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Investigating the presence and persistence of volatile methylsiloxanes in Arctic sediments

Dimitri Panagopoulos Abrahamsson[1-2], Nicholas Alexander Warner[3-4], Liisa Jantunen[5], Annika Jahnke[6], Fiona Wong[5] and Matthew MacLeod[1]

[1] Department of Environmental Science and Analytical Chemistry, ACES, Stockholm University, Svante Arrhenius väg 8, SE-114 18 Stockholm, Sweden
[2] Program on Reproductive Health and the Environment, Department of Obstetrics, Gynecology and Reproductive Sciences, University of California, San Francisco, California, USA
[3] Norwegian Institute for Air Research, NILU, N-9296, Fram Centre Tromsø, Norway
[4] Department of Arctic and Marine Biology, The Arctic University of Norway (UiT), Hansine Hansens veg 18, 9037 Tromsø, Norway
[5] Air Quality Processes Section, Environment and Climate Change Canada, Toronto, Ontario, Canada
[6] Department of Ecological Chemistry, Helmholtz Centre for Environmental Research, UFZ, Permoserstr. 15, DE-04318 Leipzig, Germany

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ABSTRACT

Volatile methylsiloxanes (VMS) have been identified as contaminants of emerging concern in aquatic systems. Here, we report on the presence of VMS in sediment and wastewater from Arctic regions in 2014 to 2016 and model their persistence in Adventfjorden in Longyearbyen, Svalbard. Total concentrations of VMS in sediment were dominated by D_4 and D_5 and ranged from 0.0024 to 1.7 ng/g at Svalbard (Longyearbyen), from 4.0 to 43 ng/g in Greenland (Nuuk) and from 0.19 to 21 ng/g in the Canadian Archipelago. Concentrations in wastewater samples from Svalbard ranged from 12 to 156 ng/L. Large variability in reported values of the partition ratio between organic carbon and water (K_{OC}) and enthalpy of sorption (ΔH_{OC}; often estimated from enthalpy of phase change between octanol and water, ΔH_{OW}) of VMS has resulted in high uncertainty in evaluating persistence in aquatic systems. We evaluated previously reported K_{OC} and ΔH_{OC} values from the literature in predicting measured VMS concentrations in sediment and wastewater in scenarios using a fugacity-based multimedia model for VMS concentrations in Svalbard. We tested two different model scenarios: (1) K_{OC} and ΔH_{OW} measurements for three cyclic VMS previously reported by Kozerski et al. (*Environ Toxicol Chem.* 2014, 33, 1937–1945) and Xu and Kropscott (*Environ Chem.* 2014, 33, 2702-2710) and (2) the K_{OC} and ΔH_{OC} measurements from Panagopoulos et al. (*Environ Sci Technol.* 2015, 49, 12161-12168 and *Environ Sci Tech Let.* 2017, 4 (6), 240-245). Concentrations of VMS in sediment predicted from concentrations in wastewater in scenario 2 were in good

agreement with measured concentrations, whereas in scenario 1, predicted concentrations were 2 to 4 orders of magnitude lower. Such large discrepancies indicate that the differences in the predicted concentrations are more likely to be attributed to K_{OC} and ΔH_{OC} than to uncertainty in environmental parameters or emission rates.

INTRODUCTION

Volatile methylsiloxanes (VMS) are a group of organosilicon chemicals with high production volumes and diverse applications. Their dominant usage is in the personal care product industry where VMS are used as carriers to aid in product application. VMS present in personal care products enter the wastewater system as down the drain chemicals and are released into the aquatic environment.[1-3] VMS have caused some concern due to their continuous presence[1-5] and their long residence times in aquatic environments[6]. The bioaccumulation of VMS in aquatic food webs is species- and site-specific, with reported bioaccumulation[7] and trophic magnification[8] factors exceeding regulatory thresholds in some studies[7-8], but not in others[9-10].

Due to their hydrophobicity, the environmental fate of VMS emitted to aquatic environments is controlled primarily by their affinity for organic carbon (OC) in suspended particles and in sediments, which is described by the OC/water partition ratio (K_{OC}).[6, 11] Measurements of K_{OC} of VMS reported in the literature vary by an order of magnitude, which has important implications for modeling calculations of persistence.[6, 11-14] Depending on which K_{OC} values one chooses to use, modeled overall residence times of VMS in the environment may differ by more than 200 days, and may or may not exceed regulatory thresholds for persistence[4, 6], rendering the choice critical for their risk assessment.

K_{OC} measurements in the lab are usually made at 21-25 °C.[11, 14] However, water temperatures in the real environment are typically substantially lower. Therefore, when modeling the fate of organic contaminants it is often necessary to correct measured K_{OC} values for differences in temperatures using the enthalpy of sorption (ΔH_{OC}).[11-12] Due to the scarcity of measurements of ΔH_{OC}, temperature corrections for K_{OC} are often made using the enthalpy of phase change between octanol and water (ΔH_{OW}).[6, 13] However, evidence from previous studies suggests that assuming $\Delta H_{OC} = \Delta H_{OW}$ can introduce considerable errors in temperature-corrected K_{OC}, which subsequently propagates to errors in estimates of overall environmental persistence and/or residence time.[6, 15]

The aim of this study was to investigate the presence and persistence of VMS in Arctic sediments. Sediment and wastewater samples from Svalbard (Adventfjorden in Longyearbyen), and sediment from Greenland (Nuuk Harbor) and 14 sites in the Canadian Archipelago were collected and analyzed for concentrations of 3 linear VMS (lVMS): decamethyltetrasiloxane (L_4), dodecamethylpentasiloxane (L_5), tetradecamethylhexasiloxane (L_6), and 3 cyclic VMS (cVMS): octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane

(D_5), dodecamethylcyclohexasiloxane (D_6) (Table S1). To our knowledge, this is the first study to report concentrations of VMS in sediments from Greenland and the Canadian Archipelago. To investigate their persistence, we used the measurements from the sediment and wastewater samples from Adventfjorden, Svalbard to model concentrations in the sediment using a fugacity-based multimedia model.[6] We chose Adventfjorden for our modeling calculations because is it a fjord system that is easily described in modeling terms, it has one single wastewater collection system that collects wastewater from the whole city, and it does not have a wastewater treatment process.

