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

Ingjerd S. Krogseth*,1,2, Xianming Zhang3, Ying D. Lei3, Frank Wania3, Knut Breivik1,4

1NILU - Norwegian Institute for Air research, Kjeller, Norway 2Department of Chemistry, Biotechnology and Food Science, Norwegian University of Life Sciences, Ås, Norway 3Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Canada 4Department of Chemistry, University of Oslo, Oslo, Norway

*Phone: +47 63 89 80 00; e-mail: isk@nilu.no; address: NILU, P.O. Box 100, NO-2027 Kjeller, Norway.

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 m³/day.

The XAD-PAS measured ∑VMS concentrations ranged from non-detects in rural areas (n = 3), to 169 ± 49 ng/m³ in the urban region (n = 21), to levels above 600 ng/m³ 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. 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. Due to their high volatility, the atmosphere is a key compartment to understand their environmental behavior. VMS have been measured in both indoor air, outdoor urban and rural air, and in Arctic air. Emissions to the atmosphere occur in particular through volatilization from use of personal care products and from sewage treatment plants (STPs) and landfills. 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.

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 and the European Arctic. 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, as well as in a global sampling campaign (GAPS). 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. 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.\textsuperscript{13-14} 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.\textsuperscript{15} 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.\textsuperscript{15}

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.\textsuperscript{16} 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.\textsuperscript{17} A pure XAD-PAS system already exists, and has been applied to a range of different compounds and environmental conditions.\textsuperscript{14,18} However, the XAD-PAS has not yet been calibrated for more volatile compounds such as the 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 the 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; 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 13C-labeled octamethylcyclotetrasiloxane (13C-D4), 608 ng/mL 13C-decamethyl-cyclopentasiloxane (13C-D5), and 880 ng/mL 13C-dodecamethylcyclohexasiloxane (13C-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
subsequently stored at -20 °C. Duplicate samples were extracted after 0, 7, 14, 21 and 28 days of storage (Table S1), and the recovery relative to day zero 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 four weeks. This implies that the field blanks for the XAD-PAS calibration are also storage blanks which 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. The SPE-cartridges were manually packed by filling a 25 mL polyethylene (PE) cartridge with approximately 120 mg ENV+ resin (hydroxylated polystyrene divinylbenzene copolymer) between two PE frits. The cartridges were pre-cleaned 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 storing of SPE-AAS samples. Cartridges were reused.

Internal standard was added directly on the frit prior to extraction (100 µL to samples, 20 µL to field blanks, mix of 768, 608, and 880 ng/mL 13C-D4, 13C-D5, and 13C-D6, respectively). The cartridges were eluted with 4 mL of hexane, and the volumetric standard (M3T, 100 µL, 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 7 sets of duplicate samples (first 17 days of the experiment). The amount of the analytes relative to the 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 single ion monitoring (SIM) mode, and only the first quadrupole was used. Details of
the method, which was similar to previously used methods for VMS,\textsuperscript{7,11} are provided in SI Section 1.2. Samples were quantified against a five-point calibration curve forced through zero based on non-labeled 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 dodecamethylcyclohexasiloxane (D6)) and three lVMS (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 meters above ground level. Duplicate samples were collected after 7, 14, 21, 28, 42, 60, 77, and 98 days (June 8) of deployment (Table S1). The VMS concentration in air at the site was monitored by collecting duplicate SPE-AAS every 2 to 3 days. The cartridges, placed inside the same type of housing as the XAD-PASs, were mounted approximately 1.5 meters above ground level with their openings facing down. The cartridges were connected with polytetrafluoroethylene (PTFE) tubing to low-volume air pumps (BGI-400 personal sampling pump, BGI Incorporated, MA, USA) calibrated using a Mini-Buck air flow calibrator M-5 (APB-80500, A. P. Buck Inc., FL, USA) before and after the sampling campaign. The average flow rates of 0.28 and 0.30 m\textsuperscript{3}/h (for the two parallel pumps A and B, respectively) during an average sampling time of 56.9 ± 11.8 h yielded an average sample volume of 16.5 ± 3.4 m\textsuperscript{3} (Table S2). Each set of XAD-PAS and SPE-AAS was accompanied by a field blank each. 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 of one of the XAD-PAS housings every 15 minutes (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 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 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.
LODs and LOQs for cVMS on a ng/m³ basis were calculated using the experimentally determined PSRs (Section 3.3), assuming the mean of all PSRs 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/m³, depending on the congener, while they ranged from 10.7 to 25.0 ng/m³ in the spatial study. This is comparable to the method detection limits (MDLs) reported for SIP-disks deployed at STPs and landfills, and up to 20 times higher than the MDLs reported for SIP-disks in the GAPS-study. However, the MDLs from the GAPS-study might have been underestimated due to an assumption of linear uptake of 6.5 m³/day for 90 days in the calculation of the MDLs, even if VMS were shown to equilibrate with the SIPs already after 21 days.

