

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

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**S** Supporting Information

**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 copolymeric resin-based passive air sampler (XAD-PAS) for VMS. Sixteen XAD-PAS were deployed for 7–98 days at a suburban site in Toronto, Canada, while the VMS concentration in air was monitored by 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<sup>3</sup>/day. The XAD-PAS measured  $\Sigma$ VMS concentrations ranged from nondetects in rural areas ( $n = 3$ ), to  $169 \pm 49$  ng/m<sup>3</sup> in the urban region ( $n = 21$ ), to levels above 600 ng/m<sup>3</sup> 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.<sup>1–3</sup> Concern with regard to their environmental behavior is focused in particular on their potential for persistence and bioaccumulation; octamethylcyclotetrasiloxane (D4) is classified as a reproductive toxicant.<sup>1–3</sup> Due to their high volatility, the atmosphere is a key compartment to understand their environmental behavior. VMS have been measured in indoor air,<sup>4</sup> in outdoor urban and rural air,<sup>5,6</sup> and in Arctic air.<sup>7</sup> Emissions to the atmosphere occur in particular through volatilization from use of personal care products and from sewage treatment plants (STPs) and landfills.<sup>8,9</sup> Reliable methods for sampling and analyzing VMS in air are a prerequisite for better characterization of their atmospheric levels and distribution and the relative importance of various emission sources. The applicability of standard air sampling methods for semivolatile 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.<sup>10</sup>

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<sup>11</sup> and the European Arctic.<sup>7</sup> A passive air sampler (PAS) with polyurethane foam (PUF) disks coated with polystyrene–divinylbenzene copolymeric resin XAD, i.e. sorbent-impregnated PUF (SIP) disks, that is, 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,<sup>8</sup> as well as in a global sampling campaign (GAPS).<sup>6</sup> PAS 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

Received: January 28, 2013

Revised: March 19, 2013

Accepted: March 26, 2013

Published: March 26, 2013

the latter the PSM has achieved equilibrium with the surrounding atmospheric gas phase.<sup>12</sup> To confidently calculate concentrations in air from the amount of a chemical accumulated in the PSM, calibration studies are necessary to establish the duration of the linear phase and the passive sampling rate (PSR) within this phase.<sup>13,14</sup> Recently it has been shown that resistance to mass transfer within the PSM influences the PSR as well as the distribution of the chemical within the PSM.<sup>15</sup> Because this resistance is related to a chemical's highly temperature-dependent sorption coefficient from the gas phase to the PSM, PSRs vary between chemicals and with temperature.<sup>15</sup>

A range of PSMs have been used in PAS for sVOC; PUF and XAD resin are currently the most common PSMs. In SIP disks, the XAD resin was reported to be the main sorbent for fluorinated compounds and not the PUF disks themselves.<sup>16</sup> Polycyclic aromatic hydrocarbons and polychlorinated biphenyls also display a stronger sorption to XAD than to PUF, and for volatile compounds the PUF is expected to quickly achieve equilibrium with the surrounding air.<sup>17</sup> A pure XAD-PAS system already exists and has been applied to a range of different compounds and environmental conditions.<sup>14,18</sup> However, the XAD-PAS has not yet been calibrated for more volatile compounds such as VMS.

The purpose of this study was to calibrate the XAD-PAS for selected cVMS and IVMS and to apply both active and passive sampling methods to study the temporal and spatial variability of VMS in urban air. We hypothesized that XAD-PAS has a higher sorptive capacity and a longer linear range for VMS than the SIP disks, allowing for longer field deployments. Uptake rates of VMS in the XAD-PAS were determined in suburban Toronto, Canada, using atmospheric VMS concentrations recorded with the SPE-AAS method for a period of 3 months. Once calibrated, XAD-PAS were deployed at selected sites in Toronto to investigate the relationship between VMS concentrations in 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;<sup>18</sup> details on materials and a drawing (Figure S1) are provided in section 1.1 in Supporting Information. Mesh cylinders (10 cm long, 2 cm diameter), prebaked at 450 °C, were filled with approximately 10 g 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  $\mu$ L of a mix containing 768 ng/mL <sup>13</sup>C-labeled octamethylcyclotetrasiloxane (<sup>13</sup>C-D4), 608 ng/mL <sup>13</sup>C-decamethylcyclopentasiloxane (<sup>13</sup>C-D5), and 880 ng/mL <sup>13</sup>C-dodecamethylcyclohexasiloxane (<sup>13</sup>C-D6)]. The XAD-hexane slurry was hand-shaken for 2 min, and excess solvent (approximately 10 mL) was drained from the separation funnel. Another 10 mL of hexane was added to the XAD and shaken for 2 min, and the solvent was drained. This step was performed twice, giving a combined

