

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

Xiaochen Tang, Pawel Misztal, William W Nazaroff, and Allen H. Goldstein

Environ. Sci. Technol. Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.estlett.5b00256 • Publication Date (Web): 29 Sep 2015

Downloaded from <http://pubs.acs.org> on October 3, 2015

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.



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

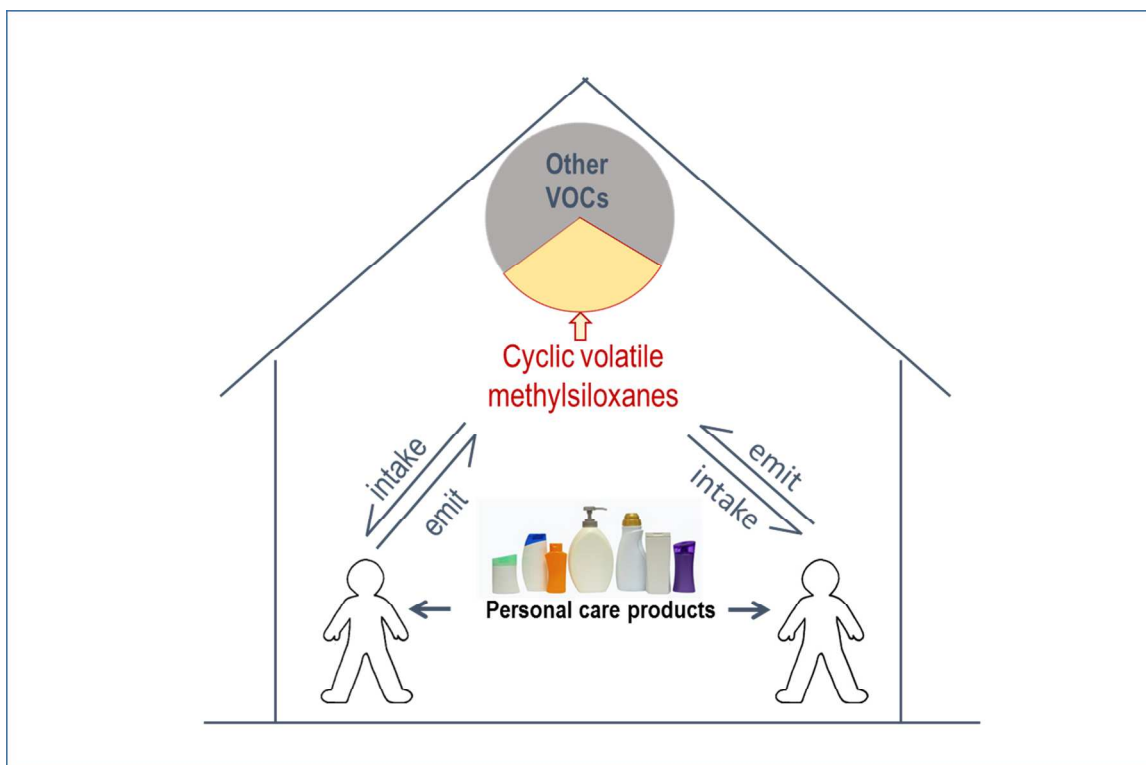
3 Xiaochen Tang*[§], Pawel K. Misztal[†], William W Nazaroff[§], Allen H.
4 Goldstein^{§†}

5 [§] Department of Civil and Environmental Engineering, University of
6 California, Berkeley, CA, USA 94720

7 [†] Department of Environmental Science, Policy and Management, University
8 of California, Berkeley, CA, USA 94720

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.



25

26

27 Introduction

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

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

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

62 **Methods**

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

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

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

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

95 The VOCs were monitored by a PTR-TOF-MS (PTR-TOF 8000, IONICON
96 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 ($\sim 8:15-17:00$ PDT). The daily-average mass concentration
123 for total VOC is the sum of that for all detected ions.

