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Determination of linear and cyclic volatile methylsiloxanes in air at a regional background site in Sweden

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HIGHLIGHTS

- Four lVMS were present in background air at concentrations of <3–540 pg m^{-3}.
- Four cVMS were present in background air at concentrations of <420–28500 pg m^{-3}.
- D3 and D4 were formed from D5 during sampling.
- The ratios of VMS emissions are similar to the ratios of concentrations in winter air.
- The VMS concentration ratio in winter can be used to estimate the ratio of emissions.

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ABSTRACT

A number of volatile methylsiloxanes have been identified as environmental contaminants and several are currently the subject of detailed risk assessments due to concerns that they may be persistent, bioaccumulative and toxic in the environment. Once emitted these chemicals reside primarily in the atmosphere. Consequently, knowledge of their concentrations in air is essential to understanding their fate in the environment and any potential adverse impacts. We developed a method to analyse 4 cyclic volatile methylsiloxanes (D3, D4, D5 and D6) and 4 linear volatile methylsiloxanes (L3, L4, L5 and L6) in air at regional background levels. The method showed good repeatability (median difference between sample pairs of 2–8%) and low limits of quantification (from 3.8 pg m^{-3} for L3 to 320 pg m^{-3} for D4). However, the analysis of D3 and D4 was confounded by the transformation of D5 to these analytes on the sampling cartridge. During a sampling campaign with a daily temporal resolution between November 4 and December 14 2011, all analytes with the exception of L5 and L6 could be quantified in all samples. It was hypothesized that the ratio of the concentrations of different VMS reflected the relative strength of their emissions to the airshed due to the slow phototransformation of the VMS at high latitudes in winter. This was supported by available emissions information.

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1. Introduction

The volatile methylsiloxanes (VMS) are a substance group that includes a range of high production volume chemicals used in consumer goods such as personal care products and cleaning agents (Horii and Kannan, 2008). Many are also present as residues in silicone polymers (Brooke et al., 2009a–c). Three cyclic volatile methylsiloxanes (cVMS), namely octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), have recently been the focus of close regulatory scrutiny in Canada and/or the European Union because of concerns that they may be persistent, bioaccumulative and toxic in the environment (Environment Canada and Health Canada, 2008a–c; Brooke et al., 2009a–c). They are emitted primarily to air, and once present in the environment they reside largely in air due to their high volatility and low water solubility (Brooke et al., 2009a–c). Therefore, knowledge of the concentrations of VMS in air is key to understanding their emissions, long range transport and environmental fate as well as the exposure of air breathing organisms.

Decamethylcyclopentasiloxane (D5) is the best studied cVMS with respect to its occurrence and fate in the atmosphere. A method to determine D5 concentrations in regional background air based

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on active sampling onto ENV+ resin has been developed and validated (Kierkegaard and McLachlan, 2010). This method was employed to measure D5 concentrations in southern Sweden with a 24 h temporal resolution, and the data were used to successfully evaluate a model of the emissions and atmospheric fate of D5 in the Northern Hemisphere (McLachlan et al., 2010). The measurements and model results showed a pronounced temporal variability of D5 concentrations on the scale of both days and seasons, with higher levels in winter. The model predictions also showed a pronounced spatial variability with high concentrations in the Arctic, particularly during winter, and lower concentrations with much stronger spatial gradients in low latitudes and during the summer months. The model predictions for the Arctic were later verified by active sampling on Svalbard (Krogseth et al., 2013a). The spatial and temporal variability in concentrations were linked to the spatial and temporal variability in the phototransformation of D5, which is the major mechanism for D5 removal from the atmosphere, as well as the spatial variability in emissions (McLachlan et al., 2010).

Passive air samplers have also been used to study cVMS. Samplers that had been deployed for 3 months at 20 stations on 3 continents were analysed for D4, D5, D6 and a fourth cVMS, hexamethylcyclotrisiloxane (D3), as well as 3 linear volatile methylsiloxanes (lVMS), namely octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), and dodecamethylpentasiloxane (L5) (Genualdi et al., 2011). Pronounced spatial gradients were observed. For D5 the measured concentrations were compared with predicted concentrations from two atmospheric transport and fate models. Positive correlations were obtained, but the magnitude of the observed spatial gradient greatly exceeded that of the modeled spatial gradient. Passive air samplers have also been used to demonstrate emissions of VMS from wastewater treatment plants and landfills (Cheng et al., 2011). Recently, a quality assured method for passive sampling of cVMS and lVMS with a one week sampling period was published (Krogseth et al., 2013b).

Chemical concentrations on a time scale of days have proven very useful for exploring the emissions and atmospheric fate of D5. However, no method is currently available for the analysis of other VMS in regional background air on a time scale of days. The goal of this work was to develop and validate such a method for D3, D4, D6, L3, L4, L5, and tetradecamethylhexasiloxane (L6) and to apply it in a limited sampling campaign in rural Sweden.