### 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 congeners over a period of 28 days (Figure S3). D6 and MD3M showed the largest, but still non-significant, losses of 0.4 % (p = 0.10) and 0.5 % (p = 0.15) per day, respectively, based on a linear regression (Figure S3). Earlier studies had shown ¹³C-D₅ to degrade to ¹³C-D₄ and ¹³C-D₃ on the ENV+ resin in the SPE-AAS cartridges when stored at -18 °C. 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 the SPE-AAS method

The LODs for cVMS ranged from 15.5 to 41.8 ng/sample depending on the congener, and the LOQs from 37.9 to 117 ng/sample (Table S5). This is 10 – 38 times higher than in the previous application of the method. The materials used in both applications were exactly the same. The increased blank levels are likely due to the laboratory environment, the solvent, or the instrumental system, which is supported by higher IDLs in this study than in the previous application. When dividing by the average sample volume (16.5 m³), the LODs ranged from 0.94 to 2.54 ng/m³ and the LOQs from 2.30 to 7.13 ng/m³ (Table S5). The mean difference between duplicates, normalized to the average of the duplicates, ranged from 6.5 % to 14 % for all congeners, when excluding D3 which was always below
LOD or LOQ (Table S6). The average recoveries of the internal standards were 85 ± 12 %, 107 ± 21 % and 102 ± 17 % for $^{13}$C-D4, $^{13}$C-D5 and $^{13}$C-D6, respectively (Table S6).

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, details in SI 1.5.2). The implication of an 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 indicates that breakthrough of IVMS is less than 1 % for 24 h sampling. Secondly, the possible degradation of D5 to D4 and D3 during sampling and during storage of the cartridges at -18 °C after sampling 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 have been made is SI section 1.5.2.

### 3.2 Temporal trends in VMS concentrations

VMS concentrations in air at UTSC measured with the SPE-AAS method were all above LOQ, except for D3 which was below or around LOD in all samples, and D6 and MD3M that were below LOQ and IQL, respectively, on a ng/sample basis in a few samples (Table S7). The results for D3 are hence not discussed further. The average concentration in air of D4, D5, and D6 was 24.2 ± 19.1, 93.5 ± 65.9, and 5.5 ± 3.8 ng/m$^3$ respectively (Figure 1, Table S7). For MDM, MD2M, and MD3M the average concentrations were 1.8 ± 1.4, 1.2 ± 0.8, and 0.5 ± 0.3 ng/m$^3$, respectively (Figure 1, Table S7). D5, followed by D4, were the dominant congeners, and the ratios between all VMS congeners stayed relatively constant throughout the sampling period. The concentrations of cVMS are up to one to two orders of magnitude higher than in rural Sweden and in the European Arctic, and comparable to those measured with SIP-disks at Downsview, approximately 25 km to the west of UTSC, in spring...
The measured IVMS concentrations are up to an order of magnitude higher than at Downsview (0.12, 0.66, and 0.45 ng/m$^3$ for MDM, MD2M, and MD3M, respectively). 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). 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). Information on wind speed and direction was available for Buttonville airport, about 17 km from UTSC. 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 (Table S8). 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°, 170°, and 180°) (Table S8). 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°, 340°, and 350°) with higher VMS levels at lower wind speeds from these directions (Table S8). 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 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, 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 the seasonality in degradation by hydroxyl radicals.\textsuperscript{5,21-22}

### 3.3 Calibration of the XAD-PAS

The levels of D5 in the 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. Due to the same reasons, levels of D6 never exceeded the LOQ, and levels of D3 never the LOD. MDM and MD2M reached levels above IQL after 21 and 42 days, respectively, while MD3M did not reach levels above IQL (Table S9). The calibration curves for the XAD-PAS samplers were plotted as the concentration in the sampler divided by the mean concentration in air ($C_{\text{PAS}}/C_{\text{Air}}$) 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 the 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).

The 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$^3$/day (Table 1). As none of the VMS reached equilibrium with the XAD-PAS within the time of deployment, partition coefficients between the PSM and the atmosphere ($K_{\text{XAD-air}}$) could not be calculated. A lower limit for $K_{\text{XAD-air}}$ 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$^3$ was used to adjust the $K_{\text{XAD-air}}$ to a unitless value.\textsuperscript{17} The lower limit of log $K_{\text{XAD-air}}$ 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 °C to +33.3 °C with a mean of 10.5 ± 7.9 °C (average of six temperature loggers) (Table S2). 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. Differences in mean temperature at six sites inside and outside of 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). The deviation between the temperature inside and outside of the housing increased with increasing temperature, with higher temperatures on the outside (Figure S4). 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).

