Article

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Volatile Organic Compound Emissions from Humans Indoors

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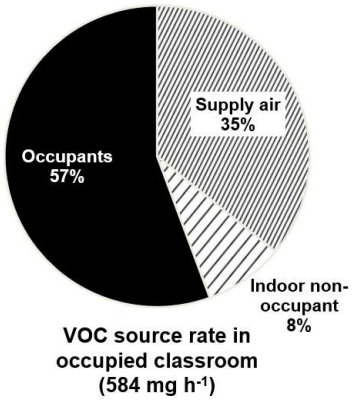
Table of Contents Art



Abstract

Research on the sources of indoor airborne chemicals has traditionally focused on outdoor air, building materials, furnishings, and activities such as smoking, cooking and cleaning. Relatively little research has examined the direct role of occupant emissions, even though this source clearly contributes to indoor volatile organic compounds (VOCs) and influences indoor chemistry. In this work, we quantify occupant-related gaseous VOC emissions in a university classroom using a proton-transfer-reaction time-of-flight mass spectrometer. Time-resolved concentrations of VOCs in room air and supply air were measured continuously during occupied and unoccupied periods. The emission factor for each human-emitted VOC was determined by dividing the occupant-associated source rate by the corresponding occupancy. Among the most abundant species detected were compounds associated with personal care products. Also prominent were human metabolic emissions, such as isoprene, methanol, acetone, and acetic acid. Additional sources included human skin oil oxidation by ozone, producing compounds such as 4-oxopentanal (4-OPA) and 6-methyl-5-hepten-2-one (6-MHO). By mass, human-emitted VOCs were the dominant source (57%) during occupied periods in a well-ventilated classroom, with ventilation supply air the second most important (35%), and indoor non-occupant emissions the least (8%). The total occupant-associated VOC emission factor was 6.3 mg h^{-1} per person.

Introduction

Human emissions of volatile organic compounds (VOCs) can strongly influence indoor air quality. Since humans spend most of their time indoors, most air inhaled by people is indoor air, and, therefore, occupant emissions of VOCs must affect humankind's aggregate inhalation exposure. Yet, notwithstanding its significance, remarkably little research has focused on characterizing occupant-associated VOC emissions to indoor environments.

Historically, ventilation rates in buildings were set at levels designed to control the perceived odors associated with human occupants.[1] Although there have been changes over time, human perception and subjective assessment of the acceptability of indoor air remains an important basis for current ventilation standards and practice.[2] In turn, building ventilation rates matter for at least two major reasons: (a) they are related to public health and well being [3,4] and (b) they contribute substantially to energy use in buildings and consequently to total energy use.[5,6]

The most prominent gaseous effluent from humans is carbon dioxide (CO_2) produced metabolically and emitted at rates of tens of grams per hour. The carbon dioxide level in an occupied indoor space is a proxy for the effectiveness of ventilation and has been found to associate with adverse health and well-being outcomes[7]. It had been long assumed that the cause of these adverse outcomes was not CO_2 itself, but rather some other as-yet-uncharacterized bioeffluent emissions whose indoor abundance would correlate with the metabolic CO_2 level. Recent studies have explored whether or not carbon dioxide is a direct-acting indoor pollutant. Satish et al.[8] and Allen et al.[9] have shown that exposure to moderate CO_2 levels (1000-2500 ppm) in the absence of other bioeffluents can impair certain attributes of decision making. However, Zhang et al.[10] found that exposure to CO_2 alone at levels up to 3000 ppm did not

degrade perceived air quality, induce acute health symptoms, or cause cognitive performance degradation. Zhang et al. did report, though, that, "exposures to bioeffluents with CO_2 at 3000 ppm reduced perceived air quality; increased the intensity of reported headache, fatigue, sleepiness, and difficulty in thinking clearly" and impaired certain indicators of cognitive functioning.

Within the indoor environment research community, VOCs are well recognized as a broad class of contaminants that pose important concerns for occupant health and well-being. Although occupants are recognized as a VOC source, relatively little work has been reported to characterize the chemical composition or rates of occupant emissions. This point is illustrated in the detailed report by Wolkoff [11] on the sources of indoor VOCs, which makes only brief mention of human occupants. A recent review by Weschler [12] does highlight the many ways that occupants influence indoor air chemistry, including through their emissions of VOCs.

From other fields of study, there are substantial emerging literatures that aim to characterize VOCs associated with the human body and its components. A recent review tabulated 1840 VOCs associated with "breath, saliva, blood, milk, skin secretions, urine, and faeces in apparently healthy individuals." [13] That review was motivated by interest in using chemical characterization of VOCs, e.g. in exhaled breath, as a potential aid for the medical diagnosis of disease.[14] Another motivation for characterizing VOC emissions from humans is to assist with rescue operations in emergencies such as the aftermath of a building collapse.[15-17] These studies provide interesting information relevant to understanding occupant emissions of VOCs to indoor spaces. However, the focus for indoor environmental quality is not just to identify emitted species, but also to characterize rates of emissions. Furthermore, the emphasis on different components of the body is less pertinent than knowledge about the totality of emissions from

building occupants, including those that originate from their metabolism, from personal care products that they have used, from their clothing, from chemical reactions occurring on their skin, and from the microbial communities that they host.

