Occurrence and seasonality of cyclic Volatile Methyl Siloxanes in Arctic air

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Abstract

Cyclic volatile methyl siloxanes (cVMS) are present in technical applications and personal care products. They are predicted to undergo long-range atmospheric transport, but measurements of cVMS in remote areas remain scarce. An active air sampling method for decamethylcyclopentasiloxane (D5) was further evaluated to include hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), and dodecamethylcyclohexasiloxane (D6). Air samples were collected at the Zeppelin observatory in the remote Arctic (79°N, 12°E) with an average sampling time of 81 ± 23 hours in late summer (August – October) and 25 ± 10 hours in early winter (November – December) 2011. The average concentrations of D5 and D6 in late summer were 0.73 ± 0.31 ng/m^3 and 0.23 ± 0.17 ng/m^3 respectively, and 2.94 ± 0.46 ng/m^3 and 0.45 ± 0.18 ng/m^3 in early winter respectively. Detection of D5 and D6 in the Arctic atmosphere

confirms their long range atmospheric transport. The D5 measurements agreed well with predictions from an Eulerian atmospheric chemistry-transport model, and seasonal variability was explained by the seasonality in the OH radical concentrations. These results extend our understanding of the atmospheric fate of D5 to high latitudes, but question the levels of D3 and D4 that have previously been measured at Zeppelin with passive air samplers.

1.   Introduction

Cyclic volatile methyl siloxanes (cVMS) are high-volume production chemicals used in the production of silicone polymers, in personal care products, and in a range of technical applications. cVMS have been found in both the physical environment and in biota, and have lately become subject to increasing scientific scrutiny by environmental scientists and regulators.[1-3] The three congeners octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) have specifically been the focus of the attention.[e.g.1-3] Hexamethylcyclotrisiloxane (D3) is an additional member of the group of cVMS. The physical-chemical properties of cVMS differ from many known organic pollutants, as they combine high volatility with extreme hydrophobicity and a considerable affinity for organic phases like octanol (Table S1).[4] Volatilization to the atmosphere is the main emission pathway of cVMS to the environment.[1-3] Hence the atmosphere is a key compartment for understanding the environmental fate and behavior of cVMS. Once in the atmosphere, cVMS are predicted to be mainly present in the gas phase, and degradation by reaction with hydroxyl radicals is understood to be the main removal mechanism.[5] The atmospheric half-lives due to reaction with hydroxyl radicals are 20.0 days for D3, 10.3 days for D4, 6.7 days for D5, and 5.8 days for D6 (Table S1).[6]

cVMS are predicted to undergo long-range atmospheric transport (LRAT). The characteristic travel distance (CTD) has been suggested as a measure of how far substances can travel in the atmosphere.[7] In a recent modeling assessment the predicted CTD was larger for D4 than for D5 than for D6, and was found to mainly depend on the phototransformation half-lives and log K_{AW}.[8] Concentrations of D5 in the atmosphere of the Northern hemisphere have been predicted using the Danish Eulerian Hemispheric Model (DEHM),[9] BETR global,[10] and Globo-POP (Table S7).[8] The DEHM-model estimated concentrations of D5 in the atmosphere of the remote Arctic from approximately 0.1 ng/m^3 in summer to more than 1 ng/m^3 in winter.[9] This predicted seasonality, with elevated concentrations in winter, was supported by the BETR global and Globo-POP simulations.[8, 10] The estimated levels of D5 from these models correspond well with observed atmospheric concentrations in the environment.[9, 11] The predicted seasonality of D5 was a consequence of the strong seasonality of the hydroxyl radical concentrations at high latitudes. During the polar night low levels of hydroxyl radicals slow down the atmospheric degradation of D5 and allow it to accumulate in the atmosphere. Similar seasonal trends can be expected for the other cVMS congeners, with more pronounced seasonality for the congeners with the highest rate constants for reaction with atmospheric hydroxyl radicals.[9, 12]

Due to a large potential for contamination during trace analysis of cVMS[13-14] as well as their high volatility, analysis of environmental trace levels of cVMS in air is challenging and measurements from remote locations are scarce. A new solid phase extraction active air sampling method (SPE-AAS) for D5 uses ENV+ resin (hydroxylated polystyrene-divinylbenzene copolymer) as the sorbent. This method was successfully applied to a rural location in Sweden, measuring D5 concentrations from 0.3 to 9 ng/m^3 over a period of four months.[15] Predicted concentrations from the DEHM-model compared well with the measurements.[9] This method is especially advantageous due to its simple extraction procedure, providing a limit of quantification almost two orders of magnitude lower compared to earlier published work.[15] A global passive air sampling study, which used sorbent impregnated polyurethane foam (SIP) disks to measure

cyclic and linear siloxanes, is to the best of our knowledge the only study that has measured concentrations of cVMS in Arctic air.[11] Four polar sites were included in the study, including the Zeppelin observatory, Svalbard, Norway, where concentrations of D3, D4, D5 and D6 were reported at respectively 17, 16, 4.0 and 0.54 ng/m^3 based on a single passive air sampler exposed from April to July 2009. At the other polar sites in Canada and Alaska the measured concentrations were similar to or lower than those at Zeppelin.[11]

The purpose of this study was to investigate the occurrence and seasonality of cVMS in Arctic air using the active air sampling method (SPE-AAS).[15] This was warranted as the current knowledge on cVMS in Arctic air mainly results from model predictions, and thorough observations are still lacking. Comparing the model predictions with measured levels would also contribute to an improved understanding of the atmospheric fate and behavior of cVMS, in particular at high latitudes, including their persistence and LRAT.

