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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 (ΔH_{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 D_5 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 D_5 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 D_5 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.

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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 $-Si(CH_3)_2-O-$ 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 (lVMS) 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 lVMS. However, Lu *et al.*[8] reported that some personal care products from the Chinese market have concentrations of lVMS 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_{OC}, as this was the parameter that was shown to be the most sensitive in the model calculations.

Environmental risk assessments for D_5 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 D_5 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 D_5 taking into consideration physicochemical properties presented by the industry representatives.[19,22,23] The Board of Review overruled the initial assessment and concluded that "D_5 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 REACH[24] 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 criterion[24] 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_{OC} for D_5 to be 6.12.[16] This K_{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_{OC} and thus on the residence times of VMS in aquatic environments is the enthalpy of sorption to OC from water (ΔH_{OC}). Due to the very limited literature data for ΔH_{OC}, it is common practice in modeling calculations to assume ΔH_{OC} is equal to the enthalpy of phase change between octanol and water (ΔH_{OW}) in order to adjust K_{OC} to different temperatures.[27–30] Xu and Kropscott[31] studied the effect of temperature on the partition ratios of VMS between octanol and water (K_{OW}) and observed that the K_{OW} of VMS decreased with decreasing temperature. In another recent study,[32] we measured the effect of temperature on the K_{OC} of VMS and observed that K_{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_{OC} measurements.

Finally, salinity has an impact on K_{OC}. In a previous study we observed that the K_{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 (ΔH_{OW} and ΔH_{OC}) will impact the model assessment. In stage 2, we used the K_{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_{OC} of VMS was corrected for temperature changes using the values for ΔH_{OC} but we also explored a scenario where ΔH_{OC} were assumed to be equal to reported values of ΔH_{OW}. Except for K_{OC}, ΔH_{OC} and ΔH_{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_{OC} and ΔH values, we have not estimated site-specific emission rates for

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

	D_4	D_5	D_6	L_4	L_5
Vapor pressure (Pa)[a]	126	20.4	2.26	40.2	6.0
log K_{OW} [b]	6.98	8.07	8.87	8.14	8.70
log K_{AW} [b]	2.74	3.16	3.01	3.45	3.13
log K_{OA} [b]	4.24	4.91	5.86	4.71	5.57
log K_{OC} Panagopoulos *et al.*[16,17]	5.13	6.30	7.13	6.24	7.26
log K_{OC} Kozerski *et al.*[26]	4.44	5.17	—	5.16	—
Salting-out constant (K^s)[c]	0.42	0.34	0.37	0.25	0.37
ΔH_{OW} (kJ mol^{-1})[d]	31.9	68.8	105.7	11.3	14.0
ΔH_{OC} (kJ mol^{-1})[e]	−79.2	−48.0	−48.3	−67.6	−45.8
ΔH_{AW} (kJ mol^{-1})[d]	73.9	123.9	173.9	65.5	81.0
ΔH_{OA} (kJ mol^{-1})[d]	−43.7	−47.3	−50.9	−46.9	−58.0
E_{act} for reaction with $^{\bullet}OH$ (kJ mol^{-1})[f]	−0.71	3.31	6.85	5	4.8
E_{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 °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 L_4 were measured experimentally in the study of Lei *et al.*,[35] whereas the vapor pressure for L_4 was estimated based on their regression.[35] [b] 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 K_{OW} and K_{AW} of L_5 were estimated from PP-LFER regressions, which were constructed as suggested by Goss[36] 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}. [c] The values for the salting-out constants (K^s) of VMS were measured by Panagopoulos *et al.*[16,17] [d] The values for ΔH_{OW}, ΔH_{AW} and ΔH_{OA} of D_4, D_5 and L_4 were measured in the study of Xu and Kropscott.[31] The values for ΔH_{OW}, ΔH_{AW} and ΔH_{OA} of D_6 and L_5 were calculated by linearly extrapolating from the measured values based on the chemicals' molecular weight. [e] The values for ΔH_{OC} were measured by Panagopoulos *et al.*[32] [f] The activation energies (E_{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 Zammit[38] and the value of L_5 was calculated by extrapolating from the data of Zammit[38] 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.[39] 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. [h] The half-lives of D_4 and D_5 in air were measured by Xiao *et al.*,[13] 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 Zammit[38] and the half-life of L_5 was estimated by extrapolating from the measurements for L_2, L_3 and L_4. [i] The half-lives of D_4 and D_5 in water at 25 °C and pH 7 and 8 were calculated by Environment Canada[4–6] 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 Miller[41–43] and the half-lives of D_6, L_4, and L_5 were estimated by extrapolating from the data for D_4 and D_5. 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 steady-state 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 km^2, 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 EQC 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.