extract of approximately 30 mL. The volumetric standard tris(trimethylsilyloxy)silane (M3T; 200  $\mu$ L, 913 ng/mL) was added to the extract. No further cleanup 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 samples (10 g) and two hexane samples (12 mL, without XAD) were spiked with native cVMS and IVMS (200  $\mu$ L, 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 subsequently stored at -20 °C. Duplicate samples were extracted after 0, 7, 14, 21, and 28 days of storage (Table S1, Supporting Information), and the recovery relative to day 0 was calculated. The storage experiment was started on the same day as the outdoor calibration of the XAD-PAS, with extractions performed jointly for the two experiments during the first 4 weeks. This implies that the field blanks for the XAD-PAS calibration are also storage blanks that have been stored in the freezer for the same number of days as the storage samples.

**2.1.2. SPE-AAS.** The SPE-AAS method has also been described earlier.<sup>7,11</sup> SPE cartridges were manually packed by filling a 25 mL polyethylene (PE) cartridge with approximately 120 mg of ENV+ resin (hydroxylated polystyrene-divinylbenzene copolymer) between two PE frits. The cartridges were precleaned by eluting them with 14 mL of dichloromethane and 14 mL of hexane, subsequently dried with purified nitrogen gas, capped with PE caps on both ends, wrapped in aluminum foil and zip-lock bags, and stored at -20 °C until sampling. Samples were extracted immediately after retrieval to avoid previously observed issues associated with storage of SPE-AAS samples.<sup>7,19</sup> Cartridges were reused.

Internal standard was added directly on the frit prior to extraction (100  $\mu$ L to samples, 20  $\mu$ L to field blanks; mix of 768, 608, and 880 ng/mL <sup>13</sup>C-D4, <sup>13</sup>C-D5, and <sup>13</sup>C-D6, respectively). The cartridges were eluted with 4 mL of hexane, and the volumetric standard (M3T; 100  $\mu$ L, 913 ng/mL) was added to the extract. To evaluate the extraction efficiency for IVMS, two fractions of 2 mL each were collected for the first seven sets of duplicate samples (first 17 days of the experiment). The amount of analytes relative to volumetric standard was calculated for both fractions and compared. For these 17 days, VMS concentrations in air could be slightly underestimated, as only the first fraction was used in the quantification of the results.

**2.1.3. Instrumental Analysis.** Instrumental analysis was carried out on an Agilent Technologies 7890A GC system connected to an Agilent Technologies 7000A GC/MS triple quad and an Agilent 7683 series injector. The instrument was operated in selected-ion monitoring (SIM) mode, and only the first quadrupole was used. Details of the method, which was similar to previously used methods for VMS,<sup>7,11</sup> are provided in section 1.2 of Supporting Information. Samples were quantified against a five-point calibration curve forced through 0 that was based on nonlabeled VMS. A six-point calibration curve was used for the XAD samples from the storage experiment and the spatial study. The samples were analyzed for four cVMS [hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethyl-

cyclohexasiloxane (D6)] and three IVMS [octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD2M), and dodecamethylpentasiloxane (MD3M)].

**2.2. Sampling.** **2.2.1. Calibration of XAD-PAS.** Sixteen XAD-PAS were deployed simultaneously on March 2, 2012, on the campus of the University of Toronto Scarborough (UTSC), in a suburban area of Toronto, Canada. The XAD-filled mesh cylinders were placed inside stainless steel housings positioned about 1.5 m above ground level. Duplicate samples were collected after 7, 14, 21, 28, 42, 60, 77, and 98 days (June 8) of deployment (Table S1, Supporting Information). The VMS concentration in air at the site was monitored by collecting duplicate SPE-AAS every 2–3 days. The cartridges, placed inside the same type of housing as the XAD-PAS, were mounted approximately 1.5 m above ground level with their openings facing down. The cartridges were connected with poly(tetrafluoroethylene) (PTFE) tubing to low-volume air pumps (BGI-400 personal sampling pump, BGI Inc.) calibrated using a Mini-Buck air flow calibrator M-5 (APB-80500, A. P. Buck Inc.) before and after the sampling campaign. The average flow rates of 0.28 and 0.30 m<sup>3</sup>/h (for the two parallel pumps A and B, respectively) during an average sampling time of  $56.9 \pm 11.8$  h yielded an average sample volume of  $16.5 \pm 3.4$  m<sup>3</sup> (Table S2, Supporting Information). Each set of XAD-PAS and SPE-AAS was accompanied by a field blank. Field blanks were brought to the sampling site but not opened. The ambient temperature at the site was recorded at six positions inside and outside one of the XAD-PAS housings every 15 min (Smartbutton, ACR Systems Inc.).

