Environmental Science Processes & Impacts



PAPER

View Article Online
View Journal | View Issue



Cite this: Environ. Sci.: Processes Impacts, 2018, 20, 183

A critical assessment of the environmental fate of linear and cyclic volatile methylsiloxanes using multimedia fugacity models

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We apply multimedia models to systematically evaluate the fate profile of cyclic volatile methyl siloxanes (VMS) D_4 , D_5 and D_6 , and the linear VMS L_4 and L_5 using recently reported measurements of their partition ratios between organic carbon and water (K_{OC}) , their salting out constants (K^s) , and their enthalpy of sorption to organic carbon ($\Delta H_{\rm OC}$). Our assessment follows a multi-stage strategy where the environmental fate of the chemicals is explored in generic regional models with increasing fidelity to the real system and in a region-specific model. Modeled emissions of VMS to air remained in air and were degraded or advected out of the system with overall residence times ranging from 2.4 to 2.5 days, while emissions to water resulted in accumulation in sediment and longer residence times ranging from 29.5 to 1120 days. When emitted to water the modeled residence times of VMS in the sediment exceeded the REACH criterion for persistence in freshwater sediments. Reported K_{OC} measurements for D₅ differ by 1 log unit, which results in a 500-day difference in the overall residence times calculated in the generic regional modeling. In the specific-region modeling assessment for Adventfjorden, Svalbard in Norway, the different K_{OC} measurements of D₅ resulted in a 200-day difference in overall residence times. Model scenarios that examined combinations of previously published ΔH_{OC} or enthalpy of phase change between octanol and water (ΔH_{OW}) for D₅ in combination with the range of the K_{OC} measurements resulted in 1100-days difference in overall residence times. Our results demonstrate that residence times of VMS in aquatic systems are highly sensitive to their degree of sorption to organic carbon, and that residence times of VMS likely exceed several persistence criteria and therefore they cannot be considered as non-persistent.

Received 1st November 2017 Accepted 18th December 2017

DOI: 10.1039/c7em00524e

rsc.li/espi

Environmental significance

Volatile methylsiloxanes (VMS) are a group of organosilicon chemicals that are used in personal care products and in the production of silicone polymers. VMS have been found at considerable levels in the air, in sediments and in aquatic organisms. We examine the fate of VMS using multimedia models in aquatic environments and we study their residence times in generic and specific environmental scenarios. Our calculations suggest that the residence times of VMS exceed several persistence criteria in aquatic environments and therefore they cannot be regarded as non-persistent chemicals.

Introduction

Volatile methylsiloxanes are a group of organosilicon chemicals that consist of -Si(CH₃)₂-O- chains in cyclic or linear form.¹⁻⁷ Cyclic volatile methylsiloxanes (cVMS) are primarily used as carriers in personal care products such as deodorants, skin creams and lotions.¹⁻⁷ On a smaller scale cVMS are also used as solvents and building blocks in the production of silicon polymers.¹⁻⁶ The most commonly used cVMS are

octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5) and dodecamethylcyclohexasiloxane (D_6).¹⁻⁶ Linear volatile methylsiloxanes (IVMS) are mainly used as intermediates in the production of silicon polymers and on a smaller scale as carriers in personal care products.⁷ Usually the concentrations of cVMS in personal care products are higher than those of IVMS. However, Lu *et al.*⁸ reported that some personal care products from the Chinese market have concentrations of IVMS that exceed those of cVMS.

Cyclic and linear VMS have been found at considerable levels in air, 9,10 sediments 11 and aquatic organisms. 12 In the air, VMS degrade within days because of their reaction with hydroxyl radicals, 13 but estimated lifetimes in sediment are substantially longer. 14-17 Whelan 18 explored the fate of cVMS in two contrasting North American lakes using multimedia models and

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underlined the importance of obtaining accurate measurements of $K_{\rm OC}$, as this was the parameter that was shown to be the most sensitive in the model calculations.

Environmental risk assessments for D5 have been conducted by Environment Canada and Health Canada, the United Kingdom Environment Agency, and the European Chemicals Agency. 1-7,20,21 In the initial report of Environment Canada and Health Canada the authors concluded that D5 was a toxic substance as defined under the Canadian Environmental Protection Act and should be added to the Toxic Substances List in Schedule 1.19,22,23 Shortly after this report was published, it was challenged by industry groups, who suggested that the assessment was not conducted using the best available scientific evidence of that time.19,22,23 The Canadian Minister of Environment responded by forming an independent Board of Review to reexamine and assess D5 taking into consideration physicochemical properties presented by the industry representatives. 19,22,23 The Board of Review overruled the initial assessment and concluded that "D5 does not pose a danger to the environment" and that "its projected future uses will not pose a danger to the environment". 19,22,23

In the risk assessment report of the United Kingdom Environment Agency the authors concluded that although D_5 meets the P and vP criteria set by REACH²⁴ for sediment, D_5 will not persist in the aquatic environment because of its plausible loss through volatilization.¹⁻³ That conclusion was consistent with recommendations articulated by Webster *et al.*,²⁵ who used model calculations to demonstrate that using compartment-specific persistence criteria to evaluate a chemical would lead to misclassification when a chemical fails the half-life criterion in an environmental compartment where it does not considerably partition. To avoid misclassification, Webster *et al.*,²⁵ recommended evaluating chemicals based on overall residence times instead of single compartment criteria, and proposed an overall environmental persistence criterion of 100 days.

