Reducing sampling artifacts in air measurements: Improvement of active air sampling methodologies for accurate measurements of cyclic volatile methylsiloxanes in remote regions

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Introduction

The presence of cyclic volatile methylsiloxanes (cVMS) and the potential hazard they pose to the environment has been an ongoing debate between industry, regulators and scientists for more than a decade. Use of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) in wash-off personal care products will be restricted (< 1%) from February 2020 within Europe Union[1] due to their classification as very persistent and very bioaccumulative compounds under REACH. Due to their volatile nature, atmospheric monitoring of cVMS is key to provide data for implementation of emission regulations by authorities as well as to evaluate effectiveness of chemical restrictions put in place, particularly in remote regions. However, the current most commonly used active sampling methodology for cVMS suffers from sampling artifacts, where degradation/formation of cVMS occurs on the sorbent (Isolute ENV+).[2, 3] This causes uncertainty in measured atmospheric concentrations for cVMS. Improvement of sampling methodologies is needed to minimize such sampling artifacts so accurate data can be delivered to evaluate cVMS atmospheric fate. In this study, we report the improvement of an active air sampler for cVMS analysis and its application to atmospheric monitoring of cVMS within the Arctic at the Zeppelin observatory located in Ny Ålesund, Svalbard (79 °N).

Materials and methods

Atmospheric sampling was carried out using two different hydroxyl-substituted polystyrene-divinylbenzene based sorbents (Isolute ENV+ and Isolute ABN Express (Biotage, Sweden)). The hydroxyl groups in ENV+ are phenolic, attached directly to the aromatic moiety (Ar-OH) whereas in ABN they are non-ionizable (Alk-OH). Bulk sorbent material was cleaned with dichloromethane followed by hexane and dried overnight in a clean cabinet to avoid contamination. ENV+ or ABN Express sorbent were packed (120 mg) between two polyethylene frits into separate 25 ml polyethylene cartridges.

Stability of cVMS on both ENV+ and ABN Express sorbent was evaluated by spiking individual cartridges with 30 ng of $^{13}C_4$-D4, $^{13}C_{10}$-D5 or $^{13}C_6$-dodecamethylcyclohexasiloxane (D6). Cartridges were stored at both - 20°C and room temperature for up to 14 days to evaluate breakdown/formation sorbent-related kinetics of cVMS.

Evaluation of the performance of the new ABN Express active air sampler, in comparison to the ENV+ sampler, for remote atmospheric sampling was carried out at the Zeppelin Station. ENV+ and ABN Express sampling cartridges were used to sample Arctic air in parallel over a 66-96 hour period (40-100 m³). Field blank cartridges for each sorbent were taken at each sampling event to assess background contamination and determine analytical detection limits. Once collection was complete, cartridges were sealed with polyethylene caps and wrapped in aluminum foil and stored at -20°C until shipped to NILU's laboratory in Tromsø, Norway. Prior to extraction, cartridges were spiked with ^{13}C-labelled cVMS (D4, D5 and D6) standards and extracted with 5 mL of hexane. The collected extract was spiked with Tetrakis(trimethylsilyloxy)silane (M4T) as a recovery standard.

Analysis was carried out by gas chromatography mass spectrometry using concurrent solvent re-condensation large volume injection (CSR-LVI) in which method details have been previously described.[4]

Results and discussion

In the storage stability experiments, highest loss rates occurred for $^{13}C_4$-D4 at room temperature on the ENV+ cartridge where over 60% of the original amount added had degraded within 14 days of storage. Observed loss

of $^{13}C_4$-D4 on ENV+ was less (16 %) when stored at -20 ºC. Loss of $^{13}C_4$-D4 on ABN Express sorbent was smaller compared to ENV+, where 90% of the initial $^{13}C_4$-D4 added to the sorbent remained at both room temperature and -20 ºC. Similar loss observed for $^{13}C_4$-D4 at both room temperature and -20 ºC on ABN Express suggests loss of may occur either through degradation and/or volatilization while spiking the cartridges, but requires further investigation. However, degradation kinetics appear to play a greater role in loss of $^{13}C_4$-D4 on ENV+ sorbent compared to volatilization.