2.   Method and materials

2.1   Method description

2.1.1   Sample preparation

The method employed was a further development of the SPE-AAS method for D5.[15] As model simulations had predicted lower concentrations of cVMS in Arctic air compared to the atmosphere of southern Sweden,[9] it was decided to increase the air flow through the samplers and thus reduce the sampling time required to reach levels above detection limits. This was achieved by using ENV+ cartridge barrels with a volume of 25 mL instead of 1 mL, giving a 13 times larger cross-sectional area for air flow through the sorbent material. In addition, the larger barrel volume reduced the risk of ice and snow clogging the cartridges during sampling. With this sampler configuration, the sampling time used in southern Sweden

(24 hours) was maintained for the sampling at Zeppelin in early winter, while it was increased to an average of 81 hours for the sampling at Zeppelin in late summer. Polyethylene (PE) cartridges were manually packed with approximately 120 mg ENV+ resin between two PE frits, providing the same height of the sorbent bed as in the previous application.[15] The packed cartridges were cleaned with 14 mL dichloromethane and 14 mL *n*-hexane. The cartridges were dried at room temperature using ENV+-purified nitrogen gas. They were capped with PE stoppers at each end and wrapped in aluminum foil. Three cartridges (for two parallel samples and one field blank) were packed together in a firmly closed PE bottle, and stored at -18 °C until use.

2.1.2 *Air sampling*

Air sampling was conducted at the Zeppelin observatory (78°54'N, 11°53'E), which is located close to the settlement of Ny Ålesund in the Svalbard archipelago. The Zeppelin station is an Arctic background station, 474 meters above sea level, and located above the local inversion layer to minimize the potential of measuring any local emissions.[16] Two sampling campaigns were carried out; one in late summer (spanning 46 days in August-October) and one in early winter (spanning 18 days in November-December) 2011. Two sampling trains were set up in parallel, each consisting of an ENV+ cartridge connected with polytetrafluoroethylene (PTFE) tubing to a GAST DOA-P509-BN air pump (GAST Manufacturing Inc., MI, USA) and a diaphragm gas volumeter (Flonidan, Denmark). The SPE-cartridges were mounted about 2 m above the ground, protected from precipitation with a plastic funnel, with the openings of the cartridges facing down. The average air flow through the cartridges was 18.0 ± 0.4 L/min. The average sampling time was 81 ± 23 hours in summer (3.4 days), and 25 ± 10 hours in winter (Table S2). Each set of parallel samples was accompanied by a field blank cartridge which was treated identically to the samples. At the sampling location, the field blank was connected to one of the pumps and air was drawn through it for 30 seconds.

2.1.3   Sample storage and extraction

After sampling the cartridges were capped, wrapped in aluminum foil, and stored at -18 °C in PE bottles. Storage time between sampling and extraction varied from 3 to 29 days. During transport the samples were outside the freezer for up to 24 hours, but they were always kept cold with refrigerating elements in an insulated box. Prior to extraction the cartridges were spiked directly on the frit with 20 µL of the internal standard containing approximately 900 pg/µL each of ^{13}C-labeled D4, D5, and D6 in *n*-hexane. The samples were eluted with 3 mL *n*-hexane directly into a vial for gas chromatography (GC). Fifty µL of 235 pg/µL (trimethylsilyloxy)silane (M3T) was added as recovery standard. The extracts were stored at -18 °C until analysis. The extracted ENV+ cartridges were reused.

2.1.4   Instrumental analysis

Instrumental analysis was carried out on a HP 6890 Series GC System connected to an Agilent 7863 Series Injector and an HP 5973 Mass Selective Detector (MSD) in positive electron ionization mode, using a similar method as in Warner et al.[17] The samples were quantified using a single-point calibration curve (concentration approximately 20 ng/mL). The linearity of the instrument was investigated, and all samples were found to be within the dynamic linear range of the instrument. Good comparability in the interlaboratory study for cVMS in fish**,** where both single- and multipoint calibrations curves were used, supports the reliability of using a single-point calibration curve.[14] The calibration solution contained non-labeled D3, D4, D5, and D6 in addition to the internal and recovery standards. Further details are provided in the Supporting Information.

2.1.5   Quality control procedures

Uttermost care was taken to avoid contamination of sampling material, as cVMS are ubiquitous in our surroundings. Sample preparation was performed in an isolated laboratory area, while the extractions were performed in a clean room facility (U.S. Federal Standard 209e) at NILU. NILU has previous experience with cVMS analysis,[17] and has also participated in an interlaboratory comparison of cVMS

analysis in rainbow trout.[14] The involved personnel refrained from using any personal care products, and samples were always handled with nitrile gloves. All glassware was burned at 450 °C for eight hours, and all plastic equipment was sonicated in *n*-hexane prior to use. The ENV+ cartridges were manually packed as experience had shown that this gives lower blank levels than commercially purchased ones.[15] After sonication in *n*-hexane, the empty PE cartridges were additionally rinsed with dichloromethane and *n*-hexane before packing. The nitrogen gas used to dry the pre-cleaned cartridges was filtered through an ENV+ cartridge to remove any cVMS contamination.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated as the average level in the field blanks plus three and ten times the standard deviation of the level in the field blanks, respectively. Background contamination resulting from the solvent and the instrumental system was assessed by frequently injecting *n*-hexane containing the internal standards and recovery standard. The results were not blank corrected, and they were only corrected for recovery during extraction and analysis.

2.2 Method evaluation

2.2.1 Elution volume and extraction recovery

A test was carried out to investigate the elution profiles of the cVMS congeners. The cartridges were spiked via the gas phase with non-labeled D3-D6, and internal standard was spiked on the frit (see Supporting Information for details). Ten fractions of 0.5 mL *n*-hexane were collected, and recovery standard was added to each fraction. Recovery of both the ^{13}C-labelled compounds and the native compounds in each fraction was calculated relative to hexane solutions containing the same amount of internal, spiking and recovery standards as had been added to the samples.

