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Journal

Environmental Science and Technology Letters, 2(11)

ISSN

2328-8930

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et al.

Publication Date

2015-11-10

DOI

10.1021/acs.estlett.5b00256

Peer reviewed

Letter

Siloxanes are the most abundant VOC emitted from engineering students in a classroom

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Environ. Sci. Technol. Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.estlett.5b00256 • Publication Date (Web): 29 Sep 2015Downloaded from <http://pubs.acs.org> on October 3, 2015

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ACS Publications

1 Siloxanes are the most abundant VOC emitted from engineering students in
2 a classroom

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9 **Abstract**

10 Direct human emissions are known to contribute volatile organic compounds
11 (VOCs) to indoor air via various mechanisms. However, few measurements
12 are available that determine the emissions of a full suite of occupant-
13 associated VOCs. We measured occupant-related VOC emissions from
14 engineering students in a classroom using a proton-transfer-reaction time-of-
15 flight mass spectrometer (PTR-TOF-MS). The dominant compound emitted
16 was a cyclic volatile methylsiloxane (cVMS), decamethylcyclopentasiloxane
17 (D5), which is a major inactive ingredient in some personal care products
18 such as antiperspirants. D5 was found to contribute ~30% of the total indoor
19 VOC mass concentration as measured by the PTR-TOF-MS.
20 Octamethylcyclotetrasiloxane (D4) and dodecamethylcyclohexasiloxane (D6)
21 were detected at one to two orders of magnitude lower abundance. The per-
22 person emission rate of these three cVMS declined monotonically from
23 morning into the afternoon, consistent with expectations for emissions from
24 daily morning application of personal care products.

Introduction

Cyclic volatile methylsiloxanes (cVMS) are manufactured chemicals, most commonly containing 4, 5, or 6 “Si-O” units (D4, octamethylcyclotetrasiloxane; D5, decamethylcyclopentasiloxane; D6, dodecamethylcyclohexasiloxane). The cVMS compounds are commonly used in personal care products, such as antiperspirants, cosmetics and hair-care products^{1, 2}. A recent review on organosiloxanes addressed environmental properties and concerns for cVMS, including bioaccumulation, toxicity and degradation³. People expose themselves to cVMS through regular application of personal care products (PCPs). A recent study indicated that inhalation may be a more significant contributor to intake of cVMS as compared with transdermal permeation⁴. Since humans spend ~90% of their time indoors^{5, 6}, indoor gaseous cVMS are likely the major cause of an individual human’s intake, whether or not they personally apply cVMS-containing products.

Airborne cVMS have been detected in both indoor and outdoor environments⁷⁻¹⁸, with much higher concentrations reported indoors^{10, 14, 19}. In 1992, Shields and Weschler¹¹ reported measurements of gaseous cVMS concentrations indoors, in a telephone switching center. Their study reported levels of D3, D4 and D5, classifying them as “indoor only” VOCs, and identified the likely sources as PCPs, such as deodorants. In 1996, Shields et al. proposed a potential correlation between occupant density and indoor D4 and D5 concentrations along with measured outdoor airborne concentrations of D4 and D5¹⁰.

Since cVMS emissions are presumed to be primarily associated with personal care product use, indoor cVMS levels should depend on occupant density and air-exchange rate. Average emission rates per occupant could be useful for assessing the impact of cVMS on indoor air quality, yet few studies have reported such values. In this study, we carried out real-time measurements of VOCs in a classroom using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). We applied a material balance calculation to determine per-person emission rates from the measured concentrations. We report here the concentrations and emission rates of the three cVMS, the relationship between occupancy and emissions, and the relative contribution of cVMS to total VOCs as measured by PTR-TOF-MS in supply air and in the occupied classroom.

Methods

Measurements were made in a normally functioning classroom at the University of California, Berkeley, California, USA. The room volume is 670 m³, and its single-pass mechanical ventilation system operates 8:00-20:45. The mechanical ventilation system provides an air-exchange rate of $5 \pm 0.5 \text{ h}^{-1}$ when operating. Outdoor air infiltration can be neglected since the classroom has no windows or exterior doors. During classes, the two interior doors are

generally closed. Additional characteristics of the classroom have been described elsewhere²⁰.

The occupant number and VOC and CO₂ concentrations in the classroom were continuously monitored with high time resolution for five weekdays (Tuesday, two Wednesdays and two Thursdays). An observer recorded minute-by-minute occupancy and remained in the classroom during the whole daytime sampling period. For each class, there was a “stable” period during which the number of room occupants ($\bar{N}$) remained relatively constant; $\bar{N}$ equaled or exceeded 17 occupants for each of the 19 stable class sessions on the five monitored days. Each class session was taught by a faculty member from the Department of Civil and Environmental Engineering, and the classroom occupants were predominately engineering students.

