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

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Objective

The atmosphere is key to understanding the environmental behavior of Volatile Methyl Siloxanes (VMS). The purpose of this study was to calibrate and evaluate an existing, polystyrene-divinylbenzene co-polymeric resin based passive air sampler (XAD-PAS)[1] for VMS. The calibration and a subsequent field test in Toronto, Canada, further allowed for investigation of the temporal and spatial variability of VMS in the region.

Cyclic VMS (cVMS)
D3: Hexamethylcyclotrisiloxane
D4: Octamethylcyclotetrasiloxane
D5: Decamethylcyclopentasiloxane
D6: Dodecamethylcyclohexasiloxane

Linear VMS (lVMS)
MDM: Octamethyltrisiloxane
MD2M: Decamethyltetrasiloxane
MD3M: Dodecamethylpentasiloxane

ΣVMS: D4,D5,MDM,MD2M,MD3M

Materials & Method

Sixteen XAD-PAS were deployed for 7 to 98 days (March – June 2012) at a suburban site in Toronto, Canada. Simultaneously the VMS concentration in air was monitored using a solid phase extraction active air sampling (SPE-AAS) method previously validated for VMS.[2,3] Subsequent to the calibration study, XAD-PAS were deployed at 26 sites in Toronto and the surrounding area (July – October 2012).

XAD-PAS were extracted by mixing the XAD with 3×10 mL hexane in a separatory funnel and draining the solvent, providing a 30 mL combined extract. SPE-AAS were extracted by elution with 4 mL hexane. All samples were analyzed with gas chromatography with mass spectrometric detection (GC-MS).

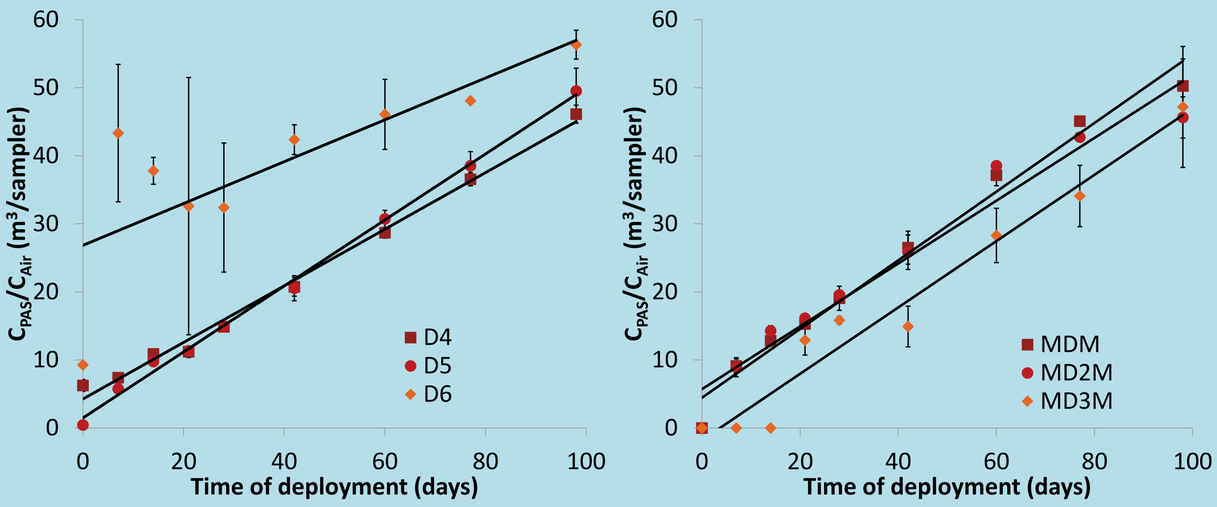

Figure 1: Calibration curves for uptake of VMS in the XAD-PAS. The averages of duplicate samples are displayed, and the error bars are the standard deviations of the duplicates.

