Chemosphere 255 (2020) 126967

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Reducing sampling artifacts in active air sampling methodology for remote monitoring and atmospheric fate assessment of cyclic volatile methylsiloxanes

Nicholas A. Warner [a, b, *], Vladimir Nikiforov [a], Ingjerd S. Krogseth [a], Stine M. Bjørneby [c], Amelie Kierkegaard [d], Pernilla Bohlin-Nizzetto [c]

[a] NILU-Norwegian Institute for Air Research, Fram Centre, NO-9296, Tromsø, Norway
[b] Department of Arctic and Marine Biology, The Arctic University of Norway (UiT), Hansine Hansens veg 18, NO-9037, Tromsø, Norway
[c] NILU-Norwegian Institute for Air Research, NO-2027, Kjeller, Norway
[d] Department of Environmental Science and Analytical Chemistry, Stockholm University, SE-106 91, Stockholm, Sweden

HIGHLIGHTS

- Improved sampling methodology for atmospheric monitoring of cVMS.
- Sorbent related artifacts (degradation/formation) avoided with new sampling sorbent.
- Higher concentrations of D5 and D6 detected in Arctic air with improved methodology.
- Insights gained on seasonal atmospheric degradation pathways for cVMS.

ARTICLE INFO

Article history:
Received 12 March 2020
Received in revised form
29 April 2020
Accepted 1 May 2020
Available online 4 May 2020

Handling Editor: Keith Maruya

ABSTRACT

Active sampling methodology for atmospheric monitoring of cyclic volatile methylsiloxanes (cVMS) was improved to reduce sampling artifacts. A new sorbent, ABN Express (ABN), was evaluated for storage stability and measurement accuracy. Storage stability of cVMS on ABN showed less than 1% degradation of the individual ^{13}C-labelled octamethylcyclotetrasiloxane ($^{13}C_4$-D4), decamethylcyclopentasiloxane ($^{13}C_5$-D5) and dodecamethylcyclohexasiloxane ($^{13}C_6$-D6) after 14 days storage at room temperature and at −20 °C whereas significant degradation was observed on ENV+ sorbent at room temperature (37–62 %) and −20 °C (9–16 %). $^{13}C_4$-D4 formed on ENV+ spiked with $^{13}C_5$-D5, and both $^{13}C_4$-D4 and $^{13}C_5$-D5 formed on ENV+ spiked with $^{13}C_6$-D6. However, this was not observed on the ABN sorbent. Performance of ABN was compared to ENV+ through an 8-month Arctic sampling campaign at the Zeppelin Observatory (Ny Ålesund, Svalbard). Good agreement between ABN and ENV+ was observed for D4 in the spring/summer months. However, D5 and D6 was found to be consistently higher on the ABN sorbent during this time period with D6 showing the greatest deviation. During the winter months, larger deviations were observed between ABN and ENV+ sorbents with a factor of 4 times higher atmospheric concentrations of both D5 and D6 found on ABN; indicating sorbent related degradation on ENV+. Our findings show that the ABN sorbent provides greater stability and accuracy for atmospheric monitoring of cVMS. Implications of these improvements towards atmospheric fate processes will be discussed.

1. Introduction

The presence of cyclic volatile methylsiloxanes (cVMS) and the potential risk they pose has been an ongoing debate between industry, regulators and scientists for more than a decade. Content of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) in wash-off personal care products is restricted below 0.1 % as of February 2020 within European Union

* Corresponding author. Department of Environmental Chemistry, NILU-Norwegian Institute for Air Research, Fram Centre, Hjalmar Johansens gate 14, NO-9296, Tromsø, Norway.
E-mail addresses: nw@nilu.no, nicholas.warner@nilu.no (N.A. Warner).

https://doi.org/10.1016/j.chemosphere.2020.126967

(ECHA, 2018) due to their classification as persistent, bioaccumulative and toxic (i.e., D4) and very persistent and very bioaccumulative (i.e., D5) under the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). These restrictions have been recently proposed to be extended to include dodecamethylcyclohexasiloxane (D6) through REACH where allowable concentration limits in all consumer and professional products is to be reduced to 0.1 % wet weight (ECHA, 2019). Due to their volatile nature and long-range transport potential (LRTP), atmospheric monitoring of cVMS is essential to provide data for implementation of emission regulations by authorities as well as to evaluate effectiveness of future chemical restrictions put in place, particularly in remote regions.

Passive and active sampling methodologies have both been utilized for atmospheric monitoring of cVMS (McLachlan et al., 2010; Genualdi et al., 2011; Kierkegaard and McLachlan, 2013; Krogseth et al. 2013a, 2013b; Ahrens et al., 2014; Companioni-Damas et al., 2014; Gallego et al., 2017; Rauert et al., 2018). Although passive sampling is advantageous considering its ease of use and flexibility in terms of deployment sites (i.e., no power requirements), it is still a semi-quantitative methodology. Consequently, active sampling is relied upon for quantitative measurements and as a tool to provide high temporal resolution in atmospheric concentrations (hours to days) compared to passive sampling techniques (weeks to months).

However, the most commonly used active sampling methodology for cVMS originally developed by Kierkegaard and McLachlan (2010); using Isolute ENV+ (hydroxylated polystyrene-divinyl benzene copolymer) as a sorbent suffers from sampling artifacts. This technique showed degradation/formation of the individual cVMS occurring on the ENV+ sorbent, requiring correction of measurements depending on the length of deployment and storage time (Kierkegaard and McLachlan, 2010, 2013; Krogseth et al., 2013). The degradation of D5 was observed in an experiment where ENV+ cartridges were spiked with $^{13}C_5$-D5 via the gas phase. In addition, subsequent formation of $^{13}C_4$-D4 and ^{13}C-hexamethylcyclotrisiloxane ($^{13}C_3$-D3) also occurred within a day after spiking and increased over a 7-day storage period (Kierkegaard and McLachlan, 2013). Loss of D4 and D6 on ENV+ with increasing storage time has also been observed, indicating degradation of both D4 and D6 (Kierkegaard and McLachlan, 2013; Krogseth et al., 2013a). However, mechanisms of loss/degradation of D6 on ENV+ have yet to be investigated. These sampling artifacts have introduced uncertainties in previously measured concentrations and hinder our knowledge and understanding of cVMS in the atmosphere. Based on this, improvements of the current active air sampling methodology for cVMS (using ENV+) is required in order to improve the accuracy of atmospheric concentrations and fate assessment of cVMS.