**2.2.2. Spatial Mapping.** Duplicate XAD-PAS were deployed for approximately 3 months (range 80–92 days for most sites, 65–70 days for the two STP sites), from July until October 2012 (Table S3, Supporting Information), 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 section 1.3 in Supporting Information). Utmost 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 was sonicated in hexane before use. The nitrogen gas used to dry the precleaned 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 and quantification (LOD and LOQ) and instrumental detection and quantification limits (IDL and IQL) were calculated from field blanks and signal-to-noise levels, respectively (section 1.4 in Supporting Information).

Results for cVMS from SPE-AAS were blank-corrected on the basis of individual field blanks, while XAD-PAS from the spatial study were blank-corrected on the basis of mean field- and procedural blank levels. Results from the storage experiment and the calibration of XAD-PAS were not blank-corrected, but the blank levels at day 0 in the calibration

experiment were incorporated in the calibration curve. The IVMS were below IDL in all field and procedural blanks, and hence results for IVMS were not blank-corrected. Recovery during extraction and analysis was accounted for by the internal standards spiked prior to extraction.

### 3. RESULTS AND DISCUSSION

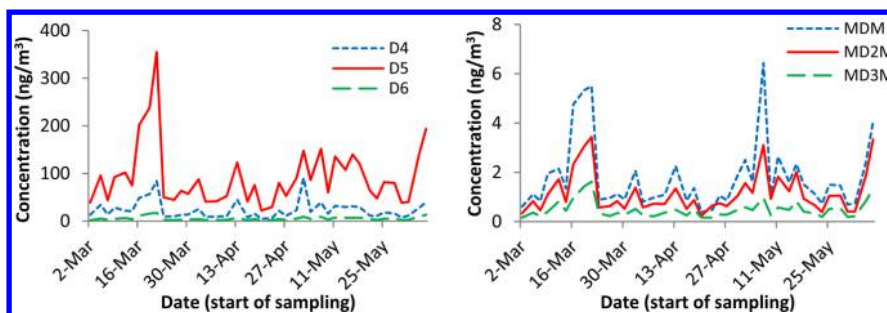
**3.1. Method Evaluation.** **3.1.1. Recovery and Repeatability for XAD-PAS.** The recovered amount of spiked VMS served as a measure of efficiency of the XAD extraction procedure. However, it is recognized that the spiking procedure may not fully simulate real uptake of VMS from the atmosphere. Details on how the results were blank-corrected are provided in section 1.5.1 in Supporting Information. 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 pure hexane samples (without XAD) were similar (Table S4, Supporting Information). 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, Supporting Information).

Mean recoveries of the internal standards were  $77\% \pm 9\%$  for <sup>13</sup>C-D4,  $104\% \pm 23\%$  for <sup>13</sup>C-D5, and  $85\% \pm 13\%$  for <sup>13</sup>C-D6, based on all samples from the XAD-PAS calibration and storage experiments ( $n = 46$ ). In the spatial study, those recoveries were  $78\% \pm 16\%$  for <sup>13</sup>C-D4,  $110\% \pm 23\%$  for <sup>13</sup>C-D5, and  $86\% \pm 9\%$  for <sup>13</sup>C-D6 ( $n = 75$ ) (Table S4, Supporting Information). The mean difference between duplicate XAD-PAS during the calibration and storage experiments, normalized to the average of duplicates, ranged from 5.2% to 18.6% ( $n = 13$ ) for all congeners. D6 and MD3M displayed the highest differences between duplicates (Table S4, Supporting Information). In the spatial study, the difference between duplicates ranged from 8.8% to 12.9% ( $n = 26$ ) when D3, which was always below LOD or LOQ, was excluded.