2.2.2 Effect of storage

As sampling in the Arctic normally requires a significant storage time between sampling and laboratory analysis, a test was carried out to evaluate the effect of storage on the samples. Fifteen cartridges were

spiked via the gas phase following the same procedure as for the elution volume (see details in Supporting Information). In addition, five blank cartridges went through the same procedure without adding the spiking mixture. All cartridges were capped at both ends, wrapped in aluminum foil, and three spiked cartridges and one blank were stored together as a set in a PE bottle. The cartridge sets were extracted after 0, 5, 11, 20 and 30 days respectively. Prior to extraction internal standard was added directly to the frit. The cartridges were eluted using 6 mL *n*-hexane, and recovery standard was added to the extract.

2.2.3   Breakthrough and sampling efficiency

Assessment of breakthrough and sampling efficiency from the gas phase was carried out at an outdoor measuring facility at Kjeller, Norway. Breakthrough is considered as the relative amount of analytes from the air that is not trapped on the cartridge during sampling. To evaluate the breakthrough during sampling, the sampling (primary) cartridge was coupled in series with a backup cartridge. Sampling was carried out for 21.4 hours (n=4) and 96.5 ± 0.2 hours (n=4) at a flow rate of 15.6 ± 0.2 L/min (n=8). Internal standard was added directly to the frit before extraction, the cartridge was extracted with 3 mL *n*-hexane, and recovery standard was added to the extract. The breakthrough was calculated as the amount of D3-D6 in the backup cartridge relative to the primary cartridge.

To evaluate the sampling efficiency from the gas phase, a PE frit and a thin disc of glass wool were inserted approximately 2 cm above the sorbent in the cartridge barrel. While air was drawn through the cartridges, the glass wool was spiked with native D3-D6. Immediately after spiking, two cartridges were coupled in series to the inlet of the spiked cartridge to remove all cVMS contribution from the air during sampling. Air was sampled for 35 ± 2 hours (n=4) and 133 ± 4 hours (n=4) at a flow rate of 13.7 ± 0.3 L/min (n=8). The sampling time was extended relative to the sampling times later used at Zeppelin to compensate for the lower flow rate. Prior to extraction the frit and the glass wool were pushed down to the sorbent, and internal standard was added on the uppermost frit. The cartridges were extracted using 6 mL *n*-hexane,

and recovery standard was added to the extract. See Supporting Information for details on volumes and concentrations of standards.

2.3 Model predictions

The concentration of D5 in the atmosphere (gaseous phase) at Zeppelin during the sampling period was predicted using the Danish Eulerian Hemispheric Model (DEHM),[18-19] previously applied for predicting concentrations of D5 in the atmosphere of the entire Northern Hemisphere for 2009.[9, 11] A simulation covering the years 1989-2011 was made. The emission estimates and the physical-chemical properties were the same as in the previous application.[9] There were no seasonal changes in the emission estimate, i.e. it was constant for the whole year. Diurnal average concentrations were calculated from the six hour mean values extracted from the model output. Back trajectories for the air masses at the sampling site during the sampling period were predicted using the HYSPLIT_4 model,[20-22] and airsheds were created following the method by Westgate et al.[23] Details for the construction of the back trajectories and airsheds have been provided in Supporting Information.

3. Results and discussion

3.1 Method evaluation

3.1.1 Method uncertainty

There is always uncertainty associated with results from analytical trace analysis. In general it can be divided into random variability influencing the precision of results, and systematic variability affecting the accuracy of results.[24] Both components can lead to either over- or underestimation of environmental concentrations. Systematic overestimation typically results from contamination of samples, while systematic underestimation is usually due to loss of analytes during sampling, storage, transport, extraction or clean-up procedures. Both can be relevant for cVMS due to their omnipresence in sampling and laboratory environments (i.e. high contamination risk) and their high volatility (i.e. susceptibility to

losses).[13-14] In this study field blank samples were extensively used to evaluate the potential overestimation of results. In addition several method evaluation tests were carried out to assess possible loss of analytes throughout the procedure, in particular during sampling, storage and extraction. In the following sections these results will be summarized.

3.1.2 Sources of underestimation of results

3.1.2.1 Elution volume and extraction recovery
Based on the elution profiles, the average recoveries after elution with 2 mL *n*-hexane were 65.6 ± 3.9 %, 89.9 ± 4.4 %, 89.5 ± 4.5 %, and 90.4 ± 5.2 % for D3, D4, D5, and D6, respectively. For the labeled compounds the recoveries were 106.0 ± 0.9 %, 99.2 ± 0.5 %, and 108.2 ± 0.7 % for ^{13}C-D4, ^{13}C-D5, and ^{13}C-D6 respectively (Figure S1). The lower recoveries for the non-labeled compounds than the labeled compounds could be due to the higher variability associated with the spiking procedure in the gas phase (non-labeled compounds) compared to spiking directly on the frit (labeled compounds). The average recovery of the internal standards during the later analysis of the samples from Svalbard was 93 ± 6 % for all congeners (Table S3), which is comparable to earlier reported values for ^{13}C-D5.[15] By quantifying the analytes with respect to the internal standards, the results were corrected for recovery of the mass-labeled analogues used as internal standards; D3 was corrected for the recovery of ^{13}C-D4.

3.1.2.2. Loss during storage
The results from the storage experiment were corrected based on the individual storage experiment blank samples (Figure S2 and S3). The recovery was variable and relatively low for most congeners. After 30 days the median blank-corrected recoveries were 17 %, 70 %, 19 %, and 19 % for D3, D4, D5 and D6 respectively (Figure S3). This is lower than reported by Kierkegaard and McLachlan, where a loss of ^{13}C-D5 of 1 % per day was observed with plastic cartridges when stored at -18 °C for 20 days.[15] However, these results are not directly comparable due to the different size of the cartridges and amount of sorbent used. See section 3.1.3.2 below for an explanation of the losses during storage.