In this study, we evaluated a new sorbent, ABN Express (Biotage, Sweden; referred from here on as ABN), in terms of its stability and sampling accuracy for atmospheric monitoring of cVMS by comparing its performance to the current sampling methodology utilizing ENV+. Performance between ABN and ENV+ was also assessed for Arctic atmospheric monitoring of cVMS through comparison of atmospheric concentrations collected over an 8-month period at the Zeppelin observatory, Ny-Ålesund, Svalbard (79 °N, 12 °E). The results of this field sampling campaign and implications towards understanding atmospheric fate processes of cVMS will be discussed.

2. Methods and materials

2.1. Active sampler preparation and extraction

Two different hydroxyl-substituted polystyrene-divinylbenzene based sorbents were evaluated in this study: Isolute ENV+ (90 μm particle diameter, Biotage, Sweden) and Isolute ABN (30 and 50 μm particle diameter, Biotage, Sweden). Although these sorbents are similar in chemistry, the properties of the OH group differ within the polystyrene-divinylbenzene structure. The OH groups in ENV+ are attached directly to the aromatic moiety and, thereby, weakly acidic (Fig. 1B) whereas in ABN they are neutral, attached to an alkyl moiety (R-OH, Fig. 1A).

Bulk sorbent material of ENV+ was purchased directly whereas 6 mL prepacked solid phase extraction (SPE) cartridges of ABN sorbent were purchased and unpacked to obtain the amount of material needed for sampler preparation. Air samplers were prepared and extracted following procedures described by Krogseth et al. (2013a) with 120 mg of ENV+ or ABN packed into 25 mL polyethylene (PE) cartridges. Briefly, the sorbent packed cartridges were cleaned with 14 mL of dichloromethane followed by equal volume of *n*-hexane and dried overnight in a clean cabinet to avoid contamination. Once dry, cartridges were capped with PE stoppers to prevent contact with air, wrapped in aluminum foil, and stored at −20 °C in sealed 1 L low density polyethylene containers until use. After sampling, cartridges were spiked with 20 μL of ^{13}C–labelled standard mixture (1 ng μL^{-1}) containing $^{13}C_8$-D4, $^{13}C_{10}$-D5, $^{13}C_6$-D6 (Cambridge Isotope Laboratories, UK) and extracted with 4 mL of *n*-hexane. The collected extract was spiked with 20 μL of Tetrakis(trimethylsilyloxy)silane (M4Q) (200 ng mL^{-1}) as a syringe standard and stored at −20 °C before analysis.

2.2. Instrumental analysis

Extracts were analyzed on an Agilent 7890A gas chromatograph (GC) connected to an Agilent 5975C mass spectrometer (MS) detector and a Gerstel MPS3 autosampler. The GC injector was equipped with a Merlin microseal septum and a 4.0 mm I.D. gooseneck splitless liner with deactivated glass wool (Restek, USA). A 5 μL volume was injected at 200 °C using concurrent solvent recondensation-large volume injection (spitless overflow) (Companioni-Damas et al., 2014) onto a 5 m Rxi guard column (Restek, 0.32 mm I.D.) coupled to a 30 m DB-5 column (Agilent

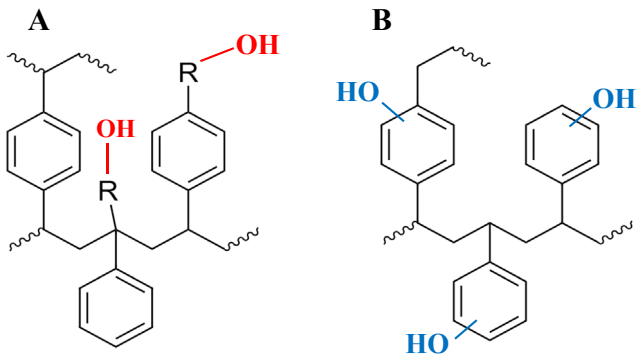

Fig. 1. Chemical structure of ABN Express (A) and ENV+ (B) sorbents.

Technologies, 0.25 mm I.D., 0.25 μm film thickness). Separation was carried out under constant flow conditions (1 mL min^{-1}) using Helium as a carrier gas (purity 5.0). The GC oven temperature program started at 40 °C for 1 min, followed by 10 °C min^{-1} up to 150 °C and 35 °C min^{-1} to 300 °C with a final hold time of 4 min. The MS ion source was operated at 230 °C and the quadrupole at 150 °C. Two ions were monitored for each compound (D4: *m/z* 207 and 281; $^{13}C_4$-D4: 284 and 285; $^{13}C_8$-D4: 287 and 288; D5: 267 and 355; $^{13}C_5$-D5: 359 and 360; $^{13}C_{10}$-D5: 364 and 272; D6: 341 and 429; $^{13}C_6$-D6: 434 and 435). Non-labelled D4 (99% purity, Fluka, Switzerland), D5 (97% purity, Fluka, Switzerland), and D6 (95% purity, Gelest Inc., PA, USA) were used in six-point calibration curves (5 ng mL^{-1} to 200 ng mL^{-1}, $R^2 = 0.99$) for quantification using MassLynx v4.2 software (Waters Corporation, USA).

2.3. Sorbent-related stability, sampling repeatability and breakthrough assessment

Individual cartridges packed with either ABN or ENV+ sorbent material was spiked with 50 μL of either $^{13}C_4$-D4 (0.84 ng μL^{-1}), $^{13}C_5$-D5 (0.63 ng μL^{-1}) or $^{13}C_6$-D6 (0.60 ng μL^{-1}) to the upper frit with single isotopically labelled standards. After spiking, one drop of water was added on top of the upper frit to simulate humidity conditions, followed by 200 μL of DCM to evenly distribute spiked standards on the sorbents. Cartridges were then left for 2 h inside a clean cabinet to dry. One set of ABN and ENV+ cartridges were immediately extracted after the drying process to determine the initial amount of isotopically labelled standard present on the sorbent. The remaining cartridges were sealed with PE stoppers and stored up to 14 days at −20 °C and room temperature (20-23 °C) conditions to assess the stability of D4-D6 on ABN and ENV+.

Repeatability experiments of cartridges packed with ABN were performed at a sampling station located outside the Norwegian Institute of Air Research in Kjeller, Norway between May to June, 2018. Average daily temperatures during sampling ranged between 8–22.5 °C in May, and 12.9–22.7 °C in June. Experimental design was similar to that described by Krogseth et al. (2013a). In brief, sampling cartridges containing ABN were connected in parallel to two separate GAST DOA-P509-BN (GAST Manufacturing Inc, Mi, USA) air pumps using polytetrafluoroethylene (PTFE) tubing. Air was sampled at a rate of 1.0 and 1.14 m^3 $hour^{-1}$ between replicate samplers using a diaphragm gas volume meter connected in series to determine the air volume sampled. To avoid contamination of the air samplers, air pumps were placed in an enclosed structure while the PTFE tubing was directed to the exterior of the structure to connect the sampling cartridges (Fig. A.1). The sampling cartridges were placed in a downwards orientation and surrounded by a plastic rain shield to protect from precipitation. Repeatability was assessed for both one- and three-day sampling periods with average air volumes of 26.0 ± 2.1 and 76.8 ± 5.7 m^3 (Table A.1), respectively.

