

# Siloxanes Are the Most Abundant Volatile Organic Compound Emitted from Engineering Students in a Classroom

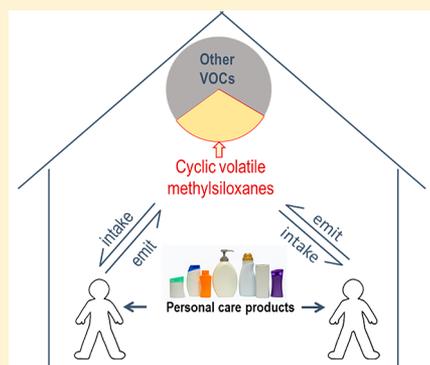
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**S** Supporting Information

**ABSTRACT:** Direct human emissions are known to contribute volatile organic compounds (VOCs) to indoor air via various mechanisms. However, few measurements that determine the emissions of a full suite of occupant-associated VOCs are available. We measured occupant-related VOC emissions from engineering students in a classroom using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). The dominant compound emitted was a cyclic volatile methylsiloxane (cVMS), decamethylcyclopentasiloxane (D5), which is a major inactive ingredient in some personal care products such as antiperspirants. D5 was found to contribute ~30% of the total indoor VOC mass concentration as measured by the PTR-TOF-MS. Octamethylcyclotetrasiloxane (D4) and dodecamethylcyclohexasiloxane (D6) were detected at abundances that were 1–2 orders of magnitude lower. The per-person emission rate of these three cVMS declined monotonically from morning into the afternoon, consistent with expectations for emissions from daily morning application of personal care products.



## INTRODUCTION

Cyclic volatile methylsiloxanes (cVMS) are manufactured chemicals, most commonly containing four, five, or six “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.<sup>1,2</sup> A recent review of organosiloxanes addressed environmental properties and concerns for cVMS, including bioaccumulation, toxicity, and degradation.<sup>3</sup> 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 than transdermal permeation.<sup>4</sup> Because humans spend ~90% of their time indoors,<sup>5,6</sup> indoor gaseous cVMS are likely the major cause of an individual human’s intake, regardless of whether they personally apply cVMS-containing products.

Airborne cVMS have been detected in both indoor and outdoor environments,<sup>7–18</sup> with much higher concentrations reported indoors.<sup>10,14,19</sup> In 1992, Shields and Weschler<sup>11</sup> reported measurements of gaseous cVMS concentrations indoors, in a telephone switching center. Their study reported levels of D3–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 D5.<sup>10</sup>

Because cVMS emissions are presumed to be primarily associated with PCP 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 conducted 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 taken in a normally functioning classroom at the University of California, Berkeley, CA. The room volume is 670 m<sup>3</sup>, and its single-pass mechanical ventilation system operates from 8:00 to 20:45. The mechanical ventilation system provides an air-exchange rate of 5 ± 0.5 h<sup>-1</sup> during operation. Outdoor air infiltration can be neglected because 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 elsewhere.<sup>20</sup>

The occupant number and VOC and CO<sub>2</sub> concentrations in the classroom were continuously monitored with high time resolution for five weekdays (one Tuesday, two Wednesdays, and

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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 min. An in-line PTFE membrane filter was deployed in front of the instrument inlet 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 occupancy.<sup>20</sup> Supply air was sampled by inserting the 0.6 cm ( $1/4$  in.) 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 CO<sub>2</sub> concentration in the classroom and supply air was measured using the same sampling lines using a LI-820 CO<sub>2</sub> analyzer (LI-COR, Inc., Lincoln, NE).

The VOCs were monitored by a PTR-TOF-MS (PTR-TOF 8000, IONICON Analytik GmbH), using H<sub>3</sub>O<sup>+</sup> as the primary reagent ion, with the mass spectrum for mass-to-charge ratio ( $m/z$ ) 30–500 recorded at an averaging time of 1 Hz. A detailed description and application of the PTR-TOF-MS can be found elsewhere.<sup>21–24</sup> The fast response time, low detection limit, and mass accuracy have made the PTR-TOF-MS an increasingly used tool for outdoor and indoor air VOC measurements.<sup>25</sup>

Individual cVMS standards (analytical grade, purity of >98%) were purchased from Sigma-Aldrich (St. Louis, MO). A 1  $\mu$ L mL<sup>-1</sup> calibration mixture was made by diluting each cVMS in hexane. A flow tube coupled with an adjustable syringe pump was utilized to produce a four-point calibration curve in air, which was in very good agreement ( $\pm 20\%$ ) with concentrations calculated using the theoretically based relative transmission method. Authentic calibration gas standards (Apel-Riemer Environmental, Inc., Broomfield, CO) were used to calibrate 22 additional VOCs, and concentrations of the rest of the observed organic ions were calculated using the relative transmission method.<sup>24,26</sup> Details of the standard gas calibration method can be found in the [Supporting Information](#).