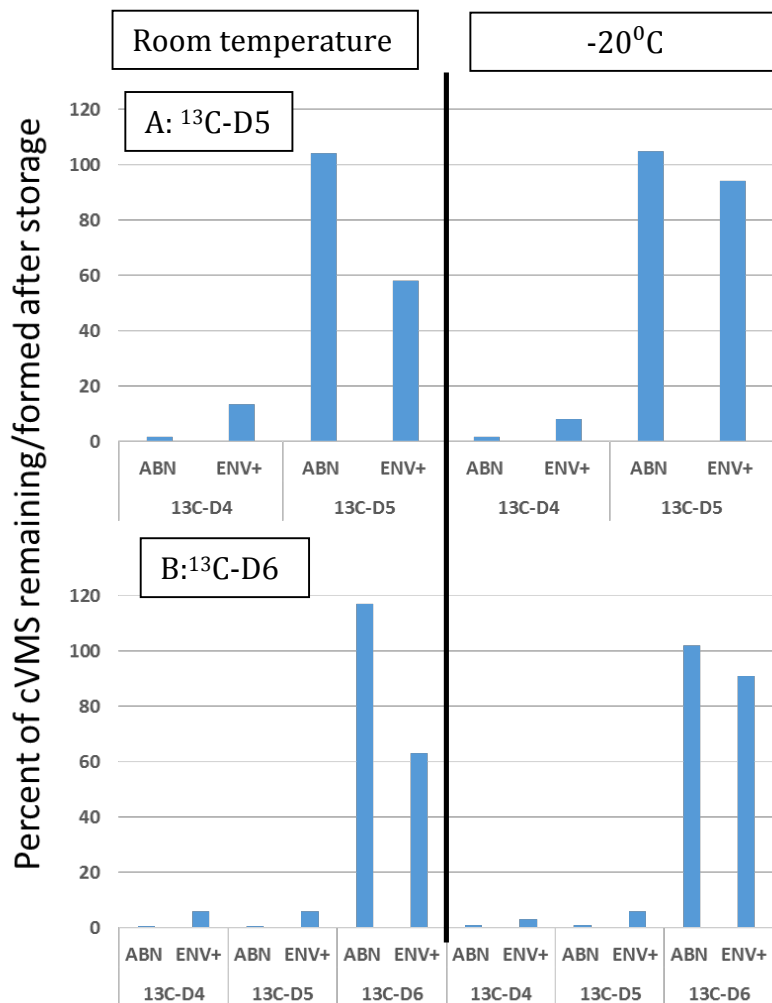Results from individual storage experiments (14 days) for $^{13}C_{10}$-D5 and $^{13}C_6$-D6 are shown in Figure 1. As was observed for ^{13}C-D4, significant loss of both $^{13}C_{10}$-D5 (Figure 1A) and $^{13}C_6$-D6 (Figure 1B) occurred on ENV+ at room temperature, whereas loss was less with storage at - 20ºC after 14 days. In addition to loss observed for $^{13}C_{10}$-D5, formation of $^{13}C_4$-D4 was observed to occur on ENV+ at both room temperature and -20 ºC (13 % and 8% on a nmol basis, respectively (Figure 1A)). This is in agreement to earlier findings by Kierkegaard and McLachlan, where they observed formation of both D3 and D4 from degradation of D5 on ENV+ sorbent[3]. In regards to $^{13}C_6$-D6, formation of $^{13}C_{10}$-D5 and $^{13}C_4$-D4 were also observed at room temperature (6% for both, respectively) and at -20 ºC (6% and 3%, respectively (Figure 1B)). To our knowledge, D6 sorbent-related degradation kinetics have not been previously studied and indicate degradation of D6 may influence levels measured in air of D4 and D5 using ENV+ sorbent.