We compared the estimated concentrations to the measured values using two different modeling scenarios. In the first scenario, we used the temperature-corrected K_{OC} values using ΔH_{OW} measurements reported by Xu and Kropscott[13] and Kozerski et al.,[14] and in the second scenario we used the K_{OC} and ΔH_{OC} measurements from Panagopoulos et al.[11-12] While uncertainties may also exist in other environmental parameters, we focused our comparison on these two scenarios because our sensitivity analysis of the Adventfjorden model in our previous study[6] showed that the parameters which the model was most sensitive to were K_{OC} and ΔH_{OC}.

MATERIALS AND METHODS

Materials

The chemicals in this study were purchased from the following vendors: L_4, L_5, L_6, D_4, D_5, methanol, potassium hydroxide (KOH), ammonium sulfate

($(NH_4)_2SO_4$), and clean sand from Sigma-Aldrich Sweden AB, Stockholm, Sweden; D_6 from Fluorochem, Derbyshire, UK; $^{13}C_4$-D_4, $^{13}C_5$-D_5 and $^{13}C_6$-D_6 (internal standards) from Moravek Biochemicals Inc., Brea, California, USA. We used the same internal standards for the lVMS because the ^{13}C chemical standards for these chemicals were not commercially available. Aldrin (volumetric standard) was purchased from Analytical Standards, Sweden; Isolute ENV+ resin (hydroxylated polystyrene-divinylbenzene copolymer) from Biotage AB (Uppsala, Sweden); dichloromethane (SupraSolv) and *n*-hexane (LiChrosolv) from Merck (Darmstadt, Germany). The water was filtered using a Milli-Q system (Merck Millipore, Solna, Sweden). Commercial corn oil was purchased from a local grocery store in Stockholm, Sweden (ICA).

Quality Control Procedures

People involved in the sample collection and analysis avoided using personal care products that contain siloxanes to prevent sample contamination. All glassware used was cleaned, rinsed with acetone and burned at 450 °C before use. All sample handling and analysis was done in a clean air cabinet to avoid contamination of the samples from siloxanes in the indoor air. Field blanks were included in all sampling occasions and were analyzed after the sample collection together with the samples. For the sediment collection, we included three different types of field blanks. The first field blank consisted of clean ammonium sulfate, the second consisted of cleaned sand purchased from Sigma Aldrich and the third consisted of sediment which was dried, baked at 200 °C for 48 hours, extracted with acetone and hexane, and finally dried again. The sediment was collected from Lake Ången, Sweden and the sample collection is described in the study of Jahnke et al.[16] For the samples from Adventfjorden and Greenland, we used all three different types of blanks (total 3 blanks per location – one of each matrix type). For the samples from Canada, we used only clean ammonium sulfate during the sampling, but we also included a sand and a sediment blank during sample handling and extraction in the lab. Batch-specific extraction blanks were used to account for variability in contamination between different batches of samples. The samples were divided into batches based on sampling location (Svalbard, Canada, Greenland). All field blanks were exposed to outdoor air and indoor air for the same duration as the sediment samples. Sample and field blank concentrations were corrected for the average extraction blank concentration detected within the same extraction batch. The blanks followed the same procedure as the samples. The process is described in the section "Sample preparation and extraction". In addition, samples were corrected for the average concentration measured within the field blanks. The limit of quantification (LOQ) for sediment samples were calculated by multiplying the standard deviation within nine extraction blanks by 10 times.

For wastewater analysis, the field blank consisted of clean water filtered through a Milli-Q system. As this matrix does not adequately reflect the matrix present in water, the LOQ was used to assess detection of VMS in wastewater. The LOQ for the wastewater samples was defined as the average field blank concentration + 10 times the standard deviation of the field blank (n= 3). For the sediment samples, we chose a less conservative calculation of LOQ due to the low concentrations in the sediment samples. This choice was made in order to avoid a substantial reduction in the dataset.

Sample collection

We collected sediment samples from boats in the summer and fall months of 2014-2016 at 5 stations in Adventfjorden, 10 stations in Nuuk harbor and 14 stations in the Canadian Archipelago using a 0.1 m^2 Van Veen grab sampler. The station coordinates and the sampling dates are presented in Table S2. The geographic locations of the stations are shown on a map in Figure S1. When the sediment grab was brought back on the boat, we collected sediment from the top 2 cm of the surface of each grab sample with a stainless-steel spoon, which had been rinsed with acetone. The sample was transferred to a clean glass jar and frozen at -20 ^{o}C.

The wastewater effluent samples from Adventfjorden were collected by the Norwegian Institute for Air Research from the wastewater facility at Adventfjorden. The wastewater facility collects the wastewater from the city (2,144 population) and deposits it without treatment in the center of the fjord. There is only one outlet for the whole city. The collection was done using clean Teflon bottles. Given that there is no collection tank, the samples were collected directly from the wastewater pipe. Two grab samples were collected in direct succession. Three subsamples were collected from each grab sample to yield a total of 6 untreated wastewater effluent samples.