3.1.2.3 Loss during sampling

Loss during sampling was evaluated in the breakthrough and sampling efficiency experiments (Section 2.2.2). The results were corrected for average levels in laboratory blanks. In cases where sample amounts were lower than average laboratory blank values, the blank-corrected mass was set to zero. One of the 21 h (20 m^3) samples in the breakthrough experiment was not included in the results because the backup cartridge contained 18 – 80 % of the sample amount in the primary cartridge, and had clearly been contaminated. The average breakthrough was less than 4 % for all congeners (n=7) (Table S3), but all levels in the backup cartridges were below quantification limits, so any correlations with sample volume or time could not be assessed.

In the sampling efficiency experiments, the average recoveries were 70 % for D3 and about 90 % for D4, D5, and D6 after 35 h (28 m^3). The results for sampling efficiency for D5 as well as the results for breakthrough were comparable to the results by Kierkegaard and McLachlan.[15] However, for the long-term sampling the sampling efficiency ranged from 59 % to 91 % after 133 h (about 5 days), with the recovery decreasing in the order D4>D5>D6>D3 (Table S3). These results were consistent with the recovery in the storage experiment after 5 days for D4, D5 and D6 (approximately 90 %, 80 % and 60 % recovery, respectively), which indicates that the sampling efficiency results are closely linked to storage losses. Only a small fraction of the loss during sampling can be explained by breakthrough. This was not the case for D3; but more than half of the D3 disappeared immediately in the storage experiment, when the samples were extracted directly after spiking. This loss of D3 could be due to volatile losses during the spiking procedure in gas phase, as D3 has a very high volatility.

3.1.3 Sources of overestimation of results

3.1.3.1 Contamination potential

Instrumental, laboratory, and method limits of detection (LOD) and quantification (LOQ) were calculated for all congeners based on laboratory and field blank samples (Table S4 and S5). The overall method LOD

based on the field blanks was 3.6, 3.5, 1.1, and 1.0 ng/sample for D3, D4, D5 and D6 respectively. This provided LODs of 0.01 – 0.14 ng/m³ depending on the season and the congener when dividing by the average volume of air sampled. The average mass of analyte in the field blanks relative to the samples ranged from 2 % for D5 to 24 % for D3 (Table S3). The method LOD for D5 in this study was twice as high on a ng/sample basis, but lower on a ng/m³ basis, compared to the study by Kierkegaard and McLachlan which used a similar SPE-AAS method with ENV+ resin.[15] This is reasonable considering that the current study used a larger sorbent mass, solvent volume, and sample volume of air compared to the study by Kierkegaard and McLachlan.[15] The LODs in this study on a ng/m³ basis are also 1-2 orders of magnitude lower for all congeners than method detection limits reported in the global study of VMS concentrations applying SIP-disks.[11]

3.1.3.2 Effect of storage

The observed losses in the storage experiment could not be explained by simple volatile losses, as the loss was greater for D6 than D5 than D4. In contrast, the volatility decreases and the octanol-air partition coefficient increases with increasing molecular weight of the cVMS congeners. However, as mentioned above, the loss of D3 observed in the storage experiment could be explained with volatilization. After the field sampling for this study had been completed, other quality assurance work for this method conducted at the Department of applied environmental science at Stockholm University revealed that ^{13}C-D3 and ^{13}C-D4 were being formed from ^{13}C-D5 during sample storage. When ^{13}C-D5 was spiked onto the sampling cartridges via the gas phase and stored frozen, ^{13}C-labeled D3 and D4 appeared in the extracts while a decrease in ^{13}C-D5 was recorded. The increase in ^{13}C-D4 was about the same magnitude as the loss of ^{13}C-D5, while the increase in ^{13}C-D3 was less. Some of the reaction occurred during or immediately following spiking, while some occurred over the 5-7 d storage period.[25]

3.1.4   Summary of method uncertainty

There was systematic uncertainty associated with the results for all four cVMS congeners in the method application, primarily as a result of the degradation of cVMS in the cartridges during storage. This section summarizes the implications of possible over- and underestimation on the results from the method application, including a description of how the measured results were corrected for loss during storage.

For D5 and D6 the main source of systematic uncertainty was possible underestimation of results due to loss during sampling and storage. It was assumed that the degradation is a first order process dependent on the amount of cVMS present on the sorbent, and hence the degradation rate should decrease exponentially with time as the amount of cVMS in the sorbent decreases. An exponential regression was made for each congener based on the results from the storage experiment (Figure S3, Table S3). The exponential regressions displayed R^2-values of 0.28 (D4) to 0.71 (D3), and the slopes of the regressions were significant for all congeners on a 95 % confidence level ($p < 0.05$) (Table S3).The measured levels of D5 and D6 were storage-corrected based on the exponential regressions using a storage time calculated from the mid-point of sampling to the time of extraction. The 95 % confidence interval of the slope of the regression was used to estimate the uncertainty in the storage-corrected values.

For D5 and D6 the only source of possible overestimation was considered to be contamination. The possibility of overestimation of D5 as a result of transformation of D6 to D5 is considered to be small due to the low concentrations of D6 compared to D5 (see Figure S4) and the extensive losses of D5 in the storage experiments in which the cVMS mixture contained similar concentrations of D5 and D6. In addition to contamination, other sources of uncertainty such as sampling efficiency were not taken into account as these were considered to be minor concerns compared to the storage artifacts.

For D3 and D4, possible overestimation of the results was the most serious concern. Since the measured concentration of D5 in the field samples was almost always considerably higher than for the other analytes

(see Figure S4), and since the storage experiment indicated that more than half of the D5 sampled could have reacted on the cartridges prior to analysis, it is likely that much of the D3 and in particular the D4 present in the extracts was formed from D5. For D3, the proximity of the quantities in many samples to the LOQ presents an additional source of uncertainty. Therefore, we cannot be sure that D3 and D4 were present in the sampled air. In addition, possible underestimation of concentrations due to loss during sampling and storage was also possible for D3 and D4 (see Figure S3). Hence the measured concentrations were storage-corrected in the same way as the concentrations of D5 and D6, and this was considered the upper boundaries of the true values for the concentrations of D3 and D4 in air at Zeppelin.