2. Methods

The method was based on the method developed for the analysis of D5 in regional background air, which entails active sampling onto an SPE cartridge prepared with Isolute ENV+ sorbent (hydroxylated polystyrene-divinylbenzene copolymer), elution with a non-polar solvent, and injection of the extract into a gas chromatograph/mass spectrometer (GC/MS) (Kierkegaard and McLachlan, 2010).

2.1. Materials

Empty cartridges, polyethylene (PE) frits and Isolute ENV+ were all purchased from Biotage AB, Uppsala, Sweden. Dichloromethane (DCM) and *n*-hexane, both lichrosolve, were from Merck (Darmstadt, Germany). For details about the chemicals and standards used see Table S1 in the Supplementary Data.

2.2. Method description

2.2.1. Air sampling

The sampling was conducted at a private home on the outskirts of Tystberga, a village with 800 inhabitants located 70 km southwest of Stockholm and 10 km west of the Swedish regional background air monitoring station of Aspvreten (see Figure S1). Samples were collected daily for 6 weeks between 4 November and 14 December 2011. Two sampling trains, each consisting of an ENV+ cartridge, were mounted under a precipitation shield with the inlets facing down. A diaphragm pump (GAST MAA-V109-HD, Gast Manufacturing, MI, USA) with the two heads operated independently was used to pull air through the cartridges at a flow rate of 12 L min^{-1}. The cartridges were connected to the pump by PTFE tubing. The air volume was recorded by gas volume meters connected to the outflows from the pump.

2.2.2. Sample preparation and extraction

The ENV+ was purchased in bulk and stored in n-hexane. 15 mL PE cartridges were packed with 85–100 mg of ENV+ held between 2 PE frits. Prior to use they were rinsed with 10 mL of DCM and 10 mL of n-hexane. The cartridges were subsequently dried using purified nitrogen, capped at both ends, and wrapped in aluminum foil. The two sample cartridges for a given sampling day and a field blank cartridge were kept together in sealed PE bags laminated with aluminum foil, and they were stored frozen before as well as after sampling. Prior to extraction, 50 μL of each of the internal standard solutions was spiked on the upper frit and after 1–2 min the cartridge was eluted with 1.3 mL of n-hexane. Column elution was via gravity flow, with eluate collection in a GC vial. All samples and field blanks were analysed within 7 days of the end of sampling.

The original intent of the sampling program was to measure D4, D5 and D6. Early in the program it was discovered that D3, L3, L4, L5 and L6 were also present in the samples. Consequently we did some method tests to evaluate whether the method was also suited for these analytes. It was observed that the elution with n-hexane resulted in insufficient extraction of D3. Tests showed that elution with 1.3 mL of DCM gave acceptable recovery of all analytes (see Results below). Therefore the second 1.3 mL fraction of n-hexane was replaced by DCM starting with the sample from November 16. A second portion of the internal standard mixture was added to this extract (elution studies had shown that 93–95% of the internal standards added to the cartridge were eluted with the first 1.3 mL of n-hexane). Prior to analysis aldrin was added to the extracts as a volumetric standard.

2.2.3. Instrumental analysis

Quantification was performed as described in Kierkegaard and McLachlan (2010), on a Trace GC Ultra (Thermo Electron Corp.) coupled to an MD800 MS detector (Fisons Instruments SpA) using electron ionization (EI). 5 μl of the extract was injected into the large volume splitless injector (Thermo Electron Corp.) equipped with a Merlin microseal® septum. In the Supplementary Data Table S2 lists the masses monitored and Figure S2 shows an examples of mass chromatograms.

2.2.4. Quantification

The internal standards used for quantification are listed in Table S1. D4, D5 and D6 were quantified using the ^{13}C labeled analogues, D3 using ^{13}C labeled D4, and L3, L4, L5 and L6 using tetrakis (trimethylsiloxy) silane (M4Q). The calibration curve included 9–11 standard solutions with a concentration range of 0.5–500 pg μL^{-1}. The concentrations in the n-hexane and DCM fractions were quantified separately and added. For the samples collected prior to November 16 for which no DCM fraction was collected, the concentrations were corrected using the average ratio of the analyte quantity in the DCM and n-hexane fractions for the samples collected after November 16 (D3: 1.69 ± 0.17; D4: 1.13 ± 0.04; D5: 1.17 ± 0.03; D6: 1.20 ± 0.03; L3: 1.02 ± 0.01).

2.2.5. QA/QC

Each pair of samples for a given day was accompanied by a field blank. The field blank and the samples were treated in an identical manner, except that air was pumped through the blank cartridge for only a few seconds. On 3 occasions an extra cartridge was mounted next to the sampling cartridges for the whole sampling period without having any air pumped through it. The samples and field blank were prepared and extracted in parallel.

A number of preventive measures were taken to reduce the possibilities for sample contamination. The cartridges were prepared and processed in a clean air cabinet under a laminar flow of charcoal (Gigapleat, Camfil International AB) and particle filtered air (HEPA H14, Trox® Technik GmbH). The hexane used in the preparation and extraction of the cartridges was treated with concentrated sulfuric acid and the nitrogen used for drying the precleaned cartridges was filtered through a 50 mg ENV+ cartridge. Measures to reduce the instrumental blanks are described in Kierkegaard and McLachlan (2010).