$$\mathrm{RT}_{CW} = \frac{I_W}{\sum D_{W\rightarrow out}} \tag{1}$$

$$\mathrm{RT}_{CX} = \frac{I_{CX}}{\sum D_{X\rightarrow out}} \tag{2}$$

$$\mathrm{RT}_{O} = \frac{I_O}{\sum D_{O\rightarrow out}} \tag{3}$$

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	2.8×10^7	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 *et al.*[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 *et al.*[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 interphase ($m\ h^{-1}$)	3×10^{-7}[b]	0.05	Mackay[45]
MTC at the air side of the air–water interphase ($m\ h^{-1}$)	3×10^{-5}[b]	5	Mackay[45]
Sediment layer depth (m)	0.05	0.05	Mackay[45]
MTC at the water side of the water-sediment interphase ($m\ h^{-1}$)	0.01	0.01	Mackay[45]

[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 $\sum D_{CW\rightarrow out}$, $\sum D_{CX\rightarrow out}$ and $\sum D_{O\rightarrow out}$ 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 main removal mechanisms (Table 4). Again, there are no notable differences between calculations using the K_{OC} measurements from Panagopoulos *et al.*[16,17] and those of Kozerski *et al.*[26]

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_{OC}				
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

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 K_{OC} 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 lVMS 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_{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						
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.*[16,17] 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 *et al.*[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_{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

		Amount (kg)				
Level III substance	Emission medium	In air	In water	In sediment	In soil	Overall residence time (h)
Panagopoulos *et al.*[16,17] 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
D_5	Air	5928	0.021	1.41	16.4	60
	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
D_6	Air	5326	0.0131	1.38	247	56
	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
L_4	Air	6175	0.00199	0.0988	9.15	62
	Water	711	16 691	826 000	1.05	8438
	Soil	3389	0.145	7.2	8271	117
	All three	10 275	16 691	826 000	8281	2872
L_5	Air	5751	0.00606	0.608	39.6	58
	Water	120	23 664	2 370 000	0.827	23 980
	Soil	680	0.915	91.8	38 433	392
	All three	6561	23 665	2 370 000	38 473	8143
Kozerski *et al.*[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
D_5	Air	5930	0.022	0.397	2.85	59
	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
L_4	Air	6177	0.0021	0.0239	1.4	62
	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