The European Chemicals Agency is currently considering a potential European-wide restriction of D_4 and D_5 in wash-off personal care products. As a part of this process, the agency published a member state committee opinion on the persistence and bioaccumulation of D_4 and D_5 . The decision of the committee is pending.^{20,21}

Mackay *et al.*¹⁹ presented an evaluation of the fate of D_5 using the equilibrium criterion (EQC) level III fugacity model. In a model scenario where 100% of the emissions are released to water, 94% of D_5 partitioned to the sediment, <6% to water and <1% to the air. The overall residence time was 140 days, which exceeds the P criterion²⁴ for freshwater sediment by only 20 days. Mackay *et al.*¹⁹ in their modeling calculations used a log K_{OC} value of 5.17, which was measured by Kozerski *et al.*²⁶

In a recent study, we measured the log $K_{\rm OC}$ for D_5 to be 6.12. ¹⁶ This $K_{\rm OC}$ value is of one order of magnitude higher than the measurements of Kozerski *et al.*, ²⁶ which would substantially increase the modeled residence time of D_5 in aquatic environments, and potentially indicate a more marked exceedance of the P criterion for sediment set by REACH. ²⁴

A parameter that could have great influence on $K_{\rm OC}$ and thus on the residence times of VMS in aquatic environments is the

enthalpy of sorption to OC from water ($\Delta H_{\rm OC}$). Due to the very limited literature data for $\Delta H_{\rm OC}$, it is common practice in modeling calculations to assume $\Delta H_{\rm OC}$ is equal to the enthalpy of phase change between octanol and water ($\Delta H_{\rm OW}$) in order to adjust $K_{\rm OC}$ to different temperatures. The partition ratios of VMS between octanol and water ($K_{\rm OW}$) and observed that the $K_{\rm OW}$ of VMS decreased with decreasing temperature. In another recent study, we measured the effect of temperature on the $K_{\rm OC}$ of VMS and observed that $K_{\rm OC}$ increased with decreasing temperatures. This difference could result in substantial differences in the modeled environmental fate and the residence times of VMS in aquatic environments at temperatures lower than the reference temperature of $K_{\rm OC}$ measurements.

Finally, salinity has an impact on $K_{\rm OC}$. In a previous study we observed that the $K_{\rm OC}$ of VMS increased with increasing salinity.¹⁷ This observation indicates that the residence times of VMS in marine environments are likely to be longer than in freshwater systems.

In this study we use a multi-stage process suggested by Mackay et al.33 as a framework to compare the environmental fate profile of VMS using property data from the Environment Canada and UK risk assessments to the fate profile using property data from our recent measurements. The stages are: (1) chemical classification, (2) evaluative assessment of chemical fate, (3) regional or far-field evaluation and (4) local or near-field evaluation. One of the focuses of this study is to assess the differences in the residence times of VMS in aquatic environments under a range of scenarios that reflect the variability in reported K_{OC} , ΔH_{OC} and ΔH_{OW} . For stages 3 and 4, we model the fjord at Longyearbyen (Adventfjorden) in the Norwegian Arctic because it is a cold system, where the K_{OC} values are expected to be substantially different from those at 21 °C and where the data on $(\Delta H_{\rm OW})$ and $\Delta H_{\rm OC}$ will impact the model assessment. In stage 2, we used the $K_{\rm OC}$ values at 21 °C. All modeling was done according to the good modeling practice guidelines as introduced by Buser et al.34

Stage 1: chemical classification

The chemicals evaluated in this study partition to all environmental media and therefore are classified as Type 1 chemicals according to the classification system suggested by Mackay et~al. ³³ The physicochemical properties of the chemicals used in the modeling calculations together with references are presented in Table 1. The $K_{\rm OC}$ of VMS was corrected for temperature changes using the values for $\Delta H_{\rm OC}$ but we also explored a scenario where $\Delta H_{\rm OC}$ were assumed to be equal to reported values of $\Delta H_{\rm OW}$. Except for $K_{\rm OC}$, $\Delta H_{\rm OC}$ and $\Delta H_{\rm OW}$ all other parameters were the same in all the modeling scenarios.

Discharge scenarios

Since this is primarily an evaluative study and the scope of the study is to evaluate the differences in the chemicals' residence times that may occur due to differences in the reported $K_{\rm OC}$ and ΔH values, we have not estimated site-specific emission rates for

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Table 1 Physicochemical properties of chemicals for the EQC and Adventfiorden models

| | D_4 | D_5 | D_6 | ${ m L}_4$ | L_5 |
|---|----------------|----------------|---------|------------|--------|
| Vapor pressure (Pa) ^a | 126 | 20.4 | 2.26 | 40.2 | 6.0 |
| $\log K_{\mathrm{OW}}^{\ \ b}$ | 6.98 | 8.07 | 8.87 | 8.14 | 8.70 |
| $\log K_{\mathrm{AW}}^{}b}$ | 2.74 | 3.16 | 3.01 | 3.45 | 3.13 |
| $\log K_{\mathrm{OA}}^{\ \ b}$ | 4.24 | 4.91 | 5.86 | 4.71 | 5.57 |
| $\log K_{\rm OC}$ Panagopoulos et al. 16,17 | 5.13 | 6.30 | 7.13 | 6.24 | 7.26 |
| $\log K_{\rm OC}$ Kozerski <i>et al.</i> ²⁶ | 4.44 | 5.17 | _ | 5.16 | _ |
| Salting-out constant $(K^s)^c$ | 0.42 | 0.34 | 0.37 | 0.25 | 0.37 |
| $\Delta H_{\rm OW}$ (kJ mol ⁻¹) ^d | 31.9 | 68.8 | 105.7 | 11.3 | 14.0 |
| $\Delta H_{\rm OC} (kJ \text{ mol}^{-1})^e$ | -79.2 | -48.0 | -48.3 | -67.6 | -45.8 |
| $\Delta H_{\rm AW}$ (kJ mol ⁻¹) ^d | 73.9 | 123.9 | 173.9 | 65.5 | 81.0 |
| $\Delta H_{\rm OA} ({\rm kJ~mol}^{-1})^d$ | -43.7 | -47.3 | -50.9 | -46.9 | -58.0 |
| $E_{\rm act}$ for reaction with 'OH (kJ mol ⁻¹) | -0.71 | 3.31 | 6.85 | 5 | 4.8 |
| $E_{\rm act}$ for hydrolysis (kJ mol ⁻¹) ^g | 87.6 | 87.2 | 93.5 | 87.6 | 87.2 |
| Half-life in air at 25 °C (h) ^h | 108 | 101 | 79 | 55 | 13 |
| Half-life in water at pH 7 and 25 °C (h) ⁱ | 89 | 1776 | 3463 | 409 | 2096 |
| Half-life in water at pH 8 and 25 $^{\circ}$ C (h) ⁱ | 70 | 216 | 362 | 98 | 244 |
| Half-life in soil at 25 °C (h) ^j | 127 | 302 | 9624 | 127 | 302 |
| Half-life in sediment at 25° C (h) ^k | 8760 | 74 400 | 140 055 | 21 228 | 86 867 |