The mixing ratio (parts per billion) and corresponding mass concentration (micrograms per cubic meter) for each ion were averaged to a time resolution of 1 min. To reduce possible effects from valve switching and sampling tube interactions, data for the first 2 min after switching between classroom and supply air sampling were discarded and data for the remaining 3 min were then averaged. Examination of the time-series results indicates that this procedure was effective for separately analyzing room and supply air concentrations. To calculate the typical VOC concentrations in an occupied classroom, the 1 min mass concentration of each ion was averaged across the stable periods for every sampling day (from ~8:15 to 17:00 Pacific Daylight Time). The daily average mass concentration for total VOC is the sum of that for all detected ions.

Occupancy-associated emission rates of the cVMS and CO<sub>2</sub> were estimated using a material-balance approach (eq 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.

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

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

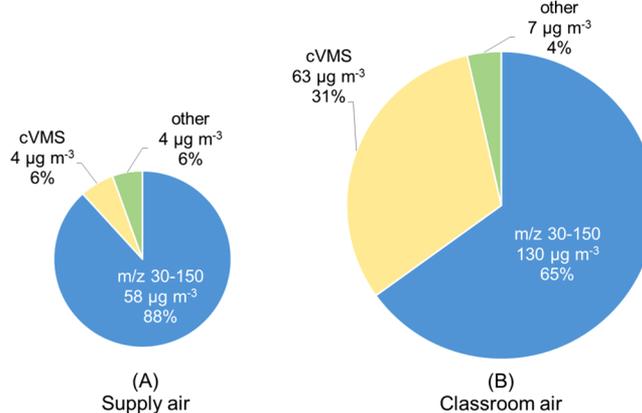
In eq 1,  $C$  is the concentration of the gaseous species (micrograms per cubic meter) at time  $t$  in the classroom air (cl) and supply air (sa),  $a$  is the air-exchange rate (inverse hours),  $E(t)$  is the emission rate of CO<sub>2</sub> or VOC species at time  $t$  associated with human occupants (micrograms per hour), and  $V$  is the volume of the indoor space (cubic meters). In eq 2,  $M$  is the total emitted mass (micrograms) from time  $t_0$  to  $t_1$ . The average per-person emission rate (ER) is evaluated, according to eq 3, as the derived quantity  $M$  divided by the average occupant number ( $\bar{N}$ ) and stable period duration ( $t_1 - t_0$ ).

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

For the cVMS, which were unambiguously associated with occupancy patterns, we report ER as analyte mass (micrograms) per hour per person.

## RESULTS AND DISCUSSION

Figure 1 shows the apportionment of the total VOCs among three categories: (i) cVMS, (ii) sum of ions in the mass range of

