Calibration and Application of a Passive Air Sampler (XAD-PAS) for Volatile Methyl Siloxanes

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Abstract

Because the atmosphere is key to understanding the environmental behavior of volatile methyl siloxanes (VMS), a variety of reliable air sampling methods are needed. The purpose of this study was to calibrate and evaluate an existing, polystyrene-divinylbenzene co-polymeric resin based passive air sampler (XAD-PAS) for VMS. Sixteen XAD-PAS were deployed for 7 to 98 days at a suburban site in Toronto, Canada, while the VMS concentration in air was monitored using an active sampling method. This calibration and a subsequent field test further allowed for investigation of the temporal and spatial variability of VMS in the region. Uptake in the XAD-PAS of octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and three linear VMS was linear throughout the whole deployment period. Sampling rates were between 0.4 and 0.5 m^3/day. The XAD-PAS measured ∑VMS concentrations ranged from non-detects in rural areas (n = 3), to 169 ± 49 ng/m^3 in the urban region (n = 21), to levels above 600 ng/m^3 at sewage treatment plants (n = 2). Levels and composition of VMS within the urban area were remarkably uniform in space. Levels, but not composition, were highly variable in time and weakly correlated with temperature, wind speed and wind direction.

1. Introduction

Volatile methyl siloxanes (VMS) are widely used in the production of silicone polymers, personal care products, and various technical applications.[e.g. 1-3] Concern with regard to their environmental behavior is focussed in particular on their potential for persistence and bioaccumulation; octamethylcyclotetrasiloxane (D4) is classified as a reproductive toxicant.[1-3] Due to their high volatility, the atmosphere is a key compartment to understand their environmental behavior. VMS have been measured in both indoor air,[4] outdoor urban and rural air,[5-6] and in Arctic air.[7] Emissions to the atmosphere occur in particular through volatilization from use of personal care products and from sewage treatment plants (STPs) and landfills.[e.g. 8-9] Reliable methods for sampling and analyzing VMS in air are a prerequisite for a better characterization of their atmospheric levels and distribution and the relative importance of various emission sources. The applicability of standard air sampling methods for semi-volatile organic compounds (sVOC) to the relatively volatile VMS cannot be assumed and must be proven. Trace analysis of VMS is additionally challenging due to their ubiquitous presence in our surroundings which leads to a high contamination potential.[10]

Two methods for sampling VMS in air have recently been developed. An active air sampling method based on solid phase extraction cartridges (SPE-AAS) provides low limits of detection and has been used successfully to measure concentrations of cyclic VMS (cVMS) in air in rural Sweden[11] and the European Arctic.[7] A passive air sampler (PAS) using sorbent-impregnated PUF-disks (SIP-disks), i.e. polyurethane foam (PUF) coated with polystyrene-divinylbenzene copolymeric resin XAD, was used for both cVMS and linear VMS (lVMS) in an indoor calibration study and subsequent deployment close to STPs and landfills in Canada,[8] as well as in a global sampling campaign (GAPS).[6] PASs are advantageous as they are cost-efficient, do not require electricity, and provide time-averaged concentrations. Chemicals are taken up in a PAS by diffusing from ambient air to a passive sampling medium (PSM) proceeding sequentially through a linear, a curvilinear, and a plateau phase. During the latter the PSM has achieved equilibrium with the surrounding atmospheric gas phase.[12] To

50   confidently calculate concentrations in air from the amount of a chemical accumulated in the PSM,

51   calibration studies are necessary to establish the duration of the linear phase and the passive

52   sampling rate (PSR) within this phase.[13-14] Recently it has been shown that resistance to mass

53   transfer within the PSM influences the PSR as well as the distribution of the chemical within the

54   PSM.[15] Because this resistance is related to a chemical's highly temperature dependent sorption

55   coefficient from the gas phase to the PSM, PSRs vary between chemicals and with temperature.[15]

56   A range of PSMs have been used in PAS for sVOC; PUF and XAD-resin are currently the most

57   common PSMs. In SIP-disks, the XAD resin was reported to be the main sorbent for fluorinated

58   compounds and not the PUF-disks themselves.[16] Polycyclic aromatic hydrocarbons and

59   polychlorinated biphenyls also display a stronger sorption to XAD than to PUF, and for volatile

60   compounds the PUF is expected to quickly achieve equilibrium with the surrounding air.[17] A pure

61   XAD-PAS system already exists, and has been applied to a range of different compounds and

62   environmental conditions.[14,18] However, the XAD-PAS has not yet been calibrated for more volatile

63   compounds such as the VMS.

64   The purpose of this study was to calibrate the XAD-PAS for selected cVMS and lVMS and to apply

65   both active and passive sampling methods to study the temporal and spatial variability of VMS in

66   urban air. We hypothesized that the XAD-PAS has a higher sorptive capacity and a longer linear

67   range for VMS than the SIP-disks, allowing for longer field-deployments. Uptake rates of VMS in the

68   XAD-PAS were determined in suburban Toronto, Canada, using atmospheric VMS concentrations

69   recorded with the SPE-AAS method for a period of 3 months. Once calibrated, XAD-PAS were

70   deployed at selected sites in Toronto to investigate the relationship between VMS concentrations in

71   air and population density and distance to STPs.

2. Materials and methods

2.1 Sample preparation, extraction and analysis

2.1.1 XAD-PAS

The XAD-PAS has been described earlier;[18] details on materials and a drawing (Figure S1) are

provided in Section 1.1 in the Supporting Information (SI). Mesh cylinders (10 cm long, 2 cm

diameter), pre-baked at 450 °C, were filled with approximately 10 grams of XAD-2 resin, capped at

each end with aluminum foil and aluminum caps, cleaned twice in a Soxhlet with hexane for 24 h,

and placed in a vacuum-desiccator overnight to dry. Cylinders that were not immediately extracted

or deployed for sampling, were wrapped in aluminum foil and zip-lock bags and stored at -20 °C.