^a The vapor pressures for all chemicals except for L₄ were measured experimentally in the study of Lei et al., ³⁵ whereas the vapor pressure for L₄ was estimated based on their regression. The values for K_{OW} and K_{AW} of D_4 , D_5 , D_6 and L_4 were measured experimentally in the studies of Xu and Kropscott.31 The Kow and Kaw of L5 were estimated from PP-LFER regressions, which were constructed as suggested by Goss36 combining the data of Abraham et al. 37 with the measurements of Xu and Kropscott 31 in their training sets. The values for K_{OA} were calculated by subtracting the values for $\log K_{AW}$ from those for $\log K_{OW}$. The values for the salting-out constants (K^5) of VMS were measured by Panagopoulos et al. 16,17 d The values for $\Delta H_{\rm OW}$, $\Delta H_{\rm AW}$ and $\Delta H_{\rm OA}$ of D₄, D₅ and L₄ were measured in the study of Xu and Kropscott.³¹ The values for $\Delta H_{\rm OW}$, $\Delta H_{\rm AW}$ and $\Delta H_{\rm OA}$ of D₆ and L₅ were calculated by linearly extrapolating from the measured values based on the chemicals' molecular weight. e The values for $\Delta H_{\rm OC}$ were measured by Panagopoulos et al. $^{32\ f}$ The activation energies ($E_{\rm act}$) for degradation in the air of D_4 and D_5 were measured in the study of Xiao et al. ¹³ The value of D_6 was calculated by extrapolating from the data for D_4 and D_5 . The value for L_4 was measured by Zammit³⁸ and the value of L_5 was calculated by extrapolating from the data of Zammit³⁸ for L_2 , L_3 and L_4 . ^g The activation energies for hydrolysis of D_4 , D_5 and D_6 were measured by Xu and Kozerski. Since no clear trend was observed between these values and the size of the molecules, the values of L_4 and L_5 were assumed to be the same as the measured ones. The half-lives of D_4 and D_5 in air were measured by Xiao et al., the half-life of D_6 was calculated by extrapolating from the measurements for D_4 and D_5 . The half-life of L_4 was measured by Zammit³⁸ and the half-life of L_5 was estimated by extrapolating from the measurements for L_2 , L_3 and L_4 . The half-lives of D_4 and D_5 in water at 25 °C and pH 7 and 8 were calculated by Environment Canada⁴⁻⁶ based on hydrolysis data from Dow Corning. The half-lives of D_6 , L_4 , and L_5 were extrapolated from the data for D_4 and D_5 . j The half-lives of D_4 , D_5 and D_6 in soil were calculated by Xu.⁴⁰ The half-lives for L_4 , and L_5 were assumed to be the same as those of D_4 and D_5 . k The half-lives of D_4 and D_5 in sediment were measured by Xu and Miller⁴¹⁻⁴³ and the half-lives of D_6 , L_4 , and L_5 were estimated by extrapolating from the data for D₄ and D₅. Since these half-lives were measured in experiments with bulk sediments we chose not to adjust them based on concentrations in pore water.

Adventfjorden. Instead, in the Adventfjorden scenarios we assumed that all chemicals were emitted to water and all emission rates were set at a constant value. The same approach is also used in the study of Mackay et al.19

Stage 2: evaluative assessment of chemical fate

As in the study by Mackay et al., 19 our evaluative assessment was conducted using the EQC model distributed by Trent University, Canada. A description of the model can be found in the studies of Mackay et al. 19,33,44 The model was run for all three levels of fugacity calculations (Level I, II and III). Level I refers to a model at steady-state and equilibrium, Level 2 refers to steadystate and equilibrium but it also includes processes of advection and reaction, Level III to steady-state non-equilibrium, and Level IV refers to non-steady-state non-equilibrium. 45 The area of the environment in the EQC model is 100 000 km², and it has environmental properties similar to the U.S. state of Pennsylvania or of South Korea. Our modeling scenarios are all direct applications of the standard scenario found in EQC.

Results from the Level I EOC calculations indicate that under equilibrium and steady state conditions the bulk of all the VMS chemicals considered here will mainly partition to the air, and that this result is not sensitive to which K_{OC} values are used as input to the model. A summary of the results of the Level 1 EQC modeling assessment is presented in Table 3.

In Level II and III we focus our assessment on the persistence of the VMS modeled as residence times in individual compartments (water and sediment), and as the overall residence time in the modeled regions. The residence times are defined as follows.

$$RT_{CW} = \frac{I_{W}}{\sum D_{W \to \text{out}}}$$
 (1)

$$RT_{CX} = \frac{I_{CX}}{\sum D_{X \to \text{out}}}$$
 (2)

$$RT_{O} = \frac{I_{O}}{\sum D_{O \to \text{out}}}$$
 (3)