2.3. Method development and evaluation

2.3.1. Elution volume

The elution profile of the analytes was studied with the samples from the first 6 d. The n-hexane was applied in 3 portions (1.2, 0.8 and 0.8 mL) and 3 fractions were collected and analysed separately to study the elution of the internal standards and the analytes. After D3 was found in the samples and observed to be almost equally distributed between the 3 n-hexane fractions, a laboratory experiment was done to assess the elution efficiency with different solvents. n-hexane solutions of D3 (25 μL) and the labeled standards (100 μL) was applied to a frit that had been wedged into a sampling cartridge upstream of the sorbent. Air was drawn through the cartridge at 0.5 L min^{-1} during application of the standard and for 5 min afterwards. The intention was that the analytes would volatilize from the frit and be carried onto the sorbent in a manner similar to that during sampling. Cartridges prepared in this manner were then eluted with 1.3 mL (n-hexane and methyl-*tert*-butylether (MTBE)) or 3 × 1.3 mL (DCM and ethyl acetate (etOac)). Each fraction was collected and analysed separately.

2.3.2. Sampling efficiency

Ten 15 mL ENV+ cartridges were spiked as described in the elution volume section with a standard containing ^{13}C labeled D4, D5 and D6 plus native D3, L3, L4, L5, L6, and PCB 209. PCB 209 was included as a conservative tracer to correct for spiking losses. Air was drawn through the cartridges at 0.5 L min^{-1} during spiking and for 5 min thereafter, after which the flow was increased to ~10 L min^{-1} for ~24 h to simulate normal sampling conditions. Two unspiked cartridges were run in parallel to assess the levels in ambient air. Each cartridge was eluted with 1.2 mL DCM.

2.3.3. Breakthrough

The breakthrough of the analytes through the sampling cartridge was assessed by mounting a second cartridge behind the primary sampling cartridge. This was done for 4 of the cartridges in the sampling efficiency experiment described above. The second cartridge had twice the diameter (and 4 times the ENV+) to offer a lower flow resistance. This cartridge was eluted with 1.2 mL DCM.

2.3.4. Repeatability

Parallel samples were collected each day of the sampling campaign. The repeatability was assessed by comparing the concentrations in these sample pairs.

2.3.5. Sample storage

During the development of the method to analyse D5 in air it was observed that D5 was lost when the samples were stored for extended periods of times (Kierkegaard and McLachlan, 2010). To investigate this for the other VMS studied here, parallel samples were collected. One of the samples was extracted immediately, whereas the second was stored at −17 °C for 5 or 7 d and then extracted. Two sets of parallel samples were collected and treated in this manner on each of 4 different days.

2.3.6. Transformation products

In order to better understand the implication of D5 loss during storage, an experiment was conducted to identify whether other analytes were formed as a result of D5 transformation. Twelve 15 mL ENV+ cartridges were spiked as described in the elution volume section with a standard containing 520 ng of ^{13}C labeled D5 only. Air was drawn through the cartridges at 0.5 L min^{-1} during spiking and for 5 min thereafter. Six of the cartridges were then spiked with 130 ng of M4Q, extracted and analyzed. The remaining 6 cartridges were capped, sealed and stored as the real samples, at −17 °C. After 7 d these cartridges were also spiked with M4Q, extracted and analyzed. This experiment was repeated using 490 ng unlabeled L6.

3. Results and discussion

3.1. Elution volume

The elution profiles in n-hexane showed that >95% of the lVMS eluted in the first 1.2 mL (see Figure S3). 93–95% of the ^{13}C-labeled D4, D5 and D6 also eluted in the first fraction. The proportion was somewhat less for the native analogues (perhaps because they had been accumulated in the cartridge over 24 h during air sampling, in contrast to the labeled standards, which had been added to the frit in solution) and decreased with decreasing molecular size (87% for D6, 81% for D5, 76% for D4). The presence of >75% of these analytes in the first fraction suggested that n-hexane was a suitable solvent for their extraction from the cartridge. However, for D3 similar quantities were extracted in each of the 3 fractions (see Figure S3), indicating that n-hexane was a poor solvent for its extraction.

The insufficient elution of D3 in n-hexane was confirmed in the experiment comparing extraction solvents; 25% was recovered in the first 1.3 mL fraction compared with 58–71% for D4-D6 (see Figure S4). Comparatively poor extraction of D3 was also observed for etOac and MTBE. For DCM, on the other hand, the recovery was similar for all four cVMS (63–71%). The second DCM fraction contained at most 2.4% of the spiked analytes, and the third less (see Figure S4), providing further evidence that DCM is an effective elution solvent. It was thus decided to modify the method, changing the elution solvent from 2 × 1.3 mL n-hexane to 1 × 1.3 mL n-hexane followed by 1 × 1.3 mL DCM.