**3.1.2. Blank Levels for XAD-PAS.** In the calibration and storage experiments (Table S5, Supporting Information), the LOD for cVMS ranged from 191 to 519 ng/sample and the LOQ ranged from 495 to 1027 ng/sample, depending on the congener. This is relatively high; see also the SPE-AAS blank levels below. In the spatial study, the LODs and LOQs were even higher. The IDL for IVMS ranged from 3.7 to 12.9 ng/sample, depending on the congener. LODs and LOQs for cVMS on a nanograms per cubic meter basis were calculated with the experimentally determined PSRs (section 3.3), with the mean of all PSRs assumed for D3 and D6, and a sampling time of 90 days. For the calibration and storage experiments the estimated LODs for cVMS ranged from 4.4 to 11.5 ng/m<sup>3</sup>, depending on the congener, while they ranged from 10.7 to 25.0 ng/m<sup>3</sup> in the spatial study. This is comparable to the method detection limits (MDLs) reported for SIP disks deployed at STPs and landfills<sup>8</sup> and up to 20 times higher than the MDLs reported for SIP disks in the GAPS study.<sup>6</sup> However, MDLs from the GAPS study might have been underestimated due to an assumption of linear uptake of 6.5 m<sup>3</sup>/day for 90 days in the calculation of MDLs,<sup>6</sup> even if VMS were shown to equilibrate with the SIPs already after 21 days.<sup>8</sup>

**3.1.3. Effect of Storage for XAD-PAS.** The results from the storage experiment showed no significant change (at the 95% confidence level) in the VMS levels with time for any of the





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

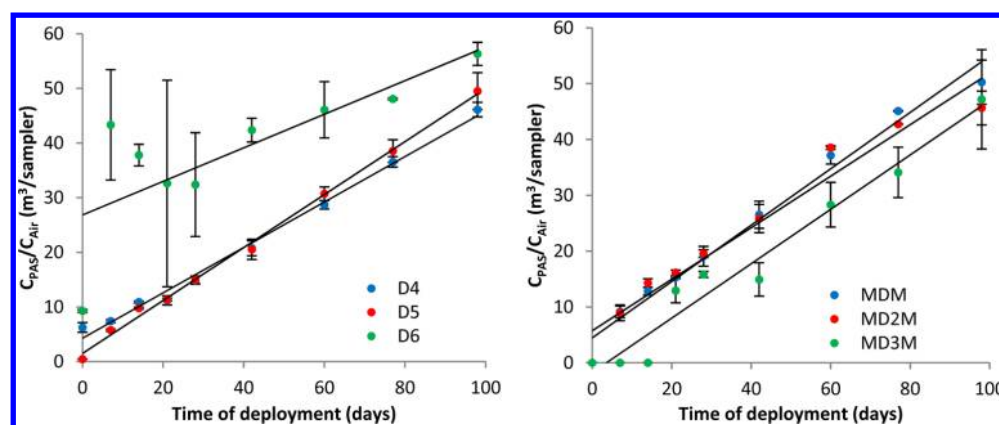
congeners over a period of 28 days. D6 and MD3M showed the largest, but still nonsignificant, losses of 0.4% ( $p = 0.10$ ) and 0.5% ( $p = 0.15$ ) per day, respectively, based on a linear regression (Figure S3, Supporting Information). Earlier studies had shown  $^{13}\text{C}$ -D5 to degrade to  $^{13}\text{C}$ -D4 and  $^{13}\text{C}$ -D3 on the ENV+ resin in SPE-AAS cartridges when stored at  $-18\text{ }^{\circ}\text{C}$ .<sup>7,19</sup> Insignificant VMS losses from the XAD-PAS suggest that a similar reaction does not occur on the XAD-2 resin within the specified time period.

**3.1.4. Evaluation of SPE-AAS Method.** The LODs for cVMS ranged from 15.5 to 41.8 ng/sample depending on the congener, and the LOQs ranged from 37.9 to 117 ng/sample (Table S5, Supporting Information). This is 10–38 times higher than in the previous application of the method.<sup>7</sup> The materials used in both applications were exactly the same. The increased blank levels are likely due to laboratory environment, solvent, or the instrumental system, which is supported by higher IDLs in this study than in the previous application. When divided by the average sample volume ( $16.5\text{ m}^3$ ), the LODs ranged from 0.94 to  $2.54\text{ ng/m}^3$  and the LOQs ranged from  $2.30$  to  $7.13\text{ ng/m}^3$  (Table S5, Supporting Information). The mean difference between duplicates, normalized to the average of the duplicates, ranged from 6.5% to 14% for all congeners when D3, which was always below LOD or LOQ, was excluded. Average recoveries of the internal standards were  $85\% \pm 12\%$  for  $^{13}\text{C}$ -D4,  $107\% \pm 21\%$  for  $^{13}\text{C}$ -D5, and  $102\% \pm 17\%$  for  $^{13}\text{C}$ -D6 (Table S6, Supporting Information).

