects the change in lipid-normalized chemical concentrations at different trophic

levels (TLs) in a food web. The TLs are usually defined in terms of the relative natural abundance of ^{15}N ($\delta^{15}\text{N}$) in different organisms, assuming a trophic enrichment factor between TLs that can vary between 3‰ and 5‰, with a value of 3.4‰ recommended by Kidd et al. (2019) when prior knowledge of the food web is low. A TMF > 1 suggests trophic magnification (i.e., an increase in concentration in animals at higher TLs). In contrast, a TMF < 1 suggests trophic dilution (i.e., a tendency for concentrations to decrease at higher TLs). A number of food web monitoring studies have been performed for VMS. Measured data from biota in two Norwegian freshwater lakes (Lakes Mjøsa and Randsfjorden) showed trophic magnification for D5 and D6, but trophic dilution for D4 (Borgå et al., 2012, 2013). In contrast, other studies in Oslofjord, Norway (Powell et al., 2018), and Tokyo Bay, Japan (Powell et al., 2018), appear to show clear trophic dilution for cVMS compounds. Similarly, McGoldrick et al. (2014) reported trophic dilution for cVMS in the Western Basin of Lake Erie, Canada. One possible explanation for differences in TMFs derived from monitoring studies is that, to some extent (and in common with chemical persistence), the TMF is an “extrinsic” metric (i.e., it depends on system characteristics as well as chemical properties). Different food webs are affected to different extents by chemical concentration gradients and species migration patterns. Concentration gradients often exist in lakes away from point sources, particularly if mixing is slow and incomplete. To explore the impact of these factors on TMF, Kim et al. (2016) extended the AQUAWEB model to include multiple compartments, which could be used to represent concentration gradients. The AQUAWEB model predicts bioaccumulation based on a balance between chemical uptake and elimination processes for each organism in a food web (Arnot & Gobas, 2004). Kim et al. (2016) showed that the timing and location of biota sample collection could, in principle, have a significant impact on the derived TMF for PCBs and phthalate esters. Similar multicompartment food web modeling is needed to illustrate the potential for biased sampling in the presence of concentration gradients to affect TMFs for VMS compounds. The findings of Mackay, Powell, et al. (2015) on the kinetics of dietary uptake, the time to reach CBR, biotransformation in higher organisms such as fish, and respiration in air-breathing organisms are also important to take into consideration in food web models, as is the assumption made about the separation of TLs from $\delta^{15}\text{N}$ data in the food web under consideration. Strictly speaking, an ecosystem-specific trophic enrichment factor should be used that incorporates ecological knowledge for the systems of interest.

Whelan and Breivik (2013) applied the marine food chain component of the ACC-HUMAN model (Czub & McLachlan, 2004a, 2004b) to predict concentrations of D4, D5, and D6 in zooplankton, herring (*Clupea harengus*), and cod (*Gadus morhua*) in the Inner Oslofjord. When the model was initiated with measured VMS concentrations in zooplankton and using metabolism rate constants derived from an independent laboratory study on D5 in rainbow trout (Domoradzki et al.,

2017), the predicted concentrations in fish were close to the measured concentrations reported by two independent monitoring studies (Powell et al., 2010; Schlabach et al., 2007). Concentrations in zooplankton were higher than those in herring, which were higher than those in cod, suggesting trophic dilution driven principally by metabolism in fish. Without metabolism, the model predicted trophic magnification. Krogseth, Undeman, et al. (2017) also measured decreasing concentrations of cVMS in biota with increasing TLs in Lake Storsvannet, northern Norway, and predicted trophic dilution using a version of the ACC-HUMAN model that was modified to include the benthic organisms at the base of the food web in this lake. The dominant loss mechanisms for cVMS removal from fish were predicted to be fecal egestion, biotransformation, and ventilation (in decreasing order of importance). VMS concentrations in benthic animals were underestimated by the model, but concentrations in fish were well predicted. This could be due to poor representation of solvent switching between sediment and the benthos (possibly resulting from poorly constrained partition coefficients between water, organic carbon, and lipids at low temperatures), as well as aleatory food web- and fish-specific parameter uncertainties.

SUMMARY AND CONCLUSIONS

Understanding chemical behaviors in the environment is important to assess whether their uses and release pose unacceptable (eco)toxicological risks and to estimate their persistence, long-range transport, and bioaccumulation potentials. Numerical models play an essential role in this process, allowing chemicals to be compared objectively and supplementing monitoring activities by helping to interpret measured data, which often represent (infrequent) spatial and temporal “snapshots” (i.e., status at a certain location and at a certain time). One important role for MFTMs is to act as a framework for capturing our broad understanding of the interactions between chemical properties and environmental processes and for filling the spatial and temporal gaps that often exist between measurements.

In this paper, we review some generic aspects of MFTMs used for evaluating chemical behavior in environmental systems, but with a specific focus on the application of MFTMs in gaining a better understanding of the environmental behavior of VMS compounds. MFTMs have been usefully employed in representing VMS behavior in wastewater treatment, in river catchments, in lakes and enclosed marine systems, in the atmosphere, and in biota. At wider scales, they have also been used to assess overall persistence, LRTP, and the propensity for atmosphere to surface exchange in remote regions. Although it is widely believed that most environmental emissions of VMS are to the atmosphere, significant emissions to water and soil can occur via the wastewater and biosolids-to-land pathways, respectively, resulting in local exposures. These emissions can be considered to be approximately steady state, although the use of different VMS compounds in personal-care and household products has and will change gradually over time

with consumer trends and in response to regulated use restrictions. Much can be learned, therefore, from steady-state (Level III) MFTMs, including estimates of current concentrations, the expected distribution between different media, and overall persistence. However, understanding system responses to variable emissions (or even the cessation of emission) and seasonally variable conditions necessitates the use of dynamic (Level IV) models. At the simplest level, when chemical half-lives are similar to, or longer than, the advective residence times of the system of interest, appropriate predictions can be made by representing each medium (water, sediment, air, or soil) with a single compartment. However, for substances with shorter half-lives (such as D3 and D4) and for systems in which strong gradients in exposure exist, a discretization of the system of interest (e.g., into multiple interconnected boxes) is useful.