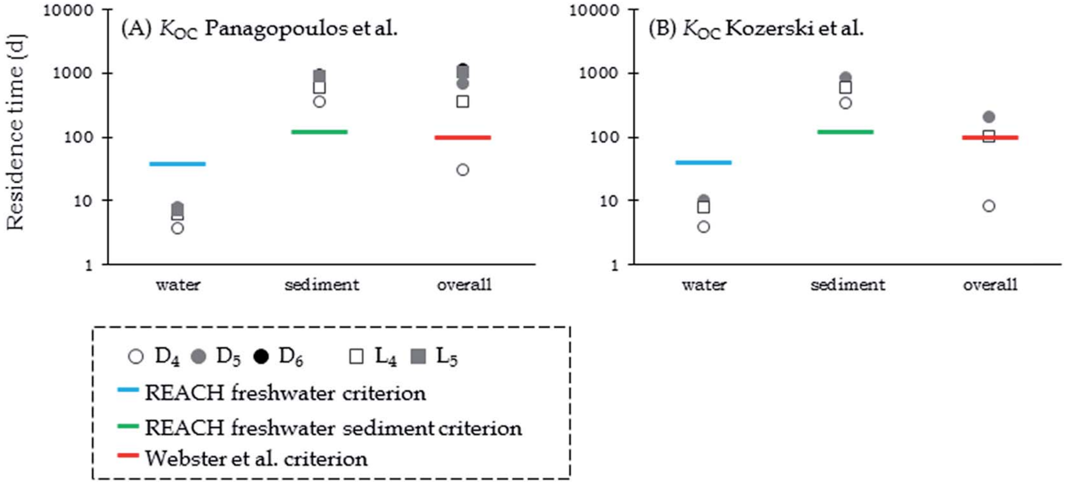

Fig. 1 Compartment-specific and overall residence times for VMS calculated in the EQC model using the K_{OC} measurements of (A) Panagopoulos *et al.*[16,17] and (B) those of Kozerski *et al.*[26] The blue line shows the REACH criterion for freshwater and the green line shows that for freshwater sediment.[24] 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.[24] However, the modeled residence times of all chemicals in the sediment compartment exceed the REACH criterion for freshwater sediment, regardless of which K_{OC} values are used.[24] Compartment specific residence times in water and sediment are almost the same for the two different K_{OC} values, however the overall residence times are substantially longer using the K_{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_{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_{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

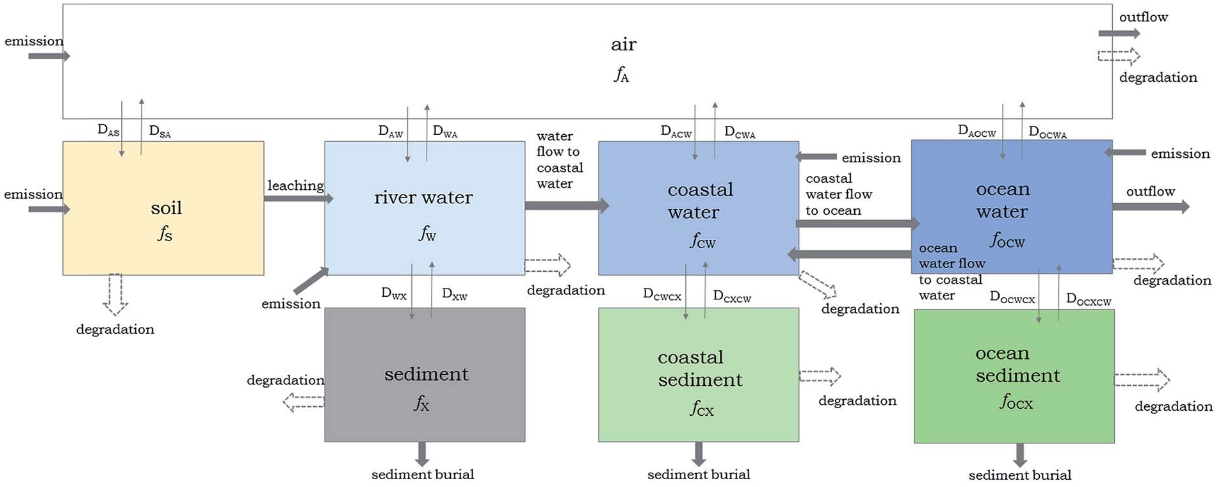

Fig. 2 Diagram of the Adventfjorden model based on the fugacity approach as introduced by Mackay.[45] f refers to the fugacity (Pa) of each individual compartment and D is the fugacity rate descriptor (mol h^{-1} Pa^{-1}) between compartments. For example, the fugacity rate descriptor from air to water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

because we wanted to see how ice coverage may affect the behavior of VMS. Adventfjorden receives wastewater from Longyearbyen without any mechanical, chemical or biological treatment. Warner *et al.*[50] showed a decrease in the concentrations of D_5 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 km^2.[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 Longyearelva with average water flows of 3 m^3 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-Kowalczuk[49] 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%