The extraction procedure was simplified as much as possible to minimize the risk of contamination

and loss of analytes. For extraction, the XAD-sorbent was transferred from the mesh cylinder to a 60

mL separation funnel, to which 22 mL of hexane was added, followed by internal standard (200 μL

mix of 768 ng/mL ^{13}C-labeled octamethylcyclotetrasiloxane (^{13}C-D4), 608 ng/mL ^{13}C-decamethyl-

cyclopentasiloxane (^{13}C-D5), and 880 ng/mL ^{13}C-dodecamethylcyclohexasiloxane (^{13}C-D6)). The XAD-

hexane slurry was hand-shaken for two minutes, and the excess solvent (approximately 10 mL)

drained from the separation funnel. Another 10 mL of hexane was added to the XAD, shaken for two

minutes, and the solvent drained. This step was performed twice, giving a combined extract of

approximately 30 mL. The volumetric standard tris(trimethylsilyloxy)-silane (M3T, 200 μL, 913

ng/mL) was added to the extract. No further clean-up or solvent reduction steps were performed to

avoid loss of analytes through volatilization and to minimize additional opportunities for sample

contamination.

To evaluate the efficiency of the extraction procedure, three XAD (10 g) and two hexane samples (12

mL, without XAD) were spiked with native cVMS and lVMS (200 μL, approximately 1000 ng/mL). Five

extracts of 10 mL each were collected, and analyzed separately to evaluate the extraction profile.

Additionally, three extracts of 10 mL each were collected for blank XAD-PAS and hexane samples. To

evaluate the effect of storage, 10 XAD-PAS were exposed to indoor laboratory air for 45 days and

98   subsequently stored at -20 °C. Duplicate samples were extracted after 0, 7, 14, 21 and 28 days of

99   storage (Table S1), and the recovery relative to day zero was calculated. The storage experiment was

100   started on the same day as the outdoor calibration of the XAD-PAS, with extractions performed

101   jointly for the two experiments during the first four weeks. This implies that the field blanks for the

102   XAD-PAS calibration are also storage blanks which have been stored in the freezer for the same

103   number of days as the storage samples.

104   ### 2.1.2   SPE-AAS

105   The SPE-AAS method has also been described earlier.[7,11] The SPE-cartridges were manually packed

106   by filling a 25 mL polyethylene (PE) cartridge with approximately 120 mg ENV+ resin (hydroxylated

107   polystyrene divinylbenzene copolymer) between two PE frits. The cartridges were pre-cleaned by

108   eluting them with 14 mL of dichloromethane and 14 mL of hexane, subsequently dried with purified

109   nitrogen gas, capped with PE caps on both ends, wrapped in aluminum foil and zip-lock bags, and

110   stored at -20 °C until sampling. Samples were extracted immediately after retrieval to avoid

111   previously observed issues associated with storing of SPE-AAS samples.[7,19] Cartridges were reused.

112   Internal standard was added directly on the frit prior to extraction (100 μL to samples, 20 μL to field

113   blanks, mix of 768, 608, and 880 ng/mL ^{13}C-D4, ^{13}C-D5, and ^{13}C-D6, respectively). The cartridges were

114   eluted with 4 mL of hexane, and the volumetric standard (M3T, 100 μL, 913 ng/mL) was added to

115   the extract. To evaluate the extraction efficiency for lVMS, two fractions of 2 mL each were collected

116   for the first 7 sets of duplicate samples (first 17 days of the experiment). The amount of the analytes

117   relative to the volumetric standard was calculated for both fractions and compared. For these 17

118   days, VMS concentrations in air could be slightly underestimated, as only the first fraction was used

119   in the quantification of the results.

120   ### 2.1.3   Instrumental analysis

121   Instrumental analysis was carried out on an Agilent Technologies 7890A GC system connected to an

122   Agilent Technologies 7000A GC/MS Triple Quad and an Agilent 7683 Series Injector. The instrument

123   was operated in single ion monitoring (SIM) mode, and only the first quadrupole was used. Details of

124   the method, which was similar to previously used methods for VMS,[7,11] are provided in SI Section

125   1.2. Samples were quantified against a five-point calibration curve forced through zero based on

126   non-labeled VMS. A six-point calibration curve was used for the XAD-samples from the storage

127   experiment and the spatial study. The samples were analyzed for four cVMS

128   (hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane

129   (D5), and dodecamethylcyclohexasiloxane (D6)) and three lVMS (octamethyltrisiloxane (MDM),

130   decamethyltetrasiloxane (MD2M), and dodecamethylpentasiloxane (MD3M)).

131   2.2   Sampling

132   2.2.1   Calibration of XAD-PAS

133   Sixteen XAD-PAS were deployed simultaneously on March 2, 2012, on the campus of the University

134   of Toronto Scarborough (UTSC), in a suburban area of Toronto, Canada. The XAD-filled mesh

135   cylinders were placed inside stainless steel housings positioned about 1.5 meters above ground

136   level. Duplicate samples were collected after 7, 14, 21, 28, 42, 60, 77, and 98 days (June 8) of

137   deployment (Table S1). The VMS concentration in air at the site was monitored by collecting

138   duplicate SPE-AAS every 2 to 3 days. The cartridges, placed inside the same type of housing as the

139   XAD-PASs, were mounted approximately 1.5 meters above ground level with their openings facing

140   down. The cartridges were connected with polytetrafluoroethylene (PTFE) tubing to low-volume air

141   pumps (BGI-400 personal sampling pump, BGI Incorporated, MA, USA) calibrated using a Mini-Buck

142   air flow calibrator M-5 (APB-80500, A. P. Buck Inc., FL, USA) before and after the sampling campaign.

143   The average flow rates of 0.28 and 0.30 m^3/h (for the two parallel pumps A and B, respectively)

144   during an average sampling time of 56.9 ± 11.8 h yielded an average sample volume of 16.5 ± 3.4 m^3

145   (Table S2). Each set of XAD-PAS and SPE-AAS was accompanied by a field blank each. Field blanks

146   were brought to the sampling site, but not opened. The ambient temperature at the site was

147   recorded at six positions inside and outside of one of the XAD-PAS housings every 15 minutes

148   (Smartbutton, ACR Systems Inc., Canada).