Sampling was conducted by drawing air through a three-way Teflon[®] solenoid valve, with switching between the supply air duct and the classroom air every 5 minutes. An in-line PTFE membrane filter was deployed in front of the instrument inlets to remove particulate matter from the sampled air. The classroom air-sampling inlet was situated at the back of the room, two meters above the floor. Previous studies provide strong evidence to support our assumption that the room air was well mixed during times of occupancy²⁰. Supply air was sampled by inserting the 0.6-cm (1/4-inch) Teflon[®] sampling tube through the ceiling diffuser into the air duct. The VOC composition in the supply air closely resembles outdoor air, with possible modifications by interactions with the air duct and thermal conditioning system. The CO₂ concentration in the classroom and supply air was measured using the same sampling lines using a LI-820 CO₂ analyzer (LI-COR, Inc., Lincoln, Nebraska).

The VOCs were monitored by a PTR-TOF-MS (PTR-TOF 8000, IONICON Analytik GmbH, Austria), using H₃O⁺ as the primary reagent ion, with the

97 mass spectrum for mass-to-charge ratio (m/z) 30-500 recorded at 1-Hz
98 averaging time. Detailed description and application of the PTR-TOF-MS can
99 be found elsewhere²¹⁻²⁴. The fast response time, low detection limit, and mass
100 accuracy have made PTR-TOF-MS an increasingly used tool for outdoor and
101 indoor air VOC measurements²⁵.

102 Individual cVMS standards (analytical grade, purity >98%) were purchased
103 from Sigma-Aldrich (St. Louis, MO, USA). A $1\mu\text{L mL}^{-1}$ calibration mixture
104 was made by diluting each cVMS in hexane. A flow tube coupled with an
105 adjustable syringe pump was utilized to produce a four-point calibration
106 curve in air, which was in very good agreement ($\pm 20\%$) with concentrations
107 calculated using the theoretically based relative transmission method.
108 Authentic calibration gas standards (Apel-Riemer Environmental, Inc.) were
109 used to calibrate for 22 additional VOCs and concentrations of the rest of the
110 observed organic ions were calculated using the relative transmission
111 method^{24, 26}. Details of the standard gas calibration method can be found in
112 the supporting information.

113 The mixing ratio (ppb) and corresponding mass concentration ($\mu\text{g m}^{-3}$) for
114 each ion was averaged to 1-min time resolution. To reduce possible effects
115 from valve switching and sampling tube interactions, data for the first two
116 minutes after switching between classroom and supply air sampling was
117 discarded and the remaining three minutes were then averaged.
118 Examination of the time-series results indicates that this procedure was
119 effective for separately analyzing room and supply air concentrations. To
120 calculate the typical VOC concentrations in an occupied classroom, the 1-min
121 mass concentration of each ion was averaged across the stable periods for
122 every sampling day ($\sim 8:15\text{-}17:00$ PDT). The daily-average mass concentration
123 for total VOC is the sum of that for all detected ions.

Occupancy-associated emission rates of the cVMS and CO₂ were estimated using a material-balance approach (Equation 1), assuming no other pathways for mass loss except air exchange. Well-mixed conditions and identical flows into and out of the room were assumed.

$$\frac{d(C_{cl})}{dt} = aC_{sa} + \frac{E(t)}{V} - aC_{cl} \quad (1)$$

$$M = \int_{t_0}^{t_1} E(t) dt \quad (2)$$

In Equation (1), C is the concentration of the gaseous species ($\mu\text{g m}^{-3}$) at time t in the classroom air (cl) and supply air (sa); a is the air exchange rate (h^{-1}); $E(t)$ is the emission rate of CO₂ or VOC species at time t associated with human occupants ($\mu\text{g h}^{-1}$); and V is the volume of the indoor space (m^3). In Equation (2), M is the total emitted mass (μg) from time t_0 to t_1 . The average per-person emission rate (ER) is evaluated, according to Equation (3), as the derived quantity M divided by the average occupant number ($\bar{N}$) and stable period duration ($t_1 - t_0$).

$$\text{ER} = \frac{M}{\bar{N}(t_1 - t_0)} \quad (3)$$

For the cVMS, which were unambiguously associated with occupancy patterns, we report ER as analyte mass per hour per person ($\mu\text{g h}^{-1} \text{p}^{-1}$).