Sample preparation and extraction

The sediment samples were extracted with a modified purge-and-trap method that has previously been published by Kierkegaard et al.[17] A detailed description of the method modification has been previously published in Panagopoulos et al.[11-12, 18] Briefly, the sediment samples were centrifuged to separate the sediment solids from the water. The water was removed with a glass pipette and discarded and 10 mL dichloromethane containing ^{13}C stable isotope-labeled internal standards were added to the sample. The samples were shaken for 3 minutes and the two phases were allowed to separate for 10 minutes. The extract was moved to the purge-and-trap flask and the process was repeated for 4 times in total. After adding 4 drops of clean corn oil to act as a keeper, the extract was evaporated to dryness at room temperature and then heated to 100 °C for 2 h to drive VMS to the gas phase and onto an ENV+ column (25 mg). The ENV+ column was then eluted with 1 mL dichloromethane, which was analyzed without further treatment using Gas Chromatography Mass Spectrometry (GC/MS). The GC/MS method is described in detail in Panagopoulos at al.[11] The field blanks and extraction blanks followed the same procedure, at the same time as the corresponding samples. The sediment samples were also analyzed for their total organic carbon (TOC) content. The sediment was dried at 70 °C and pulverized using a mortar and pestle. The pulverized sediment was then analyzed using an elemental analyzer (CarloErba NC2500).

The wastewater samples were extracted and analyzed with a headspace GC/MS (HS-GC/MS). The methods are described in detail in Krogseth et al.[15] Briefly, 15 mL of wastewater were transferred to a 20 mL headspace vial and equilibrated at 80 °C for 10 min using a Gerstel MPS 3 autosampler. Samples were mixed for 1 minute and 1.5 mL of headspace was extracted and injected into the GC inlet equipped with a Merlin microseal septum (Merlin Instrument Company, CA, USA) and direct 2.0 mm I.D. liner (Agilent Technologies). Samples were injected in split mode with a 1:10 split at a total flow of 14 mL/min, a septum purge of 3 mL/min and a column flow of 1 mL/min. Chromatographic and instrumental conditions have been previously described in detail in Krogseth et al.[15]

Statistics

For all values below the LOQ, we considered a series of approaches that have been previously proposed for working with censored data[19]: (i) treating values below LOQ as zero; (ii) treating values below LOQ as the absolute LOQ value; (iii) substituting values below LOQ with a value between LOQ and zero; and (iv) excluding all values below LOQ. All four approaches carry some uncertainties and, whichever approach is used, the resulting data have certain limitations with regards to their interpretation.[19] More specifically, when treating values below LOQ as the absolute value of LOQ or when excluding values below LOQ, the resulting averages tend to be overestimated.[19] On the other hand, when treating below LOQ values as zeros, the resulting averages tend to be underestimated. Substituting below LOQ values with a value between LOQ and zero may result in over- or underestimations of the true averages depending on the dataset.[19] For the purposes of our study, we decided to treat values below LOQ as zeros. This approach allows us to know a priori the direction of the error (underestimation). As discussed later, underestimation of average concentrations biases the measured data towards the first modeling scenario (values of Xu and Kropscott[13] and Kozerski et al.[14]); see results and discussion for more details.

Modeling

We used a steady state, non-equilibrium (Level III) model, which has previously been parametrized to describe the environmental fate of organic chemicals in Adventfjorden, Svalbard.[6] The model describes the behavior of organic chemicals using the fugacity concept as it was introduced in environmental contaminant modeling by Mackay.[20] We chose to focus our modeling calculation on cVMS because for more than half of the sediment samples the concentrations of lVMS were below LOQ (Table S6). All environmental parameters and the physicochemical properties of cVMS used in the modeling calculations along with the rationale behind the choice for each parameter are presented in detail in Panagopoulos and MacLeod.[6] We used the average measured concentrations of cVMS in wastewater to predict concentrations of cVMS in sediment. We calculated the inflow emissions (mol/h) of cVMS to the fjord by first estimating the total wastewater flow for the population of Longyearbyen using the average per capita wastewater flows (0.171 m^3/cap/day) measured in Gatidou et al[21]. The wastewater treatment plants used in the study of Gatidou et al.[21] received wastewater from populations comparable (26,000, 1250, and 1,600 people) to that of Longyearbyen around Adventfjorden (2,144 population). We then multiplied the estimated wastewater flow for Adventfjorden (15 m^3/h) with the average concentration of cVMS measured in wastewater. It is important to note that there is no wastewater treatment plant in Longyearbyen and the wastewater is released in the middle of the fjord from a single pipe which collects wastewater from the whole city. It is worth noting that population habits and other contributing emissions from sewer flows could theoretically impact these estimates. However, in the case of Longyearbyen, the population is not expected to have substantially different habits from other parts of Europe, and because of the city's small population we assume that urban runoff or sewer overflows will not have a significant impact on the emissions to the fjord.