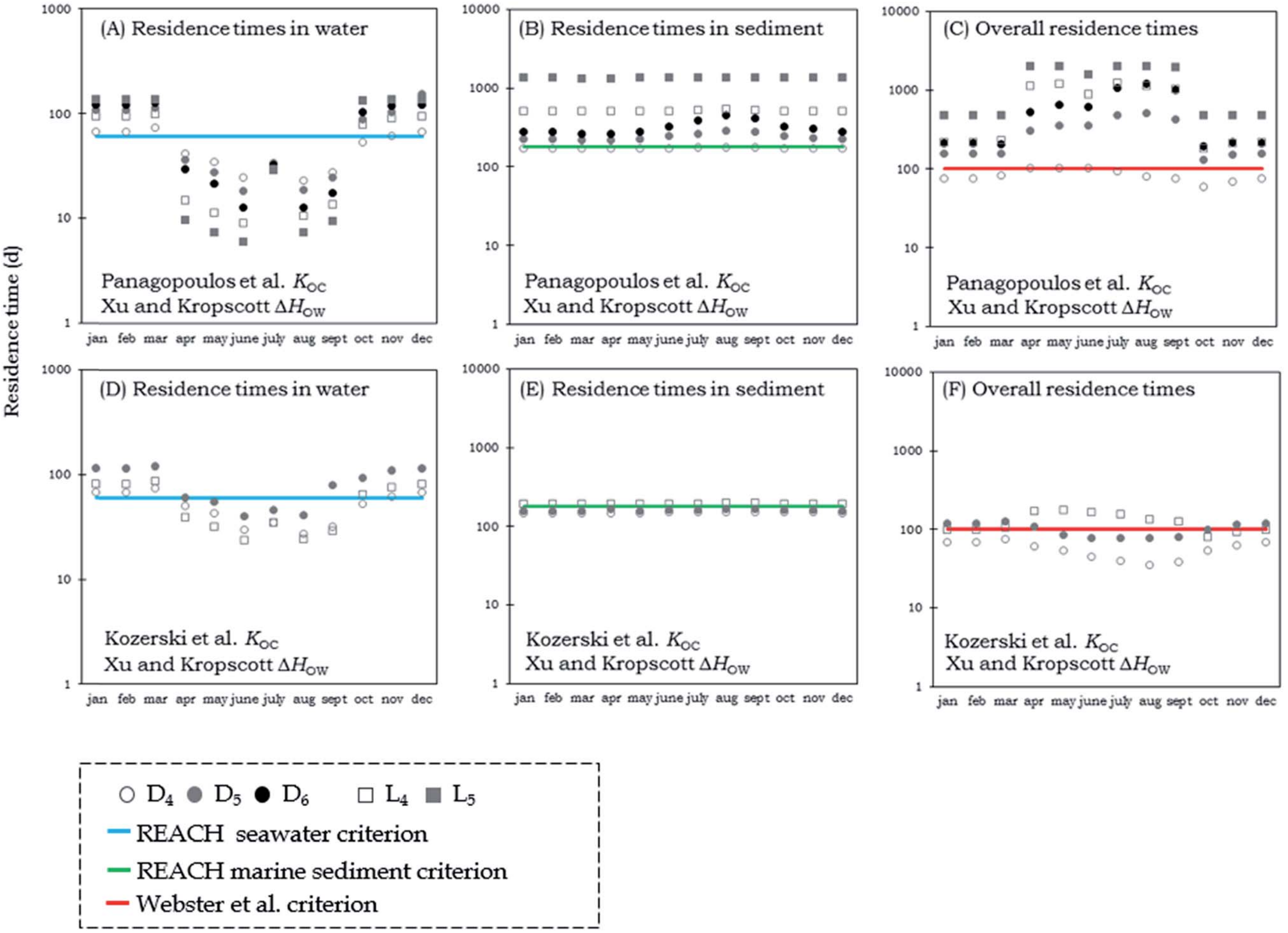

Fig. 3 Water, sediment and overall residence times for cVMS (circles) and lVMS (squares) using both the K_{OC} measurements of Kozerski *et al.*[26] (lower panels) and those of Panagopoulos *et al.*[16,17] (upper panels). The K_{OC} was corrected for temperature changes using the ΔH_{OW} measurements of Xu and Kropscott.[31] 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 unsteady-state (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 ΔH_{OW} measurements of Xu and Kropscott[31] and results in Fig. 4 are for a scenario in which K_{OC} was corrected for temperature changes using the ΔH_{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