3.2 cVMS levels in Arctic air

All measured cVMS concentrations were above method detection and quantification limits (on a ng/sample basis) except for D3 in some of the winter samples, which were above LOD, but below or equal to LOQ (Table S6). However, the D3 and D4 data are subject to the caveats outlined above due to their possible formation from D5 on the sorbent. The average difference between the parallel samples from Zeppelin, normalized to the average of the two parallel samples, ranged from 8 % (D5) to 21 % (D3) (Table S3), and was comparable to earlier reported values for D5.[15]

The results are presented as point estimates for D5 and D6, while the results for D3 and D4 are presented as ranges, as these congeners were possibly only present as a result of the storage artifacts (Figure 1, Table 1). The average concentrations in air for D5 and D6 were 0.73 ± 0.31 ng/m^3 and 0.23 ± 0.17 ng/m^3 in summer and 2.94 ± 0.46 ng/m^3 and 0.45 ± 0.18 ng/m^3 in winter, respectively. The D3 and D4 concentration windows extended from n.d. - 2.20 ng/m^3 and n.d. - 0.95 ng/m^3 in summer, and from n.d. - 2.98 ng/m^3 and n.d. - 2.13 ng/m^3 in winter, respectively (Figure 1). D5 was the cVMS with the highest measured concentration in most of the samples, except for in August and September when the upper boundaries of the concentration windows of D4 and sometimes also D3 was higher (Figure S4). However,

the upper boundaries of the concentration windows of D3 and D4 represents the situation that D3 and D4 has been subject to loss during storage and not formation from degradation of D5. This is considered unlikely for the samples in question in light of the current knowledge of degradation of D5. The concentration of D5 was higher than D6 in all samples (Figure S4). The D5 concentrations in this study are of the same order of magnitude but somewhat lower than measured with the SPE-AAS method in Sweden in 2009 (up to 9 ng/m^3).[9, 15]

In comparison to the concentrations measured with the SPE-AAS method in this study, Genualdi et al. reported concentrations of 17 ng/m^3, 16 ng/m^3, 4.0 ng/m^3, and 0.54 ng/m^3 for D3, D4, D5, and D6 at the Zeppelin observatory using SIP-disks that had been deployed from April until July 2009.[11] For D3 and D4 this is 17 and 31 times higher than the mean of the upper boundary of the concentrations measured in August and September of the current study. The reported concentrations of D5 and D6 at Zeppelin in the GAPS-study were also slightly higher than in this study, in particular when the time of sampling is considered. The reported concentrations for April – July (midnight sun period, which is the season with the lowest expected concentrations) in the GAPS-study are comparable to the levels for November – December (polar night period, which is the season with the highest expected concentrations) in this study. There has been no report on the effect of storage on cVMS in the SIP-disks yet.

The seasonality of cVMS in Arctic air can be illustrated by the ratio between the median concentration in winter and the median concentration in summer. The empirical seasonality ratios in this study are expected to be underestimated as the time of the year where the concentration in air of D5 is expected to be at its maximum (January-March) and its minimum (June-July) respectively[8-9] were not included in the sampling periods in this study. For D5 at Zeppelin the seasonality ratio was 3.8. This is in accordance with the hypothesis that lower concentration of hydroxyl radicals in the atmosphere during the Arctic winter leads to higher concentrations of D5 in the air. The observed seasonality ratio is lower than the

maximum model-predicted seasonality ratios of about 10 in the DEHM and GloboPOP-models.[8-9] However, the predicted seasonality ratio based on the median concentrations from DEHM for the specific sampling periods used in this study was 4.3, which compares well with the observed ratio of 3.8. Inspection of the airsheds of the samples did not reveal any differences in the atmospheric transport patterns between sampling periods in late summer and early winter that could explain the observed seasonality in cVMS concentrations (Figure S5 and S6).

The main factor affecting differences in the seasonality ratios between the cVMS congeners is the reaction rate with hydroxyl radicals. The reaction rate constants of D3, D4, and D6 with hydroxyl radicals are 0.3, 0.7, and 1.2 times the reaction rate constant of D5 (Table S1). The application of the DEHM-model to D5 in Sweden showed that the sensitivity of the predicted concentration of D5 in air to the reaction rate constant of D5 with hydroxyl radicals varied seasonally.[9] In late spring the concentration of D5 showed a near linear relationship to the reaction rate constant; increasing the rate constant by a factor of 4 also decreased the predicted concentrations by about a factor of 4. In winter the relationship was non-linear, and the concentration in air was relatively independent of the reaction rate constant. Based on this, a semi-quantitative assessment of the expected seasonality ratios for D3, D4, and D6 can be made. The seasonality ratio for the cVMS congeners relative to D5 can be assumed to differ by the same factor as the reaction rate constant with hydroxyl radicals differs. I.e. as D4 has a reaction rate constant which is 0.7 times the rate constant of D5, the seasonality ratio of D4 is expected to be only 0.7 times the seasonality ratio of D5. This makes sense as a lower rate of degradation in summer leads to a smaller difference between summer and winter levels. The resulting expected seasonality ratios for D3, D4, and D6 are 1.1, 2.7, and 4.6 respectively, compared to 3.8 for D5. Based on the upper limits of the concentration windows for D3 and D4, the seasonality ratios were 1.4 and 2.7, respectively. These results agree well with the expected values, but in light of the uncertainty of the measured data this may be a chance result. For D6 the seasonality ratio was 2.2. This is in contradiction to the expectation that D6

16

should display a more pronounced seasonality than D5. One possible explanation is the uncertainty in the reaction rate constant of D6; it has not yet been experimentally determined and could only be estimated using a quantitative structure activity relationship (QSAR).