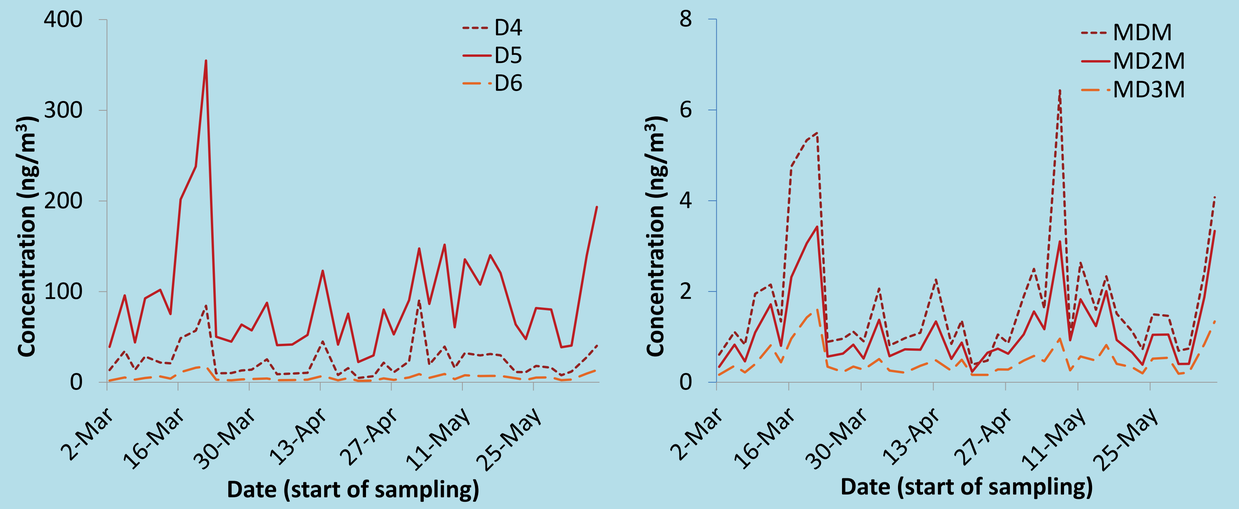

Figure 2: VMS concentrations in air measured with the SPE-AAS method, as the average of duplicates, throughout the sampling period for the calibration experiment.

Calibration & Method Evaluation

- Uptake of D4, D5, MDM, MD2M, and MD3M in the XAD-PAS was highly linear throughout the whole deployment period **(Fig 1)**.
- Sampling rates were between 0.4 and 0.5 m^3/day for these congeners **(Table 1)**.
- Blank levels were high for cVMS in both XAD-PAS and SPE-AAS, and uptake of D3 and D6 in XAD-PAS could not be quantified because levels were below quantification limits **(Table 1)**.
- No loss of VMS was observed during storage of the XAD-PAS.

Temporal & Spatial Variability

- Levels, but not composition, were highly variable in time **(Fig 2)** and weakly correlated with temperature, wind speed, and wind direction.
- No consistent seasonal trend, as previously seen for VMS,[2,3] was observed.
- ΣVMS concentrations measured with XAD-PAS ranged from nondetects 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) **(Fig 3)**.

Table 1: Limits of detection and quantification (LOD and LOQ) for cVMS and instrumental detection and quantification limits (IDL and IQL) for lVMS in XAD-PAS. Sampling rate, lower limit for the partition coefficient between XAD and the atmosphere ($K_{XAD\text{-}air}$), and duration of linear uptake period for uptake in the XAD-PAS.

	LOD & IDL (ng/sample)	LOQ & IQL (ng/sample)	Sampling rate (m^3/day)	Min log $K_{XAD\text{-}air}$	Linear uptake period (days)
D3	519	1027	-	-	-
D4	226	548	0.42	6.47	>98
D5	191	495	0.49	6.50	>98
D6	243	636	-	-	-
MDM	7.71	25.7	0.50	6.51	>98
MD2M	7.73	25.8	0.46	6.47	>98
MD3M	12.9	42.9	0.49	6.48	>98