Results and Discussion

Figure 1 shows the apportionment of the total VOCs among three categories: (i) cVMS, (ii) sum of ions in mass range m/z 30-150, and (iii) sum of “other” ions in mass range m/z 151-500 excluding the three cVMS. The measured total VOC mass concentration in the classroom air averaged 3 times higher than in the supply air ($200 \mu\text{g m}^{-3}$ versus $66 \mu\text{g m}^{-3}$, respectively) for times when at least 17 students were present. The mass concentration of three cVMS ($63 \pm 33 \mu\text{g m}^{-3}$) contributed $\sim 31\%$ of the total VOC measured in the occupied classroom. For the combined cVMS, the occupied classroom-air

concentration was an order of magnitude higher than that in the supply air ($4.1 \pm 1.7 \mu\text{g m}^{-3}$, Table S1), indicating that these species primarily originated from indoor emission sources. Among the three cVMS, D5 was clearly dominant, comprising >90% of the total ($60 \pm 32 \mu\text{g m}^{-3}$ for classroom air, $3.8 \pm 1.5 \mu\text{g m}^{-3}$ for supply air; see Table S2). The predominance of D5, and the lesser contributions from D4 and D6, are consistent with other indoor cVMS measurements^{9, 12, 14, 27}. The D5 mass concentration was also comparable with previous reported values. For example, the average D5 concentration in offices in the UK and Italy⁹ was 54 and $7.5 \mu\text{g m}^{-3}$; the range of D5 concentration in a classroom in Albany, New York, USA with 5 occupants was $0.1\text{--}1.0 \mu\text{g m}^{-3}$ ¹² and in two offices in Barcelona, Spain was $2.4 \pm 0.2 \mu\text{g m}^{-3}$ and $1.7 \pm 0.2 \mu\text{g m}^{-3}$ ²⁷. Air samples collected in hair salons have had the highest reported concentrations of D5¹², which could be attributed to the extensive use of PCPs in that setting.

Time resolved (10-min average) mixing ratios of D4, D5, D6 and CO₂ in the supply and the classroom air on one sampling day (13 November 2014) are shown in Figure 2. As expected, because of occupant metabolism, we observed synchronous changes of indoor CO₂ concentration with occupant number and the starting and ending times of a class session. The time series of cVMS levels showed a clear association with occupancy, but differed interestingly from the CO₂ trend. A clear peak in concentrations of D5 and D6 occurred at the beginning of each class, likely resulting from increased emissions associated with elevated body temperatures due to active movement en route to the classroom, and/or from shedding of outer layers of clothing after entering the classroom. For D4, one prominent indoor peak appeared around 8:10 when the first class started, then the mixing ratio decayed toward the background level throughout the class period. The maximum mixing ratios for D5 and D6 occurred during the second class, with ~54 occupants, instead of during the next two classes, which had more occupants (see Figure 2). A

one-time prominent emission event was observed for D4 that was much larger than any other during the two-week study. No stable concentration plateau was reached for any of the three cVMS species, indicating that their emission sources were not related to metabolism as with CO₂, but instead emissions occurred more as a “burst” source when occupants first entered the room and then declined with time. Further examination focuses on the average per person emission rates.

The per-person emission rates (ER, mg h⁻¹ p⁻¹) of D4, D5 and D6 are shown for 14 classes on four weekdays (two Wednesdays and two Thursdays) in Figure 3. The ERs were consistently higher in the morning and lower in the afternoon. This finding is consistent with previously reported temporal evaporation loss of D5 after the application of PCPs^{28, 29}. In contrast, the average per-person ER of CO₂ was 21 ± 3 g h⁻¹ p⁻¹, exhibiting a consistent average metabolism rate for occupants throughout each stable class period and also across all class periods. Thus, the time series of cVMS emissions was consistent with PCPs being applied by student occupants mainly in the morning before coming to school, and exhibited a different pattern than a metabolic source.

The cVMS ERs were dominated by D5. The D4 and D6 ERs were at least one order of magnitude lower than D5, except for one class period on 11/13/2014 when the ER of D4 was comparable to that of D5, consistent with the mixing ratios shown in Figure 2. Good agreement was found for the per-capita ER of D5 between our calculation (4–235 mg p⁻¹ d⁻¹) and the few previous studies that have estimated emission rates^{30–32}. Results from models simulating ambient air measurements in Zurich³¹ and Chicago³⁰ were 170–690 mg d⁻¹ p⁻¹ and 100–420 mg d⁻¹ p⁻¹, respectively. The model-estimated per-capita ER for D6 in Zurich, Switzerland (19–81 mg d⁻¹ p⁻¹) is an order of magnitude higher than our measured values of 0.5–7.3 mg d⁻¹ p⁻¹, suggesting the

207 potential importance for this compound of emission sources other than
208 PCPs³¹.