Table 2 Model parameters for Adventfjorden for the months January and July

| Parameter | Value for January | Value for July | Source |
|--|----------------------|---------------------|---|
| Air temperature | -7 | 8 | Weslawski ⁴⁸ |
| Water temperature | 0 | 5 | Weslawski ⁴⁸ |
| Fjord area (m ²) | 2.8×10^{7} | $2.8 	imes 10^7$ | Weslawski ⁴⁸ |
| Fjord mean depth (m) | 75 | 75 | Weslawski ⁴⁸ |
| Fjord volume (m ³) | 2.10×10^{9} | 2.10×10^{9} | Weslawski ⁴⁸ |
| Precipitation (m h ⁻¹) | 2.28×10^{-5} | 2.28×10^{-5} | Hanssen-Bauer ⁵¹ |
| Residence time of water (months) | 6^a | 5^a | Weslawski ⁴⁸ and Basedow <i>et al.</i> ⁵² |
| Concentration of suspended particles (mg L ⁻¹) | 35.3 | 223.5 | Zajaczkowski and |
| , | | | Wlodarska-Kowalczuk ⁴⁹ |
| OC fraction of suspended particles (%) | 2 | 2 | Warner et al. ⁵⁰ |
| OC fraction of sediment particles (%) | 2 | 2 | Warner <i>et al.</i> ⁵⁰ |
| Sediment deposition rate (g m ⁻² d ⁻¹) | 4.2 | 464.1 | Zajaczkowski and Wlodarska-Kowalczuk ⁴⁹ |
| Sediment resuspension rate (g m ⁻² d ⁻¹) | 0.634 | 0.634 | Mackay ⁴⁵ |
| Sediment burial rate (g m ⁻² d ⁻¹) | 1.96 | 1.96 | Mackay ⁴⁵ |
| MTC at the water side of the air-water | $3 	imes 10^{-7b}$ | 0.05 | Mackay ⁴⁵ |
| interphase (m h ⁻¹) | | | • |
| MTC at the air side of the air-water interphase (m h ⁻¹) | $3 	imes 10^{-5b}$ | 5 | Mackay ⁴⁵ |
| Sediment layer depth (m) | 0.05 | 0.05 | Mackay ⁴⁵ |
| MTC at the water side of the water-sediment | 0.01 | 0.01 | Mackay ⁴⁵ |
| interphase (m h ⁻¹) | | | • |

^a We assumed a residence time of water in the fjord of 6 months for winter and 5 months for summer. This assumption is based on the observations of Basedow *et al.*⁵² for Kongsfjorden in Svalbard. No measurements were found for Adventfjorden. Basedow *et al.*⁵² measured a residence time of water in Kongsfjorden of about 6 days. Kongsfjorden is directly exposed to the Atlantic Ocean, while Adventfjorden is a small fjord inside a larger fjord (Isfjorden) and the water exchange there is expected to be substantially slower. For that reason, we chose the value of 6 months. The difference between winter and summer is due to additional water flowing into the fjord from the rivers and due to the ice cover melting. ⁴⁸ The residence times of water are primarily controlled by the inflow of ocean water into the fjord and by the outflow of fjord water into the ocean. ^b The values for MTCw and MTCa in winter were assumed to be extremely low because the fjord is covered with ice and there is no volatilization.

where, RT_{CW}, RT_{CX} and RT_O are the residence times of the VMS in water, sediment and overall residence time; I_{CW} , I_{CX} and I_{O} are the amounts of chemical (mol) in water, sediment and the total amount in the model environment, and $\sum D_{\text{CW} \to \text{out}}$, $\sum D_{\text{CX} \to \text{out}}$ and $\sum D_{\text{O} \to \text{out}}$ are the sum of the chemical fluxes moving out of each compartment (CW and CX) or out of the region (O) (mol h⁻¹).

The Level II EQC modeling assessment shows that the overall persistence of all VMS are similar, and dominated by processes in the air compartment. Advection and reaction in the air are the

Table 3 Summary of the Level 1 EQC modeling assessment

| | Amount (kg) | | | | | | |
|--|-----------------------|----------|-------------|---------|--|--|--|
| Level I substance | In air | In water | In sediment | In soil | | | |
| Panagopoulos et al. | 16,17 K _{OC} | | | | | | |
| D_4 | 99 891 | 0.364 | 2.35 | 106 | | | |
| D_5 | 99 570 | 0.148 | 9.34 | 420 | | | |
| D_6 | 94 495 | 0.185 | 120 | 5381 | | | |
| L_4 | 99 728 | 0.0708 | 5.9 | 266 | | | |
| L_5 | 94 374 | 0.14 | 122 | 5500 | | | |
| Kozerski et al. ²⁶ K _O | C | | | | | | |
| D_4 | 99 986 | 0.364 | 0.297 | 13.4 | | | |
| D_5 | 99 951 | 0.148 | 1.05 | 47.3 | | | |
| L_4 | 99 979 | 0.0709 | 0.459 | 20.7 | | | |

main removal mechanisms (Table 4). Again, there are no notable differences between calculations using the $K_{\rm OC}$ measurements from Panagopoulos *et al.*^{16,17} and those of Kozerski *et al.*²⁶

The Level III EQC modeling assessment shows that for all VMS the medium of release strongly affects the distribution of the chemicals between air, water, soil and sediment. When released in the air all VMS tend to remain in air and they are removed from the environment through advection and reaction. When the VMS are released in water they tend to partition to the sediment, which substantially prolongs their overall residence times compared to the release to air scenario due to lack of advection and slower degradation rates. When emissions occur to soil the VMS with lower Koc tend to mainly partition to air while those with higher K_{OC} mainly reside in soil. Out of all three emission scenarios, emissions to water showed the longest overall residence times (Table 5), and residence times increased with increasing hydrophobicity. When cVMS are emitted to water the overall residence times range from 8 to 1123 days and those of IVMS range from 97 to 1194 days. Emissions to water result in the longest residence times, and will occur through wastewater treatment plants, so we focused our comparisons on that scenario.