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

$$128 \quad \frac{d(C_{cl})}{dt} = aC_{sa} + \frac{E(t)}{V} - aC_{cl} \quad (1)$$

$$129 \quad M = \int_{t_0}^{t_1} E(t) dt \quad (2)$$

130 In Equation (1), C is the concentration of the gaseous species ($\mu\text{g m}^{-3}$) at time
131 t in the classroom air (cl) and supply air (sa); a is the air exchange rate (h^{-1});
132 $E(t)$ is the emission rate of CO₂ or VOC species at time t associated with
133 human occupants ($\mu\text{g h}^{-1}$); and V is the volume of the indoor space (m^3). In
134 Equation (2), M is the total emitted mass (μg) from time t_0 to t_1 . The average
135 per-person emission rate (ER) is evaluated, according to Equation (3), as the
136 derived quantity M divided by the average occupant number (\bar{N}) and stable
137 period duration ($t_1 - t_0$).

$$138 \quad \text{ER} = \frac{M}{\bar{N}(t_1 - t_0)} \quad (3)$$

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

141 Results and Discussion

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

150 concentration was an order of magnitude higher than that in the supply air
151 ($4.1 \pm 1.7 \mu\text{g m}^{-3}$, Table S1), indicating that these species primarily originated
152 from indoor emission sources. Among the three cVMS, D5 was clearly
153 dominant, comprising >90% of the total ($60 \pm 32 \mu\text{g m}^{-3}$ for classroom air,
154 $3.8 \pm 1.5 \mu\text{g m}^{-3}$ for supply air; see Table S2). The predominance of D5, and the
155 lesser contributions from D4 and D6, are consistent with other indoor cVMS
156 measurements^{9, 12, 14, 27}. The D5 mass concentration was also comparable with
157 previous reported values. For example, the average D5 concentration in
158 offices in the UK and Italy⁹ was 54 and $7.5 \mu\text{g m}^{-3}$; the range of D5
159 concentration in a classroom in Albany, New York, USA with 5 occupants
160 was $0.1\text{-}1.0 \mu\text{g m}^{-3}$ ¹² and in two offices in Barcelona, Spain was $2.4 \pm 0.2 \mu\text{g m}^{-3}$
161 and $1.7 \pm 0.2 \mu\text{g m}^{-3}$ ²⁷. Air samples collected in hair salons have had the
162 highest reported concentrations of D5¹², which could be attributed to the
163 extensive use of PCPs in that setting.

164 Time resolved (10-min average) mixing ratios of D4, D5, D6 and CO₂ in the
165 supply and the classroom air on one sampling day (13 November 2014) are
166 shown in Figure 2. As expected, because of occupant metabolism, we observed
167 synchronous changes of indoor CO₂ concentration with occupant number and
168 the starting and ending times of a class session. The time series of cVMS
169 levels showed a clear association with occupancy, but differed interestingly
170 from the CO₂ trend. A clear peak in concentrations of D5 and D6 occurred at
171 the beginning of each class, likely resulting from increased emissions
172 associated with elevated body temperatures due to active movement en route
173 to the classroom, and/or from shedding of outer layers of clothing after
174 entering the classroom. For D4, one prominent indoor peak appeared around
175 8:10 when the first class started, then the mixing ratio decayed toward the
176 background level throughout the class period. The maximum mixing ratios
177 for D5 and D6 occurred during the second class, with ~54 occupants, instead
178 of during the next two classes, which had more occupants (see Figure 2). A

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

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

197 The cVMS ERs were dominated by D5. The D4 and D6 ERs were at least one
198 order of magnitude lower than D5, except for one class period on 11/13/2014
199 when the ER of D4 was comparable to that of D5, consistent with the mixing
200 ratios shown in Figure 2. Good agreement was found for the per-capita ER of
201 D5 between our calculation (4–235 mg p⁻¹ d⁻¹) and the few previous studies
202 that have estimated emission rates^{30–32}. Results from models simulating
203 ambient air measurements in Zurich³¹ and Chicago³⁰ were 170–690 mg d⁻¹
204 p⁻¹ and 100–420 mg d⁻¹ p⁻¹, respectively. The model-estimated per-capita ER
205 for D6 in Zurich, Switzerland (19–81 mg d⁻¹ p⁻¹) is an order of magnitude
206 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;

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

237 This material is available free of charge via the Internet at <http://pubs.acs.org>.

238 AUTHOR INFORMATION

239 Corresponding author

240 *Email: xtang@berkeley.edu. Phone: 951-961-8295.