2.2.2   Spatial mapping

Duplicate XAD-PAS were deployed for approximately 3 months (range 80 to 92 days for most sites, 65-70 days for the two STP sites), from July until October 2012 (Table S3), at 26 sites in Toronto and Ontario, varying widely in terms of population density and proximity to STPs. Two of the locations were directly within STPs and three were at rural to remote locations. Field blanks (n = 10) were brought to selected sites, and two procedural blanks (n = 12) were extracted for each batch of sample extractions.

2.3   Quality control

All sample preparations and extractions were performed in the ALFONSE (Advanced Laboratory for Fluorinated and Other New Substances in the Environment) clean-lab facility at UTSC (see SI section 1.3). Uttermost care was taken to avoid contamination, and personal care products containing VMS were not used by the personnel handling the samples. All glass equipment was baked at 450 °C overnight and all plastic equipment sonicated in hexane before use. The nitrogen gas used to dry the pre-cleaned SPE-AAS cartridges was filtered through an ENV+ cartridge to remove any VMS contamination. Contamination from the solvent and the instrumental system was continuously monitored by injecting hexane containing the internal and volumetric standards. Method limits of detection (LOD) and quantification (LOQ), and instrumental detection and quantification limits (IDL and IQL) were calculated based on field blanks and signal-to-noise levels, respectively (SI section 1.4).

Results for cVMS from the SPE-AAS were blank-corrected based on the individual field blanks, while the XAD-PAS from the spatial study were blank-corrected based on mean field- and procedural blank levels. Results from the storage experiment and the calibration of the XAD-PAS were not blank-corrected, but the blank levels at day zero in the calibration experiment were incorporated in the calibration curve. The lVMS were below IDL in all field and procedural blanks, and hence results for lVMS were not blank-corrected. Recovery during extraction and analysis was accounted for by the internal standards spiked prior to extraction.

3. Results and discussion

3.1 Method evaluation

3.1.1 Recovery and repeatability for XAD-PAS

The recovered amount of spiked VMS served as a measure of the efficiency of the XAD extraction

procedure. However, it is recognized that the spiking procedure may not fully simulate real uptake of

VMS from the atmosphere. Details on how the results were blank-corrected are provided in SI

section 1.5.1. The mean blank-corrected recoveries from XAD-samples after three extractions ranged

from 84 % to 101 % for MDM, MD2M, MD3M, D5, and D6. D3 and D4 displayed higher mean

recoveries of 179 % and 120 %, respectively. The results for the pure hexane samples (without XAD)

were similar (Table S4). Hence the major part is extracted in the first three fractions, in particular for

congeners with low blank levels, and sample load in the last two fractions is to a large degree

contamination (Figure S2).

The mean recoveries of the internal standards were 77 ± 9 %, 104 ± 23 %, and 85 ± 13 % for ^{13}C-D4,

^{13}C-D5, and ^{13}C-D6, respectively, based on all samples from the XAD-PAS calibration and storage

experiments (n = 46) (Table S4). In the spatial study, those recoveries were 78 ± 16 %, 110 ± 23 %,

and 86 ± 9 % for ^{13}C-D4, ^{13}C-D5, and ^{13}C-D6, respectively (n = 75) (Table S4). The mean difference

between duplicate XAD-PAS during the calibration and storage experiments, normalized to the

average of the duplicates, ranged from 5.2 % to 18.6 % (n = 13) for all congeners. D6 and MD3M

displayed the highest differences between duplicates (Table S4). In the spatial study, the difference

between duplicates ranged from 8.8 % to 12.9 % (n = 26), when excluding D3 which was always

below LOD or LOQ.

3.1.2 Blank levels for XAD-PAS

In the calibration and storage experiments, the LOD for cVMS ranged from 191 to 519 ng/sample,

and the LOQ from 495 to 1027 ng/sample, depending on the congener (Table S5). This is relatively

high; see also the SPE-AAS blank levels below. In the spatial study, the LODs and LOQs were even

higher (Table S5). The IDL for lVMS ranged from 3.7 to 12.9 ng/sample, depending on the congener

201 (Table S5). LODs and LOQs for cVMS on a ng/m^3 basis were calculated using the experimentally

202 determined PSRs (Section 3.3), assuming the mean of all PSRs for D3 and D6, and a sampling time of

203 90 days. For the calibration and storage experiments the estimated LODs for cVMS ranged from 4.4

204 to 11.5 ng/m^3, depending on the congener, while they ranged from 10.7 to 25.0 ng/m^3 in the spatial

205 study. This is comparable to the method detection limits (MDLs) reported for SIP-disks deployed at

206 STPs and landfills,[8] and up to 20 times higher than the MDLs reported for SIP-disks in the GAPS-

207 study.[6] However, the MDLs from the GAPS-study might have been underestimated due to an

208 assumption of linear uptake of 6.5 m^3/day for 90 days in the calculation of the MDLs,[6] even if VMS

209 were shown to equilibrate with the SIPs already after 21 days.[8]

3.1.3 Effect of storage for XAD-PAS

211 The results from the storage experiment showed no significant change (at the 95 % confidence level)

212 in the VMS levels with time for any of the congeners over a period of 28 days (Figure S3). D6 and

213 MD3M showed the largest, but still non-significant, losses of 0.4 % (p = 0.10) and 0.5 % (p = 0.15) per

214 day, respectively, based on a linear regression (Figure S3). Earlier studies had shown ^{13}C-D5 to

215 degrade to ^{13}C-D4 and ^{13}C-D3 on the ENV+ resin in the SPE-AAS cartridges when stored at -18 °C.[7,19]

216 Insignificant VMS losses from the XAD-PAS suggest that a similar reaction does not occur on the

217 XAD-2 resin within the specified time period.

3.1.4 Evaluation of the SPE-AAS method

219 The LODs for cVMS ranged from 15.5 to 41.8 ng/sample depending on the congener, and the LOQs

220 from 37.9 to 117 ng/sample (Table S5). This is 10 – 38 times higher than in the previous application

221 of the method.[7] The materials used in both applications were exactly the same. The increased blank

222 levels are likely due to the laboratory environment, the solvent, or the instrumental system, which is

223 supported by higher IDLs in this study than in the previous application. When dividing by the average

224 sample volume (16.5 m^3), the LODs ranged from 0.94 to 2.54 ng/m^3 and the LOQs from 2.30 to 7.13

225 ng/m^3 (Table S5). The mean difference between duplicates, normalized to the average of the

226 duplicates, ranged from 6.5 % to 14 % for all congeners, when excluding D3 which was always below

227   LOD or LOQ (Table S6). The average recoveries of the internal standards were 85 ± 12 %, 107 ± 21 %

228   and 102 ± 17 % for ^{13}C-D4, ^{13}C-D5 and ^{13}C-D6, respectively (Table S6).