There are two important limitations of the SPE-AAS method. The method, including sampling and extraction, had not yet been evaluated for IVMS prior to this study. The extraction efficiency was good for IVMS, with only 1–2% remaining in the second fraction (Table S6 and details in section 1.5.2 in Supporting Information). The implication of incomplete sampling efficiency for IVMS would be underestimation of IVMS concentrations in air, and if consistent throughout the sampling period, the PSRs of XAD-PAS for IVMS would be overestimated. However, recent method evaluation by McLachlan and Kierkegaard<sup>19</sup> indicates that breakthrough of IVMS is less than 1% for 24 h sampling. Second, the possible degradation of D5 to D4 and D3 during sampling and during storage of the cartridges at  $-18\text{ }^{\circ}\text{C}$  after sampling<sup>7,19</sup> would result in possible under- and overestimation of the D5 and D3–D4 concentrations, respectively. Due to the short sampling time and no storage time, as well as the currently limited knowledge about mechanisms, products, conditions, and rates of D5 and possibly D6 degradation, no corrections have been made in this study. However, a rough estimate of the extent of possible over- and underestimation has been made in section 1.5.2 in Supporting Information.

**3.2. Temporal Trends in VMS Concentrations.** VMS concentrations in air at UTSC measured by the SPE-AAS method were all above LOQ except for D3, which was below or around LOD in all samples, and D6 and MD3M, which were below LOQ and IQL, respectively, on a nanograms per sample basis in a few samples (Table S7, Supporting Information). The results for D3 are hence not discussed further. The average concentrations in air of D4, D5, and D6 were  $24.2 \pm 19.1$ ,  $93.5 \pm 65.9$ , and  $5.5 \pm 3.8\text{ ng/m}^3$ , respectively. For MDM, MD2M, and MD3M, the average concentrations were  $1.8 \pm 1.4$ ,  $1.2 \pm 0.8$ , and  $0.5 \pm 0.3\text{ ng/m}^3$ , respectively (Figure 1; Table S7, Supporting Information). D5, followed by D4, was the dominant congener, and the ratios between all VMS congeners stayed relatively constant throughout the sampling period. The concentrations of cVMS are up to 1–2 orders of magnitude higher than in rural Sweden and in the European Arctic<sup>7,11</sup> and are comparable to those measured with SIP disks at Downsview, approximately 25 km to the west of UTSC, in spring 2009 ( $11$ ,  $55$ , and  $6.2\text{ ng/m}^3$  for D4, D5, and D6, respectively).<sup>6</sup> The measured IVMS concentrations are up to an order of magnitude higher than at Downsview ( $0.12$ ,  $0.66$ , and  $0.45\text{ ng/m}^3$  for MDM, MD2M, and MD3M, respectively).<sup>6</sup>

The VMS concentrations in air were highly variable during the sampling period (Figure 1), with no readily apparent seasonal trend. Peak concentrations in the middle of March coincided with a period of warm weather (Table S2, Supporting Information). Overall, correlations between measured VMS levels and ambient temperature were weak but significant for D5, D6, MD2M, and MD3M at the 95% confidence level, with higher concentrations at higher temperatures (Table S8, Supporting Information). Information on wind speed and direction was available for Buttonville Airport, about 17 km from UTSC.<sup>20</sup> As the Toronto area is very flat, the predominant wind pattern is expected to be similar at the two sites. Correlations were weak but significant between wind speed and VMS concentrations at the 95% confidence level, with higher concentrations at lower wind speeds. There was a significant positive correlation, at the 95% confidence level, between VMS levels and the relative frequency of wind from south–southeast (directions  $150^{\circ}$ ,  $170^{\circ}$ , and  $180^{\circ}$ ). When wind speed was taken into account, there was a significant negative correlation, at the 95% confidence level, between VMS levels and wind from north–northwest (directions  $310^{\circ}$ ,  $340^{\circ}$ , and  $350^{\circ}$ ), with higher VMS levels at lower wind speeds from these directions (Table S8, Supporting Information). The Highland Creek STP is located approximately 3 km to the southeast of UTSC, which indicates that higher VMS levels could be associated with atmospheric transport from the STP. One of the three samples in March with elevated VMS concentrations



**Figure 2.** Calibration curves for (left) cVMS and (right) IVMS. Averages of duplicate samples are displayed, and error bars are 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 0.