241 Notes

242 The authors declare no competing financial interest.

243 ACKNOWLEDGEMENTS

244 This work was funded by the Alfred P. Sloan Foundation under grant number
245 2013-10-04. We thank Seema Bhangar and Robin Weber for technical
246 assistance.

247 REFERENCES

- 248 1. Horii, Y.; Kannan, K. Survey of organosilicone compounds, including cyclic and linear
249 siloxanes, in personal-care and household products. *Arch. Environ. Con. Tox.* **2008**, *55*, 701-
250 710.
- 251 2. Wang, R.; Moody, R. P.; Koniecki, D.; Zhu, J. Low molecular weight cyclic volatile
252 methylsiloxanes in cosmetic products sold in Canada: Implication for dermal exposure.
253 *Environ. Int.* **2009**, *35*, 900-904.
- 254 3. Rücker, C.; Kümmerer, K. Environmental Chemistry of Organosiloxanes. *Chem. Rev.*
255 **2015**, *115*, 466-524.
- 256 4. Biesterbos, J. W. H.; Beckmann, G.; van Wel, L.; Anzion, R. B. M.; von Goetz, N.;
257 Dudzina, T.; Roeleveld, N.; Ragas, A. M. J.; Russel, F. G. M.; Scheepers, P. T. J. Aggregate dermal
258 exposure to cyclic siloxanes in personal care products: Implications for risk assessment.
259 *Environ. Int.* **2015**, *74*, 231-239.
- 260 5. de Bruin, Y. B.; Koistinen, K.; Kephelopoulos, S.; Geiss, O.; Tirendi, S.; Kotzias, D.
261 Characterisation of urban inhalation exposures to benzene, formaldehyde and acetaldehyde
262 in the European union: comparison of measured and modelled exposure data. *Environ. Sci.*
263 *Pollut. Res.* **2008**, *15*, 417-430.
- 264 6. Sarigiannis, D. A.; Karakitsios, S. P.; Gotti, A.; Liakos, I. L.; Katsoyiannis, A. Exposure to
265 major volatile organic compounds and carbonyls in European indoor environments and
266 associated health risk. *Environ. Int.* **2011**, *37*, 743-765.
- 267 7. Hodgson, A. T.; Faulkner, D.; Sullivan, D. P.; DiBartolomeo, D. L.; Russell, M. L.; Fisk, W.
268 J. Effect of outside air ventilation rate on volatile organic compound concentrations in a call
269 center. *Atmos. Environ.* **2003**, *37*, 5517-5527.