Figure 1. Percentage of A) ^{13}C-D5 and B) ^{13}C-D6 remaining on ENV+ and ABN Express sorbents stored at room temperature and -20 ºC, as well as ^{13}C-D4 and ^{13}C-D5 formed on the sorbent. Percentages determined on a nmol

Contrary to results observed on ENV+, little loss was observed for $^{13}C_{10}$-D5 and $^{13}C_6$-D6 on the ABN Express sorbent after 14 days. Formation of $^{13}C_4$-D4 and $^{13}C_{10}$-D5
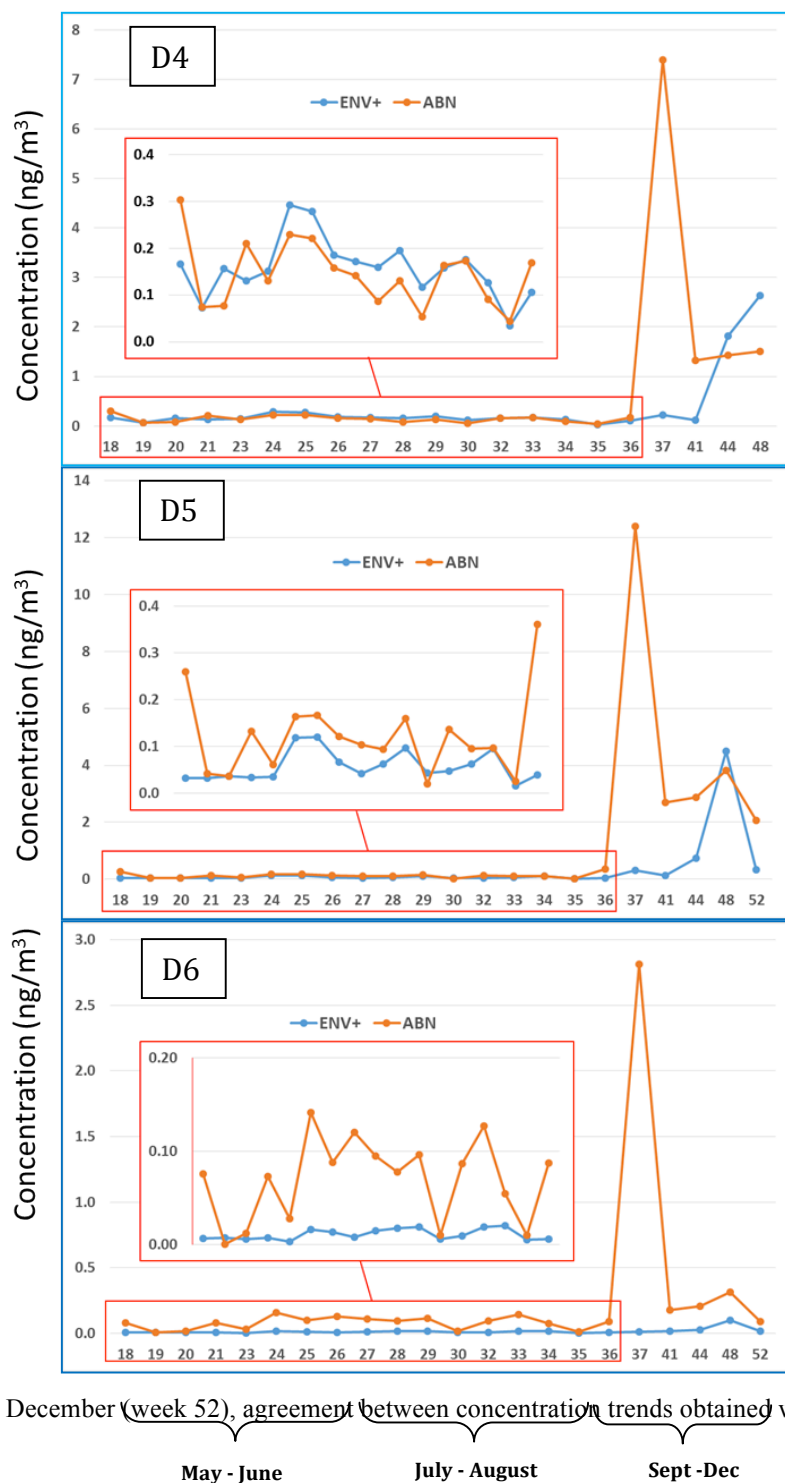
was similar at both room temperature and -20 ºC storage conditions and account for less than 2% and 1% of the initial spiked amount of $^{13}C_{10}$-D5 and $^{13}C_6$-D6, respectively. These findings indicate that ABN Express is a more stable and reliable sorbent compared to ENV+ for accurate determination of atmospheric cVMS concentrations.