When emitted to water in the generic EQC model, all VMS except D_4 exceed the 100-day persistence criterion suggested by Webster *et al.*²⁵ (Fig. 1). Large differences were observed between the simulations based on the $K_{\rm OC}$ measurements of Panagopoulos *et al.*^{16,17} and those of Kozerski *et al.*²⁶ The largest

Table 4 Summary of the Level II EQC modeling assessment

| | Amount | Amount | | | | | | | |
|--|----------------------|----------|-------------|---------|-------------------|------------------|----------------------------|--|--|
| Level II substance | In air (kg) | In water | In sediment | In soil | Lost by advection | Lost by reaction | Overall residence time (h) | | |
| Panagopoulos et al.1 | 6,17 K _{OC} | | | | | | | | |
| D_4 | 60 892 | 0.222 | 1.44 | 64.6 | 609 | 391 | 61 | | |
| D_5 | 59 273 | 0.0879 | 5.56 | 250 | 593 | 407 | 60 | | |
| D_6 | 53 259 | 0.104 | 67.4 | 3033 | 533 | 467 | 56 | | |
| L_4 | 61 721 | 0.0438 | 3.65 | 164 | 617 | 382 | 62 | | |
| L_5 | 57 123 | 0.0847 | 74 | 3329 | 571 | 421 | 61 | | |
| Kozerski <i>et al.</i> ²⁶ K _{OC} | | | | | | | | | |
| D_4 | 60 911 | 0.222 | 0.181 | 8.14 | 609 | 391 | 61 | | |
| D_5 | 59 303 | 0.0879 | 0.624 | 28.1 | 593 | 407 | 59 | | |
| L_4 | 61 772 | 0.0438 | 0.284 | 12.8 | 618 | 382 | 62 | | |

difference observed was for D_5 emitted to water. Using the $K_{\rm OC}$ measurements of Kozerski et al.26 the overall residence time for D_5 is 203 d while using the K_{OC} measurements of

Panagopoulos et al. 16,17 the overall residence time is 676 d. The difference of one log unit in the K_{OC} of D_5 resulted in almost 500-days difference in the modeled overall residence times.

Table 5 Summary of the Level III EQC modeling assessment

| | Emission medium | Amount (kg) | | | | | |
|--|------------------------------|-------------|----------|-------------|---------|---------------------------|--|
| Level III substance | | In air | In water | In sediment | In soil | Overall residence time (h | |
| Panagopoulos et al. 16,1 | ⁷ K _{OC} | | | | | | |
| D_4 | Air | 6090 | 0.00488 | 0.0344 | 5.01 | 61 | |
| | Water | 1094 | 8649 | 60 955 | 0.9 | 707 | |
| | Soil | 4566 | 0.0716 | 0.505 | 4590 | 92 | |
| | All three | 11 750 | 8649 | 60 956 | 4596 | 287 | |
| | Air | 5928 | 0.021 | 1.41 | 16.4 | 60 | |
| D_5 | Water | 1183 | 23 871 | 1 600 000 | 3.28 | 16 236 | |
| | Soil | 3839 | 0.406 | 27.2 | 15 389 | 193 | |
| | All three | 10 951 | 23 872 | 1 600 000 | 15 409 | 5496 | |
| | Air | 5326 | 0.0131 | 1.38 | 247 | 56 | |
| D_6 | Water | 158 | 25 307 | 2 670 000 | 7.33 | 26 975 | |
| · · | Soil | 4333 | 6.6 | 697 | 259 000 | 2638 | |
| | All three | 9817 | 25 314 | 2 670 000 | 259 000 | 9889 | |
| | Air | 6175 | 0.00199 | 0.0988 | 9.15 | 62 | |
| L_4 | Water | 711 | 16 691 | 826 000 | 1.05 | 8438 | |
| 24 | Soil | 3389 | 0.145 | 7.2 | 8271 | 117 | |
| | All three | 10 275 | 16 691 | 826 000 | 8281 | 2872 | |
| | Air | 5751 | 0.00606 | 0.608 | 39.6 | 58 | |
| L_5 | Water | 120 | 23 664 | 2 370 000 | 0.827 | 23 980 | |
| 25 | Soil | 680 | 0.915 | 91.8 | 38 433 | 392 | |
| | All three | 6561 | 23 665 | 2 370 000 | 38 473 | 8143 | |
| Kozerski <i>et al.</i> ²⁶ K _{OC} | | | | | | | |
| D_4 | Air | 6091 | 0.00496 | 0.0051 | 0.983 | 61 | |
| • | Water | 1310 | 8831 | 9095 | 0.211 | 192 | |
| | Soil | 5792 | 0.0493 | 0.0508 | 901 | 67 | |
| | All three | 13 193 | 8831 | 9095 | 902 | 107 | |
| | Air | 5930 | 0.022 | 0.397 | 2.85 | 59 | |
| D_5 | Water | 3044 | 25 361 | 457 000 | 1.46 | 4859 | |
| | Soil | 5568 | 0.128 | 2.31 | 2672 | 82 | |
| | All three | 14 542 | 25 361 | 457 000 | 2676 | 1667 | |
| | Air | 6177 | 0.0021 | 0.0239 | 1.4 | 62 | |
| L_4 | Water | 2372 | 18 704 | 213 000 | 0.536 | 2338 | |
| —·± | Soil | 5752 | 0.0376 | 0.427 | 1262 | 70 | |
| | All three | 14 302 | 18 704 | 213 000 | 1264 | 823 | |

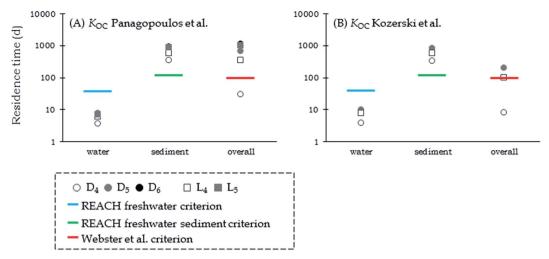


Fig. 1 Compartment-specific and overall residence times for VMS calculated in the EQC model using the $K_{\rm OC}$ measurements of (A) Panagopoulos *et al.*^{16.17} and (B) those of Kozerski *et al.*²⁶ The blue line shows the REACH criterion for freshwater and the green line shows that for freshwater sediment.²⁴ The red line shows the 100-day criterion for overall persistence suggested by Webster *et al.*²⁵

The modeled residence times in the water compartment of all chemicals are below the REACH criterion for freshwater. However, the modeled residence times of all chemicals in the sediment compartment exceed the REACH criterion for freshwater sediment, regardless of which $K_{\rm OC}$ values are used. Compartment specific residence times in water and sediment are almost the same for the two different $K_{\rm OC}$ values, however the overall residence times are substantially longer using the $K_{\rm OC}$ measured by Panagopoulos *et al.* 16,17 (Fig. 1). The explanation lies in the distribution of cVMS among the different compartments and the total inventory. The larger inventory of cVMS in the sediment when using the $K_{\rm OC}$ value of Panagopoulos *et al.* 16,17 results in much longer overall residence times but it does not strongly affect the compartment specific residence times for sediment.