Breakthrough experiments of cartridges packed with ABN were carried out in the same manner as the repeatability experiments except with a second cartridge packed with ABN connected in series (Fig. A.2). Air was sampled at a rate of 0.81 and 0.9 m^3 $hour^{-1}$ between replicate samplers. The sampling cartridge (front cartridge) and the breakthrough cartridge (back cartridge) were extracted separately after 3 days sampling to evaluate if breakthrough occurred over the 3-day sampling period.

2.4. Field sampling comparison of active air sampling methodology

Performance of ABN sorbent was evaluated against ENV+ sorbent during a weekly field sampling campaign from May 2017 to January 2018 (week 18 (2017) – week 1 (2018)) at the Zeppelin observatory station located in Ny Ålesund, Svalbard. Active air sampling was carried out in parallel with one ABN and one ENV+ sorbent with a sampling time of approximately 3 days. The air volume sampled was 40–60 m^3 for ABN and 60–80 m^3 for ENV+ (Table A.2). Difference in volumes collected between the sorbents is attributed to smaller particle diameter size of ABN utilized in the field campaign (i.e., 30 μm), with less volume being collected over time due to higher air flow restriction. Air concentrations reported using ENV+ as a sampling sorbent in this study, as well as previous reports for cVMS at Zeppelin station have been corrected using methodology described by Krogseth et al., 2013a to account for sorbent mediated degradation with sampling/storage time.

2.5. Quality assurance/quality control

All glassware was burned at 450 °C for 8 h with all sample preparation and handling occurring within an ISO class 7 clean cabinet (Bigneat Ltd. UK) equipped with HEPA and carbon filters for particle and gas phase filtration, respectively, to avoid contamination from the indoor air. Only newly opened bottles of solvents were used in sample processing and extraction and were only opened within the clean cabinet to avoid contamination. Personnel involved in sample preparation, field sampling, extraction and analysis did not use personal care products, which siloxanes are used in as major ingredients (Horii and Kannan, 2008).

A minimum of three lab blanks were run for each extraction batch of samples. In repeatability and breakthrough experiments, lab blanks consisted of clean SPE sorbent cartridges that were not exposed in the field. Samples were blank corrected based on the average concentrations determined in laboratory blanks. Blank results for repeatability and breakthrough experiments are reported in Table A.3. Field blanks for sampling at the Zeppelin Observatory consisted of clean SPE sorbent cartridges that were connected to the pump, having air drawn through for 15 s, then removed and sealed to account for any background contamination occurring during sample mounting and transport. Method detection limits (MDL) and quantification limits (MQL) were calculated on a ng/sample basis using 3- and 10-times lab or field blank signal variation, respectively (Tables A.3 and A.4). Detection and quantification limits on a ng/m^3 basis were calculated by using the average volumes collected for 1-day (26.0 m^3) and 3-day (76.8 m^3) sampling collections (i.e., repeatability and breakthrough experiments) and average volumes collected on ENV+ (76 m^3) and ABN sorbents (49 m^3) for field sampling at Zeppelin station.

3. Results and discussion

3.1. Sorbent storage stability for cVMS

Comparison of sorbent storage stability for $^{13}C_4$-D4 on ABN and ENV+ sorbents showed the highest losses to occur on ENV+ after 14 days at room temperature with over 60% loss of the original amount spiked. Whereas loss of $^{13}C_4$-D4 was less (16 %) on ENV+ when stored at −20 °C (Fig. A.3). On ABN, loss of $^{13}C_4$-D4 (10 %) was smaller compared to ENV+ at both room temperature and −20 °C. Similar losses observed for $^{13}C_4$-D4 on ABN at room temperature and −20 °C suggests that the losses are due to volatilization while spiking the cartridges and not due to degradation during storage. Similar observations were observed by Krogseth et al. (2013a) where after spiking ENV+ sorbent cartridges followed by immediate extraction gave lower recoveries of both D3 (60 %) and D4 (90 %), indicating losses from volatilization had occurred. The addition of water to the sorbent to simulate humidity could also promote volatilization of $^{13}C_4$-D4 considering its

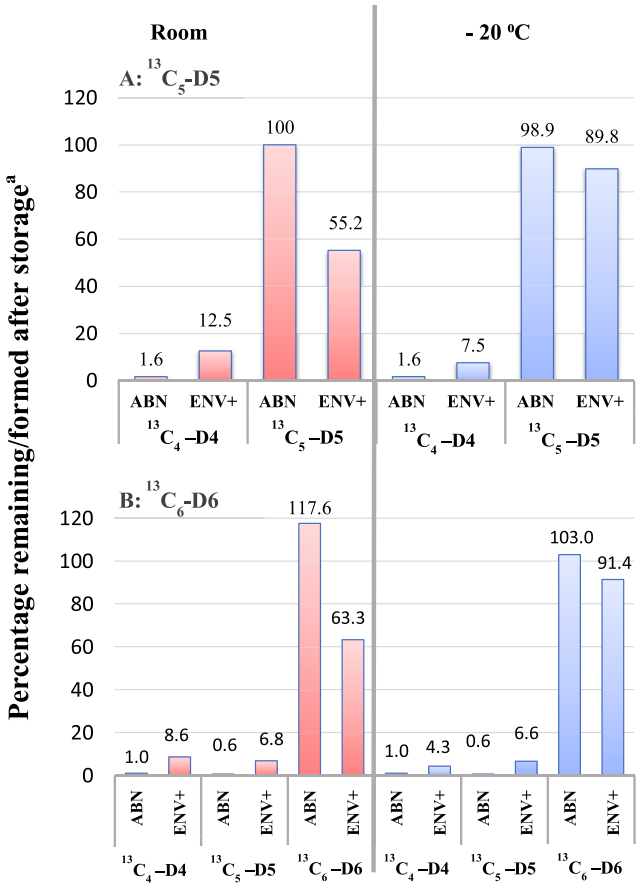

Fig. 2. Percentage of $^{13}C_5$-D5 (A) and $^{13}C_6$-D6 (B) remaining and percentage of $^{13}C_4$-D4 and $^{13}C_5$-D5 formed on ENV+ and ABN Express sorbents after storage for 14 days at room temperature and −20 °C. [a]All percentages are determined on a nanomole basis.

appreciable Log K_{ow} (6.9) and higher volatility compared to D5 and D6. However, loss of $^{13}C_4$-D4 on ABN is independent of storage temperature whereas 60 % loss was observed on ENV+ at room temperature; showing ABN to display far greater stability compared to ENV+.