Comparison of performance of ABN Express and ENV+ sorbents for remote atmospheric monitoring of cVMS at Zeppelin Station is shown in Figure 2. Based on storage stability experiments[2], concentrations measured on ENV+ were corrected to account for losses occurring during storage. No correction was applied to ABN Express results as loss observed was less than 2%.

Atmospheric concentrations of cVMS were seasonally dependent with lowest concentrations occurring between spring (May, week 18) to late fall (September, week 36) followed by an increase in concentration into the winter months for all cVMS on both sorbents. This concentration trend has been previously reported at Zeppelin Station[2], which is attributed to a decrease in atmospheric degradation via photochemical oxidation as atmospheric hydroxyl radical concentration decreases towards the winter months.

Concentration trends obtained with ENV+ and ABN Express sorbent were in good agreement, during the spring to late fall for D4 and D5 (Figure 2). However, levels of D4 present on ENV+ will be influenced from formation from D5 and D6 degradation, and thus may actually be lower compared to findings presented here. For D5, 70% of the samples showed higher concentrations on the ABN Express sorbent compared to those obtained on ENV+. In particular, at week 18 and 36, concentrations of D5 were between 7-9 times higher on the ABN Express sorbent. This observed pattern is even more prominent for D6, where observations on the two sorbents clearly deviate. Of the weeks sampled during the spring to fall period, 50% of the concentrations reported on ABN Express were at least 7 times higher to those found on ENV+ for D6.

Between September (week 37) to December (week 52), agreement between concentration trends obtained with ENV+ and ABN Express is poor. Concentrations for cVMS were higher at all sampling times with ABN than ENV+ with exception for week 44 and 48 for D4 and week 48 for D5. In particular, a high exposure event occurring at week 37 was observed on ABN Express

Figure 2. Comparison of atmospheric concentrations of cVMS measured at Zeppelin collected using ENV+ and ABN Express sorbent. Week number of 2017 is presented on the x-axis

sorbent but not on ENV+. Although cVMS concentrations did increase between week 36 and 37 on ENV+ by a factor of two, it was far below the increase observed on ABN Express (factor of 43). However, the reason for this high increase on ABN Express is unknown and requires further investigation.

Based on the findings within this study, ENV+ cannot be considered a suitable sorbent to carry out routine atmospheric monitoring of cVMS in background sites/remote regions in which extraction cannot be carried out immediately. ABN Express showed much greater stability towards sorbent mediated degradation/formation kinetics. Although correction for sorbent-mediated degradation/formation showed good correlation between the two sorbents during the spring/summer months (week 18-36) for D4 and D5, greater deviation was observed for atmospheric concentrations of D6. Deviation between the two sorbents was also greater for all cVMS during the winter months and further evaluation is needed to determine the source of this variation. However, our initial findings indicate that D5 and D6 concentrations previously reported using ENV+ sampling sorbent may potentially be higher in the Arctic atmosphere, particularly during the fall/winter season (week 37-52). In addition, D4 concentrations were often higher on ENV+ compared to ABN Express, indicating that earlier findings of D4 are influenced by D5 and D6 degradation and warrants further investigation using the newly developed ABN sorbent.

References:

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