229   There are two important limitations of the SPE-AAS method. The method, including sampling and

230   extraction, had not yet been evaluated for lVMS prior to this study. The extraction efficiency was

231   good for lVMS, with only 1-2 % remaining in the second fraction (Table S6, details in SI 1.5.2). The

232   implication of an incomplete sampling efficiency for lVMS would be underestimation of lVMS

233   concentrations in air, and if consistent throughout the sampling period, the PSRs of XAD-PAS for

234   lVMS would be overestimated. However, recent method evaluation by McLachlan and Kierkegaard

235   indicates that breakthrough of lVMS is less than 1 % for 24 h sampling.[19] Secondly, the possible

236   degradation of D5 to D4 and D3 during sampling and during storage of the cartridges at -18 °C after

237   sampling[7,19] would result in possible under- and overestimation of the D5 and D3-D4 concentrations,

238   respectively. Due to the short sampling time and no storage time, as well as the currently limited

239   knowledge about mechanisms, products, conditions and rates of D5 and possibly D6 degradation, no

240   corrections have been made in this study. However, a rough estimate of the extent of possible over-

241   and underestimation have been made is SI section 1.5.2.

242   ## 3.2   Temporal trends in VMS concentrations

243   VMS concentrations in air at UTSC measured with the SPE-AAS method were all above LOQ, except

244   for D3 which was below or around LOD in all samples, and D6 and MD3M that were below LOQ and

245   IQL, respectively, on a ng/sample basis in a few samples (Table S7). The results for D3 are hence not

246   discussed further. The average concentration in air of D4, D5, and D6 was 24.2 ± 19.1, 93.5 ± 65.9,

247   and 5.5 ± 3.8 ng/m^3 respectively (Figure 1, Table S7). For MDM, MD2M, and MD3M the average

248   concentrations were 1.8 ± 1.4, 1.2 ± 0.8, and 0.5 ± 0.3 ng/m^3, respectively (Figure 1, Table S7). D5,

249   followed by D4, were the dominant congeners, and the ratios between all VMS congeners stayed

250   relatively constant throughout the sampling period. The concentrations of cVMS are up to one to

251   two orders of magnitude higher than in rural Sweden and in the European Arctic,[7,11] and comparable

252   to those measured with SIP-disks at Downsview, approximately 25 km to the west of UTSC, in spring

253   2009 (11, 55, and 6.2 ng/m^3 for D4, D5, and D6, respectively).[6] The measured lVMS concentrations

254   are up to an order of magnitude higher than at Downsview (0.12, 0.66, and 0.45 ng/m^3 for MDM,

255   MD2M, and MD3M, respectively).[6]

256   The VMS concentrations in air were highly variable during the sampling period (Figure 1), with no

257   readily apparent seasonal trend. Peak concentrations in the middle of March coincided with a period

258   of warm weather (Table S2). Overall, correlations between measured VMS levels and ambient

259   temperature were weak but significant for D5, D6, MD2M, and MD3M at the 95 % confidence level,

260   with higher concentrations at higher temperatures (Table S8). Information on wind speed and

261   direction was available for Buttonville airport, about 17 km from UTSC.[20] As the Toronto area is very

262   flat, the predominant wind pattern is expected to be similar at the two sites. Correlations were weak

263   but significant between wind speed and VMS concentrations at the 95 % confidence level, with

264   higher concentrations at lower wind speeds (Table S8). There was a significant positive correlation,

265   at the 95 % confidence level, between VMS levels and the relative frequency of wind from south-

266   southeast (directions 150°, 170°, and 180°) (Table S8). When wind speed was taken into account,

267   there was a significant negative correlation, at the 95 % confidence level, between VMS levels and

268   wind from north-northwest (directions 310°, 340°, and 350°) with higher VMS levels at lower wind

269   speeds from these directions (Table S8). The Highland Creek STP is located approximately 3 km to

270   the southeast of UTSC, which indicates that higher VMS levels could be associated with atmospheric

271   transport from the STP. One of the three samples in March with elevated VMS concentrations was

272   dominated by wind from south-southeast, while the other two displayed winds from variable

273   directions.

274   In rural Sweden and in the Arctic, a seasonality with higher D5 concentrations in the atmosphere in

275   winter than in summer was observed,[5,7] but the same trend was not seen in this study. This fits with

276   model predictions, which suggest seasonality is less pronounced in source regions than in remote

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277   areas, as constant emissions in source regions reduce the impact of the seasonality in degradation

278   by hydroxyl radicals.[5,21-22]

3.3   Calibration of the XAD-PAS

280   The levels of D5 in the XAD-PAS were above LOQ after 14 days of deployment, and after 60 days for

281   D4 due to higher blank levels and lower concentrations in air. Due to the same reasons, levels of D6

282   never exceeded the LOQ, and levels of D3 never the LOD. MDM and MD2M reached levels above IQL

283   after 21 and 42 days, respectively, while MD3M did not reach levels above IQL (Table S9). The

284   calibration curves for the XAD-PAS samplers were plotted as the concentration in the sampler

285   divided by the mean concentration in air (C_{PAS}/C_{Air}) against time of deployment (Figure 2). Results for

286   D3 have not been included as levels were below LOD in both active and passive samples throughout

287   the whole sampling period. While the levels of D6 in the XAD-PAS were also around LOD for the

288   whole sampling period, their increase with time indicates that a linear uptake period could probably

289   have been observed if the blank levels were lowered and/or the deployment period was extended

290   (Figure 2).