Although VMS materials lie within the applicability domain of MFTMs, particularly careful selection of model inputs is needed because their physico-chemical properties are very different from those of most organic compounds (including so-called legacy contaminants and POPs). This prohibits effective use of some empirical property estimation methods. For example, compared with organic compounds with similar molecular weights or similar K_{OW} values, the K_{AW} values for VMS are very high and K_{OA} values are, as a consequence, relatively low. In addition, K_{OC} values are substantially lower than expectations based on K_{OW} . Importantly, this means that models that predict K_{OC} from K_{OW} using empirical relationships derived from general organic compounds are not appropriate for predicting the environmental behavior of VMS. Instead, K_{OC} should be specified explicitly as an input (Whelan, 2013). This is essential because both exposure and persistence of VMS compounds in surface waters and sediments tend to be very sensitive to K_{OC} . There is also some uncertainty about the strength and direction of the temperature dependence of different partition coefficients for VMS materials, particularly for K_{OC} . Most model applications assume that the temperature dependence of K_{OC} is the same as that determined experimentally for K_{OW} . However, this assumption has recently been challenged by Panagopoulos Abrahamsson et al. (2020), and further work is required to investigate the extent to which this challenge is supported by other evidence. The fact that MFTM-predicted concentrations in sediments from mid-latitude lakes and near-shore marine areas often appear to agree with measured data (notwithstanding uncertainties in emissions) suggests that model sensitivity to this temperature dependence is not critical, except perhaps in cold environments. Although half-life estimates in water (and derived half-lives in sediments) based on hydrolysis are believed to be reasonable, the lack of observed soil degradation half-life data under environmentally realistic conditions is a key data gap. The experimental values reported by S. Xu and Chandra (1999) were derived using soils with volumetric moisture contents that were much lower than those expected in most field soils in humid zones, which may have yielded unrealistically low half-lives. Good

agreement between the modeled and measured concentrations in air and in sediment also indicates that our level of understanding of environmental fate processes for VMS is reasonable. Model simulations of VMS in the atmosphere confirm our expectations that they are principally degraded by reactions with OH radicals, at rates that are consistent with model parameters derived from atmospheric chamber experiments. The principal reaction product from this process is believed to be DMSD, which is expected to be removed from the atmosphere in wet deposition. However, there are still some uncertainties about the fate of DMSD in surface water, sediment, and soil. Again, additional research is required here.

MFTMs have also been shown to show reasonable agreement with VMS concentrations measured in aquatic organisms sampled from the field (Krogseth, Undeman, et al., 2017; Whelan & Breivik, 2013). This work has shown that metabolism is an important elimination process in many taxa, which can drive trophic dilution of VMS compounds. Modeling work has also been used to aid interpretation of disparities in TMFs from different sampled ecosystems. For example, Kim et al. (2016) showed that the TMF for phthalate esters and PCBs can be influenced by spatial gradients in concentrations and by the spatial migration of the sampled organisms in measured food webs. However, similar modeling is needed for VMS compounds to illustrate the potential for biased sampling in the presence of concentration gradients to affect TMFs.

Although metrics like chemical persistence and LRTP are independent of emissions, good estimates of total emissions and the mode of emission are critical for making reasonable predictions of environmental concentrations. Total emissions can, in principle, be estimated from commercial production and use data, but major uncertainties remain about how much of the VMS used in different product types is lost to the atmosphere and how much is typically emitted to the wastewater stream. The most reliable way to estimate emission to surface waters is, therefore, to monitor the inputs to MWWTPs (measuring both concentrations and the wastewater flow and taking account of the pronounced diurnal variability in both of these variables: van Egmond et al., 2013). Although several such monitoring studies have been conducted, additional information is still needed, particularly to reveal differences in emissions of different VMS compounds in different parts of the world. These are likely to vary with product availability, but socioeconomic status will also be a key driver for use because wealthier countries and more affluent sectors of the population are more likely to use a greater number of VMS-containing products. Cultural practices may also be important. MWWTP removal efficiencies are also likely to vary with location, the technology types used, and (sometimes) the season. Provided that reasonable estimations can be made for emission patterns, MFTMs can be used to help to anticipate exposure patterns in current and future scenarios (e.g., in response to regulatory restrictions in use: see Kim et al., 2018), which can be used to help design monitoring

strategies (e.g., by guiding the frequency and location of sampling in different media).

In all applications of MFTMs, credibility in model outputs as a guide for increasing understanding and for making regulatory decisions can be enhanced by being transparent about the model version used, the assumptions made (e.g., parameter values used and their provenance), and the outputs generated, such that the application is reproducible. Following the principles of Good Modeling Practice can help ensure that this is achieved (Buser et al., 2012). This includes conducting sensitivity and uncertainty analyses to identify the most important parameters for which accurate values are needed and to direct future research to close knowledge gaps.

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CONFLICT OF INTEREST

M. J. W. is an independent research scientist and declares no conflict of interest. J. K. is an employee of the Dow Chemical Company. The work described in the paper could, therefore, have been subject to biases that could constitute a potential conflict of interest. However, we maintain that the study was conducted objectively and was not influenced by commercial or other drivers, from either the funders or employers.

DATA AVAILABILITY STATEMENT

This paper is a critical review based on data and findings presented elsewhere. Some novel calculations and plots have been generated using calculation tools that are available in the public domain.

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