As was observed for $^{13}C_4$-D4, significant loss of both $^{13}C_5$-D5 (Fig. 2A) and $^{13}C_6$-D6 (Fig. 2B) occurred on ENV+ at room temperature, whereas the degree of loss was less (≤10 %) with storage at −20 °C. In addition to loss observed for $^{13}C_5$-D5, formation of $^{13}C_4$-D4 was also observed to occur on ENV+ at both room temperature and −20 °C (13 % and 8 % on a nanomole basis, respectively (Fig. 2A)). This is in agreement to earlier findings by Kierkegaard and McLachlan (2013), where formation of both $^{13}C_3$-D3 and $^{13}C_4$-D4 from degradation of $^{13}C_5$-D5 on ENV+ sorbent was observed. Worth noticing is the large difference in loss for $^{13}C_5$-D5 on ENV+ between room temperature and −20 °C storage conditions. However, little difference is observed in formation of $^{13}C_4$-D4 between these storage conditions. This is likely attributed to greater reaction activity occurring at room temperature where degradation loss of $^{13}C_4$-D4 was much greater (52 %) compared to −20 °C (6 %) (Fig. A.3). This indicates that the majority of $^{13}C_4$-D4 formed through degradation/rearrangement of $^{13}C_5$-D5 is further degraded at room temperature. In storage experiments for $^{13}C_6$-D6, formation of $^{13}C_5$-D5 and $^{13}C_4$-D4 were also observed at room temperature (6.8 and 8.6 %, respectively) and at −20 °C (6.6 % and 4.3 %, respectively (Fig. 2B)). Products of D6 sorbent-related degradation have not been previously studied. Contrary to the results observed on ENV+, no losses were observed for $^{13}C_5$-D5 and $^{13}C_6$-D6 on the ABN sorbent after 14 days at room temperature and −20 °C storage conditions. Formation of $^{13}C_4$-D4 and $^{13}C_5$-D5 accounted for less than 2 % of the initial spiked amount for both $^{13}C_5$-D5 and $^{13}C_6$-D6 under both storage conditions. Higher degradation on the ENV+ sorbent is hypothesized to be attributed to the somewhat acidic phenolic substituent within the divinylbenzene structure of the sorbent (Fig. 1B).

cVMS investigated in this study are known to degrade much faster under acidic conditions (i.e., hydrolysis half-life: 33 h to 4 days at pH 5 and 25 °C) compared to environmentally neutral conditions (hydrolysis half-life: 2.2–71 days at pH 7 and 25 °C) (Brooke et al., 2009a, b, c) where ring opening of the cyclic ring structure occurs. After ring opening of cVMS, formation of other cVMS oligomers has been shown to occur in soil media via hydrolysis and/or rearrangement reactions (Xu, 1998, 1999). This is supported by our findings here with the formation of $^{13}C_4$-D4 from $^{13}C_5$-D5 degradation, and formation of $^{13}C_4$-D4 and $^{13}C_5$-D5 from $^{13}C_6$-D6 degradation, most likely occurring through an acid-catalyzed hydrolysis and rearrangement reaction on the ENV+ sorbent. Thus, the reaction rate of cVMS degradation/formation may not only be affected by temperature (Fig. 2) but also by humidity/water content present on the sorbent.

3.2. Repeatability and breakthrough experiments

Evaluation of repeatability experiments was carried out for ABN over two different sampling durations; one- and three-day continuous sampling. For each sampling, two ABN samplers were connected in parallel to two separate sampling pumps where concentrations were compared to assess method repeatability. All concentrations from one- and three-day collections were above MQL for D4 (0.02–0.4 ng m^{-3}), D5 (0.04–0.5 ng m^{-3}), and D6 (0.02–0.1 ng m^{-3}), respectively. For one day sampling, good repeatability was observed between parallel samplers with average relative standard deviation (RSD) ranging from 5.5 to 6.7 % for the cVMS investigated (Table A.5A supporting information). Similar results were observed for three-day sampling collections where average RSD ranged from 2.1 to 6.8 % (Table A.5B). Methodology developed by Kierkegaard and McLachlan (2010) using 10 mg ENV+ cartridges reported difference in replicate samplers normalized to their mean concentration for D5 was less than 22 % for 88 % of their parallel samplings. With ABN, the normalized difference between replicate samplers to the mean concentration for D5 ranged from 1.7 to 13.5 %, showing acceptable sampling repeatability on ABN.

Breakthrough experiments were carried out over several three-day sampling periods for the ABN sorbent. Concentrations detected on the front and back sorbent cartridges connected in series (Fig. A.2) are reported in Table A.6. Concentrations for all cVMS were below the MQL on the back-sorbent cartridge. Percentage breakthrough was less than 0.41 % for D4 and D5 after 3 days of sampling (Table A.6). For D6, percent breakthrough of 2.4 and 2.5 % was observed in two of the three experiments (Table A.6).

3.3. Field sampling evaluation of ABN and ENV+ sorbent

Concentrations of cVMS in air at Zeppelin observatory were measured in parallel on ENV+ and ABN sorbent from week 18, 2017 to week 1, 2018 (Fig. 3 and Table A.7). Atmospheric concentrations of all cVMS on both sorbents were low during the spring and summer months and increased in the winter months, reflecting seasonality in OH radical mediated atmospheric degradation (McLachlan et al., 2010; Krogseth et al., 2013a). Reasonable agreement was observed for D4 on both ABN and ENV+ sorbents from