209 Class schedules were the same during the two weeks of the study. Thus, the
210 same group of students was expected to be present in each of the classes (by
211 day and time), as supported by the consistency in numbers of occupants
212 (Table 1). The ERs for the two Wednesdays were comparable with each other,
213 whereas the ER for the second Thursday was much higher than on the first
214 Thursday. The amount and types of products used by occupants each day
215 may cause variability in the emitted mass of cVMS as well as in the relative
216 amounts of D4, D5 and D6. The second Thursday (11/13/2014) was the only
217 rainy day during the sampling period, and we speculate that the enhanced
218 cVMS emissions per person on that day might be due to wearing of coats and
219 sweaters which were removed upon entering the classroom, causing a burst
220 of emissions.

221 To summarize, in this study, we employed PTR-TOF-MS to examine the
222 sources of VOCs in a university classroom and found that D5 was the
223 dominant chemical emitted. Furthermore, we found that cVMS accounted for
224 ~1/3 of the total observed VOC mass concentration in the occupied classroom.
225 The effective emission rates we determined for D4, D5, and D6 provide useful
226 input data for indoor air quality and exposure assessment models. Further
227 investigations on indoor cVMS emissions from different populations are
228 needed to help validate and add to the accuracy of such models.

229 **ASSOCIATED CONTENT**

230 Supporting Information

231 Supporting Information available:

232 Method for the measurement of AER and details on the PTR-TOF-MS
233 parameters and calibration;

Table S1 and S2 provide data on mass concentration and relative fraction of the three categories of ions to the total measured VOC mass as well as D4, D5 and D6 in the total cVMS mass.

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.

ACKNOWLEDGEMENTS

This work was funded by the Alfred P. Sloan Foundation under grant number 2013-10-04. We thank Seema Bhangar and Robin Weber for technical assistance.

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Figure and Table captions:

Fig 1. Distribution of cVMS, organic ions in mass range m/z 30-150, and other ions (m/z range 151-500, excluding the three cVMS) comprising the total VOCs measured by PTR-TOF-MS in the supply air (A) and classroom air (B), respectively. The numerical labels represent the average mass concentration ($\mu\text{g m}^{-3}$) and fraction for each category under occupied conditions during the five sampling days. Size (area) of each chart represents the total average VOC mass concentration.

Fig 2. Time-resolved concentrations of D4, D5, D6 and CO₂ in the supply air (dashed line) and the classroom air (solid line with markers) on 13 Nov 2014 as measured by PTR-TOF-MS. The vertical dashed lines define the duration of each class; the average number of occupants in each class is noted in the top panel.

363

364 Fig 3. Per person emission rates, ER ($\text{mg h}^{-1} \text{p}^{-1}$) of D4, D5 and D6 during
365 occupied class periods for four weekdays (two Wednesdays and two
366 Thursdays). The emissions of cVMS were dominated by D5 and declined over
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369 Table 1 Measured emission rates (ER) for D4, D5, D6 and total cVMS in each
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Figure 1

Figure 2

Figure 3

Table 1 Measured emission rates (ER) for D4, D5, D6 and total cVMS in each class period, with number of occupants, class time, and date indicated.

Date	Class period	Occupant (person)	Emission rate (ER)			
			D4 ($\mu\text{g h}^{-1} \text{p}^{-1}$)	D5 ($\mu\text{g h}^{-1} \text{p}^{-1}$)	D6 ($\mu\text{g h}^{-1} \text{p}^{-1}$)	Total ($\text{mg h}^{-1} \text{p}^{-1}$)
11/4/2014	0820-0930	26	58	2480	76	2.6
	0940-1010	58	31	4260	303	4.6
	1250-1400	69	6	764	83	0.9
	1410-1600	17	3	183	19	0.2
11/5/2014	1020-1100	62	41	5950	240	6.2
	1120-1200	36	11	3670	116	3.8
	1210-1300	66	20	1900	48	2.0
	1310-1400	29	4	718	26	0.7
11/6/2014	0810-0910	24	15	4640	103	4.8
	0940-1100	57	37	3680	97	3.8
	1110-1150	58	13	2450	105	2.6
	1300-1400	64	2	336	36	0.4
11/12/2014	1020-1100	61	19	7610	156	7.8
	1120-1200	31	11	3880	97	4.0
	1210-1300	65	13	2360	66	2.4
11/13/2014	0810-0910	26	1270	9800	211	11.3
	0940-1100	54	64	8890	157	9.1
	1110-1150	64	13	4110	88	4.2
	1300-1400	67	17	2430	72	2.5