The coefficients of variation for the D5 and D6 concentrations were larger in summer (42 % and 75 %) than in winter (16 % and 41 %), respectively (Table S1), despite the fact that the sampling period was longer in summer (3-4 d) than in winter (≈1 d), which would tend to reduce variability. This corresponds with the DEHM-predictions, where the relative standard deviation also was larger in summer (73 %) than in winter (54 %) for the predicted daily mean concentrations of D5, when the divide between the two seasons was set at the 15th of October. Greater variability during summer was also observed in the previous predictions of D5 concentrations with the DEHM-model, but not discussed.[9] This is in accordance with the Junge relationship, namely that the temporal or spatial variability in the distribution of tropospheric trace constituents is inversely related to the residence time of the constituent.[26-27] In other words, when the degradation of cVMS is greater due to higher hydroxyl radical concentrations in the atmosphere, the residence time is shorter, and the temporal (and spatial) variability is greater due to decreased opportunities for mixing.

The D5 concentrations predicted by the DEHM-model compared well with the measured concentrations for D5 (Figure 1). On average the ratio of the modeled concentration to the measured concentration was 1.3 ± 0.5, with a minimum value of 0.2 and a maximum value of 2.6. Given the uncertainties in the measured concentrations, this is considered a good fit between modeled and observed values. In winter the overestimation was slightly higher than in summer with an average ratio of modeled to measured concentrations of 1.5 ± 0.5 and 1.1 ± 0.5 respectively. In the previous application of the model, a better fit was also observed between modeled/measured values in summer than in winter.[9] It has been suggested that reaction of cVMS on aerosols could make a discernable contribution to cVMS removal

when gas phase reactions of cVMS with OH radicals are slow.[28] This could explain some of the greater

disagreement between the modeled and the measured concentrations during the polar winter. However,

the overall good agreement with the measurements increases the confidence in the ability of the DEHM

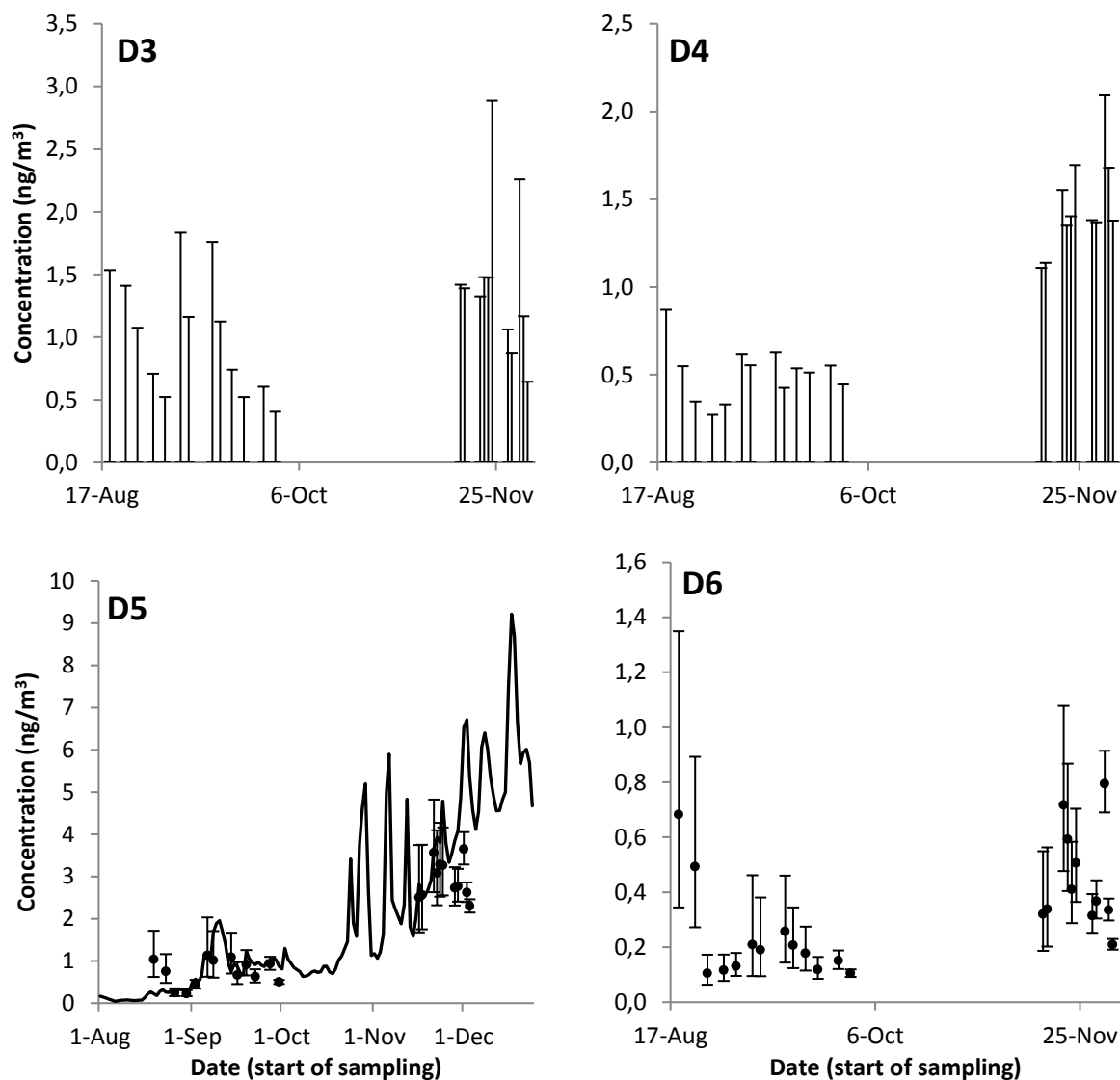model to predict D5 concentrations in the atmosphere.

Figure 1: Concentrations of D3, D4, D5, and D6 in air for all samples at Zeppelin in 2011. The concentrations are shown as ranges for D3 and D4, taking both possible under- and overestimation due to the storage artifacts into account. The concentrations for D5 and D6 are the storage-corrected concentrations with the uncertainties as error bars. The DEHM-model estimate for D5 concentrations in Arctic air from August to December 2011 is displayed as a line. Note the different scales on the y-axes.