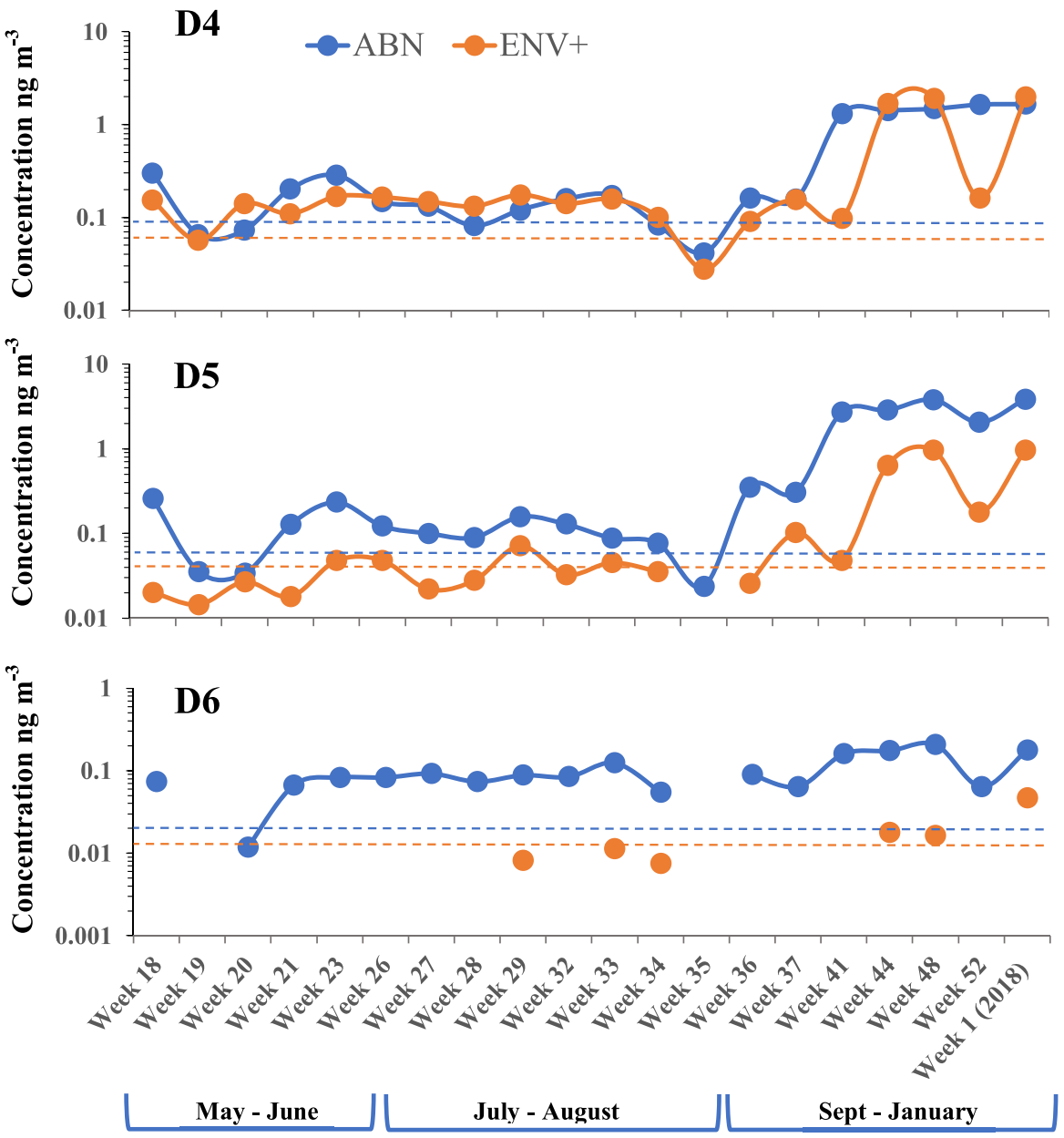

Fig. 3. Comparison of log normalized atmospheric concentration (ng m^{-3}) of cVMS measured at Zeppelin station from week 18 (2017) to week 1 (2018) between parallel samplers of ABN (blue line) and ENV+ sorbent (orange line). Dashed lines represent the MQL for ABN (blue) and ENV+ (orange). Weeks with no data reported represents concentrations below method detection limit (MDL). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

week 18 to week 37 with the ABN/ENV+ ratio for D4 ranging between 0.68 and 2.31. No clear difference was observed between the two sorbents. However, as concentrations increased during the fall to winter months (week 41 – week 1), larger deviations were observed between the two sorbents with higher concentrations occurring on ABN compared to ENV+ in most cases (ABN/ENV+ ratio: 0.77–13.5). Higher concentrations for D4 on ENV+ compared to ABN were only observed during weeks 44, 48 and week 1, whereas higher concentrations were observed on ABN during week 41 and 52, (Fig. 3, Table A.7). During the winter season, OH radical driven atmospheric degradation is limited due to the polar night conditions and low OH radical concentrations. Thus, we would expect levels of D4 to be consistently higher on ENV+ sorbent due to formation from D5, which is present in the atmosphere at higher concentrations. Degradation of D4 can continue to occur on the ENV+ sorbent, thus affecting its overall concentration. However, a decrease in atmospheric concentrations of D5 was also observed during weeks 41 and 52, while D6 was below MDL. This suggests a sampling error may have occurred during these time points on ENV+, thus explaining the lower reported cVMS concentrations.

In contrast to D4, atmospheric concentrations of D5 on the ABN sorbent were consistently higher compared to ENV+ throughout the entire sampling campaign (Fig. 3, Table A.7). ABN/ENV+ ratio for D5 during the spring/summer months (week 18 to week 37) ranged from 1.4 to 16 (median ratio: 3.1). After week 41, the ABN/ENV+ ratio increased further ranging from 3.0 to 56 (median ratio: 4.5). Formation of D5 can occur on ENV+ through sorbent mediated degradation of D6. However, considering that the degree of formation of D5 from D6 is small (7 %, Fig. 2) and atmospheric

concentrations of D6 are considerably lower compared to D5 (Fig. 3), sorbent mediated formation of D5 from D6 on ENV+ will have less of an impact on the overall atmospheric concentrations. This is supported by our findings where D5 is consistently higher on ABN sorbent.

The concentration ratio of D4/D5 also helps providing insights into the relative performance between the two sorbents. D4/D5 ratios on the ABN during the spring/summer months (weeks 18 to week 37) range between 0.46 and 2.67 (average: 1.45 ± 0.66) with D4 detected at comparable or higher levels to D5 (Fig. 4).

D4/D5 ratios were less than one (0.38–0.80, average: 0.52 ± 0.16) during the fall/winter months (week 41 – week 1 (2018)) where D5 was consistently more abundant (Fig. 4). This supports documented atmospheric stability of cVMS (D4 > D5 > D6) (Atkinson, 1991; MacLeod et al., 2013; Safron et al., 2015; Kim and Xu, 2017; Bernard et al., 2018), as relative abundance of D4 would be greater during spring/summer months compared to D5 due to its higher atmospheric stability. During the winter months, low OH radical concentrations during the polar night will limit atmospheric degradation, causing D5 to be more abundant than D4 due to its higher use/emission into the environment. However, on the ENV+ sorbent, D4/D5 ratio was 2–8 times higher (except week 52) compared to the ABN sorbent, indicating D4 dominates, independent of season (Fig. 4). This is unlikely considering the emission profiles between these two chemicals (D5 > D4) and limited atmospheric degradation (OH radical mediated) occurring in the fall/winter months. This provides further evidence that artifacts occurring on the ENV+ sorbent will alter the true D4/D5 ratio by overestimating the atmospheric concentrations of D4 and underestimating atmospheric concentrations of D5 and that more reliable data for cVMS can be obtained on the ABN sorbent. Largest differences in atmospheric concentrations between the two sorbents were observed for D6 (Fig. 3). D6 was below the MDL in 70 % of all ENV+ samples whereas the detection frequency was much higher on ABN Express (95 %). The ABN/ENV+ ratio in samples with concentrations above the MQL on both sorbents (n = 2, Table A.7) were 3.8 and 9.8, showing clear loss of D6 on the ENV + sorbent.