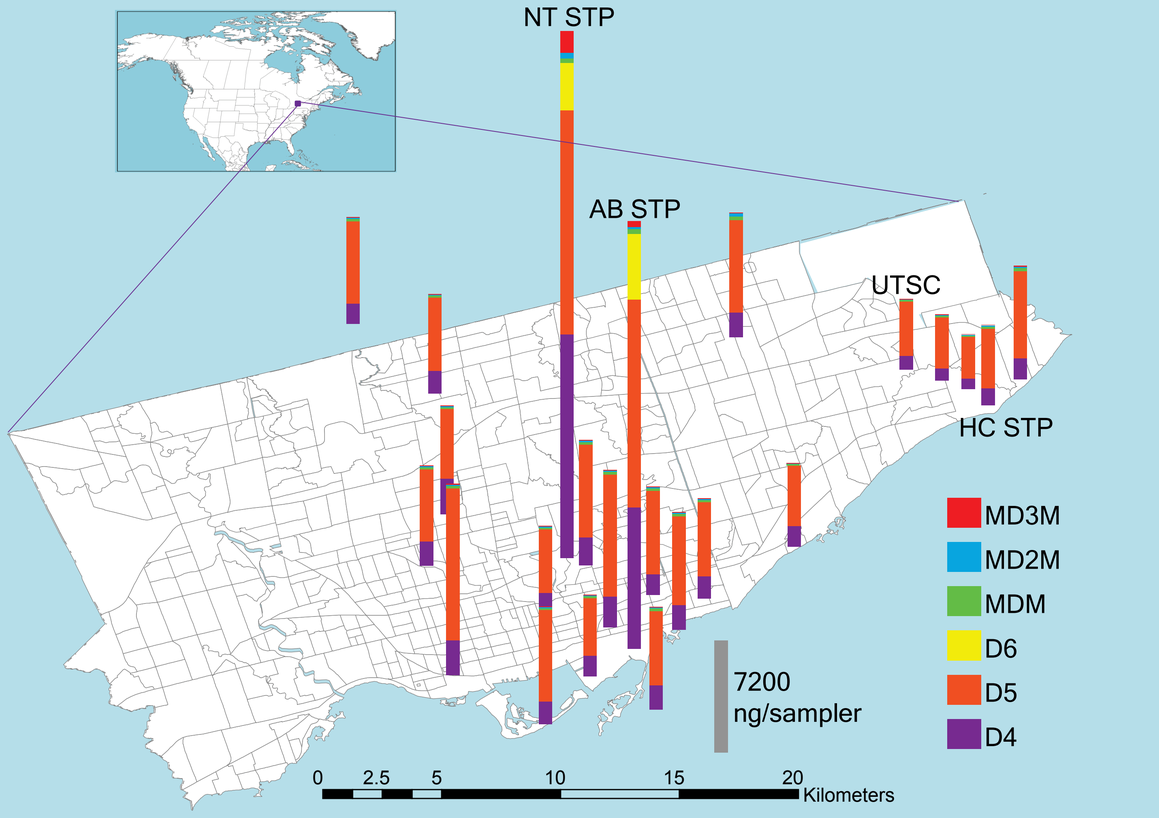

Figure 3: VMS concentrations (ng/sample/85 days) in the atmosphere of Toronto, corrected for blank-levels and deployment time. Only levels above detection limits are displayed. NT STP, AB STP, and HC STP are abbreviations for North Toronto, Ashbridges Bay, and Highland Creek Wastewater Treatment Plants,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

Conclusions

- The XAD-PAS successfully measured VMS levels that are in agreement with expected trends.
- 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.
- Lowering of the blank levels is required for determination of cVMS with XAD-PAS in rural and remote locations.
- Additional calibration studies would be required to establish the longest deployment period for VMS in XAD-PAS and sampling rates in climates other than the temperate outdoors.

References:
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[3]Krogseth, I. S. et al. *Environ. Sci. Technol.* 2013, 47, 502-509. All data published in: Krogseth, I. S. et al. *Environ Sci. Technol.* DOI: 10.1021/es400427h.

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