We compared the predicted concentrations of cVMS to their measured concentrations in two different scenarios. In the first scenario, we used the K_{OC} measurements of Kozerski et al.[14] and the ΔH_{OW} of Xu and Kropscott.[13] In the second scenario, we used the K_{OC} and ΔH_{OC} measurements of Panagopoulos et al.[11-12]

To further understand the differences in the predictions between the two scenarios, we expanded on our modeling calculations to study how environmental parameters can impact the partitioning of cVMS in Adventfjorden. During the first stage of this optimization exercise, the parameters in the model were adjusted one at a time so that the modeled concentrations matched the measured concentrations. During the second stage, the parameters were increased simultaneously following a 2-fold and 3-fold increase. We repeated the process for both models and we compared the required adjustments for both models. These parameters were: the fraction of organic carbon in sediment solids (FOSS), the fraction of organic carbon in suspended particles in water (FOPW), the density of sediment solids (ρSS), the density of suspended particles in water (ρP) and the mass transfer coefficient for particle deposition (MTCdep), emission rates to water (Ew), the wastewater flow rate (WW G) and the concentration of cVMS in wastewater (Fig.4). During the simultaneous adjustment, we also included K_{OC} as one of the parameters. The parameters to be adjusted were selected based on the sensitivity analysis of the model that was presented in the study of Panagopoulos and MacLeod.[6] All details about the environmental and physicochemical parameters tested during the sensitivity analysis are presented in Panagopoulos and MacLeod.[6]

RESULTS AND DISCUSSION

Sample analysis

Our field blanks showed on average lower levels of lVMS compared to cVMS (Table S3). The ammonium sulfate field blanks showed on average slightly lower levels of VMS compared to the sand and the sediment field blanks (Table S3). The concentrations determined in the extraction blanks are shown in Table S4.

The average recoveries in the sediment extraction for VMS ranged from 60 to 91% (Table S5). The average recoveries for cVMS in the wastewater extractions ranged from 66 to 82% (Table S5). We focused our wastewater analysis and modeling calculations on cVMS only because for more than half of the sediment samples the concentrations of lVMS were below LOQ. We present our measurements in sediment as ng/g wet weight (ww) since it is not possible to obtain direct dry weight measurements for VMS. Drying the sediment sample would lead to volatilization of VMS from the sediment and likely substantial loss from the sample. Previous studies on VMS in sediment also report concentrations of VMS as ng/g wet weight.[15, 22]

On average, the highest concentrations of VMS in sediments were observed in Nuuk Harbor, while the lowest were observed in Adventfjorden (Figure1 and Table S6). This observation is most likely due to the higher population of Nuuk (17,984)[23] compared to Longyearbyen (2,144)[24] and the Canadian Archipelago (mostly remote areas). The levels of VMS in sediments are known to be strongly dependent on the number of people that live in proximity. That explains why we see substantially higher concentrations of VMS in sediments from China[25] or urban centers in Northern Europe[26] compared to less populated regions like Svalbard.[22] The cVMS concentrations were consistently higher than those of the lVMS, with D_4 and D_5 at highest concentrations. In the wastewater samples from Adventfjorden, D_5 showed the highest concentrations followed by D_4 and then D_6 (Table S7). These observations are in good agreement with previous findings about the presence of VMS in the Arctic.[26] Kaj et al.[26] reported measured concentrations of VMS in sediments from the European Arctic (Sweden, Norway, Denmark, Finland, Iceland and Faroe Islands). In their report, cVMS also showed higher levels than lVMS and D5 was present on average at highest concentrations in all locations.

The concentrations of D_5 that we observed in the sediment samples in Adventfjorden (0.54 ± 0.32 ng/g ww, Table S6) were consistent with the range of values observed by Warner et al.[22] for Advenfjorden (0.74 ± 0.29 ng/g ww). When comparing the wastewater concentrations of cVMS to the sediment concentrations of cVMS in Adventfjorden, we observed that the concentration of D_4 in the sediment samples were slightly higher than what one would expect based on the wastewater emissions (Fig.3). This observation could be the result of long-term emissions and the slower hydrolysis rate of D_4 compared to that of D_5 [27-29]. In a study of VMS in a lake near a small town in the Arctic (Storvannet near Hammerfest, Norway)[15], the average concentrations of D_4, D_5 and D_6 were a factor of 10 higher than the concentrations we observed in Nuuk harbor. Nuuk has a similar population as Hammerfest (17,984 vs 10,287). However, Nuuk harbor is located in an open fjord that exchanges water with the Atlantic

Ocean, while Storvannet is a freshwater lake with a narrow opening to the nearby fjord. Thus, the water in Nuuk harbor is expected to have a shorter residence time than the water in Storvannet. Shorter water residence times should result in lower concentrations of cVMS in sediment, as observed in the two studies.[6, 30] In addition, Storvannet has historically received untreated wastewater emissions, which would likely result in elevated levels of VMS in the lake sediment.[15]

We examined the relationship between the concentrations of VMS and TOC for all three locations separately, but we did not find any significant correlations (Table S8). The concentrations of VMS in sediment have previously been shown to decrease rapidly with increasing distance from the emission source.[22] This behavior is presumably due to their strong affinity to OC.[11-12, 18] Correspondingly, one could assume that if VMS in aquatic environments remain very close to their emission source, there could be neighboring areas of sediment with high OC content but with low concentrations of VMS. This could perhaps explain the absence of a significant relationship between VMS and TOC in our data.

Considering the large geographical spread of the samples from the Canadian Archipelago, we divided the samples from Canada into two groups for each of three criteria: (i) their median distance from the nearest settlement, (ii) their median distance from the nearest coastline and (iii) their median distance from the nearest major river mouth, such as the Mackenzie River mouth. For every criterion, we split each group of samples and we compared them using a t-test (Table S9). The average concentrations of VMS in most cases were higher in the group of samples that were closer to settlements, closer to land and closer to a major river mouth. However, none of the observed differences were statistically significant (Table S9).