This evaluative assessment confirms the modeling results presented by Whelan $et~al.^{14,15}$ in that it underlines the importance of $K_{\rm OC}$ and the importance of the emission medium, especially when emissions are to water, in the chemical fate and persistence of VMS in the environment. These results also agree with the studies of Hughes $et~al.^{46}$ and Xu and Wania.⁴⁷

Stage 3 and 4: regional/local or near-field evaluation

The fate of cVMS and lVMS in Adventfjorden, Svalbard is particularly interesting because it is a coastal system with low water temperatures all year round, seasonal variability in particle deposition, and ice coverage during winter. 48,49 Since 2006–2007 the ice thickness and coverage of the fjord has been declining. However, we kept that parameter in our modeling

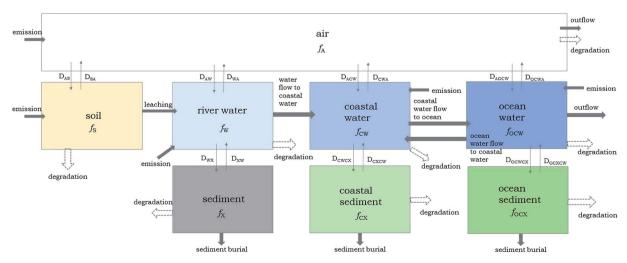


Fig. 2 Diagram of the Adventfjorden model based on the fugacity approach as introduced by Mackay.⁴⁵ f refers to the fugacity (Pa) of each individual compartment and D is the fugacity rate descriptor (mol h⁻¹ Pa⁻¹) between compartments. For example, the fugacity rate descriptor from air to water is shown as D_{AW} .

because we wanted to see how ice coverage may affect the behavior of VMS. Adventfjorden receives wastewater from Longvearbyen without any mechanical, chemical or biological treatment. Warner et al.50 showed a decrease in the concentrations of D₅ in the sediment with increasing distance from the wastewater outlet indicating that wastewater is the main source of VMS. The effluent is released to the fjord at 62 m depth about 1.5 km away from the coast.

Our Adventfjorden model is a non-equilibrium Level III and Level IV model, which was specifically parameterized to describe the environmental fate of chemicals in coastal environments. The model is similar to the EQC model in structure, and describes chemical behavior using the fugacity concept by Mackay.45 A diagram of the model environment is shown in Fig. 2.

The physical characteristics of Adventfjorden are summarized in Table 2. Adventfjorden is a small fjord located close to Longyearbyen in Svalbard, Norway, with a total area of about 28 km².48 It has an average depth of 75 m and is rather steep, with a 50 m km⁻¹ depth increase for the first km from the coast.48 The main source of water into the fjord is exchange of seawater from the ocean. Adventfjorden receives freshwater primarily from the rivers Adventelva and Longvearelva with average water flows of 3 m³ s⁻¹ for each river and from sea ice and snow cover melting. 48 The residence time of the water in the fjord is controlled by the inflow of ocean water into the fjord and by the outflow of fjord water into the ocean. The freshwater from the rivers and the ice cover melting are minor contributions to the overall residence time.48 Zajaczkowski and Wlodarska-Kowalczuk49 measured the concentrations of suspended particles and the sedimentation rates at different sites across the fjord. Based on their observations an average concentration of suspended particles of 223.5 mg L⁻¹ was used in our model scenarios for July and 35.3 mg L⁻¹ was used for model scenarios for January. For the months in between we calculated the concentration of suspended particles assuming that it increases logarithmically. A value of 464.1 g m⁻² per day sedimentation rate was used in scenarios for July and a value of 4.2 g m⁻² per day was used for January. For the months between, the sedimentation rates were calculated as described above for the concentration of suspended particles. The fraction of total OC in the sediment of Adventfjorden is around 2%

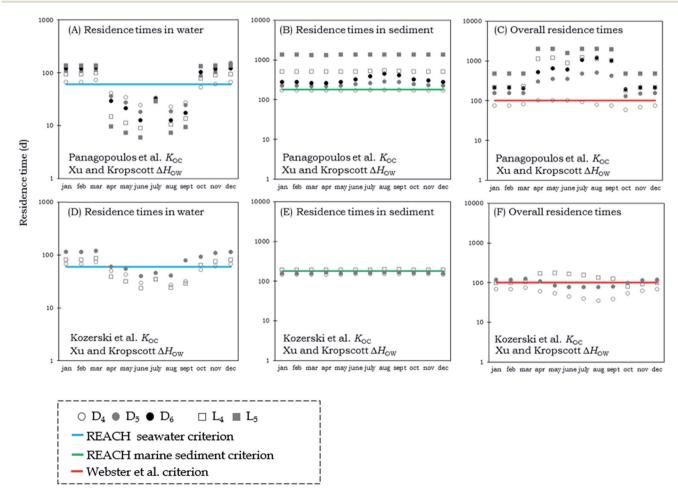


Fig. 3 Water, sediment and overall residence times for cVMS (circles) and IVMS (squares) using both the K_{OC} measurements of Kozerski et al.²⁶ (lower panels) and those of Panagopoulos et al. 16,17 (upper panels). The $K_{\rm OC}$ was corrected for temperature changes using the $\Delta H_{\rm OW}$ measurements of Xu and Kropscott.⁵¹ The blue line shows the REACH criterion for persistence in marine waters and the green line shows the REACH criterion for persistence in marine sediments.²⁴ The red line shows the 100-day overall persistence criterion suggested by Webster et al.²⁵

(Warner et al.50). The same OC content was assumed for the suspended particles.