3.2. Sampling efficiency

Of the analytes, only D3 was present in the unspiked cartridges at levels >0.5% of those in the spiked cartridges. The D3 levels in the spiked cartridges were corrected for the levels present in the ambient air in order to be able to calculate the recovery of the spike. This correction amounted to 15–38%.

The recovery of the siloxanes relative to PCB 209, the conservative, involatile tracer in the spike solution, is illustrated in Figure S5. It ranged from 70 to 80% for most of the analytes, indicating that there were small losses. The notable exception was D3, with a mean recovery of 44%. There are several possible explanations for the small losses, including volatilization during spiking,

Table 1
Repeatability and LOQ of the analytical method. The repeatability was evaluated using the % difference between sample pairs that had been collected in parallel (28–41 pairs).

	Repeatability (median % diff.)[a]	LOQ (pg m^{-3})[b]
L3	3.4	3.8
L4	3.6	7.0
L5	5.1	8.9
L6	8.0	16
D3	4.4	270
D4	2.6	210
D5	1.7	150
D6	2.4	130

[a] Difference in concentration between the two samples divided by the mean of the two concentrations.
[b] Based on a sampling volume of 12 m^3 of air.

transformation in the cartridge, or incomplete extraction from the cartridge. The low recovery of D3 suggests that it may be less stable. Transformation is discussed further below.

3.3. Breakthrough

The results of the breakthrough experiment of all analytes except D3 are shown in Figure S6. In all cases it was negligible (<0.2%). The second cartridge contained 5% of the D3 in the first cartridge. However, since the D3 quantity in the second cartridge was in the same range as the method blank, this must be regarded as an upper limit for possible breakthrough.

3.4. Repeatability

The median % difference between the sample pairs collected during the field campaign is shown in Table 1. The median % difference ranged from 2% for D5 to 8% for L6. This indicates that the repeatability of the method was good.

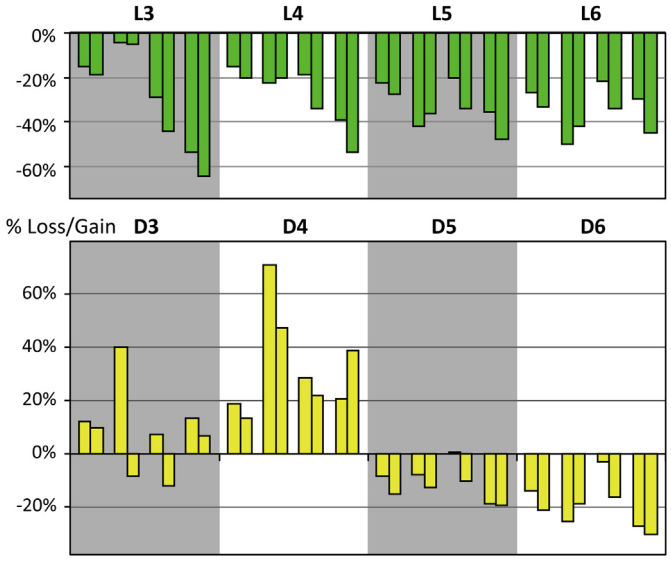

Fig. 1. Change in the quantity of VMS in air samples following storage in the freezer at −17 °C. Each pair of bars represents a pair of samples collected on the same day. The first pair of samples was stored for 5 d, the other 3 pairs for 7 d. In each case the change was calculated with respect to a parallel sample collected on the same pump that was extracted immediately after the end of the 24 h sampling period. The upper panel shows the results for the lVMS; the lower panel shows the results for the cVMS.

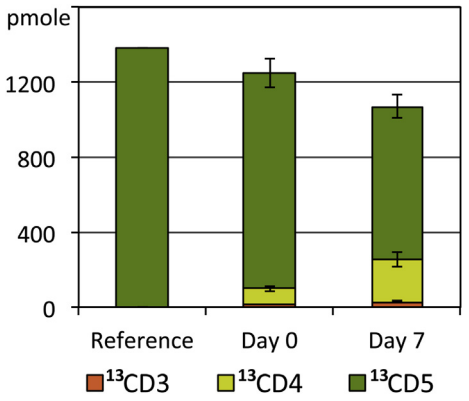

Fig. 2. Formation of $^{13}C_3$-D3 and $^{13}C_4$-D4 following application of $^{13}C_5$-D5 to the sampling cartridge via the gas phase. The amounts (in pmole) in the reference standard applied to the cartridges, in cartridges extracted immediately after standard application, and in cartridges extracted after 7 d of storage (mean, standard deviation, $n = 6$ for each group) are shown.