Table 1: cVMS concentrations in air at Zeppelin. Data for parallel samples (A and B) are reported. Results for D3 and D4 are given as the lower and upper boundaries of the concentration window.

Sample start	Sample end	Concentration (ng/m^3)							
		D3		D4		D5		D6	
		A	B	A	B	A	B	A	B
19.08.11	23.08.11	n.d.-1.66	n.d.-1.41	n.d.-0.95	n.d.-0.79	1.05	1.01	0.66	0.71
23.08.11	26.08.11	n.d.-1.43	n.d.-1.39	n.d.-0.57	n.d.-0.53	0.76	0.73	0.52	0.46
26.08.11	30.08.11	n.d.-1.24	n.d.-0.91	n.d.-0.35	n.d.-0.35	0.25	0.24	0.11	0.10
30.08.11	02.09.11	n.d.-0.68	n.d.-0.73	n.d.-0.27	n.d.-0.28	0.22	0.23	0.11	0.12
02.09.11	06.09.11	n.d.-0.57	n.d.-0.47	n.d.-0.34	n.d.-0.32	0.46	0.41	0.15	0.11
06.09.11	08.09.11	n.d.-2.20	n.d.-1.47	n.d.-0.78	n.d.-0.46	1.26	0.99	0.25	0.17
08.09.11	13.09.11	n.d.-1.28	n.d.-1.04	n.d.-0.58	n.d.-0.53	1.06	0.97	0.20	0.18
14.09.11	16.09.11	n.d.-1.94	n.d.-1.58	n.d.-0.69	n.d.-0.57	1.17	0.99	0.28	0.23
16.09.11	19.09.11	n.d.-1.24	n.d.-1.01	n.d.-0.45	n.d.-0.40	0.68	0.65	0.24	0.18
19.09.11	22.09.11	n.d.-0.80	n.d.-0.68	n.d.-0.56	n.d.-0.51	0.93	0.89	0.19	0.16
22.09.11	27.09.11	n.d.-0.56	n.d.-0.48	n.d.-0.54	n.d.-0.49	0.65	0.60	0.13	0.11
27.09.11	30.09.11	n.d.-0.65	n.d.-0.55	n.d.-0.57	n.d.-0.53	0.94	0.92	0.16	0.14
30.09.11	04.10.11	n.d.-0.36	n.d.-0.45	n.d.-0.43	n.d.-0.46	0.50	0.50	0.10	0.11
16.11.11	17.11.11	n.d.-1.55	n.d.-1.29	n.d.-1.14	n.d.-1.08	2.49	2.52	0.33	0.31
17.11.11	18.11.11	n.d.-1.56	n.d.-1.22	n.d.-1.19	n.d.-1.09	2.61	2.51	0.35	0.33
21.11.11	22.11.11	n.d.-1.39	n.d.-1.26	n.d.-1.57	n.d.-1.53	3.86	3.25	0.76	0.67
22.11.11	23.11.11	n.d.-1.20	n.d.-1.76	n.d.-1.27	n.d.-1.43	2.92	3.24	0.57	0.61
23.11.11	24.11.11	n.d.-1.60	n.d.-1.35	n.d.-1.41	n.d.-1.39	3.25	3.31	0.37	0.45
24.11.11	25.11.11	n.d.-2.80	n.d.-2.98	n.d.-1.67	n.d.-1.72	3.30	3.22	0.50	0.51
28.11.11	29.11.11	n.d.-0.93	n.d.-1.19	n.d.-1.39	n.d.-1.38	2.66	2.79	0.30	0.33
29.11.11	01.12.11	n.d.-0.84	n.d.-0.91	n.d.-1.38	n.d.-1.35	2.71	2.82	0.37	0.37
01.12.11	02.12.11	n.d.-1.92	n.d.-2.59	n.d.-2.06	n.d.-2.13	3.56	3.74	0.76	0.82
02.12.11	03.12.11	n.d.-1.38	n.d.-0.95	n.d.-1.76	n.d.-1.60	2.66	2.57	0.35	0.32
03.12.11	04.12.11	n.d.-0.62	n.d.-0.67	n.d.-1.34	n.d.-1.42	2.23	2.36	0.20	0.22

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Supporting Information

Supporting Information containing more detailed descriptions of methods and results is available. This material is available free of charge via the Internet at http://pubs.acs.org.

References

1.   Brooke, D.; Crookes, M.; Gray, D.; Robertson, S. *Environmental risk assessment report: Decamethylcyclopentasiloxane*; Environment Agency of England and Wales: Bristol, 2009.

2.   Brooke, D.; Crookes, M.; Gray, D.; Robertson, S. *Environmental risk assessment report: Octamethylcyclotetrasiloxane*; Environment Agency of England and Wales: Bristol, 2009.

3.   Brooke, D.; Crookes, M.; Gray, D.; Robertson, S. *Environmental risk assessment report: Dodecamethylcyclohexasiloxane*; Environment Agency of England and Wales: Bristol, 2009.

4.   Xu, S.; Kropscott, B. Method for simultaneous determination of partition coefficients for cyclic volatile methylsiloxanes and dimethylsilanediol. *Anal. Chem.* **2012,** *84* (4), 1948-1955.

5.   Whelan, M. J.; Estrada, E.; van Egmond, R. A modelling assessment of the atmospheric fate of volatile methyl siloxanes and their reaction products. *Chemosphere* **2004,** *57* (10), 1427-1437.

6.   Atkinson, R. Kinetics of the gas-phase reactions of a series of organosilicon compounds with OH and NO3 radicals and O3 at 297 +/- 2K. *Environ. Sci. Technol.* **1991,** *25* (5), 863-866.

7.   Bennett, D. H.; McKone, T. E.; Matthies, M.; Kastenberg, W. E. General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment. *Environ. Sci. Technol.* **1998,** *32* (24), 4023-4030.