The concentrations of VMS in Canadian samples were unexpectedly high. Samples C1, C7 and C10 were collected close to the mouth of the Mackenzie River (Table S6 and Figure S1), indicating that the Mackenzie River may be acting as a contributing source. Previous studies at the Mackenzie River delta have reported concentrations of polycyclic aromatic hydrocarbons (PAHs) and hexachlorohexanes (HCHs) at similar levels to the ones we found for cVMS.[31-33] Sites close to the North Shore of Baffin Island (C11-14) were taken close to the controlled oil spill region[34], which could impact the levels of VMS in the sediment. Finally, there is commercial and tourist boat traffic throughout the Canadian Archipelago and several construction activities around Cambridge Bay[35], which could perhaps explain the elevated levels of VMS in samples C5 and C6.

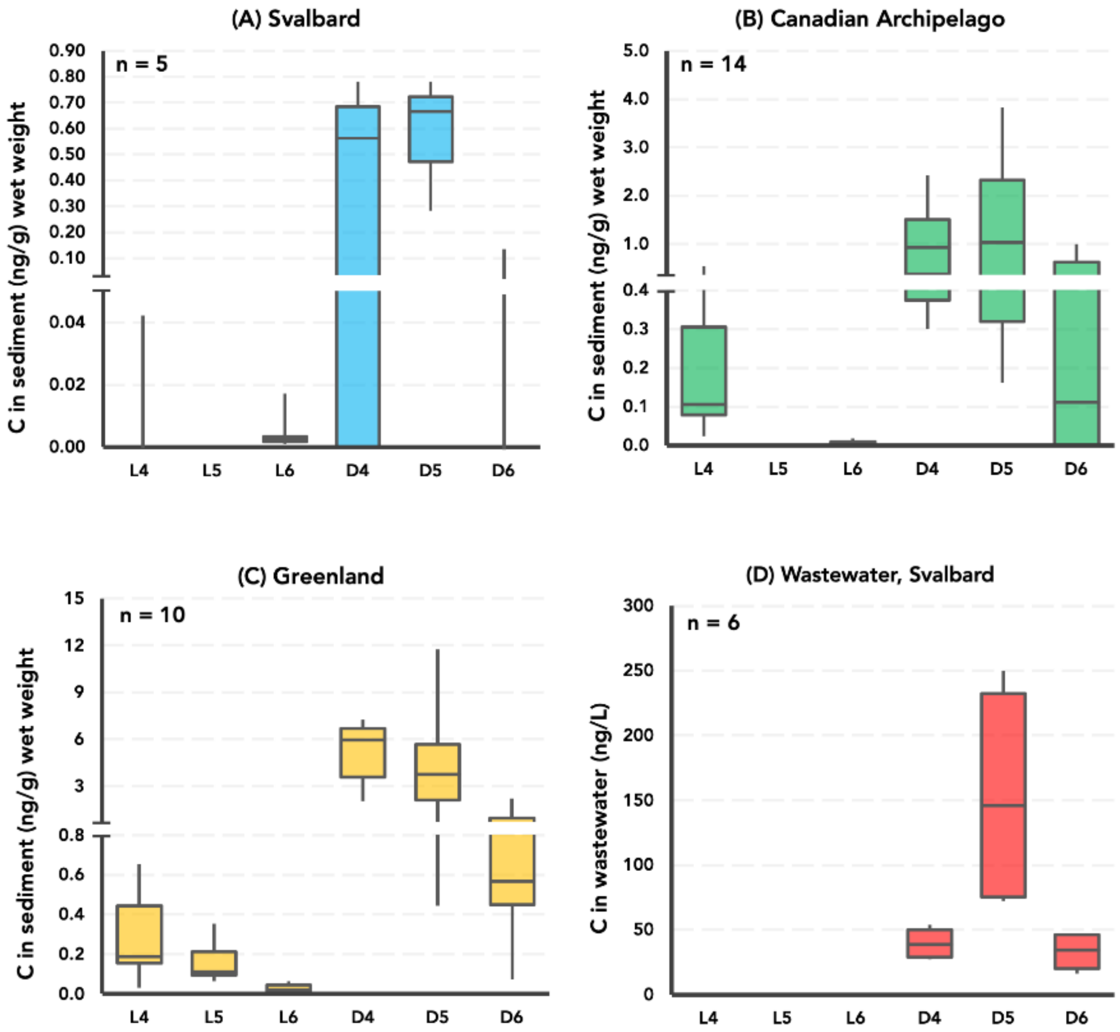

Figure 1: Box-plot graphs of the concentrations of VMS in the sediment samples from the three different areas in the Arctic (A) Adventfjorden, Svalbard, (B) Canadian archipelago, (C) Nuuk harbor, Greenland and (D) in the wastewater samples from Adventfjorden, Svaldbard. The error bars represent the 10th and 90th percentile of each group, the bottom part of the box shows the 25th percentile, the line in the middle shows the median, and the top part of the box shows the 75th percentile. The data in plots (A), (B) and (C) are shown with a broken y-axis due to their large spread. For the purposes of descriptive

statistics, the median and the percentiles were calculated after assigning a value of 0 to the samples that were below the LOQ. Note that in plot (A) only the 90th percentile is shown for L_4 and D_6 because all the other box plot elements (median, 25th and 75th percentile) were 0. In plot (A) and (B), all data points for L5 were below LOQ and thus 0 in these plots.