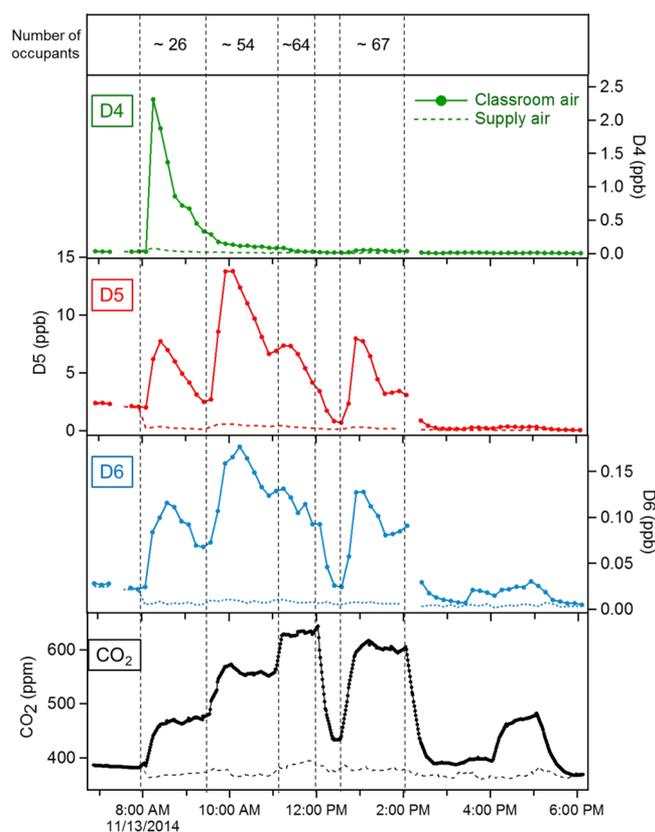


**Figure 1.** Distribution of cVMS, organic ions in the mass range of  $m/z$  30–150, and other ions (mass range of  $m/z$  151–500, excluding the three cVMS) comprising the total VOCs measured by the PTR-TOF-MS in the (A) supply air and (B) classroom air. The numerical labels represent the average mass concentration (micrograms per cubic meter) and the fraction for each category under occupied conditions during the five sampling days. The size (area) of each chart represents the total average VOC mass concentration.

$m/z$  30–150, and (iii) sum of “other” ions in the mass range of  $m/z$  151–500 excluding the three cVMS. The measured total VOC mass concentration in the classroom air ( $200 \mu\text{g m}^{-3}$ ) was on average 2 times higher than in the supply air ( $66 \mu\text{g m}^{-3}$ ) 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 1 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 and  $3.8 \pm 1.5 \mu\text{g m}^{-3}$  for supply air (see Table S2)]. The predominance of D5, and the smaller contributions from D4 and D6, are consistent with other indoor cVMS measurements.<sup>9,12,14,27</sup> The D5 mass concentration was also comparable with previous reported values. For example, the average D5 concentrations in offices in the U.K. and Italy<sup>9</sup> were 54 and  $7.5 \mu\text{g m}^{-3}$ , respectively; the range of D5 concentration in a classroom in Albany, NY, with five occupants was  $0.1\text{--}1.0 \mu\text{g m}^{-3}$ <sup>12</sup> and in two offices in Barcelona, Spain, was  $2.4 \pm 0.2$  and  $1.7 \pm 0.2 \mu\text{g m}^{-3}$ .<sup>27</sup> Air samples collected in hair salons have had the highest reported concentrations of D5,<sup>12</sup> which could be attributed to the extensive use of PCPs in that setting.

Time-resolved (10 min average) mixing ratios of D4–D6 and CO<sub>2</sub> in the supply and the classroom air on one sampling day (November 13, 2014) are shown in Figure 2. As expected,



**Figure 2.** Time-resolved concentrations of D4–D6 and CO<sub>2</sub> in the supply air (dashed line) and the classroom air (solid line with markers) on November 13, 2014, as measured by the 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.

because of occupant metabolism, we observed synchronous changes in indoor CO<sub>2</sub> 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 CO<sub>2</sub> 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

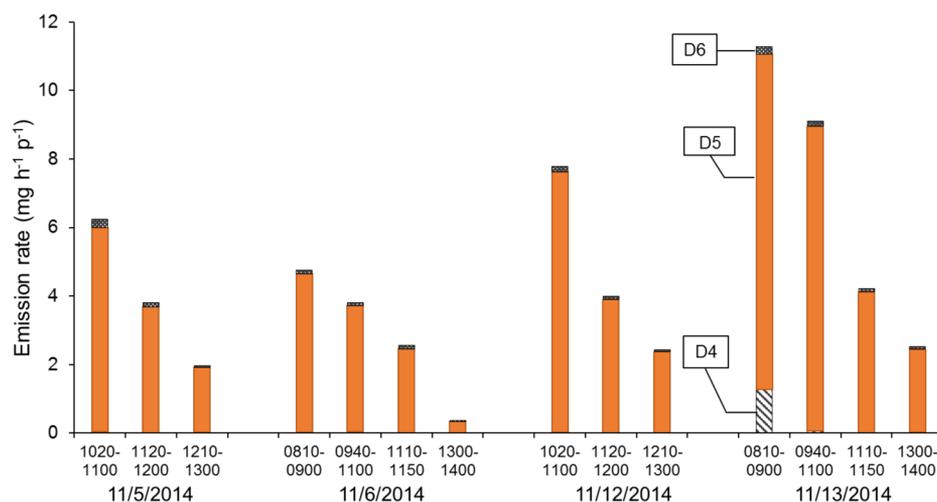
entering the classroom. For D4, one prominent indoor peak appeared around 8:10 when the first class started, and then the mixing ratio decayed toward the background level throughout the class period. The maximal mixing ratios for D5 and D6 occurred during the second class, with ~54 occupants, instead 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 CO<sub>2</sub>, 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, milligrams per hour per person) of D4–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.<sup>28,29</sup> In contrast, the average per-person ER of CO<sub>2</sub> was  $21 \pm 3 \text{ g h}^{-1} \text{ person}^{-1}$ , 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 pattern different from that of a metabolic source.