**Table 1.** Experimentally Determined and Estimated Sorption Characteristics of VMS to XAD-PAS<sup>a</sup>

	experimentally determined				predicted			
	PSR (m <sup>3</sup> /day)	R <sup>2</sup> of linear regression	min log $K_{XAD-air}$	linear uptake period (days)	$\Delta H_S$ (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

<sup>a</sup>PSR is the passive sampling rate of XAD-PAS, and R<sup>2</sup> is the coefficient of determination of the linear regression used to calculate PSR. Experimentally determined partition coefficients between the sampler and the surrounding air ( $K_{XAD-air}$ ) are estimated lower limits of the real values. See text for details on PP-LFER predictions, which are adjusted to the mean environmental temperature (10.5 °C).  $\Delta H_S$  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.

was dominated by wind from south-southeast, while the other two displayed winds from variable directions.

In rural Sweden and in the Arctic, a seasonality with higher D5 concentrations in the atmosphere in winter than in summer was observed,<sup>5,7</sup> but the same trend was not seen in this study. This fits with model predictions, which suggest seasonality is less pronounced in source regions than in remote areas, as constant emissions in source regions reduce the impact of seasonality in degradation by hydroxyl radicals.<sup>5,21,22</sup>

**3.3. Calibration of XAD-PAS.** The levels of D5 in XAD-PAS were above LOQ after 14 days of deployment, and after 60 days for D4 due to higher blank levels and lower concentrations in air. For the same reasons, levels of D6 never exceeded LOQ and levels of D3 never exceeded LOD. MDM and MD2M reached levels above IQL after 21 and 42 days, respectively, while MD3M did not reach levels above IQL (Table S9, Supporting Information). Calibration curves for the XAD-PAS samplers were plotted as the concentration in the sampler divided by the mean concentration in air ( $C_{PAS}/C_{air}$ ) against time of deployment (Figure 2). Results for D3 have not been included, as levels were below LOD in both active and passive samples throughout the whole sampling period. While the levels of D6 in XAD-PAS were also around LOD for the whole sampling period, their increase with time indicates that a linear uptake period could probably have been observed if the blank levels were lowered and/or the deployment period was extended (Figure 2).

Calibration curves for D4, D5, MDM, MD2M, and MD3M were highly linear throughout the whole sampling period of 98

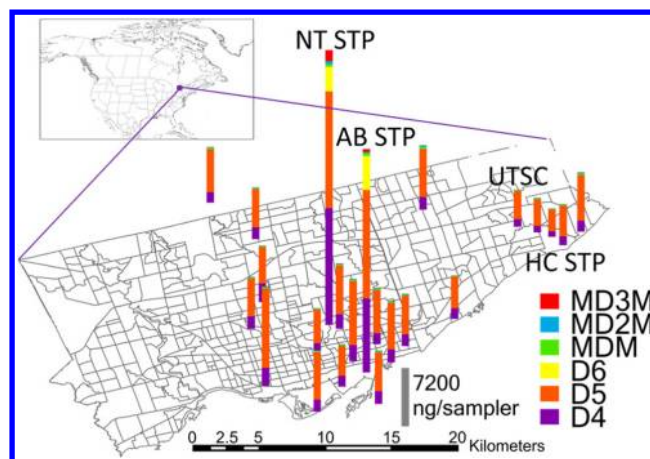
days. The PSRs of the XAD-PAS for VMS, calculated from the slopes of these calibration curves, ranged from 0.42 to 0.50 m<sup>3</sup>/day (Table 1). As none of the VMS reached equilibrium with XAD-PAS within the time of deployment, partition coefficients between the PSM and the atmosphere ( $K_{XAD-air}$ ) could not be calculated. A lower limit for  $K_{XAD-air}$  was calculated by dividing the amount of VMS accumulated in the XAD at the end of the deployment period by the average VMS concentrations in air during that period. A sorbent density of 640 kg/m<sup>3</sup> was used to adjust the  $K_{XAD-air}$  to a unitless value.<sup>17</sup> The lower limit of log  $K_{XAD-air}$  was 6.5 for all congeners, which reflects the similarity in their PSRs as they had not reached equilibrium (Table 1).