3.4. Implications towards remote monitoring and atmospheric fate processes of cVMS

Concentrations found in the present study for both ABN and ENV+ sorbent for cVMS at Zeppelin observatory can be compared to earlier findings. Krogseth et al. (2013a) utilized ENV+ as an active sampling sorbent in 2011, and no statistical difference ($p < 0.05$, unpaired *t*-test with Welch's correction, GraphPad, Prism version 8.3.1) is observed in atmospheric concentrations for D5 and D6 during the same sampling time periods measured in 2011 and in this study using the ABN sorbent (Table A.8.). Atmospheric concentrations of D4 detected in this study fall within the range reported by Krogseth et al. (2013a), despite high uncertainty surrounding D4 measurements on ENV+. Krogseth et al. (2013a) applied storage correction to their results to account for sorbent related artifacts occurring on the ENV+ sorbent. However, despite this correction, concentrations may be underestimated based on uncertainty surrounding storage correction.

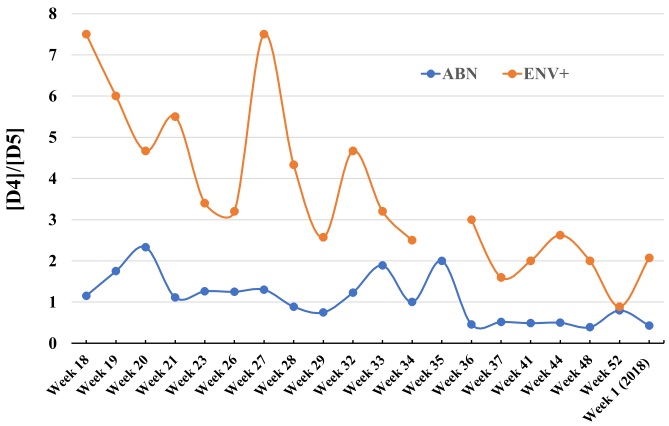

Fig. 4. Atmospheric concentration ratio of D4/D5 on ABN (blue) and ENV+ (orange) measured at Zeppelin station from week 18 (2017) to week 1 (2018). Black solid line represents atmospheric concentrations of D4 and D5 are equal. Concentrations below MQL but above MDL are included. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Remote monitoring of cVMS has also been carried out using passive air sampling techniques. Earlier work by Genualdi et al. (2011) using sorbent-impregnated polyurethane foam (SIP) disks reported concentrations of 16, 4.0, and 0.54 ng m^{-3} for D4, D5 and D6, respectively at Zeppelin station between April to July 2009. Similar concentrations were found in 2013 (D4: 32 ng m^{-3}, D5: 6.4 ng m^{-3}, D6: 1.3 ng m^{-3}) and 2015 (D4: 18 ng m^{-3}, D5: 6.6 ng m^{-3}, D6: 1.6 ng m^{-3}) at Zeppelin station for the same sampling time period with follow up studies using SIP disk sampling methodology (Rauert et al., 2018). In the same study, SIP-disk measurements during the winter months (January–April) from Zeppelin station in 2013 were higher (D4: 67 ng m^{-3}, D5: 25 ng m^{-3}, D6: 3.8 ng m^{-3}) compared to the spring/summer season, reflecting seasonal atmospheric degradation (McLachlan et al., 2010; Krogseth et al., 2013a). Concentrations reported on SIP-disks are considerably higher compared to concentrations reported here using active sampling with the ABN sorbent during both spring/summer (week 18 – week 31) and winter (week 41 - week 1) (Fig. 3, Table A.7). Difference in concentrations may reflect temporal changes in cVMS emission, although Rauert et al. (2018) reported an increase and/or stable trends of D4, D5 and D6 in the atmosphere from various sites within the Global Atmospheric Passive Sampling (GAPS) network from 2009 to 2015. Differences may be attributed to the SIP-disks representing a time-integrated signature over several months, while active samplers provide higher temporal resolution (i.e., days) in measurements. Concentration ratios of D4/D5 from SIP-disk passive samplers ranged from 2.7 to 4, whereas ratios on the ABN sorbent were below this range (Fig. 4), potentially indicating issues surrounding cVMS stability over the long deployment times and warrants further investigation.

Long-range transport potential and atmospheric persistence based on global measurements have been recently evaluated by Xu et al. (2019). In this study, D5/D6 concentration ratios derived from empirical measurements decreased from a south (source region) to north (remote region) trajectory, contrary to modeled predictions and known atmospheric degradation behavior (i.e., half-lives: D5 > D6). The authors hypothesized that the observed south to north decline in empirically derived D5/D6 ratios may be attributed to additional degradation mechanisms (i.e., aerosol facilitated hydrolysis) not accounted for in model simulations (i.e., Globo-POP, Xu and Wania (2013)). However, the authors also highlight several limitations in their data analysis, particularly sampling artifacts as monitoring data performed at remote locations have used ENV+ as a sampling sorbent. Comparison of D5/D6 concentration ratios collected on ABN in this study to data collected previously using ENV+ by Krogseth et al. (2013a) and NILU (Nizzetto et al., 2014, 2015; Nizzetto and Aas, 2016; Nizzetto et al., 2017) as well as GloboPOP model simulations (Xu and Wania, 2013) at Zeppelin station are shown in Fig. 5. During the winter season, an increasing trend is observed in the D5/D6 ratio from 2011 to 2017. Concentrations reported using the ABN sorbent (in 2017) were statistically higher than all concentrations reported from previous years (Fig. 5,