- 270 8. Katsoyiannis, A.; Anda, E. E.; Cincinelli, S.; Martellini, T.; Leva, P.; Goetsch, A.;
271 Sandanger, T. M.; Huber, S. Indoor air characterization of various microenvironments in the
272 Arctic. The case of Tromsø, Norway. *Environ. Res.* **2014**, *134*, 1-7.
- 273 9. Pieri, F.; Katsoyiannis, A.; Martellini, T.; Hughes, D.; Jones, K. C.; Cincinelli, A.
274 Occurrence of linear and cyclic volatile methyl siloxanes in indoor air samples (UK and Italy)
275 and their isotopic characterization. *Environ. Int.* **2013**, *59*, 363-371.
- 276 10. Shields, H. C.; Fleischer, D. M.; Weschler, C. J. Comparisons among VOCs measured in
277 three types of U.S. commercial buildings with different occupant densities. *Indoor Air* **1996**,
278 *6*, 2-17.
- 279 11. Shields, H. C.; Weschler, C. J. Volatile organic compounds measured at a telephone
280 switching center from 5/30/85-12/6/88: a detailed case-study. *J. Air Waste Manage.* **1992**,
281 *42*, 792-804.
- 282 12. Tran, T. M.; Kannan, K. Occurrence of cyclic and linear siloxanes in indoor air from
283 Albany, New York, USA, and its implications for inhalation exposure. *Sci. Total Environ.*
284 **2015**, *511*, 138-144.
- 285 13. Xu, L.; Shi, Y.; Liu, N.; Cai, Y. Methyl siloxanes in environmental matrices and human
286 plasma/fat from both general industries and residential areas in China. *Sci. Total Environ.*
287 **2015**, *505*, 454-463.
- 288 14. Yucuis, R. A.; Stanier, C. O.; Hornbuckle, K. C. Cyclic siloxanes in air, including
289 identification of high levels in Chicago and distinct diurnal variation. *Chemosphere* **2013**, *92*,
290 905-910.
- 291 15. Genualdi, S.; Harner, T.; Cheng, Y.; MacLeod, M.; Hansen, K. M.; van Egmond, R.;
292 Shoeib, M.; Lee, S. C. Global distribution of linear and cyclic volatile methyl siloxanes in air.
293 *Environ. Sci. Technol.* **2011**, *45*, 3349-3354.
- 294 16. Kierkegaard, A.; McLachlan, M. S. Determination of decamethylcyclopentasiloxane in
295 air using commercial solid phase extraction cartridges. *J. Chromatogr. A.* **2010**, *1217*, 3557-
296 3560.
- 297 17. McLachlan, M. S.; Kierkegaard, A.; Hansen, K. M.; van Egmond, R.; Christensen, J.
298 H.; Skjøth, C. A. Concentrations and fate of decamethylcyclopentasiloxane (D-5) in the
299 atmosphere. *Environ. Sci. Technol.* **2010**, *44*, 5365-5370.
- 300 18. Wang, X. M.; Lee, S. C.; Sheng, G. Y.; Chan, L. Y.; Fu, J. M.; Li, X. D.; Min, Y. S.; Chan, C. Y.
301 Cyclic organosilicon compounds in ambient air in Guangzhou, Macau and Nanhai, Pearl
302 River Delta. *Appl. Geochem.* **2001**, *16*, 1447-1454.
- 303 19. Wang, D. G.; Norwood, W.; Alae, M.; Byer, J. D.; Brimble, S. Review of recent
304 advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl
305 siloxanes in the environment. *Chemosphere* **2013**, *93*, 711-725.
- 306 20. Bhangar, S.; Huffman, J. A.; Nazaroff, W. W. Size-resolved fluorescent biological
307 aerosol particle concentrations and occupant emissions in a university classroom. *Indoor*
308 *Air* **2014**, *24*, 604-617.
- 309 21. Cappellin, L.; Karl, T.; Probst, M.; Ismailova, O.; Winkler, P. M.; Soukoulis, C.; Aprea, E.;
310 Märk, T. D.; Gasperi, F.; Biasioli, F. On quantitative determination of volatile organic
311 compound concentrations using proton transfer reaction time-of-flight mass spectrometry.
312 *Environ. Sci. Technol.* **2012**, *46*, 2283-2290.
- 313 22. Graus, M.; Müller, M.; Hansel, A. High resolution PTR-TOF: quantification and formula
314 confirmation of VOC in real time. *J. Am. Soc. Mass Spectr.* **2010**, *21*, 1037-1044.
- 315 23. Hayeck, N.; Maillot, P.; Vitrani, T.; Pic, N.; Wortham, H.; Gligorovski, S.; Temime-
316 Roussel, B.; Mizzi, A.; Poulet, I. In cleanroom, sub-ppb real-time monitoring of volatile
317 organic compounds using proton-transfer reaction/time of flight/mass spectrometry. *Proc*
318 *Spie* **2014**, *Metrology, Inspection, and Process Control for Microlithography XXVII*.