291   The calibration curves for D4, D5, MDM, MD2M, and MD3M were highly linear throughout the

292   whole sampling period of 98 days. The PSRs of the XAD-PAS for VMS, calculated from the slopes of

293   these calibration curves, ranged from 0.42 to 0.50 m^3/day (Table 1). As none of the VMS reached

294   equilibrium with the XAD-PAS within the time of deployment, partition coefficients between the

295   PSM and the atmosphere ($K_{XAD-air}$) could not be calculated. A lower limit for $K_{XAD-air}$ was calculated by

296   dividing the amount of VMS accumulated in the XAD at the end of the deployment period by the

297   average VMS concentrations in air during that period. A sorbent density of 640 kg/m^3 was used to

298   adjust the $K_{XAD-air}$ to a unitless value.[17] The lower limit of log $K_{XAD-air}$ was 6.5 for all congeners, which

299   reflects the similarity in their PSRs as they had not reached equilibrium (Table 1).

300   The temperature throughout the whole sampling period ranged from -14.4 °C to +33.3 °C with a

301   mean of 10.5 ± 7.9 °C (average of six temperature loggers) (Table S2). It has previously been

302   hypothesized that the temperature inside the PUF-PAS housing differs from the ambient

303   temperature, and that this can affect observed partition coefficients and PSRs.[23] Differences in mean

304   temperature at six sites inside and outside of one XAD-PAS housing were negligible (range 10.1 -

305   11.0 °C), as were differences with data from a nearby weather station (mean 10.4 ± 7.9 °C,

306   Buttonville airport).[20] The deviation between the temperature inside and outside of the housing

307   increased with increasing temperature, with higher temperatures on the outside (Figure S4). The

308   deviation ranged from -4 to +10 °C and was largest in the morning and around noon, when the sun is

309   typically at its strongest (Figure S4).

310   A poly-parameter linear free energy relationship (PP-LFER) for XAD and solute descriptors for VMS

311   were used to predict $K_{XAD-air}$ for VMS.[17,24] The predictions were adjusted to the mean environmental

312   temperature (10.5 °C) using a PP-LFER predicted sorption enthalpy and the van't Hoff equation.[17]

313   The predicted log $K_{XAD-air}$ ranged from 5.1 to 7.3 for all VMS (Table 1), and were lower than the

314   experimentally determined minima (log $K_{XAD-air}$ = 6.5) for D4, MDM, and MD2M. Based on a sorbent

315   mass of 10 grams, the experimentally determined PSRs (assuming the mean PSR for D3 and D6) and

316   the PP-LFER predicted $K_{XAD-air}$, the times required to reach 25 % (t_{25}) and 95 % (t_{95}) of equilibrium

317   could be estimated.[17] The time t_{25} can be considered as the upper limit of the linear uptake phase.

318   The t_{25} and t_{95} for VMS ranged from 1 day (D3) to 184 days (D6) and from 13 days (D3) to more than

319   5 years (D6), respectively (Table 1). This is shorter than the observed linear uptake period (98 days)

320   for most (with regard to t_{25}) or some (with regard to t_{95}) of the congeners, and indicates that

321   sorption of VMS to XAD is stronger than predicted. However, the PP-LFER predictions are strongly

322   temperature dependent (Table S10), which makes direct comparison difficult as the temperature

323   ranged over almost 50 degrees during the sampling period. To further evaluate the effect of

324   temperature, the calibration curves were compared to model predictions at various temperature

325   scenarios, which showed that the temperature has a negligible effect on the XAD-PAS uptake curves

326   (SI section 1.6).

327   SIP-disks displayed linear uptake regions for all analyzed VMS of about 21 days, with PSRs of 1.8 to

328   3.7 m^3/day and log $K_{PSM\text{-}air}$ of 5.5 to 6.2.[8] The shorter linear uptake periods and the smaller partition

329   coefficients illustrate a larger uptake capacity for VMS of the pure XAD in the XAD-PAS than of the

330   XAD-impregnated PUF-disks. The studies are not directly comparable as the calibration of the SIP-

331   disks was performed indoors. When SIP-disks were applied to measure VMS in air at STPs and

332   landfills, the PSRs from the indoor calibration were used.[8] It is not advisable to use PSRs from indoor

333   calibrations to calculate volumetric concentrations in air from the amounts sequestered in PAS

334   deployed outdoors, because air turbulence and therefore uptake kinetics are likely to be very

335   different indoors and outdoors. When SIPs were applied in the GAPS network, site-specific PSRs

336   derived from the loss of semi-volatile depuration compounds from PUF-disks (average 6.5 m^3/day,

337   range 2.25 to 16.5 m^3/day) were used to calculate VMS concentrations.[6] Considering that uptake in

338   passive samplers was recently shown to be subject to a resistance on the PSM side and therefore

339   related to the equilibrium partition coefficient between PSM and the gas phase,[15] it is unlikely that

340   PSRs obtained for one type of chemical in one type of PSM can be applied to estimate the kinetics of

341   uptake of another type of chemical in another type of PSM.