Modeling Calculations

The two modeling scenarios resulted in substantially different distributions of cVMS in the environment. In scenario 1, all cVMS, with the exception of D6 in the summer, partitioned primarily in the water compartment of the fjord (Figure 2). In scenario 2, however, all cVMS partitioned primarily to the sediment compartment of the fjord, which is expected to increase the residence times of VMS in the fjord. These differences are attributed to the differences in the reported K_{OC}, ΔH_{OW} and ΔH_{OC} in the studies of Kozerski et al.[14], Xu and Kropscott[13] and the studies of Panagopoulos et al.[11-12]. In both scenarios, the amount of cVMS in the sediment increased with increasing hydrophobicity of cVMS and also increased from winter to summer. Note that for the purposes of this exercise, the emission rates for all VMS were assumed to be the same (1 mol/h). The seasonal increase is due to the increased amounts of suspended particles flowing into the fjord from the nearby rivers in the summer. In the winter the rivers are mostly frozen and the fjord receives water mainly from the ocean.[6]

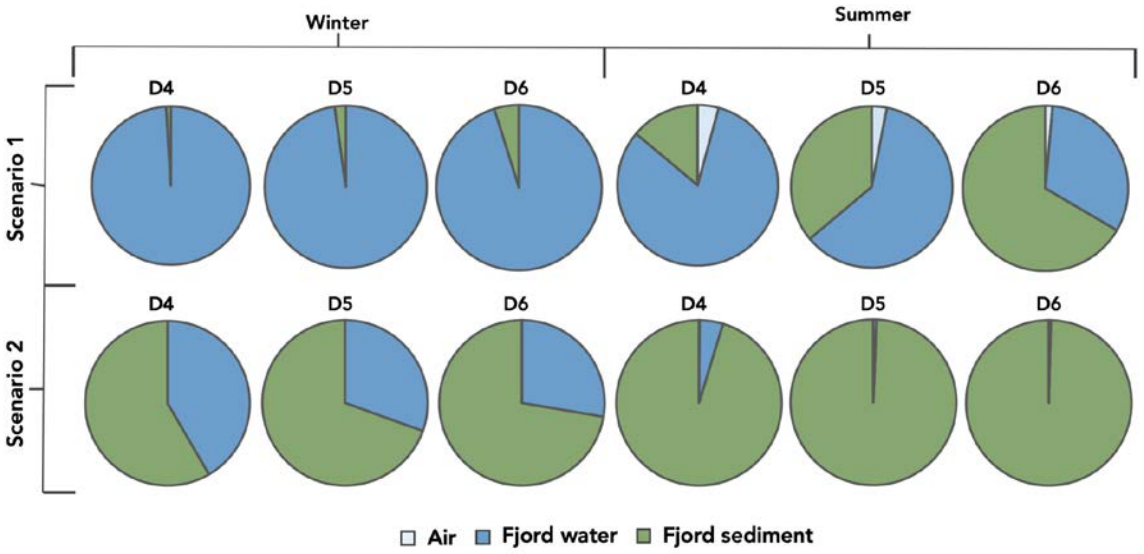

Figure 2: Modeled distributions of cVMS in Adventfjorden for scenarios 1 and 2 in winter and summer. In scenario 1, we used the K_{OC} values of Kozerski et al.[14] and the ΔH_{OW} of Xu and Kropscott.[13] In scenario 2, we used the K_{OC} and ΔH_{OC} values from our previous studies.[11-12]

The two different scenarios resulted in substantially different predictions of concentrations of cVMS in sediment (Figure 3). For all three cVMS, the predictions of scenario 2 were closer to the measured values, compared to the predictions of scenario 1. Scenario 1 underpredicted the concentrations of D_4 D_5 and D_6 by 3, 2 and 1.5 log units, respectively (Fig. 3).