A poly-parameter linear free energy relationship (PP-LFER) for XAD and solute descriptors for VMS were used to predict $K_{XAD-air}$ for VMS. The predictions were adjusted to the mean environmental temperature (10.5 °C) using a PP-LFER predicted sorption enthalpy and the van’t Hoff equation. The predicted log $K_{XAD-air}$ ranged from 5.1 to 7.3 for all VMS (Table 1), and were lower than the experimentally determined minima (log $K_{XAD-air}$ = 6.5) for D4, MDM, and MD2M. Based on a sorbent mass of 10 grams, the experimentally determined PSRs (assuming the mean PSR for D3 and D6) and the PP-LFER predicted $K_{XAD-air}$, the times required to reach 25 % ($t_{25}$) and 95 % ($t_{95}$) of equilibrium could be estimated. 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), which makes direct comparison difficult as the temperature ranged over almost 50 degrees during the sampling period. To further evaluate the effect of temperature, the 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 (SI section 1.6).
SIP-disks displayed linear uptake regions for all analyzed VMS of about 21 days, with PSRs of 1.8 to 3.7 m³/day and log $K_{PSM-air}$ of 5.5 to 6.2. The shorter linear uptake periods and the smaller partition coefficients illustrate a larger uptake capacity for VMS of the pure XAD in the 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. 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 semi-volatile depuration compounds from PUF-disks (average 6.5 m³/day, range 2.25 to 16.5 m³/day) were used to calculate VMS concentrations. Considering that uptake in passive samplers was recently shown to be subject to a resistance on the PSM side and therefore related to the equilibrium partition coefficient between PSM and the gas phase, 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

The results from the deployment of the XAD-PAS samplers in the Toronto area were corrected for mean blank levels and normalized to deployment time (Figure 3, Table S11). 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 (Table S11). 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 based on the calibration standard with the highest concentration (Table S11). Levels of MDM and MD2M were above IDL and IQL at all except the rural sites, while MD3M was normally between IDL and IQL (Table S11).

VMS concentrations in air were estimated based on the PSRs from the calibration of XAD-PAS, assuming linear uptake for the whole deployment period. The estimated concentrations of $\Sigma$VMS
(D4, D5, MDM, MD2M, MD3M) ranged from non-detects at the rural sites to levels above 600 ng/m³ at the two STP sites. The mean ∑VMS concentration of the urban sites was 169 ± 49 ng/m³ (n = 21), with D4 and D5 concentrations of 41 ± 12 and 122 ± 39 ng/m³ (n = 21), respectively. The estimated IVMS concentrations were 3.3 ± 0.9, 1.8 ± 0.7, and 0.7 ± 0.2 ng/m³ (n = 21) for MDM, MD2M, and MD3M, respectively. At UTSC (site 4) the estimated concentrations from the XAD-PAS were a factor of 0.9 to 1.3, depending on the congener, of the average concentrations measured with the SPE-AAS in spring. The mean temperature during the autumn sampling period (18.2 ± 5.5 °C) was higher than during the calibration,²⁰ which could influence the PSRs and hence the concentrations. The ratios between the VMS congeners were similar at all urban sites.

The sites could be binned into three groups; the two STP sites, the urban sites, and the three rural sites, with elevated, medium and low VMS levels, respectively. The elevated levels at the STPs demonstrate that the STPs emit VMS to the atmosphere, in accordance with previous results.⁸ VMS concentrations in air at STPs in Ontario were measured with the SIP-disks at 1230 – 8140 ng/m³ in July – September 2009, with the highest concentrations above the aeration tanks.⁸ 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/m³ for sites 25 and 26, respectively). The urban sites closest to the 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.²⁵ 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 (SI Section 1.7). Most importantly, the levels of VMS in air measured with the XAD-PAS demonstrate the capability of the sampler to measure VMS concentrations which 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, considering the much higher blank-levels for the instrumental system and the SPE-AAS method in this study compared to the previous application, it should be possible to also achieve considerably lower blank-levels of the XAD-PAS method. This could be done by e.g. using cleaner solvents, a more extensive pre-cleaning of the XAD-2 resin, or by meticulously removing any other sources of cVMS contamination from the laboratory environment and the instrumental system. If blank-levels are lowered, the XAD-PAS can be extended to applications in non-urban areas. No indication of slowing in uptake, as would be indicative of an approach to equilibrium, could be observed in the field over a three 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 one year (as in GAPS) could still be interpreted quantitatively using 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.

Figure 1: Concentrations in air of cVMS (left) and IVMS (right), as the average of duplicates, throughout the sampling period for the calibration experiment.
Figure 2: Calibration curves for cVMS (left) and IVMS (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.

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 ($K_{\text{PAS-air}}$) 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). $\Delta H_S$ 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.

<table>
<thead>
<tr>
<th></th>
<th>Experimentally determined</th>
<th>Predicted</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PSR (m$^3$/day)</td>
<td>$R^2$ of linear regression</td>
<td>Minimum $K_{\text{PAS-air}}$ (log)</td>
</tr>
<tr>
<td>D3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MDM</td>
<td>0.50</td>
<td>0.980</td>
<td>6.51</td>
</tr>
<tr>
<td>D4</td>
<td>0.42</td>
<td>0.993</td>
<td>6.47</td>
</tr>
<tr>
<td>MD2M</td>
<td>0.46</td>
<td>0.952</td>
<td>6.47</td>
</tr>
<tr>
<td>D5</td>
<td>0.49</td>
<td>0.997</td>
<td>6.50</td>
</tr>
<tr>
<td>MD3M</td>
<td>0.49</td>
<td>0.961</td>
<td>6.48</td>
</tr>
<tr>
<td>D6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
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.

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.
Acknowledgements

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

References