342   **3.4   Spatial mapping in an urban area**

343   The results from the deployment of the XAD-PAS samplers in the Toronto area were corrected for

344   mean blank levels and normalized to deployment time (Figure 3, Table S11). Levels of D3 and D6

345   were below LOD at all sites, except for D6 at two STP sites. Levels of D4 and D5 were below LOD or

346   LOQ at five sites, including the three rural locations (Table S11). The two STP sites had levels of D4

347   and D5 outside the upper range of the calibration curve, and a lower limit for the mass of D4 and D5

348   in these samples was estimated based on the calibration standard with the highest concentration

349   (Table S11). Levels of MDM and MD2M were above IDL and IQL at all except the rural sites, while

350   MD3M was normally between IDL and IQL (Table S11).

351   VMS concentrations in air were estimated based on the PSRs from the calibration of XAD-PAS,

352   assuming linear uptake for the whole deployment period. The estimated concentrations of ∑VMS

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353   (D4, D5, MDM, MD2M, MD3M) ranged from non-detects at the rural sites to levels above 600 ng/m^3

354   at the two STP sites. The mean ∑VMS concentration of the urban sites was 169 ± 49 ng/m^3 (n = 21),

355   with D4 and D5 concentrations of 41 ± 12 and 122 ± 39 ng/m^3 (n = 21), respectively. The estimated

356   lVMS concentrations were 3.3 ± 0.9, 1.8 ± 0.7, and 0.7 ± 0.2 ng/m^3 (n = 21) for MDM, MD2M, and

357   MD3M, respectively. At UTSC (site 4) the estimated concentrations from the XAD-PAS were a factor

358   of 0.9 to 1.3, depending on the congener, of the average concentrations measured with the SPE-AAS

359   in spring. The mean temperature during the autumn sampling period (18.2 ± 5.5 °C) was higher than

360   during the calibration,[20] which could influence the PSRs and hence the concentrations. The ratios

361   between the VMS congeners were similar at all urban sites.

362   The sites could be binned into three groups; the two STP sites, the urban sites, and the three rural

363   sites, with elevated, medium and low VMS levels, respectively. The elevated levels at the STPs

364   demonstrate that the STPs emit VMS to the atmosphere, in accordance with previous results.[8] VMS

365   concentrations in air at STPs in Ontario were measured with the SIP-disks at 1230 − 8140 ng/m^3 in

366   July − September 2009, with the highest concentrations above the aeration tanks.[8] This is up to an

367   order of magnitude higher than the estimated minimum total VMS concentrations (without D3 and

368   D6) at the STP sites in this study (600 − 800 ng/m^3 for sites 25 and 26, respectively). The urban sites

369   closest to the STPs did not show elevated VMS levels, indicating that the emissions are rapidly

370   diluted. While the samplers at site 25 and 26 were placed directly on the facilities of the STPs, the

371   samplers at site 1 were placed just outside the boundaries of an STP and showed much lower levels

372   than the two other STP sites. Rapid dilution of sVOCs from urban source areas in Toronto to rural

373   areas has previously been demonstrated.[25] The considerably lower levels of VMS at the rural sites

374   demonstrate that urban regions are also sources of VMS. Regression analysis of urban VMS levels

375   indicated that population density could be a more significant explaining variable than proximity to

376   STPs, likely due to the rapid dilution of VMS outside the STP boundaries (SI Section 1.7). Most

377   importantly, the levels of VMS in air measured with the XAD-PAS demonstrate the capability of the

378   sampler to measure VMS concentrations which are in agreement with expected trends.

379   Currently high LOD and LOQ of the XAD-PAS method renders it unsuitable for quantitative

380   determination of cVMS levels in rural and remote locations. However, considering the much higher

381   blank-levels for the instrumental system and the SPE-AAS method in this study compared to the

382   previous application,[7] it should be possible to also achieve considerably lower blank-levels of the

383   XAD-PAS method. This could be done by e.g. using cleaner solvents, a more extensive pre-cleaning

384   of the XAD-2 resin, or by meticulously removing any other sources of cVMS contamination from the

385   laboratory environment and the instrumental system. If blank-levels are lowered, the XAD-PAS can

386   be extended to applications in non-urban areas. No indication of slowing in uptake, as would be

387   indicative of an approach to equilibrium, could be observed in the field over a three month period.

388   Longer calibration studies would be required to establish the longest deployment period for VMS in

389   XAD-PAS, in particular, whether VMS amounts sequestered in XAD-PAS deployed for one year (as in

390   GAPS)[26] could still be interpreted quantitatively using the PSRs determined here. Also, PSRs under

391   different conditions would need to be established if XAD-PAS are to be confidently used for VMS in

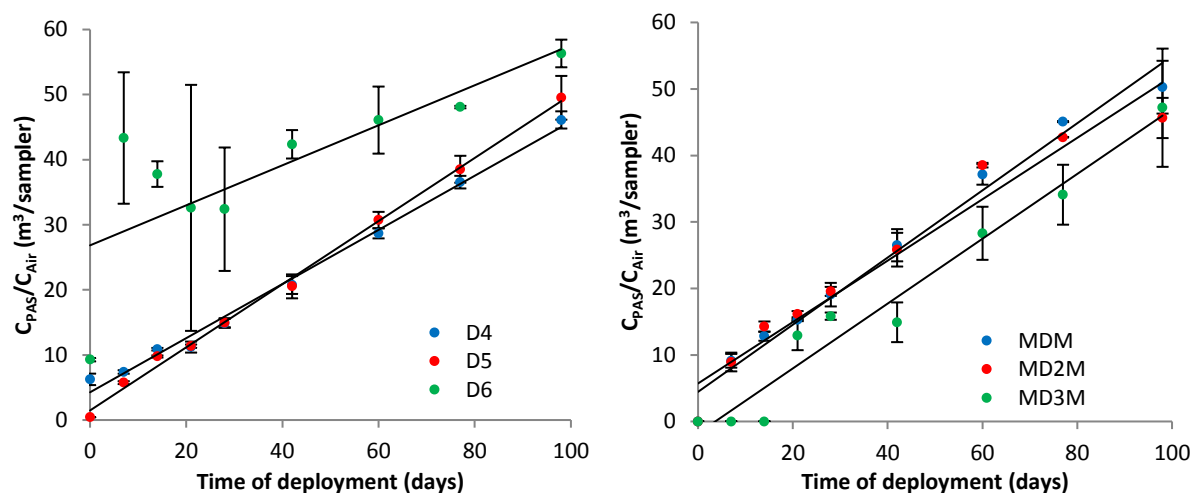392   climates other than the temperate outdoors.