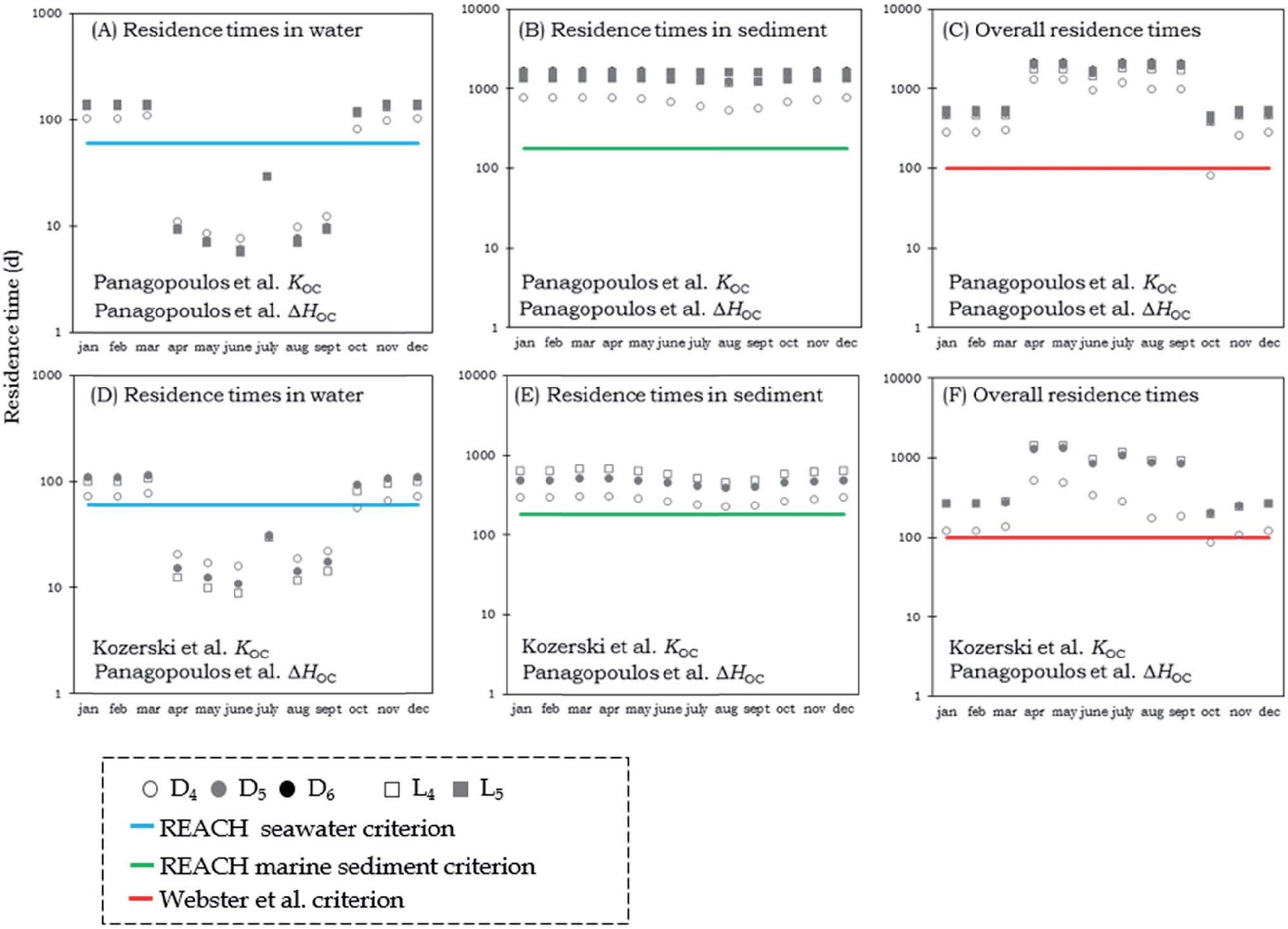

Fig. 4 Water, sediment and overall residence times for cVMS (circles) and lVMS (squares) using both the K_{OC} measurements of Kozerski *et al.*[26] (lower panels) and those of Panagopoulos *et al.*[16,17] (upper panels). The K_{OC} was corrected for temperature changes using the ΔH_{OC} measurements 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_{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 ΔH_{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 ΔH_{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 D_4, 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 ΔH_{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 ΔH_{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 Agency[1–3] and Environment Canada,[4–6] VMS cannot be categorized as non-persistent since their residence times exceed by far the REACH criterion for marine sediments[24] and the 100-day criterion of Webster *et al.*[25] One could expect to see longer residence times in the winter than in the summer due to the ice-melting 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 ΔH_{OW} measurements of Xu and Kropscott,[31] 1 year after the end of emissions the modeled amount of D_5 in Adventfjorden decreases to almost 0% of the initial amount. However, in the scenarios using K_{OC} measurements and ΔH_{OC} of Panagopoulos *et al.*[16,17,32] the modeled amount of D_5 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