The cVMS ERs were dominated by D5. The D4 and D6 ERs were at least 1 order of magnitude lower than that of D5, except for one class period on November 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 ( $4\text{--}235 \text{ mg person}^{-1} \text{ day}^{-1}$ ) and the few previous studies that have estimated emission rates.<sup>30–32</sup> Results from models simulating ambient air measurements in Zurich<sup>31</sup> and Chicago<sup>30</sup> were  $170\text{--}690$  and  $100\text{--}420 \text{ mg day}^{-1} \text{ person}^{-1}$ , respectively. The model-estimated per-capita ER for D6 in Zurich, Switzerland ( $19\text{--}81 \text{ mg day}^{-1} \text{ person}^{-1}$ ), is an order of magnitude higher than our measured values of  $0.5\text{--}7.3 \text{ mg day}^{-1} \text{ person}^{-1}$ , suggesting the potential importance for this compound of emission sources other than PCPs.<sup>31</sup>

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

In summary, in this study, we employed the PTR-TOF-MS to examine the sources of VOCs in a university classroom and found that D5 was the dominant chemical emitted. Furthermore, we found that cVMS accounted for approximately one-third of the total observed VOC mass concentration in the occupied classroom. The effective emission rates we determined



**Figure 3.** Per-person emission rates, ER, of D4–D6 during occupied class periods for four weekdays (two Wednesdays and two Thursdays). The emissions of cVMS were dominated by D5 and declined over the course of each day.

**Table 1.** Measured Emission Rates (ERs) for D4–D6 and Total cVMS during Each Class Period, with the Number of Occupants, Class Time, and Date Indicated

| date              | class period | occupant (person) | emission rate (ER)                            |   |   | total (mg h <sup>-1</sup> person <sup>-1</sup> ) |
|-------------------|--------------|-------------------|---|---|---|--|
|                   |              |                   | D4 (μg h <sup>-1</sup> person <sup>-1</sup> ) | D5 (μg h <sup>-1</sup> person <sup>-1</sup> ) | D6 (μg h <sup>-1</sup> person <sup>-1</sup> ) |  |
| November 4, 2014  | 8:20–9:30    | 26                | 58  | 2480  | 76  | 2.6  |
|                   | 9:40–10:10   | 58                | 31  | 4260  | 303   | 4.6  |
|                   | 12:50–14:00  | 69                | 6   | 764   | 83  | 0.9  |
|                   | 14:10–16:00  | 17                | 3   | 183   | 19  | 0.2  |
| November 5, 2014  | 10:20–11:00  | 62                | 41  | 5950  | 240   | 6.2  |
|                   | 11:20–12:00  | 36                | 11  | 3670  | 116   | 3.8  |
|                   | 12:10–13:00  | 66                | 20  | 1900  | 48  | 2.0  |
|                   | 13:10–14:00  | 29                | 4   | 718   | 26  | 0.7  |
| November 6, 2014  | 8:10–9:10    | 24                | 15  | 4640  | 103   | 4.8  |
|                   | 9:40–11:00   | 57                | 37  | 3680  | 97  | 3.8  |
|                   | 11:10–11:50  | 58                | 13  | 2450  | 105   | 2.6  |
|                   | 13:00–14:00  | 64                | 2   | 336   | 36  | 0.4  |
| November 12, 2014 | 10:20–11:00  | 61                | 19  | 7610  | 156   | 7.8  |
|                   | 11:20–12:00  | 31                | 11  | 3880  | 97  | 4.0  |
|                   | 12:10–13:00  | 65                | 13  | 2360  | 66  | 2.4  |
| November 13, 2014 | 8:10–9:10    | 26                | 1270  | 9800  | 211   | 11.3   |
|                   | 9:40–11:00   | 54                | 64  | 8890  | 157   | 9.1  |
|                   | 11:10–11:50  | 64                | 13  | 4110  | 88  | 4.2  |
|                   | 13:00–14:00  | 67                | 17  | 2430  | 72  | 2.5  |

for D4–D6 provide useful input data for indoor air quality and exposure assessment models. Further investigations of indoor cVMS emissions from different populations are needed to help validate and add to the accuracy of such models.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.estlett.5b00256](https://doi.org/10.1021/acs.estlett.5b00256).

Method for the measurement of AER and details on the PTR-TOF-MS parameters and calibration and data on the mass concentration and relative fraction of the three categories of ions to the total measured VOC mass as well as D4–D6 in the total cVMS mass (Tables S1 and S2) (PDF)

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### Notes

The authors declare no competing financial interest.

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