A few recent studies are directly relevant to the interest of characterizing occupant VOC emission rates. Veres et al.[18] reported on the air quality impacts of humans in a soccer stadium. Even for an open-roofed arena, the influence of the 31,000 attendees and their associated activities could be detected and quantified for several chemical analytes. Noteworthy are the emission rates (normalized to exhaled carbon dioxide) of ethanol, acetone, isoprene, 6-methyl-5-hepten-2-one (6-MHO), and decanal. Elevated ethanol emissions were associated with heavy beer consumption. The 6-MHO and decanal emissions were associated with ozone reactions with human skin oils. Clear signals of human occupancy could be seen and quantified in this environment even though the increment of metabolic carbon dioxide — about 80 ppm above ambient levels — indicates a much higher per-person effective ventilation rate than commonly applies to indoor spaces that are densely occupied. Williams et al.[19] found that human emission rates of certain volatile organic compounds varied according to audiovisual stimuli in the cinema. These interesting studies reveal information about VOC emissions in highly occupied spaces, but do not capture directly the circumstances that dominate for indoor occupancy, such as being in one's own residence, being at work in an office, or being at school.[20]

Two studies have characterized human emissions of VOCs in university classrooms. In seminal work, Wang [19] applied time-integrated sorbent sampling with analysis by gas chromatography to characterize the emissions rate from university students of several compounds: acetone, acetaldehyde, allyl alcohol, acetic acid, amyl alcohol, butanoic acid, diethyl ketone, ethyl acetate, ethyl alcohol, methanol, phenol, and toluene. Analytical methods available

for characterizing emissions have improved markedly in the four decades since Wang undertook his research. Liu et al.[22] monitored in real time the VOC levels in university classroom using a proton-transfer reaction mass spectrometer. They utilized positive matrix factorization to detect a "human influence" component that varied with level of occupancy and with ventilation in a manner analogous to CO_2. They reported that this component made an "average contribution of 40% to the measured daytime VOC concentration."

To add new knowledge about the emission rates of VOCs from human occupants in an ordinary indoor environment, we conducted an intensive sampling campaign in a university classroom. Carried out over a two-week period, we made near continuous, time-resolved and chemically differentiated measurements of the broadest suite of VOCs that has been technologically possible thus far. We sampled from both the air supply and the classroom air and we monitored during both occupied and unoccupied periods. The application of a material balance model allows us to extract from the measured concentrations the chemical-specific net effective source rate entering the classroom air. The combination of sampling times and locations permits an apportionment of these source rates into contributions from occupants, indoor sources not related to occupancy, and outdoor air supplied by the ventilation system. For those chemicals substantially associated with occupancy, we are able to determine a per-occupant emission factor by combining the occupancy-associated aggregate emission rates with direct observations of the time-varying level of classroom occupancy.

The preliminary assessment of data from this field campaign revealed an unexpectedly strong contribution from cyclic volatile methylsiloxanes (cVMS). We reported briefly on those specific findings.[21] In this paper, we report on the other major results from this campaign, focusing on the emission rates of VOCs from human occupants of a university classroom.

Methods

Experimental Approach. Air sampling was carried out in a normally functioning classroom (volume = 670 m^3; air-exchange rate = 5 ± 0.5 h^{-1}; mechanically ventilated, without recirculation, during the hours 8:00-20:45) at the University of California, Berkeley, California. Previous characterization of the classroom suggested negligible infiltration of air from other parts of the building because of the single-pass ventilation system and the absence of windows or exterior doors.[24] Details of the sampling strategy have been described.[23] Briefly, the monitoring phase was conducted over a two-week period in November 2014, including periods of stable occupancy for nineteen separate class periods on five weekdays during which at least seventeen occupants were in the classroom. One class period was excluded due to limited data availability, so results in this paper include eighteen of the nineteen class periods.

We continuously monitored concentrations of chemically differentiated VOCs, along with CO_2 and O_3 in the classroom air and in the ventilation air supplied to the classroom (supply air). A Teflon solenoid three-way valve enabled the sampling of the classroom air and supply air alternating at five-minute intervals. From each interval, the first two minutes of data were excluded and the remaining three were averaged. The resulting processed data set includes time-series measurements with six points per hour for the supply air and the classroom air, with each point representing the average condition over three contiguous minutes.

VOC Measurements. Mixing ratios of VOCs (in parts per billion) were measured using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS; PTR-TOF 8000, IONICON Analytik GmbH). The PTR-TOF-MS recorded the mass spectrum for mass-to-charge ratios (m/z) 30−500 at a rate of 1 Hz, using H_3O^+ as the primary reagent ion. VOCs with proton affinities greater than that of water undergo proton transfer reactions with H_3O^+ in the drift tube,

158 and are detected by the mass spectrometer. PTR-TOF-MS is highly sensitive to alkenes,
159 aromatics, alcohols, aldehydes, ketones, acids, esters, ethers, and many other compounds, but
160 alkanes generally have proton affinities lower than water and are therefore not detected
161 efficiently using H_3O^+.[25,26] However, even in the H_3O^+ mode, there is up to 5% presence of
162 impurity ions (i.e. O_2^+, and NO^+), which are sensitive to alkanes;[27,28] therefore, it is possible that
163 abundant episodes or bursts of alkane emissions may have contributed to the signals seen by our
164 instrument. VOCs reported here include all those detectable by PTR-TOF-MS as deployed in the
165 classroom.