- 319 24. Jordan, A.; Haidacher, S.; Hanel, G.; Hartungen, E.; Mark, L.; Seehauser, H.;
320 Schottkowsky, R.; Sulzer, P.; Märk, T. D. A high resolution and high sensitivity proton-
321 transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). *Int. J. Mass Spectrom.*
322 **2009**, *286*, 122-128.
- 323 25. Schripp, T.; Etienne, S.; Fauck, C.; Fuhrmann, F.; Märk, L.; Salthammer, T. Application
324 of proton-transfer-reaction-mass-spectrometry for indoor air quality research. *Indoor Air*
325 **2014**, *24*, 178-189.
- 326 26. Holzinger, R.; Kasper-Giebl, A.; Staudinger, M.; Schauer, G.; Röckmann, T. Analysis of
327 the chemical composition of organic aerosol at the Mt. Sonnblick observatory using a novel
328 high mass resolution thermal-desorption proton-transfer-reaction mass-spectrometer (hr-
329 TD-PTR-MS). *Atmos. Chem. Phys.* **2010**, *10*, 10111-10128.
- 330 27. Companioni-Damas, E. Y.; Santos, F. J.; Galceran, M. T. Linear and cyclic
331 methylsiloxanes in air by concurrent solvent recondensation-large volume injection-gas
332 chromatography-mass spectrometry. *Talanta* **2014**, *118*, 245-252.
- 333 28. Montemayor, B. P.; Price, B. B.; van Egmond, R. A. Accounting for intended use
334 application in characterizing the contributions of cyclopentasiloxane (D5) to aquatic
335 loadings following personal care product use: antiperspirants, skin care products and hair
336 care products. *Chemosphere* **2013**, *93*, 735-740.
- 337 29. Gouin, T.; van Egmond, R.; Sparham, C.; Hastie, C.; Chowdhury, N. Simulated use and
338 wash-off release of decamethylcyclopentasiloxane used in anti-perspirants. *Chemosphere*
339 **2013**, *93*, 726-734.
- 340 30. Buser, A. M.; Bogdal, C.; MacLeod, M.; Scheringer, M. Emissions of
341 decamethylcyclopentasiloxane from Chicago. *Chemosphere* **2014**, *107*, 473-475.
- 342 31. Buser, A. M.; Kierkegaard, A.; Bogdal, C.; MacLeod, M.; Scheringer, M.; Hungerbühler,
343 K. Concentrations in ambient air and emissions of cyclic volatile methylsiloxanes in Zurich,
344 Switzerland. *Environ. Sci. Technol.* **2013**, *47*, 7045-7051.
- 345 32. Bzdek, B. R.; Horan, A. J.; Pennington, M. R.; Janecek, N. J.; Baek, J.; Stanier, C.
346 O.; Johnston, M. V. Silicon is a frequent component of atmospheric nanoparticles. *Environ. Sci.*
347 *Technol.* **2014**, *48*, 11137-11145.

348

349 Figure and Table captions:

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

357

358 Fig 2. Time-resolved concentrations of D4, D5, D6 and CO₂ in the supply air
359 (dashed line) and the classroom air (solid line with markers) on 13 Nov 2014
360 as measured by PTR-TOF-MS. The vertical dashed lines define the duration
361 of each class; the average number of occupants in each class is noted in the
362 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
367 the course of each day.

368

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

Figure 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 CO_2 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.

Fig 3. Per person emission rates, ER ($\text{mg h}^{-1} \text{p}^{-1}$) of D4, D5 and 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.