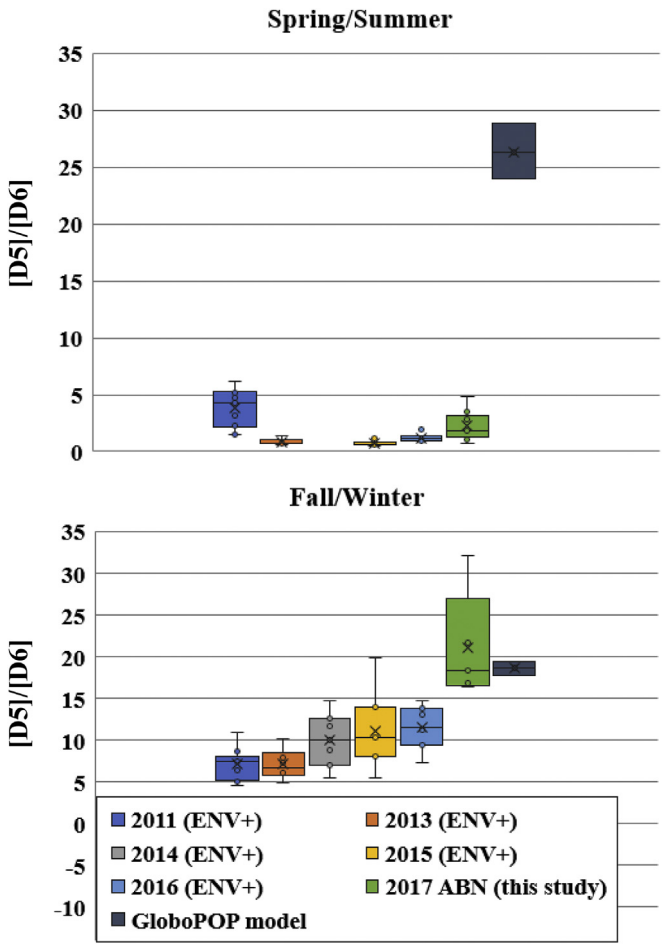

Fig. 5. Comparison of GloboPOP model estimates and measured D5/D6 atmospheric concentration ratio on ABN Express and ENV+ at Zeppelin station in spring/summer (2011, 2013, 2014, 2017) and fall/winter (2011, 2013–2015, 2017). Additional data on D5/D6 ratios was obtained from Krogseth et al. 2013a and Nizzetto et al. (2014, 2015, 2016, 2017, 2018). GloboPOP model estimates obtained from Xu and Wania (2013). Average of box-plot distribution represented by "x", solid black line represents the median, and box edges represent 25th and 75th percentile of the distribution. Distribution for GloboPOP model estimates represents error from sensitivity analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table A.9) ($p < 0.05$, ANOVA with Tukey multiple comparisons test, GraphPad, Prism version 8.3.1). Lower D5/D6 ratios observed on ENV+ compared to ABN can be attributed to degradation of D5 on the ENV+ sorbent during the fall/winter season. Atmospheric concentrations of D6 are much lower compared to D5 and will unlikely have a significant impact on the overall measured concentrations of D5 through degradation on the sorbent (i.e., D6 → D5). Xu et al. (2019) hypothesized that the observed south to north decline in empirically derived D5/D6 ratios may be attributed to additional degradation mechanisms (i.e., aerosol facilitated hydrolysis) not accounted for in model simulations. However, D5/D6 ratios obtained from empirical measurements with ABN were in good agreement with estimates predicted by GloboPOP model at 80 °N during the fall/winter using emission scenarios outlined by Xu and Wania (2013) (Fig. 5, Table A.9). Measurements from previous years were statistically lower compared to GloboPOP model estimates ($p < 0.05$, ANOVA with Tukey multiple comparisons test, GraphPad, Prism version 8.3.1) with exception to measurements made in 2016, although the p value for this year (adjusted p-value: 0.067) was just outside the threshold ($\alpha < 0.05$) for statistical significance. During the summer period, no clear trend can be observed in the temporal analysis of D5/D6 ratios (Fig. 5, Table A.10). However, all measured ratios were significantly different ($p < 0.05$, Brown-Forsythe and Welch ANOVA multiple comparisons test, GraphPad, Prism version 8.3.1) than GloboPOP model estimates ranging between 5 and 54 times lower. Considering aerosol facilitated degradation mechanism proposed by Xu et al. (2019), our observations may be attributed to seasonal particle formation within the Arctic. Several studies have documented the seasonal production of aerosols during the onset of the Arctic Haze period (March–May) as well as high concentrations of ultrafine particles during the Polar summer (June–August) (Tunved et al., 2013; Asmi et al., 2016). This may explain the seasonal discrepancy between empirical measured D5/D6 ratios and GloboPOP model predictions, indicating that aerosol formation may assist in cVMS degradation, but only during the spring/summer season.

4. Conclusions

As restrictions on the cVMS use are beginning to be implemented by regulatory agencies, continued atmospheric monitoring is needed to assess the effectiveness of such initiatives from both an environmental and policy performance standpoint. However, reliable sampling methodology is needed to avoid artifacts that can hinder understanding of atmospheric behavior for decisions on chemical management. cVMS stability was far greater on the ABN sorbent compared to the traditionally used ENV+ sorbent, thus minimizing impacts of sampling derived artifacts. Concentration ratios determined for D5/D6 on the ABN sorbent were in good agreement with GloboPOP model predictions during the winter season. However, deviation between model estimates and measurements during the summer season is not explained by sorbent related degradation and may be attributed to additional degradation mechanisms associated with seasonal aerosol production in the Arctic (i.e., aerosol facilitated hydrolysis). Additional work is needed to investigate differences between passive and active sampling measurements and the impact atmospheric humidity towards cVMS stability on sampling sorbents. As cVMS are prone to undergo hydrolysis/rearrangement interactions (Xu, 1998, 1999), accumulation of water vapor on sampling sorbents over time may facilitate degradation.

Declaration of competing interest

The authors declare no competing financial interests.

CRediT authorship contribution statement

Nicholas A. Warner: Conceptualization, Methodology, Validation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration. **Vladimir Nikiforov:** Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - review & editing, Visualization. **Ingjerd S. Krogseth:** Conceptualization, Writing - review & editing. **Stine M. Bjørneby:** Investigation. **Amelie Kierkegaard:** Conceptualization, Methodology, Writing - review & editing. **Pernilla Bohlin-Nizzetto:** Writing - review & editing, Funding acquisition.

Acknowledgements

This study was funded by the Norwegian Ministry of Climate and Environment through the Strategic Institute Programs, granted by the Norwegian Research Council (Arctic, the herald of Chemical

Substances of Environmental Concern, Clean Arctic, project #117031). Financial support for monitoring activities at Zeppelin station provided by the Norwegian Environment Agency (Norwegian monitoring programme for long-range atmospheric transported contaminants, project # 16078187). We would also thank Dr. Shihe Xu from Dow Chemical for providing output data from the GloboPOP model simulations.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2020.126967.

References

Ahrens, L., Harner, T., Shoeib, M., 2014. Temporal variations of cyclic and linear volatile methylsiloxanes in the atmosphere using passive samplers and high-volume Air samplers. Environ. Sci. Technol. 48, 9374–9381.

Asmi, E., Kondratyev, V., Brus, D., Laurila, T., Lihavainen, H., Backman, J., Vakkari, V., Aurela, M., Hatakka, J., Viisanen, Y., Uttal, T., Ivakhov, V., Makshtas, A., 2016. Aerosol size distribution seasonal characteristics measured in Tiksi, Russian Arctic. Atmos. Chem. Phys. 16 (3), 1271–1287.