3.5. Storage

The percentage difference between the sample pairs is shown in Fig. 1. For all lVMS as well as D5 and D6, the sample that had been stored contained less than the sample that had been extracted immediately. The difference averaged 12% for D5, or ~1.8% per day, which can be compared with the ~1% per day observed in the earlier study (Kierkegaard and McLachlan, 2010). It was somewhat higher for D6 (20%), while the lVMS all showed an average deviation of ~30%. These values can be compared with the repeatability results in which sample pairs from the same pump were compared in the same manner, albeit without differences in storage. Here no consistent bias for one of the sampling heads was observed and the average difference ranged from 2% for D5 to 8% for L6 (see above). The differences for the storage experiment show both a clear bias and are larger. Possible explanations include transformation of the chemicals in the cartridge (see below) or a decrease in extractability during storage.

For D3 and D4 the opposite trend was observed; the stored samples contained on average 9% (D3) and 33% (D4) higher concentrations than the samples extracted immediately (Fig. 1). The corresponding numbers from the repeatability experiment are 7% and 3%. For D4 the storage resulted in a systematic variability that clearly deviated from the reproducibility experiment.

To account for the influence of storage, the mean storage effect in % per day was used to correct the data from the sampling campaign for all analytes. Since the maximum storage period was 6 d, the minimum and maximum correction factors were 0.66 (L6) and 1.3 (D4).

3.6. Transformation products

The amounts of ^{13}CD3, ^{13}CD4, and ^{13}CD5 in the reference standard applied to the cartridges, in the extracts of the cartridges that were processed immediately, and in the extracts of the cartridges that were processed after 7 d of storage are shown in Fig. 2. A clear formation of ^{13}CD4 and ^{13}CD3 was observed. While the amount of ^{13}CD5 decreased by ~20% after application and a further ~20% following storage, this was accompanied by an increase in both ^{13}CD3 and ^{13}CD4. In the case of ^{13}CD4 the increase amounted to 40% of the loss of ^{13}CD5, expressed on a molar basis, suggesting that much of the ^{13}CD5 was converted into ^{13}CD4. The formation of ^{13}CD3 was approximately an order of magnitude lower (5% of the

loss of ^{13}CD5) than for ^{13}CD4. No formation of ^{13}CD6 or of ^{13}CL3-^{13}CL5 was observed.

It is known that when D4 is heated in solvent in the presence of a catalyst a series of cVMS is formed that contain up to >100 siloxane units (Brown and Slusarczuk, 1965; Carmichael et al., 1967). Clearly cVMS can under appropriate conditions react by ring opening, loss of a siloxane unit, followed by ring closing. The ring-chain equilibria for cVMS show D4 to be the most stable ring size, and that the stability decreases with increasing ring size with the exception of a small second maximum at 15 siloxane units (Brown and Slusarczuk, 1965). Thus one could expect that at trace levels larger cVMS would under appropriate conditions react to form smaller cVMS. The ENV+ cartridges would appear to be an appropriate environment for such reactions. It remains to be explored whether such reactions are common in media in the natural environment.

The observed formation of D3 and D4 between the cartridges processed immediately and those stored for 7 d is consistent with the results of the storage experiment, where storage was observed to lead to an increase in concentrations (Fig. 1). The fact that the relative increase in D3 and D4 concentrations was greater than the relative decrease in D5 concentrations can be explained by the higher absolute concentrations of D5. The measured D5 concentration in the storage experiment was 4–6 times higher than the D4 concentration and 19–28 times higher than the D3 concentration. Thus the transformation of a small fraction of the D5 can have a large impact on the concentration of D3 and D4.

The presence of ^{13}CD3 and ^{13}CD4 in the cartridges that were processed immediately indicates that ^{13}CD5 also reacts during sampling to form these products. This is not necessarily inconsistent with the results of the sampling efficiency experiment which showed a mean recovery of D4 of 79% versus 77% for D5. In that experiment the standard mixture contained similar concentrations of D3, D4, and D5, so the transformation of a modest quantity of D5 to D4 and D3 would have resulted in only a modest change in the concentrations of all 3 analytes. However, in the environment the concentrations of D5 are much higher, and the transformation of a modest quantity of D5 can have a significant impact on the concentrations of D3 and D4. If one assumes that the formation rates measured during the transformation experiment can be applied to the storage experiment, on the order of 40% of the D3 and 80% of the D4 concentrations can be explained by this artifact. However, since we have no understanding of the variables that influence this reaction and thus how the reaction rate may vary with sampling conditions, we do not consider it justifiable to apply the formation rates measured in the transformation experiment to the field data. Instead we have reported the D3 and D4 data corrected for storage formation only. They must be regarded as upper boundaries for the concentrations; the true values may be considerably lower.

The experiment with L6 showed no evidence for the formation of shorter chained lVMS or cVMS.

3.7. LOQ

The method's limit of quantification (LOQ) was limited by blank contamination for all the cVMS and by noise in the detection signal for lVMS (no lVMS were detected in the blanks). For the cVMS the LOQ was calculated as the mean blank plus 10 times their standard deviation (based on 28–30 field blanks). For the lVMS the LOQ was calculated from a signal to noise ratio of 10. The results, using a representative sample volume of 12 m^3, are shown in Table 1. They ranged from 3.8 pg m^{-3} for L3 to 270 pg m^{-3} for D4. The LOQs were lower than the minimum concentrations measured in the field campaign for D3–D6, L3 and L4.