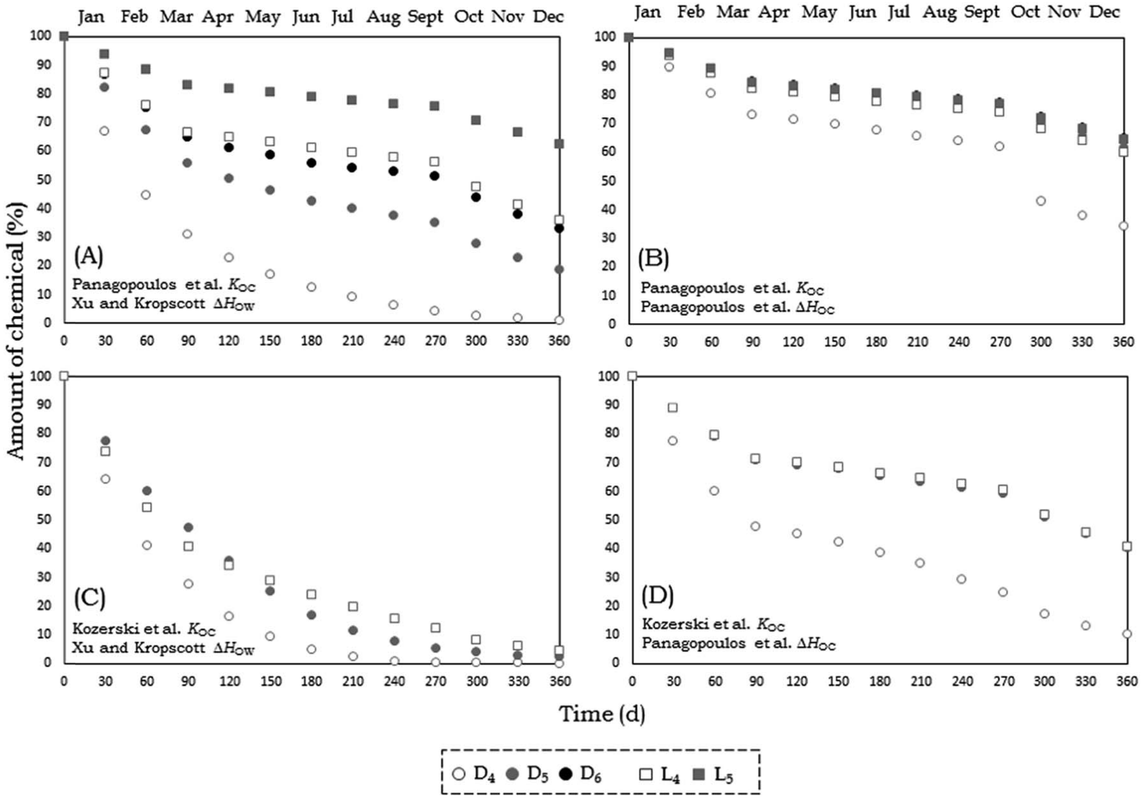

Fig. 5 Elimination of cVMS (circles) and lVMS (squares) from Adventfjorden over the course of one year if emissions stopped at time 0. Panels A and B show the elimination data for cVMS and lVMS using the K_{OC} measurements of Panagopoulos *et al.*[16,17] and panels C and D show the elimination data for cVMS and lVMS 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 lVMS using the ΔH_{OW} measurements of Xu and Kropscott[31] to correct for temperature and the panels on the right show the elimination data for cVMS and lVMS using the ΔH_{OW} measurements of Panagopoulos *et al.*[32]