The temperature throughout the whole sampling period ranged from -14.4 to +33.3 °C with a mean of 10.5 ± 7.9 °C (average of six temperature loggers) (Table S2, Supporting Information). It has previously been hypothesized that the temperature inside the PUF-PAS housing differs from the ambient temperature and that this can affect observed partition coefficients and PSRs.<sup>23</sup> Differences in mean temperature at six sites inside and outside one XAD-PAS housing were negligible (range 10.1–11.0 °C), as were differences with data from a nearby weather station (mean 10.4 ± 7.9 °C, Buttonville Airport).<sup>20</sup> The deviation between the temperature inside and outside the housing increased with increasing temperature, with higher temperatures on the outside. The deviation ranged from -4 to +10 °C and was largest in the morning and around noon, when the sun is typically at its strongest (Figure S4, Supporting Information).

A polyparameter linear free energy relationship (PP-LFER) for XAD and solute descriptors for VMS were used to predict  $K_{\text{XAD-air}}$  for VMS.<sup>17,24</sup> Predictions were adjusted to the mean environmental temperature (10.5 °C) by use of a PP-LFER predicted sorption enthalpy and the van't Hoff equation.<sup>17</sup> The predicted  $\log K_{\text{XAD-air}}$  ranged from 5.1 to 7.3 for all VMS (Table 1) and were lower than the experimentally determined minima ( $\log K_{\text{XAD-air}} = 6.5$ ) for D4, MDM, and MD2M. On the basis of a sorbent mass of 10 g, the experimentally determined PSRs (with the mean PSR assumed for D3 and D6) and the PP-LFER predicted  $K_{\text{XAD-air}}$ , the times required to reach 25% ( $t_{25}$ ) and 95% ( $t_{95}$ ) of equilibrium could be estimated.<sup>17</sup> The time  $t_{25}$  can be considered as the upper limit of the linear uptake phase. 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 5 years (D6), respectively (Table 1). This is shorter than the observed linear uptake period (98 days) for most (with regard to  $t_{25}$ ) or some (with regard to  $t_{95}$ ) of the congeners and indicates that sorption of VMS to XAD is stronger than predicted. However, the PP-LFER predictions are strongly temperature-dependent (Table S10, Supporting Information), which makes direct comparison difficult as the temperature ranged over almost 50 °C during the sampling period. To further evaluate the effect of temperature, calibration curves were compared to model predictions at various temperature scenarios, which showed that the temperature has a negligible effect on the XAD-PAS uptake curves (section 1.6 in Supporting Information).

SIP disks displayed linear uptake regions for all analyzed VMS of about 21 days, with PSRs of 1.8–3.7 m<sup>3</sup>/day and  $\log K_{\text{PSM-air}}$  of 5.5–6.2.<sup>8</sup> The shorter linear uptake periods and smaller partition coefficients illustrate a larger uptake capacity for VMS of the pure XAD in XAD-PAS than of the XAD-impregnated PUF disks. The studies are not directly comparable, as the calibration of the SIP disks was performed indoors. When SIP disks were applied to measure VMS in air at STPs and landfills, the PSRs from the indoor calibration were used.<sup>8</sup> It is not advisable to use PSRs from indoor calibrations to calculate volumetric concentrations in air from the amounts sequestered in PAS deployed outdoors, because air turbulence and therefore uptake kinetics are likely to be very different indoors and outdoors. When SIPs were applied in the GAPS network, site-specific PSRs derived from the loss of semivolatile depuration compounds from PUF disks (average 6.5 m<sup>3</sup>/day, range 2.25–16.5 m<sup>3</sup>/day) were used to calculate VMS concentrations.<sup>6</sup> When it is considered that uptake in passive samplers was recently shown to be subject to resistance on the PSM side and therefore related to the equilibrium partition coefficient between PSM and the gas phase,<sup>15</sup> it is unlikely that PSRs obtained for one type of chemical in one type of PSM can be applied to estimate the kinetics of uptake of another type of chemical in another type of PSM.

**3.4. Spatial Mapping in an Urban Area.** Results from deployment of XAD-PAS samplers in the Toronto area were corrected for mean blank levels and normalized to deployment time (Figure 3; Table S11, Supporting Information). Levels of D3 and D6 were below LOD at all sites, except for D6 at two STP sites. Levels of D4 and D5 were below LOD or LOQ at five sites, including the three rural locations. The two STP sites had levels of D4 and D5 outside the upper range of the calibration curve, and a lower limit for the mass of D4 and D5 in these samples was estimated from the calibration standard with the highest concentration. Levels of MDM and MD2M were above IDL and IQL at all except the rural sites, while



**Figure 3.** VMS concentrations (nanograms per sample per 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.

MD3M was normally between IDL and IQL (Table S11, Supporting Information).