During a period of 2 weeks from 10 to 23 November highly elevated blanks of D3, D4, and D6 were observed. This was linked to a plastic rod used to push the upper frit onto the ENV+ bed when packing the cartridges. Despite cleaning with solvents, this rod still contaminated the cartridges. After it was replaced with a glass rod the blanks returned to normal. These elevated blanks were not used to calculate the LOD and LOQ in Table 1. They were used to calculate separate LOQs for these 2 weeks however, which were used to censor the data.

Table 2
Summary statistics of the VMS concentrations in air at Tystberga (minimum, maximum and mean, n = 56–82). The concentrations reported for Malin Head, Ireland, are listed for comparison. Rate constants for the reaction of some VMS with OH radicals are also given.

	Concentrations Tystberga (ng m^{-3})			Malin head[a] (ng m^{-3})	Rate Constant ($\times 10^{-12}$ cm^3 mol^{-1} s^{-1})
	Minimum	Maximum	Mean		
L3	0.056	0.54	0.20		1.83[b]
L4	0.012	0.048	0.025	0.073	2.66[b]
L5	<0.003	0.033	0.013	0.043	
L6	<0.008	0.080	0.022		
D3[c]	0.42	2.4	0.94	11	
D4[c]	1.8	8.0	3.5	6.2	1.01[d]
D5	5.6	28	13	15	1.55[d]
D6	0.48	2.7	1.0	1.9	

[a] Genualdi et al. (2011).
[b] Markgraf and Wells (1997).
[c] Upper boundary of true concentration due to formation from D5 during sampling.
[d] Atkinson (1991).

3.8. VMS concentrations in Swedish background air

The air concentrations measured during the field campaign are given in Table S3, while summary statistics (minimum, maximum and mean) are given in Table 2.

The concentrations of D5 measured in this study (5.6–28 ng m^{-3}) were comparable with the concentrations measured during January 2009 at another rural site in Sweden located 115 km west of Tystberga (4.7–8.8 ng m^{-3}) (McLachlan et al., 2010). In that earlier paper it was reported that the measured D5 concentrations agreed well with the D5 concentrations predicted by an atmospheric fate and transport model of the northern hemisphere using D5 emissions estimates based on sales statistics for personal care products.

The concentrations of D4 (1.8–8.0 ng m^{-3}) from this study (which are upper estimates, see above) can be compared with earlier reports of 35, 78 and 300 ng m^{-3} in air at a background station in Sweden (Kaj et al., 2005a) and 2400 ng m^{-3} for a rural site in Denmark (Kaj et al., 2005b). An analogous comparison can be made for D6; the 0.5–2.7 ng m^{-3} from this study versus the earlier reports of <12, 11 and 77 ng m^{-3} in air at a background station in Sweden (Kaj et al., 2005a) and 440 ng m^{-3} for a rural site in Denmark (Kaj et al., 2005b). Similar discrepancies between the earlier screening studies and our measurements were also observed for D5, but it was not possible to explore possible explanations due to the lack of QA/QC information in the earlier screening studies.

Recently Krogseth et al. (2013a) reported cVMS concentration in air on Svalbard. They collected samples at the same time as the samples in this study (Nov.–Dec. 2011). The concentrations of D5 (2.3–3.7 ng m^{-3}) and D6 (0.2–0.8 ng m^{-3}) measured at this Arctic location were somewhat lower than the concentrations measured in this study. The relatively small gradient between Tystberga and the remote Arctic site is a reflection of the long atmospheric half-life of these chemicals during the polar winter when the photo-transformation rate is low.