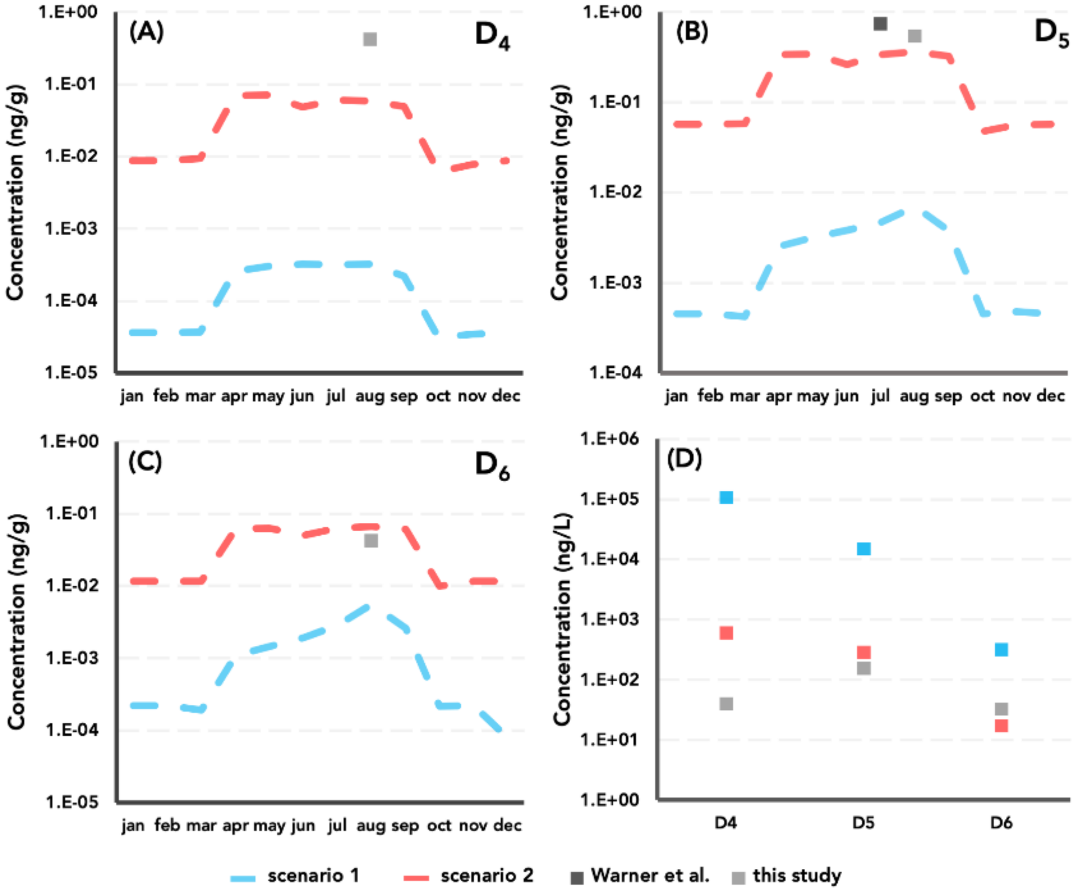

Figure 3: Panels A, B and C show monthly predicted concentrations of cVMS (A) D_4, (B) D_5, (C) D_6 in sediment in Adventfjorden for scenarios 1 and 2, and average measured concentrations of cVMS in this study and in Warner et al.[22] Panel D shows the average measured concentrations of cVMS in wastewater and the back-calculated concentrations in wastewater using scenarios 1 and 2. The averages were calculated after assigning the value 0 to the samples that were below the LOQ. The measurements for all samples together with the standard deviations of the measurements are shown in Table S6.

Our optimization exercise for the environmental parameters (Figure 4) showed that the parameters that required the smallest adjustment for the predictions to match the measured values were the emission rates to water, the wastewater flow and the concentrations of cVMS in wastewater. However, even in these parameters the necessary adjustment for the predictions of scenario 1 to reach the measured values were on average 4 orders of magnitude for D_4, about 2 orders of magnitude for D_5 and about 1 order of magnitude for D_6. This observation practically means that for scenario 1 to be accurate, the wastewater flow or the concentrations of D_4 in the wastewater would have to have been underestimated by 4 orders of magnitude and those of D_5 and D_6 by 2 and 1 orders of magnitude, respectively (Figure 3D). If we take D_5 as an example, the concentration of D_5 in wastewater would have to be 15,000 ng/L instead of the measured 150 ng/L. Such high concentrations of D_5 in wastewater are comparable to levels found in influents of wastewater treatment plants in Oslo, Norway[36], in Ontario, Canada[37] and in Beijing, China[38] and are hence not expected in remote areas, such as the Arctic with very small populations. If on the other hand the error lies in the wastewater flow estimate, then for D_5 the wastewater flow would have to be 1,528 m^3/h instead of the estimated 15.3 m^3/h, which would be inconsistent with our knowledge about wastewater discharge for a town of 2,144 people.[21] Interestingly, Krogseth et al.[15] observed a similar difference of about 2 log units in their modeling study about the fate of cVMS in a lake in Northern Norway evaluating two similar modeling scenarios, where they compared the K_{OC} and ΔH_{OC} values measured by Panagopoulos et al.[11-12] to the K_{OC} and ΔH_{OW} values measured by Kozerski et al.[14] and by Xu and Kropscott.[13]

The simultaneous adjustment of the modeling parameters (Figure 5) showed that for the modeled concentrations of scenario 1 to reach the measured values, there would need to be a more than 3-fold increase of all parameters for D_4 (Figures 5A and B) and a 2-fold increase of all parameters for D_5 (Figures 5C and D). These changes, even though smaller than the changes required for when the parameters were adjusted one at a time, are still substantial and they reinforce our observations in the first step of the optimization. It seems unlikely that we have underestimated all the above-mentioned parameters 3-fold for D4 and 2-fold for D5. In addition, it should be noted that there is some variability in K_{OC} for different types of organic matter[11, 14]. However, it seems unlikely that that variability would be so large that it could explain the observed 2-3 log units difference between the measured and modeled values for D_4 and D_5 (Fig. 3).

Our observations lead us to the conclusion that the observed differences in the predicted concentrations in the two modeling scenarios are more likely to be attributed to K_{OC} and ΔH_{OC} than to environmental parameters and that scenario 2 seems to predict the concentrations of VMS in Adventfjorden more accurately than scenario 1. It should be noted, however, that more studies from additional locations are needed in order to corroborate these findings.