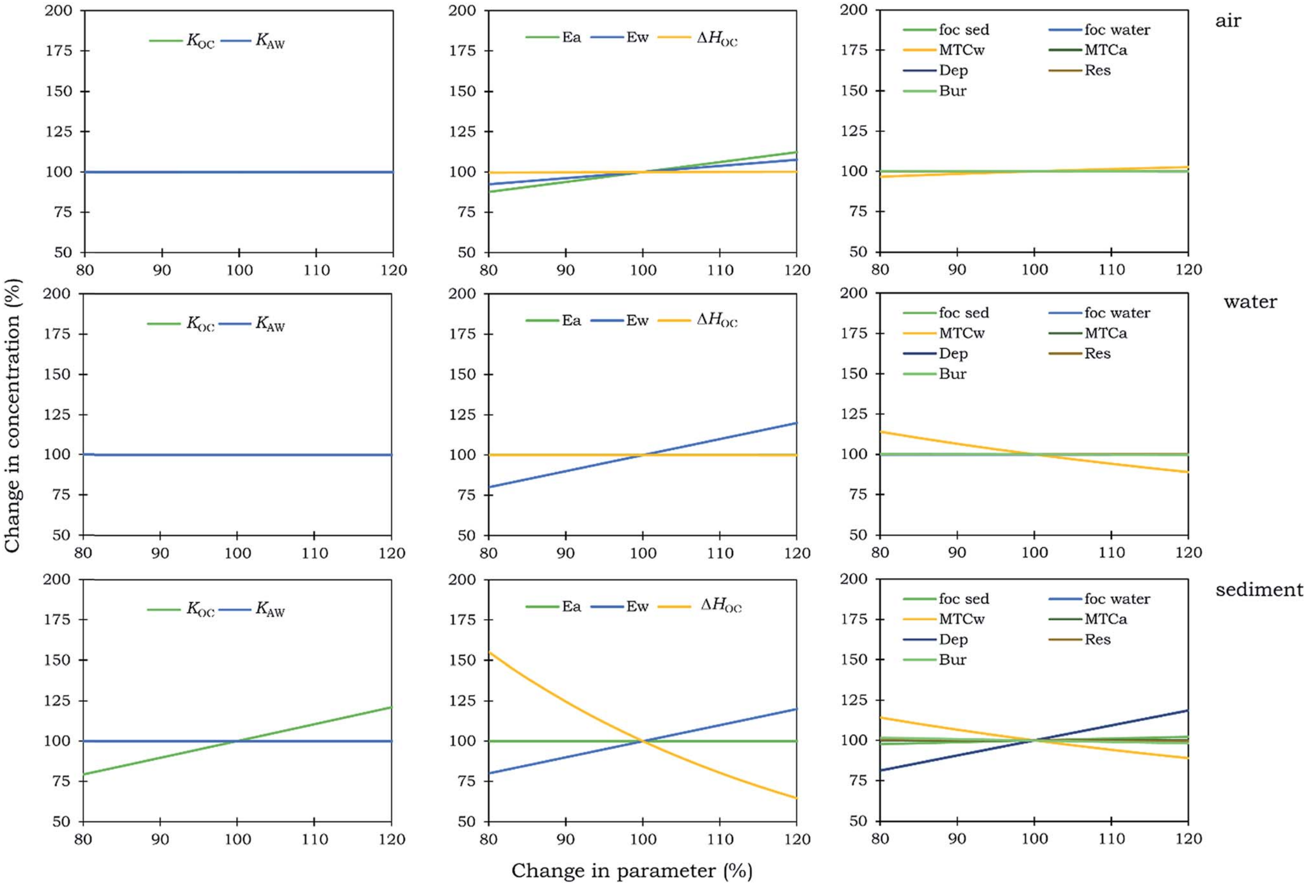

Fig. 6 Results of the sensitivity analysis for the Adventfjorden model. Changes in concentration (%) in air (first row), water (second row) and sediment (third row) as a response of changes in K_{OC} and K_{AW} (first column); emissions to air (E_a), emissions to water (E_w) and ΔH_{OC} (second column); 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 ΔH_{OC}, K_{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 ΔH_{OC}, K_{OC}, f_{OC} and Dep. The results of the sensitivity analysis underline the importance of accurately determining the K_{OC} and ΔH_{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_{OC} and ΔH_{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 K_{OC} measurements of Kozerski *et al.*[26] and those of Panagopoulos *et al.*[16,17] in combination with differences in reported ΔH_{OW} and ΔH_{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 ΔH_{OC} instead of ΔH_{OW} in the modeling calculations of VMS. Also because of the difference in the sign (+ or −) of ΔH_{OW} and ΔH_{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 ΔH_{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

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