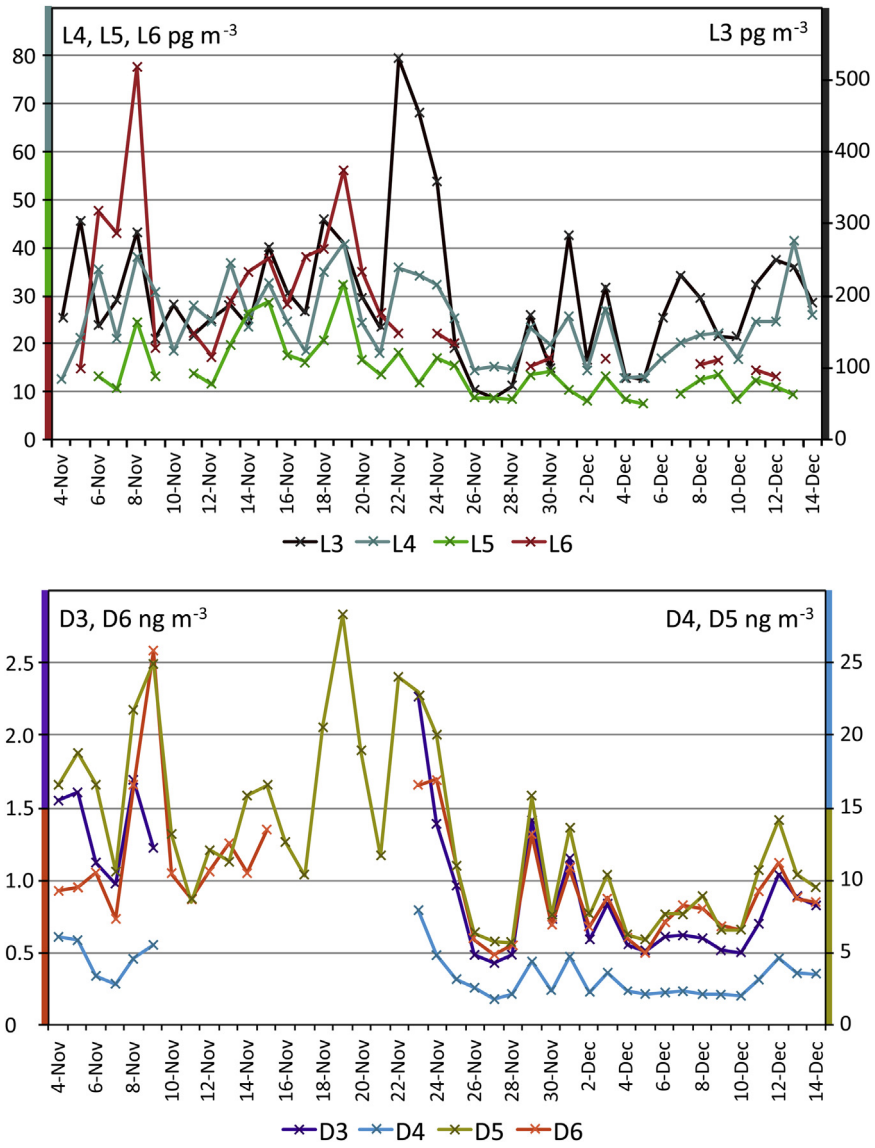

Fig. 3. Concentrations of lVMS (upper panel) and cVMS (lower panel) in air in Tystberga, Sweden. Note the different units used in the two panels.

Genualdi et al. (2011) determined L3–L5 and D3–D6 concentrations in air using passive samplers deployed at several locations around the world. Malin Head, a background station in Ireland, was the location closest to Tystberga. The concentrations in their sampler are shown in Table 2. For most chemicals they are a factor 2–3 higher than measured in this study. One possible explanation is the closer proximity of Malin Head to major source regions. The model simulations of D5 concentrations in the Northern Hemisphere in McLachlan et al. (2010) indicate that concentrations will be higher at Malin Head than at Tystberga. On the other hand, the samples from Malin Head were collected in the late spring and early summer when atmospheric concentrations are expected to be at a minimum due to phototransformation, whereas the samples from this study were collected in the later autumn and early winter, which is expected to represent the peak in the seasonal cycle of D5 concentrations (McLachlan et al., 2010). Much larger differences between the two studies were observed for D3, with the concentrations at Tystberga (which are upper boundaries, see above) 15 times lower than at Malin Head. No explanation can be offered for this. Measurements from wastewater treatment plants and landfills have shown concentrations of D3 that are an order of magnitude less than D4 (Rasi et al., 2010). In this study the concentration of D3 was approximately 5 times lower, while D3 was reported to be almost twice as high as D4 at Malin Head.

The temporal variability of the VMS concentrations is illustrated in Fig. 3. The concentrations fluctuate by a factor of 2–3 on a time scale of 1–4 d. This is similar to the variability observed in the previous study of D5 (McLachlan et al., 2010). As discussed there, the variability in D5 concentrations was due to changing patterns in atmospheric transport. Air masses that pass over highly populated areas of Europe on their way to Tystberga will load up with VMS and display higher concentrations. In winter temporal variability in regional sink mechanisms is not expected to influence the concentrations. Phototransformation is the primary removal process for D5 in the atmosphere. Model sensitivity studies showed that the concentrations of D5 during the winter months are insensitive to the reaction rate constant for phototransformation (McLachlan et al., 2010). This indicates that phototransformation at the regional scale does not influence D5 concentrations. The primary mechanism for D5 elimination in winter is hemispheric scale

Table 3
Matrix of the Pearson correlation coefficients for the concentrations of the different VMS. All correlations were significant at the 1% level unless otherwise labeled.

Versus	D3	D4	D5	D6	L3	L4	L5
D4	0.94						
D5	0.91	0.89					
D6	0.70	0.72	0.89				
L3	0.77	0.75	0.70	0.53			
L4	0.56	0.50	0.69	0.64	0.64		
L5	0.57	0.40[a]	0.65	0.47	0.39[a]	0.62	
L6	0.45[b]	0.06[b]	0.45[a]	0.20[b]	0.16[b]	0.55	0.63

[a] Significant at the 5% level.
[b] Not significant at the 5% level.

advection to lower latitudes, where phototransformation is an effective sink.