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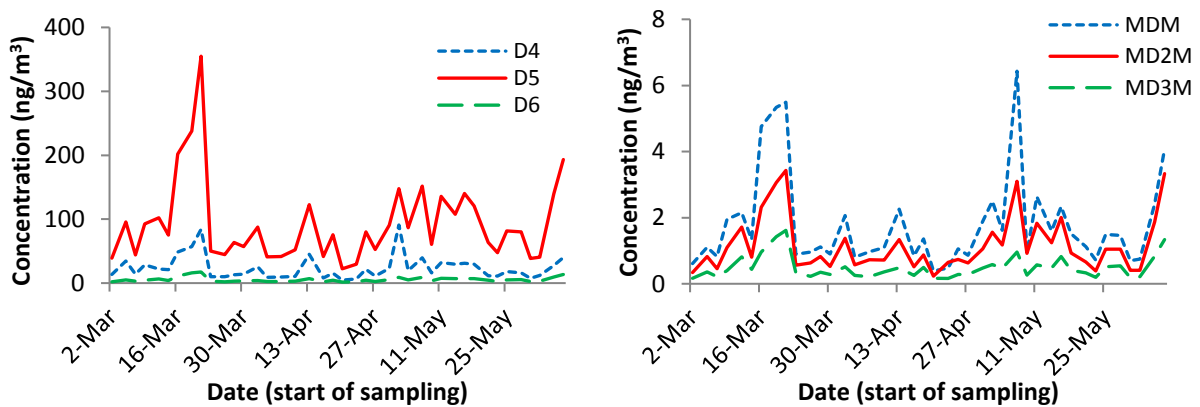
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395   **Figure 1: Concentrations in air of cVMS (left) and lVMS (right), as the average of duplicates, throughout the sampling**
396   **period for the calibration experiment.**

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Figure 2: Calibration curves for cVMS (left) and lVMS (right). The averages of duplicate samples are displayed, and the
error bars are the standard deviations of the duplicates. Results for blank samples extracted at the start of the
experiment (*n* = 2), divided by the average concentration in air for the whole deployment period, have been included at
time zero.

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Table 1: Experimentally determined and estimated sorption characteristics of VMS to XAD-PAS. PSR is the passive
sampling rate of XAD-PAS, and R^2 is the coefficient of determination of the linear regression used to calculate the PSR.
The experimentally determined partition coefficients between the sampler and the surrounding air ($K_{PAS-air}$) are
estimated lower limits of the real values. See the text for details on the PP-LFER predictions, which are adjusted to the
mean environmental temperature (10.5 °C). ΔH_S is the sorption enthalpy, and t_{25} and t_{95} are the estimated times to 25 %
and 95 % of equilibrium between the PAS and the surrounding air, respectively.

	Experimentally determined				Predicted			
	PSR (m³/day)	R^2 of linear regression	Minimum log $K_{XAD-air}$	Linear uptake period (days)	ΔH_S (kJ/mol)	log $K_{XAD-air}$	t_{25} (days)	t_{95} (days)
D3	-	-	-	-	-36.47	5.11	1	13
MDM	0.50	0.980	6.51	>98	-37.87	5.47	3	27
D4	0.42	0.993	6.47	>98	-39.12	5.90	9	89
MD2M	0.46	0.952	6.47	>98	-40.66	6.31	20	207
D5	0.49	0.997	6.50	>98	-41.43	6.58	35	367
MD3M	0.49	0.961	6.48	>98	-43.23	7.08	111	1152
D6	-	-	-	-	-43.76	7.28	184	1914

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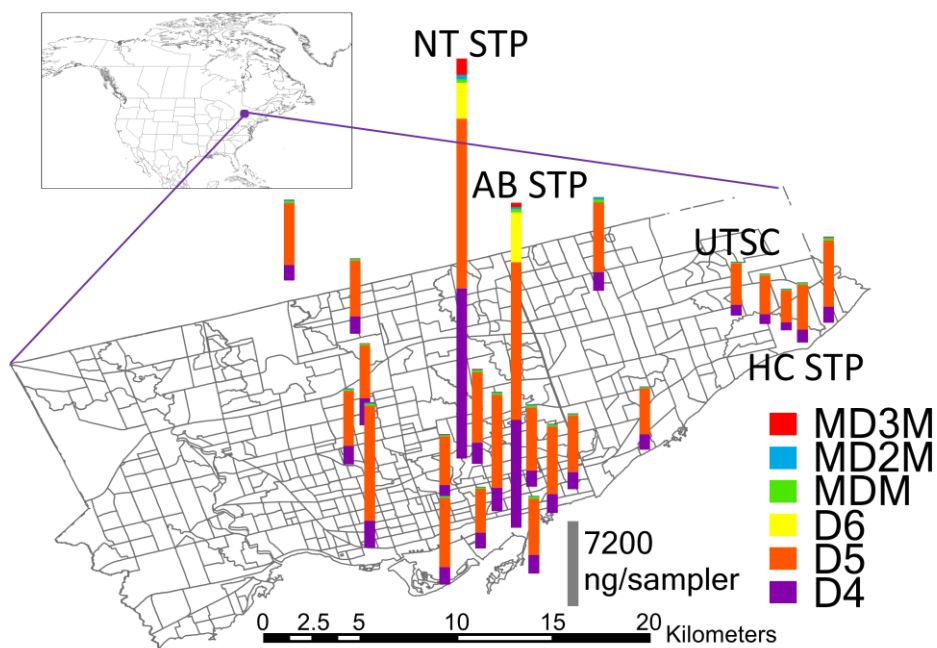
Figure 3: VMS concentrations (ng/sample/85 days) in the atmosphere of Toronto, corrected for blank-levels and deployment time. Only levels above detection limits are displayed. NT STP, AB STP, and HC STP are abbreviations for North Toronto, Ashbridges Bay, and Highland Creek Wastewater Treatment Plants, respectively.

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420   TOC/Abstract art

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Supporting Information

Supporting information containing more detailed descriptions of methods and results is available

free of charge via the Internet at http://pubs.acs.org.