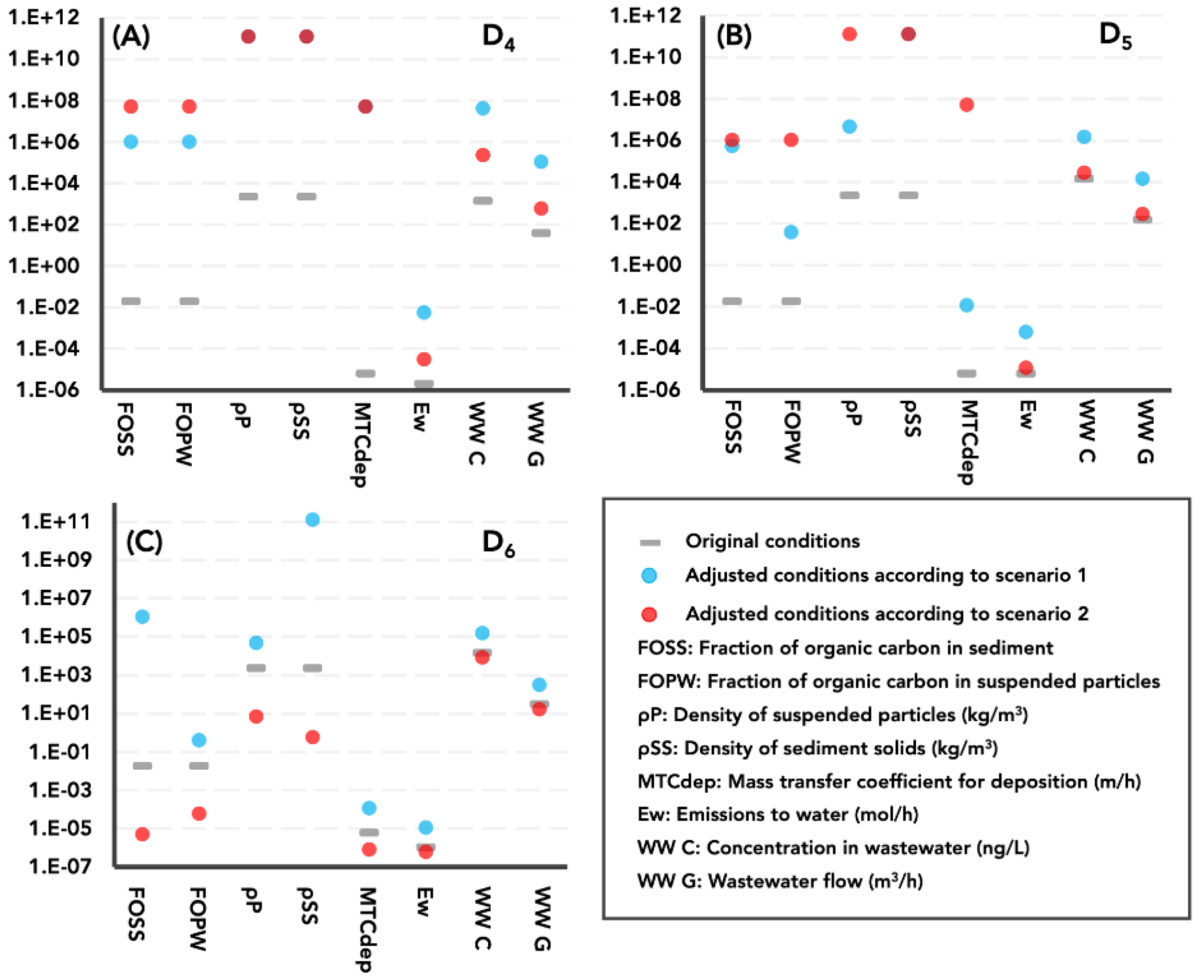

Figure 4: Original parameters (gray) and adjustments needed (red and blue) for the predicted concentrations in scenarios 1 and 2 to reach the measured concentrations in the sediment. In these calculations we included all parameters that have an important impact on the partitioning of cVMS according to the sensitivity analysis from our previous study.[6] Note that the overlap between red and blue dots appears as a darker shade of red. The y-axis shows the number corresponding to each parameter. The units for each parameter are shown in the lower right side of the figure.

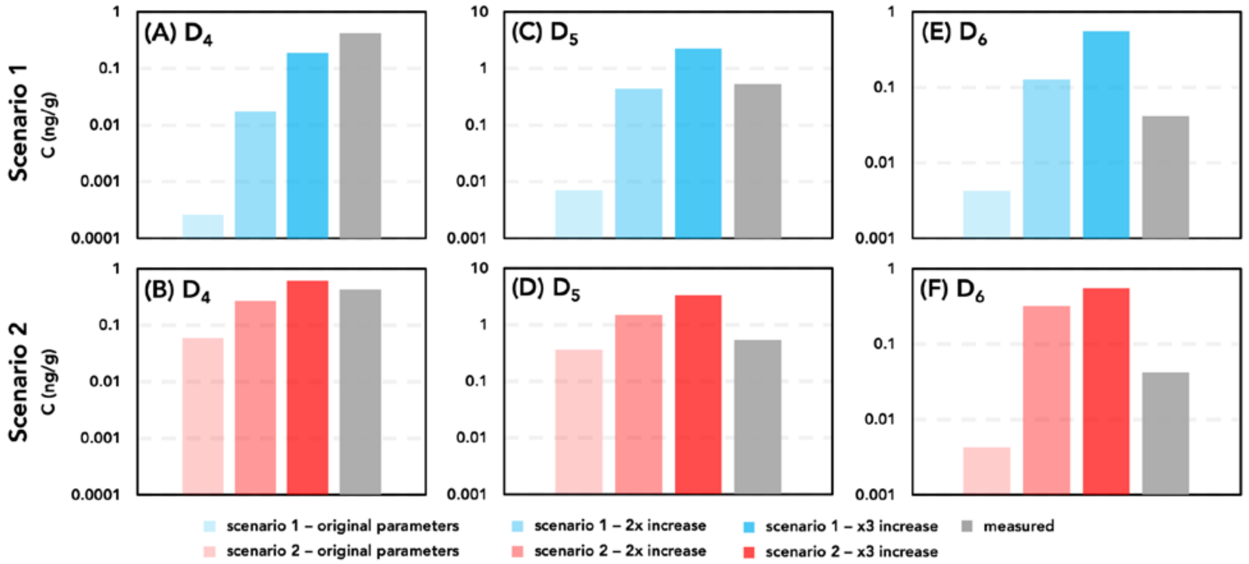

Figure 5: Measured and modeled concentrations of cVMS in Adventfjorden using the original modeling parameters and adjusted parameters. In this case, the parameters were increased simultaneously following a 2-fold and a 3-fold increase.

CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

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