The temporal variability of the different VMS was compared by correlating the concentrations (mean of the sample pairs) against each other. The matrix of Pearson correlation coefficients r is given in Table 3. All correlations were significant at the 1% level with the exception of L6, which correlated only with L4 and L5 at the 1% level and D5 at the 5% level, and L5, for which the correlation with D4 and L3 was only significant at the 5% level. There was a strong correlation amongst the D3, D4 and D5, with r of 0.89 or more, and D5 was also strongly correlated with D6 ($r = 0.89$). This is also apparent in Fig. 3, where the cVMS show similar patterns of temporal variability. It is possible that the transformation of D5 to D4 and D3 contributed to the good correlations between these chemicals. The correlations amongst the lVMS and between the lVMS and cVMS were weaker. The particularly weak correlations for L6 indicated that its temporal variability differed the most from that of the other chemicals.

There are different possible explanations for the differences in the temporal variability of the VMS. One is differences in the mechanisms for removal from the atmosphere. The VMS are very volatile chemicals, so that atmospheric deposition is expected to be negligible compared to phototransformation (Whelan et al., 2004). The rate constants for the reaction with OH radicals of L3, L4 and D4 are similar to that of D5 (see Table 2). Given that the modeled concentrations of D5 in winter are insensitive to the reaction rate constant (a factor of 4 increase in the rate constant decreased the predicted D5 concentration by ~25% (McLachlan et al., 2010)), these small differences in reaction rate constants are unlikely to explain differences in the temporal variability between these VMS. A trend of increasing reaction rate constant with increasing number of siloxane groups is seen for both the cVMS and the lVMS. Thus L6 can be expected to have the highest reaction rate constant. This is the chemical for which phototransformation on a regional scale is most likely to be a significant removal process. This may explain why the temporal variability of L6 differed the most from that of the other compounds.

If differences in the atmospheric removal rates of the chemicals were insignificant for most of the VMS, then the differences in the concentrations of the chemicals must have been related to differences in the emissions. Consequently, the differences in the temporal variability of the VMS concentrations must have been due to differences in the temporal or the spatial distribution of emissions in the air shed that impacted the sampling site. The good correlations amongst the cVMS indicate that there were no large differences in the temporal and spatial distribution of the emissions of these compounds. Emissions of D4, D5, and D6 to air in Europe have been estimated to originate primarily from personal care product use and residuals of monomers in PDMS, whereby the fraction attributed to residual monomers varies from 5% for D5 to 66% for D4 (Brooke et al., 2009a–c). The poorer correlations of the lVMS with the cVMS indicate that the lVMS may have had a different temporal or spatial distribution of emissions. Much less information is available on the sources of lVMS emissions to air. A Canadian screening assessment of L3 identified sources for emissions to air that were similar to those for the cVMS (personal care products, residual monomers), but no quantitative information was available (Environment Canada and Health Canada, 2011). Hence no further conclusions can be drawn about the causes of the differences in temporal variability between the chemicals.

As noted above, in winter the major mechanism for the elimination of D5 from the atmosphere is hemispheric scale advection to lower latitudes where it is subjected to phototransformation. This is expected to be the case for the other VMS, given their high volatility and comparable phototransformation rate constants. Since the rate constant for advection to lower latitudes is the same for all chemicals, differences in concentrations of the chemicals will be largely due to differences in emissions. Referring to Table 2, this indicates that the emissions of D5 were highest and that the emissions of the other chemicals decreased in the order D4 (27% of D5) > D6 (8%) > D3 (7%) > L3 (2%) > L4 (0.2%) > L6 (0.2%) > L5 (0.1%). Note that there are some uncertainties with this assessment. Since L6 has the highest rate constant for phototransformation, this may have been a significant loss process on a regional scale, in which case the emissions would be higher. D3 is subject to rapid hydrolysis, and thus hydrolysis in aqueous aerosols may be a significant additional loss mechanism for this chemical. Finally, the reported values for D3 and D4 were upper boundaries, and the true concentrations may have been markedly lower.

The concentration ratios can be compared with emissions estimates. The emissions of D4, D5, and D6 to air in Europe have been estimated to be > 1.4, >15.6, and 2.2 kilotonnes per year, respectively (Brooke et al., 2009). Normalized, the estimated emissions of D4 are 9% of the estimated emissions of D5, which is considerably lower than the 27% derived from the concentrations in air (Table 2). This discrepancy could be due to the fact that the D4 concentrations in air were upper boundaries. For D6 the agreement is better: 14% according to the emissions estimates and 8% according to the concentrations in air. It should be noted that the emissions estimates for D4 and D5 represented lower boundaries, as emissions from some source classes could not be reported for proprietary reasons (Brooke et al., 2009a–b). This illustrates one of the problems in estimating emissions via emissions inventories. For these chemicals, estimating emissions from the concentrations in air during winter is an attractive alternative. Note that extrapolation of emissions from winter to summer is reasonable when personal care product use is the primary source of emissions, but it may not be when emissions have other sources.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.08.001.

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