8.   Xu, S.; Wania, F. Chemical fate, latitudinal distribution and long-range transport of cyclic volatile methylsiloxanes in the global environment: A modeling assessment. *Chemosphere* (In Press). DOI: 10.1016/j.chemosphere.2012.10.056.

9.   McLachlan, M. S.; Kierkegaard, A.; Hansen, K. M.; van Egmond, R.; Christensen, J. H.; Skjoth, C. A. Concentrations and fate of decamethylcyclopentasiloxane (D(5)) in the atmosphere. *Environ. Sci. Technol.* **2010,** *44* (14), 5365-5370.

10.   MacLeod, M.; von Waldow, H.; Tay, P.; Armitage, J. M.; Wohrnschimmel, H.; Riley, W. J.; McKone, T. E.; Hungerbuhler, K. BETR global - A geographically-explicit global-scale multimedia contaminant fate model. *Environ. Pollut.* **2011,** *159* (5), 1442-1445.

11.   Genualdi, S. G. S.; Harner, T.; Cheng, Y.; MacLeod, M.; Hansen, K. M.; van Egmond, R.; Shoeib, M.; Lee, S. C. Global distribution of linear and cyclic volatile methyl siloxanes in air. *Environ. Sci. Technol.* **2011,** *45* (8), 3349-3354.

12.   Beyer, A.; Wania, F.; Gouin, T.; Mackay, D.; Matthies, M. Temperature dependence of the characteristic travel distance. *Environ. Sci. Technol.* **2003,** *37* (4), 766-771.

13.	Varaprath, S.; Stutts, D.; Kozerski, G. A primer on the analytical aspects of silicones at trace levels - challenges and artifacts – a review. *Silicon Chemistry* **2006,** *3* (1), 79-102.

14.	McGoldrick, D. J.; Durham, J.; Leknes, H.; Kierkegaard, A.; Gerhards, R.; Powell, D. E.; McLachlan, M. S. Assessing inter-laboratory comparability and limits of determination for the analysis of cyclic volatile methyl siloxanes in whole rainbow trout (Oncorhynchus mykiss). *Chemosphere* **2011,** *85* (8), 1241-1247.

15.	Kierkegaard, A.; McLachlan, M. S. Determination of decamethylcyclopentasiloxane in air using commercial solid phase extraction cartridges. *J. Chromatogr. A* **2010,** *1217* (21), 3557-3560.

16.	Berg, T.; Kallenborn, R.; Mano, S. Temporal trends in atmospheric heavy metal and organochlorine concentrations at Zeppelin, Svalbard. *Arct. Antarct. Alp. Res.* **2004,** *36* (3), 284-291.

17.	Warner, N. A.; Evenset, A.; Christensen, G.; Gabrielsen, G. W.; Borga, K.; Leknes, H. Volatile siloxanes in the european Arctic: assessment of sources and spatial distribution. *Environ. Sci. Technol.* **2010,** *44* (19), 7705-7710.

18.	Hansen, K. M.; Christensen, J. H.; Brandt, J.; Frohn, L. M.; Geels, C.; Skjoth, C. A.; Li, Y. F. Modeling short-term variability of alpha-hexachlorocyclohexane in Northern Hemispheric air. *J. Geophys. Res.-Atmos.* **2008,** *113* (D2).

19.	Brandt, J.; Silver, J. D.; Frohn, L. M.; Geels, C.; Gross, A.; Hansen, A. B.; Hansen, K. M.; Hedegaard, G. B.; Skjøth, C. A.; Villadsen, H.; Zare, A.; Christensen, J. H. An integrated model study for Europe and North America using the Danish Eulerian Hemispheric Model with focus on intercontinental transport of air pollution. *Atmos. Environ.* **2012,** *53* (0), 156-176.

20.	Draxler, R. R.; Hess, G. D. An overview of the HYSPLIT_4 modelling system for trajectories, dispersion and deposition. *Aust. Meteorol. Magazine* **1998,** *47*, 295-308.

21.	Draxler, R. R.; Hess, G. D. *Description of the HYSPLIT_4 modeling system*; NOAA Tech. Memo. ERL ARL-224; NOAA Air Resources Laboratory: Silver Spring, MD, 1997.

22.	Draxler, R. R. *HYSPLIT4 user's guide*; NOAA Tech. Memo. ERL ARL-230; NOAA Air Resources Laboratory: Silver Spring, MD, 1999.

23.	Westgate, J. N.; Wania, F. On the construction, comparison, and variability of airsheds for interpreting semivolatile organic compounds in passively sampled air. *Environ. Sci. Technol.* **2011,** *45* (20), 8850-8857.

24.	Harris, D. C., *Quantitative chemical analysis, 6th ed.*; W. H. Freeman and Company: USA, 2003.

25.	McLachlan, M. S.; Kierkegaard, A. *Linear and cyclic VMS in rural Swedish air*, Presented at 3rd Workshop on Organosilicones in the Environment, Canada Centre for Inland Waters, Burlington, Ontario, Canada, May 8th-9th, 2012.

26.	Becker, S.; Halsall, C. J.; MacLeod, M.; Scheringer, M.; Jones, K. C.; Hungerbuhler, K. Empirical Investigation of the Junge Variability-Lifetime Relationship Using Long-Term Monitoring Data on Polychlorinated Biphenyl Concentrations in Air. *Environ. Sci. Technol.* **2009,** *43* (8), 2746-2752.

27.	Junge, C. E. Residence time and variability of tropospheric trace gases. *Tellus* **1974,** *26* (4), 477-488.

28.	Navea, J. G.; Young, M. A.; Xu, S. H.; Grassian, V. H.; Stanier, C. O. The atmospheric lifetimes and concentrations of cyclic methylsiloxanes octamethylcyclotetrasiloxane (D(4)) and decamethylcyclopentasiloxane (D(5)) and the influence of heterogeneous uptake. *Atmos. Environ.* **2011,** *45* (18), 3181-3191.