Figure 1

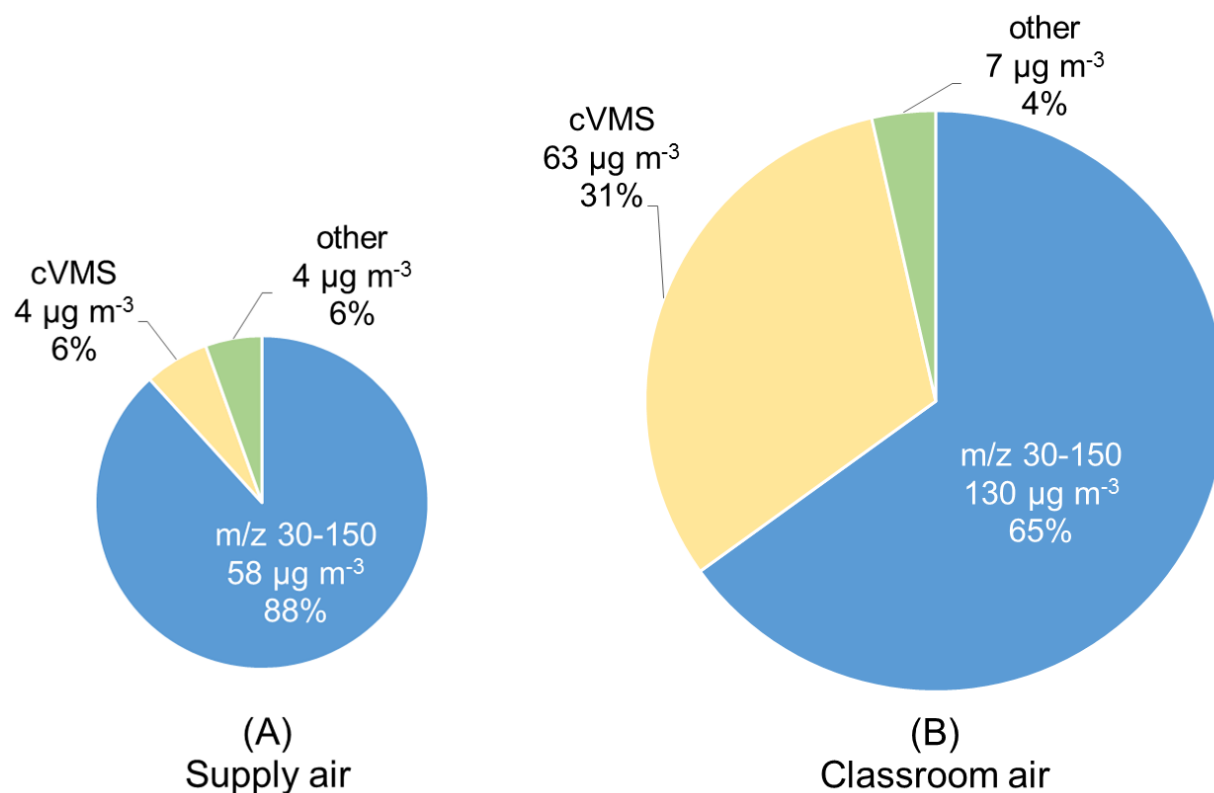


Figure 2

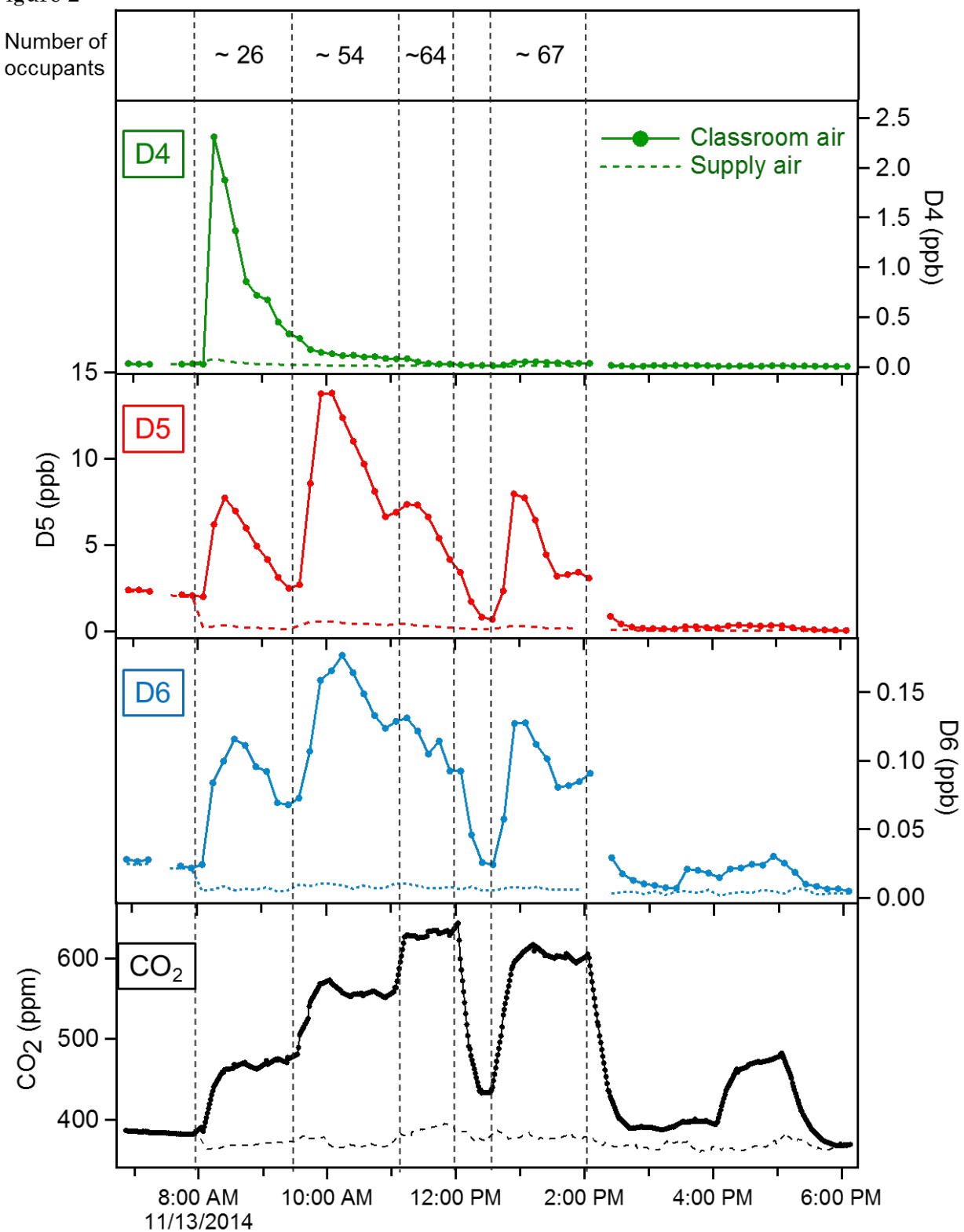


Figure 3

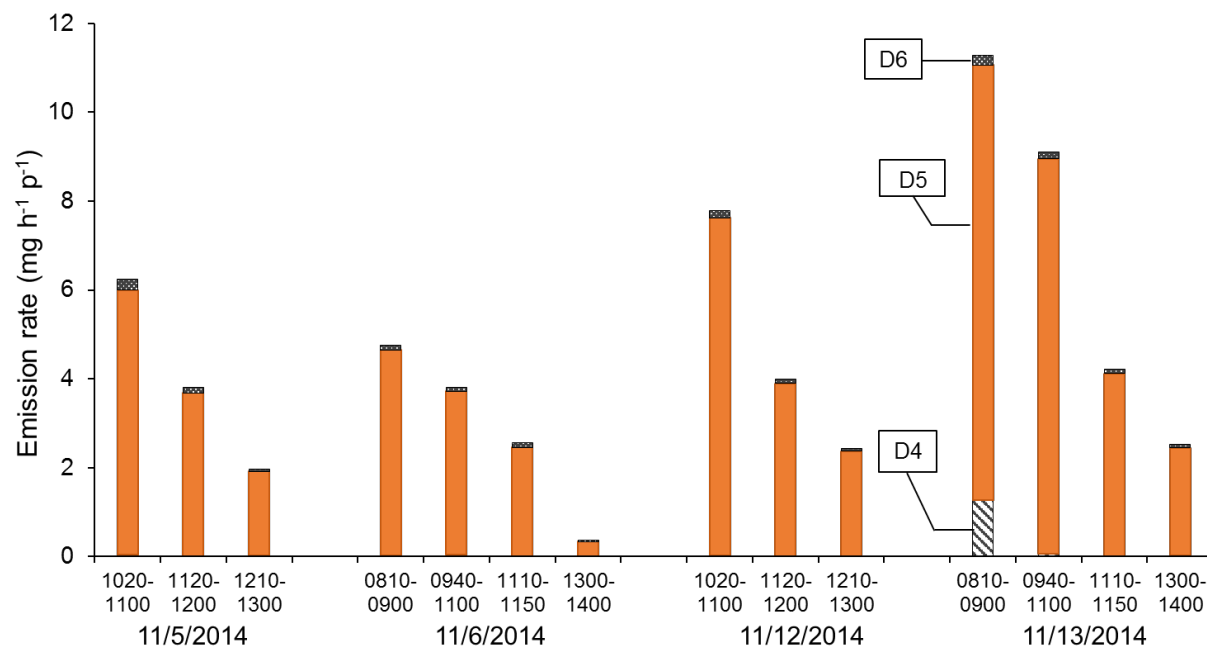


Table 1 Measured emission rates (ER) for D4, D5, D6 and total cVMS in each class period, with number of occupants, class time, and date indicated.

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