References

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

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

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

4. Wu, X. M.; Apte, M. G.; Maddalena, R.; Bennettt, D. H. Volatile organic compounds in small- and medium-sized commercial buildings in California. *Environ. Sci. Technol.* **2011,** *45*, 9075-9083.

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

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

7. Krogseth, I. S.; Kierkegaard, A.; McLachlan, M. S.; Breivik, K.; Hansen, K. M.; Schlabach, M. Occurrence and seasonality of cyclic volatile methyl siloxanes in Arctic air. *Environ. Sci. Technol.* **2013,** *47*, 502-509.

8. Cheng, Y.; Shoeib, M.; Ahrens, L.; Harner, T.; Ma, J. Wastewater treatment plants and landfills emit volatile methyl siloxanes (VMSs) to the atmosphere: Investigations using a new passive air sampler. *Environ. Pollut.* **2011,** *159*, 2380-2386.

451 9.   Montemayor, B. P.; Price, B. B.; van Egmond, R. A. Accounting for intended use application in

452   characterizing the contributions of cyclopentasiloxane (D5) to aquatic loadings following

453   personal care product use: Antiperspirants, skin care products and hair care products.

454   Chemosphere **2012,** DOI: http://dx.doi.org/10.1016/j.chemosphere.2012.10.043.

455 10. Warner, N. A.; Kozerski, G.; Durham, J.; Koerner, M.; Gerhards, R.; Campbell, R.; McNett, D.

456   A. Positive vs. false detection: A comparison of analytical methods and performance for

457   analysis of cyclic volatile methylsiloxanes (cVMS) in environmental samples from remote

458   regions. Chemosphere **2012,** DOI: http://dx.doi.org/10.1016/j.chemosphere.2012.10.045.

459 11. Kierkegaard, A.; McLachlan, M. S. Determination of decamethylcyclopentasiloxane in air

460   using commercial solid phase extraction cartridges. *J. Chromatogr. A* **2010,** *1217*, 3557-3560.

461 12. Shoeib, M.; Harner, T. Characterization and comparison of three passive air samplers for

462   persistent organic pollutants. *Environ. Sci. Technol.* **2002,** *36*, 4142-4151.

463 13. Bartkow, M. E.; Booij, K.; Kennedy, K. E.; Muller, J. F.; Hawker, D. W. Passive air sampling

464   theory for semivolatile organic compounds. *Chemosphere* **2005,** *60*, 170-176.

465 14. Tuduri, L.; Millet, M.; Briand, O.; Montury, M. Passive air sampling of semi-volatile organic

466   compounds. *TrAC - Trend. Anal. Chem.* **2012,** *31*, 38-49.

467 15. Zhang, X. M.; Wania, F. Modeling the Uptake of Semivolatile Organic Compounds by Passive

468   Air Samplers: Importance of Mass Transfer Processes within the Porous Sampling Media.

469   *Environ. Sci. Technol.* **2012,** *46*, 9563-9570.

470 16. Shoeib, M.; Harner, T.; Lee, S. C.; Lane, D.; Zhu, J. P. Sorbent-impregnated polyurethane foam

471   disk for passive air sampling of volatile fluorinated chemicals. *Anal. Chem.* **2008,** *80*, 675-682.

472 17. Hayward, S. J.; Lei, Y. D.; Wania, F. Sorption of a diverse set of organic chemical vapors onto

473   XAD-2 resin: Measurement, prediction and implications for air sampling. *Atmos. Environ.*

474   **2011,** *45*, 296-302.

475   18.   Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G. Development and calibration of a

476   resin-based passive sampling system for monitoring persistent organic pollutants in the

477   atmosphere. *Environ. Sci. Technol.* **2003,** *37*, 1352-1359.

478   19.   McLachlan, M. S.; Kierkegaard, A. Linear and cyclic VMS in rural Swedish air. Presented at *3rd*

479   *Workshop on Organosilicones in the Environment*; Canada Centre for Inland Waters,

480   Burlington, Ontario, Canada, May 8-9th, 2012.

481   20.   Environment Canada. National Climate Data and Information Archive.

482   www.climate.weatheroffice.gc.ca (accessed November 21, 2012).

483   21.   Xu, S.; Wania, F. Chemical fate, latitudinal distribution and long-range transport of cyclic

484   volatile methylsiloxanes in the global environment: A modeling assessment. Chemosphere

485   **2012**, DOI: http://dx.doi.org/10.1016/j.chemosphere.2012.10.056.

486   22.   MacLeod, M.; von Waldow, H.; Tay, P.; Armitage, J. M.; Wohrnschimmel, H.; Riley, W. J.;

487   McKone, T. E.; Hungerbuhler, K. BETR global - A geographically-explicit global-scale

488   multimedia contaminant fate model. *Environ. Pollut.* **2011,** *159*, 1442-1445.

489   23.   Kennedy, K.; Hawker, D. W.; Bartkow, M. E.; Carter, S.; Ishikawa, Y.; Mueller, J. F. The

490   potential effect of differential ambient and deployment chamber temperatures on PRC

491   derived sampling rates with polyurethane foam (PUF) passive air samplers. *Environ. Pollut.*

492   **2010,** *158*, 142-147.

493   24.   Ahmed, H.; Poole, C. F.; Kozerski, G. E. Determination of descriptors for organosilicon

494   compounds by gas chromatography and non-aqueous liquid-liquid partitioning. *J.*

495   *Chromatogr. A* **2007,** *1169*, 179-192.

496   25.   Melymuk, L.; Robson, M.; Helm, P. A.; Diamond, M. L. PCBs, PBDEs, and PAHs in Toronto air:

497   Spatial and seasonal trends and implications for contaminant transport. *Sci. Total Environ.*

498   **2012,** *429*, 272-280.

499   26.   Shunthirasingham, C.; Oyiliagu, C. E.; Cao, X. S.; Gouin, T.; Wania, F.; Lee, S. C.; Pozo, K.;

500   Harner, T.; Muir, D. C. G. Spatial and temporal pattern of pesticides in the global

501   atmosphere. *J. Environ. Monit.* **2010,** *12*, 1650-1657.