VMS concentrations in air were estimated from PSRs from the calibration of XAD-PAS, with linear uptake assumed for the whole deployment period. The estimated concentrations of  $\sum\text{VMS}$  (D4, D5, MDM, MD2M, MD3M) ranged from nondetection at the rural sites to levels above 600 ng/m<sup>3</sup> at the two STP sites. The mean  $\sum\text{VMS}$  concentration of the urban sites was  $169 \pm 49$  ng/m<sup>3</sup> ( $n = 21$ ), with D4 and D5 concentrations of  $41 \pm 12$  and  $122 \pm 39$  ng/m<sup>3</sup> ( $n = 21$ ), respectively. The estimated IVMS concentrations were  $3.3 \pm 0.9$ ,  $1.8 \pm 0.7$ , and  $0.7 \pm 0.2$  ng/m<sup>3</sup> ( $n = 21$ ) for MDM, MD2M, and MD3M, respectively. At UTSC (site 4), the estimated concentrations from XAD-PAS were a factor of 0.9–1.3, depending on the congener, of the average concentrations measured with SPE-AAS in spring. The mean temperature during the autumn sampling period ( $18.2 \pm 5.5$  °C) was higher than during the calibration,<sup>20</sup> which could influence the PSRs and hence the concentrations. The ratios between VMS congeners were similar at all urban sites.

The sites could be binned into three groups: two STP sites, urban sites, and three rural sites, with elevated, medium, and low VMS levels, respectively. The elevated levels at STPs demonstrate that the STPs emit VMS to the atmosphere, in accordance with previous results.<sup>8</sup> VMS concentrations in air at STPs in Ontario were measured with SIP disks at 1230–8140 ng/m<sup>3</sup> in July–September 2009, with the highest concentrations above the aeration tanks.<sup>8</sup> This is up to an order of magnitude higher than the estimated minimum total VMS concentrations (without D3 and D6) at the STP sites in this study (600–800 ng/m<sup>3</sup> for sites 25 and 26, respectively). The urban sites closest to STPs did not show elevated VMS levels, indicating that the emissions are rapidly diluted. While the samplers at site 25 and 26 were placed directly on the facilities of the STPs, the samplers at site 1 were placed just outside the boundaries of an STP and showed much lower levels than the two other STP sites. Rapid dilution of sVOCs from urban source areas in Toronto to rural areas has previously been demonstrated.<sup>25</sup> The considerably lower levels of VMS at the rural sites demonstrate that urban regions are also sources of VMS. Regression analysis of urban VMS levels indicated that



population density could be a more significant explaining variable than proximity to STPs, likely due to the rapid dilution of VMS outside the STP boundaries (section 1.7 in Supporting Information). Most importantly, the levels of VMS in air measured with XAD-PAS demonstrate the capability of the sampler to measure VMS concentrations that are in agreement with expected trends.

Currently high LOD and LOQ of the XAD-PAS method renders it unsuitable for quantitative determination of cVMS levels in rural and remote locations. However, when the much higher blank levels for the instrumental system and the SPE-AAS method in this study compared to the previous application are considered,<sup>7</sup> it should be possible to also achieve considerably lower blank levels of the XAD-PAS method. This could be done, for example, by use of cleaner solvents, by more extensive precleaning of the XAD-2 resin, or by meticulous removal of any other sources of cVMS contamination from the laboratory environment and the instrumental system. If blank levels are lowered, XAD-PAS can be extended to applications in nonurban areas. No indication of slowing in uptake, as would be indicative of an approach to equilibrium, could be observed in the field over a 3-month period. Longer calibration studies would be required to establish the longest deployment period for VMS in XAD-PAS: in particular, whether VMS amounts sequestered in XAD-PAS deployed for 1 year (as in GAPS)<sup>26</sup> could still be interpreted quantitatively by use of the PSRs determined here. Also, PSRs under different conditions would need to be established if XAD-PAS are to be confidently used for VMS in climates other than the temperate outdoors.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Additional text, four figures, and 11 tables with more detailed descriptions of methods and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank the Research Council of Norway (196191/S30 and 218812/F11) for financing the study. We also thank Shihe Xu at Dow Corning for <sup>13</sup>C-labeled standards, Scott Wilton at Toronto Water for access to STPs, and Abha Parajulee, Anya Gawor, and James Armitage for assistance.

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