Atkinson, R., 1991. 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. 25, 863–866.

Bernard, F., Papanastasiou, D.K., Papadimitriou, V.C., Burkholder, J.B., 2018. Temperature dependent rate coefficients for the gas-phase reaction of the OH radical with linear (L2, L3) and cyclic (D3, D4) permethylsiloxanes. J. Phys. Chem. 122, 4252–4264.

Brooke, D.N., Crookes, M.J., Gray, D., Robertson, S., 2009a. Environmental Risk Assessment Report: Decamethylcyclopentasiloxane. Environment Agency of England and Wales, Bristol, U.K.

Brooke, D.N., Crookes, M.J., Gray, D., Robertson, S., 2009b. Environmental Risk Assessment Report: Dodecamethylcyclohexasiloxane. Environment Agency of England and Wales, Bristol, U.K., 2009.

Brooke, D.N., Crookes, M.J., Gray, D., Robertson, S., 2009c. Environmental Risk Assessment Report. Octamethylcyclotetrasiloxane Environment Agency of England and Wales, Bristol, U.K., 2009.

Companioni-Damas, E.Y., Santos, F.J., Galceran, M.T., 2014. Linear and cyclic methylsiloxanes in air by concurrent solvent recondensation–large volume injection–gas chromatography–mass spectrometry. Talanta 118, 245–252.

ECHA, 2018. REACH Restricted Substance List 2018 (REACH Annex XVII). https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.006.01.0045.01.ENG&toc=OJ:L:2018:006:TOC.

ECHA, 2019. REACH annex XV restriction report. Octamehylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6). https://echa.europa.eu/documents/10162/11f77453-8a0d-411b-38c3-7f992a136cca.

Gallego, E., Perales, J.F., Roca, F.J., Guardino, X., Gadea, E., 2017. Volatile methyl siloxanes (VMS) concentrations in outdoor air of several Catalan urban areas. Atmos. Environ. 155, 108–118.

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

Horii, Y., Kannan, K., 2008. Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. Arch. Environ. Contam. Toxicol. 55, 701–710.

Kierkegaard, A., McLachlan, M.S., 2010. Determination of decamethylcyclopentasiloxane in air using commercial solid phase extraction cartridges. J. Chromatogr. A 1217, 3557–3560.

Kierkegaard, A., McLachlan, M.S., 2013. Determination of linear and cyclic volatile methylsiloxanes in air at a regional background site in Sweden. Atmos. Environ. 80, 322–329.

Kim, J., Xu, S., 2017. Quantitative structure-reactivity relationships of hydroxyl radical rate constants for linear and cyclic volatile methylsiloxanes. Environ. Toxicol. Chem. 36, 3240–3245.

Krogseth, I.S., Kierkegaard, A., McLachlan, M.S., Breivik, K., Hansen, K.M., Schlabach, M., 2013a. Occurrence and seasonality of cyclic volatile methyl siloxanes in arctic air. Environ. Sci. Technol. 47, 502–509.

Krogseth, I.S., Zhang, X., Lei, Y.D., Wania, F., Breivik, K., 2013b. Calibration and application of a passive air sampler (XAD-PAS) for volatile methyl siloxanes. Environ. Sci. Technol. 47, 4463–4470.

MacLeod, M., Kierkegaard, A., Genualdi, S., Harner, T., Scheringer, M., 2013. Junge relationships in measurement data for cyclic siloxanes in air. Chemosphere 93, 830–834.

McLachlan, M.S., Kierkegaard, A., Hansen, K.M., van Egmond, R., Christensen, J.H., Skjøth, C.A., 2010. Concentrations and fate of decamethylcyclopentasiloxane (D5) in the atmosphere. Environ. Sci. Technol. 44, 5365–5370.

Nizzetto, P.B., Aas, W., Krogseth, I.S., 2014. Monitoring of Environmental Contaminants in Air and Precipitation, Annual Report 2013. Kjeller, NILU. Norwegian Environmental Agency report M-368/2015. http://www.miljodirektoratet.no/Documents/publikasjoner/M202/M202.pdf.

Nizzetto, P.B., Aas, W., Warner, N., 2015. Monitoring of Environmental Contaminants in Air and Precipitation, Annual Report 2014. Kjeller, NILU. Norwegian Environmental Agency report M-368/2015.

Nizzetto, P.B., Aas, W., 2016. Monitoring of Environmental Contaminants in Air and Precipitation, Annual Report 2015. Norwegain Environment Agency report M-579/2016. http://tema.miljodirektoratet.no/Documents/publikasjoner/M579/M579.pdf.

Nizzetto, P.B., Aas, W., Warner, N., 2017. Monitoring of Environmental Contaminants in Air and Precipitation, Annual Report 2016. Norwegian Environmental Agency report M-757/2016. https://www.miljodirektoratet.no/globalassets/publikasjoner/M1062/M1062.pdf.

Rauert, C., Shoieb, M., Schuster, J.K., Eng, A., Harner, T., 2018. Atmospheric concentrations and trends of poly- and perfluoroalkyl substances (PFAS) and volatile methyl siloxanes (VMS) over 7 years of sampling in the Global Atmospheric Passive Sampling (GAPS) network. Environ. Pollut. 238, 94–102.

Safron, A., Strandell, M., Kierkegaard, A., Macleod, M., 2015. Rate constants and activation energies for gas-phase reactions of three cyclic volatile methyl siloxanes with the hydroxyl radical. Int. J. Chem. Kinet. 47, 420–428.

Tunved, P., Ström, J., Krejci, R., 2013. Arctic aerosol life cycle: linking aerosol size distributions observed between 2000 and 2010 with air mass transport and precipitation at Zeppelin station, Ny-Å lesund, Svalbard. Atmos. Chem. Phys. 13.

Xu, S., 1998. Hydrolysis of poly(dimethylsiloxanes) on clay minerals as influenced by exchangeable cations and moisture. Environ. Sci. Technol. 32, 3162–3168.

Xu, S., Wania, F., 2013. Chemical fate, latitudinal distribution and long-range transport of cyclic volatile methylsiloxanes in the global environment: a modeling assessment. Chemosphere 93, 835–843.

Xu, S., Warner, N., Bohlin-Nizzetto, P., Durham, J., McNett, D., 2019. Long-range transport potential and atmospheric persistence of cyclic volatile methylsiloxanes based on global measurements. Chemosphere 228, 460–468.

Xu, S.H., 1999. Fate of cyclic methylsiloxanes in soils. 1. The degradation pathway. Environ. Sci. Technol. 33, 603–608.