In winter the mass transfer coefficients at the water side (MTCw) and at the air side (MTCa) of the air-water interface were assumed to be extremely low in January and December to simulate ice cover, and to logarithmically increase in the months in between (Table 2). For all other parameters, we used data from the literature for each month.

In Fig. 3 and 4 we present steady-state calculations of the residence times of VMS in Adventfjorden for each month over a period of one year. In all scenarios, the emissions of the chemicals were directed 100% into water. In cases where residence times exceed 1 month, the modeled steady-state conditions will not be approached in the real system, and unsteadystate (Level IV) model results are presented below. However, we chose to model hypothetical steady-state conditions for each month in order to explore bounding scenario for variability in the system that illustrate the effects of temperature, ice coverage and varying sedimentation rates on the residence times of the chemicals in the fjord. Results in Fig. 3 are for K_{OC} corrected for temperature using the $\Delta H_{\rm OW}$ measurements of Xu and

Kropscott³¹ and results in Fig. 4 are for a scenario in which K_{OC} was corrected for temperature changes using the $\Delta H_{\rm OC}$ measurements of Panagopoulos et al.32 We present both compartment-specific and overall residence times.

The residence times of the chemicals in water were found to vary considerably in the steady state scenarios for different months (Fig. 3 & 4). The variation depends on the ice formation and melting in the fjord. In the winter months when the fjord is covered with ice the residence times of the chemicals in water exceed the REACH criterion for marine waters.24 In the summer months when the ice has melted and volatilization is not restricted the residence times are below the REACH criterion for marine waters.24 In July the concentrations of VMS increase substantially compared to the values for June and August. The reason behind that difference is that in July we have the highest concentration of suspended particles. The larger amount of organic carbon in water in July increases the residence times in water.

The residence times of VMS in sediment are less variable in the range of scenarios. Ice formation and melting does not affect the sediment residence times substantially. In the

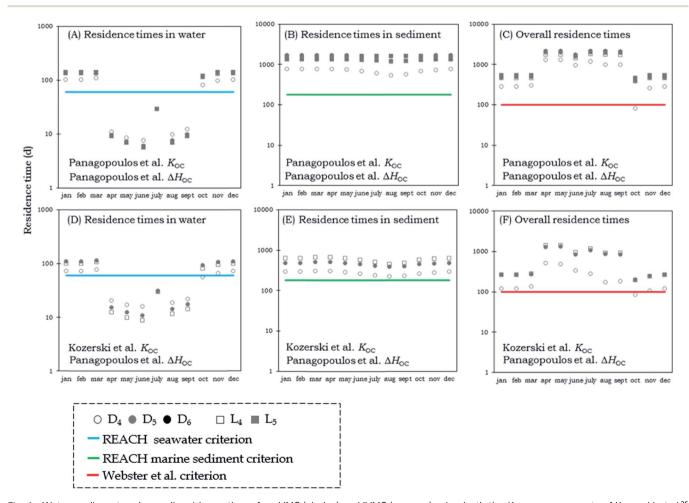


Fig. 4 Water, sediment and overall residence times for cVMS (circles) and IVMS (squares) using both the K_{OC} measurements of Kozerski et al.²⁶ (lower panels) and those of Panagopoulos et al. 16,17 (upper panels). The K_{OC} was corrected for temperature changes using the ΔH_{OC} measurements of Panagopoulos et al.³² The blue line shows the REACH criterion for persistence in marine waters and the green line shows the REACH criterion for persistence in marine sediments.²⁴ The red line shows the 100-day overall persistence criterion suggested by Webster et al.²⁵

scenarios using the $K_{\rm OC}$ measurements of Kozerski et al., 26 the residence times were all shorter than in scenarios using the measurements of Panagopoulos et al.16,17 and in the case where we used the $\Delta H_{\rm OW}$ measurements of Xu and Kropscott,³¹ the residence times were very close to the criterion values for persistence in marine sediments. On the other hand, scenarios using the $\Delta H_{\rm OC}$ measurements of Panagopoulos et al.³² had residence times of VMS that exceeded the REACH criterion for marine sediments in all cases except for D4, where residence times were almost equal to the residence time of the REACH criterion.24

Similar results were observed for the overall residence times. In the majority of scenarios, the overall residence times exceed the 100-day criterion of Webster et al.25 but the magnitude of that exceedance varies considerably among the different scenarios. In the scenario using K_{OC} measurements of Kozerski et al. 26 and $\Delta H_{\rm OW}$ measurements of Xu and Kropscott 31 the overall residence times were in all cases between 50 and 200 days, while in the scenario using the K_{OC} measurements and $\Delta H_{\rm OC}$ of Panagopoulos et al. 16,17,32 the majority of calculated overall residence times were between 100 and 1000 days. Our calculations using scenarios based on measurements of Panagopoulos et al. 16,17,32 suggest that, in contrast to findings in the study of Mackay et al.19 and the assessments of UK Environment Agency¹⁻³ and Environment Canada,⁴⁻⁶ VMS cannot be categorized as non-persistent since their residence times exceed by far the REACH criterion for marine sediments²⁴ and the 100day criterion of Webster et al.25 One could expect to see longer residence times in the winter than in the summer due to the icemelting and warmer water temperatures. However, the effect of higher sediment deposition rates in the summer outweighs the effect of ice-melting and higher water temperatures.

In Fig. 5 we present the modeled elimination of VMS from Adventfjorden in a Level IV unsteady-state model scenario over the course of one year if the system starts at steady-state conditions for average values of environmental parameters and emissions are stopped at time 0. Large differences are observed for the different scenarios. In the scenario using K_{OC} measurements of Kozerski et al. 26 and $\Delta H_{\rm OW}$ measurements of Xu and Kropscott, 31 1 year after the end of emissions the modeled amount of D₅ in Adventfjorden decreases to almost 0% of the initial amount. However, in the scenarios using $K_{\rm OC}$ measurements and $\Delta H_{\rm OC}$ of Panagopoulos et al. 16,17,32 the modeled amount of D₅ declines to only about 65% of the initial amount.

Fig. 6 shows results of a sensitivity analysis of the steady-state (Level III) version of the Adventfjorden model. The parameters that were included in the sensitivity analysis were selected based on whether they have an influence on the residence times of the chemicals in the sediment and the overall residence times. Parameters that influence only the residence times of the

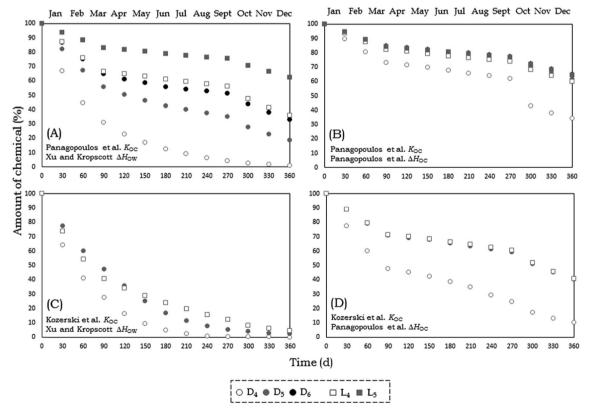


Fig. 5 Elimination of cVMS (circles) and IVMS (squares) from Adventfjorden over the course of one year if emissions stopped at time 0. Panels A and B show the elimination data for cVMS and IVMS using the K_{OC} measurements of Panagopoulos et al. 16.17 and panels C and D show the elimination data for cVMS and IVMS using the K_{OC} measurements of Kozerski et al. ²⁶ The panels on the left (A and C) show the elimination data for cVMS and IVMS using the $\Delta H_{\rm OW}$ measurements of Xu and Kropscott³¹ to correct for temperature and the panels on the right show the elimination data for cVMS and IVMS using the $\Delta H_{\rm OW}$ measurements of Panagopoulos et al. 32

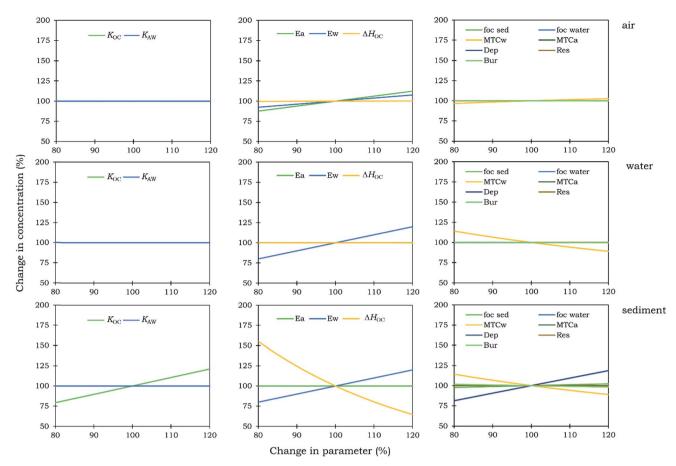


Fig. 6 Results of the sensitivity analysis for the Adventiforden model. Changes in concentration (%) in air (first row), water (second row) and sediment (third row) as a response of changes in K_{OC} and K_{AW} (first column); emissions to air (E_a), emissions to water (E_w) and ΔH_{OC} (second column); f_{OC} in sediment and water, MTCw, MTCa, deposition, resuspension and burial (third column).

chemicals in water, such as the residence time of water in the fjord were not included in the sensitivity analysis. The parameters that were found to be most sensitive are $\Delta H_{\rm OC}$, $K_{\rm OC}$, the fraction of organic carbon in the water (f_{OC}) and the deposition rate of sediment particles (Dep). This observation is also supported by the findings of Krogseth et al.53 Out of all compartments, these parameters were found to be especially sensitive for the concentrations of VMS in the sediment. One could expect to see large differences in the concentrations of VMS in water too but the amount of siloxane in the water compartment is small under all scenarios and thus appears insensitive to changes in $\Delta H_{\rm OC}$, $K_{\rm OC}$, $f_{\rm OC}$ and Dep. The results of the sensitivity analysis underline the importance of accurately determining the $K_{\rm OC}$ and $\Delta H_{\rm OC}$ of VMS in order to study their environmental fate using multimedia models. Our findings from the sensitivity analysis are in good agreement with those of Whelan. ^{14,15} Both studies agree that K_{OC} and other parameters directly related to K_{OC} , such as sediment deposition and resuspension rates are the most sensitive parameters of the models.

Conclusions

A major challenge in modeling the environmental fate of VMS in aquatic environments using multimedia models has been

obtaining reliable data for $K_{\rm OC}$ and $\Delta H_{\rm OC}$. Our work demonstrates that these two parameters are the most sensitive in the region-specific modeling assessment. The difference of one log unit between the Koc measurements of Kozerski et al.26 and those of Panagopoulos et al. 16,17 in combination with differences in reported $\Delta H_{\rm OW}$ and $\Delta H_{\rm OC}$ resulted in substantial differences in the environmental fate and residence times of VMS. Our results suggest that residence times of VMS may be substantially longer when using $\Delta H_{\rm OC}$ instead of $\Delta H_{\rm OW}$ in the modeling calculations of VMS. Also because of the difference in the sign (+ or -) of $\Delta H_{\rm OW}$ and $\Delta H_{\rm OC}$ of VMS, modeling calculations of the effect of temperature on the residence times of VMS may show contradictory results. Calculations using ΔH_{OW} would indicate that the residence times of VMS are shorter in cold waters,54 while calculations using $\Delta H_{\rm OC}$ would indicate that they are longer in cold waters. In the light of these new results we suggest that VMS are monitored in aquatic environments in order to assess their persistence and the potential environmental threat they may pose in the future.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We thank the Swedish Research Council FORMAS for funding this project (project number 2011-484) and Mick Whelan for useful comments and suggestions.

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