166 The instrument was calibrated daily with two multicomponent VOC gas standard mixtures,
167 including a total of 22 compounds with their protonated parent ion corresponding to these *m*/*z*
168 values (5 of which are in both mixtures): 45.033, 33.034, 42.034, 59.048, 63.027, 69.069,
169 71.049, 73.028, 79.054, 83.086, 87.081, 93.07, 99.081, 107.086, 121.101, 137.133, and 146.977.
170 Each chemical in the standard gas was present at a level of 1 ppm and was dynamically diluted to
171 3 concentrations (3, 6 and 9 ppb) using zero air of similar humidity to that of classroom air.

172 **Data Analysis: Material Balance, Source Rates and Emission Factors.** The total mass
173 supply rate of each species entering the classroom was computed by material balance, assuming
174 that the species is conserved and that the room air is well mixed. This mass supply rate was
175 computed for the stable occupancy duration of each class period by applying an integral material
176 balance in which the total supply rate is balanced by the change in the room air abundance and
177 the total removal by means of ventilation. Each VOC in the classroom air could have one or
178 more sources. We interpreted the data with the goal of apportioning the source rate for each
179 VOC into three categories: (a) supply air (primarily from outdoor air), (b) human occupants
180 (including their belongings), and (c) indoor sources that are not occupancy related, i.e., from the

181 building materials and room furnishings. The contributions from category (c) were determined
182 utilizing classroom measurements during unoccupied periods at the end of each day. For this
183 purpose, we analyzed data from periods of duration 40-min to 1-h beginning at least one hour
184 after the room became vacant. This protocol ensured that these periods had minimal
185 contributions from human occupants and consequently the differences between the classroom air
186 and the supply air are likely to be associated with emissions from indoor sources other than
187 occupants. We assumed that this non-occupancy emission rate was constant so that the value
188 determined from end-of-day sampling could also be applied during periods of occupancy. In
189 summary, the apportionment utilized direct measurements of supply air concentrations and the
190 room ventilation rate to assess the contributions from ventilation supply. Measurements of the
191 differences between supply air and room air when the room was vacant were interpreted to
192 determine the non-occupant contribution of indoor sources. Measurements of the differences
193 between supply air and room air when the room was occupied, after correction for non-
194 occupancy contributions, were assigned to occupancy-associated emissions.
195 Detailed calculation procedures are reported in the Supporting Information. An emission
196 factor (EF, μg person^{-1} h^{-1}) for each human-emitted VOC was calculated by dividing the
197 occupancy-associated source rate for a given class session by the average number of the
198 occupants in the classroom during that class session.[23]

199 ## Results and Discussion

200 Considering the whole sampling campaign, more than 400 ions were detected in the
201 classroom air and supply air by the PTR-TOF-MS, which were filtered for internal ions and
202 reduced using an abundance threshold. Consequently, 220 ions had mixing ratios (averaged over
203 occupied periods for each sampling day) above 10 ppt in the classroom air and were evaluated

204 further. Almost all of these 220 ions were on average more abundant in the classroom air than in
205 the supply air. We focus on these 220 ions in this paper.
206 The detected chemicals were categorized into hydrocarbons (C_xH_y); oxygenated organic
207 compounds with 1 or 2 oxygen atoms in the molecule (C_xH_yO, $C_xH_yO_2$) such as carbonyls,
208 alcohols, ethers, acids, diols, dicarbonyls, hydroxyl carbonyls and esters; and nitrogen (N)-,
209 sulfur (S)- and silicon (Si)-containing organic compounds.
210 **Temporal Variation of Indoor VOCs.** Indoor VOC mixing ratios are expected to change
211 temporally with ventilation, emission or uptake by indoor materials and humans. The temporal
212 patterns of some representative VOCs are discussed here to provide evidence for their
213 contributions to the composition of classroom air. The time series of CO_2 mixing ratio in the
214 classroom and supply air (top panel of Fig. 1) serves as an independent tracer providing evidence
215 for changes associated with ventilation and occupancy. Before the ventilation system was turned
216 on at 8 AM, air that remained overnight in the classroom had the same stable CO_2 mixing ratio
217 as air in the supply duct. Following the beginning of ventilation system operation and occupancy
218 (which occurred almost simultaneously), the CO_2 level in the classroom is clearly higher than in
219 the supply air and varies with the average number of occupants in the room during each class
220 session (as labeled above the arrows in Fig. 1). The average production rate of CO_2 from
221 occupants during all class periods was stable at 21 ± 3 g h^{-1} $person^{-1}$.[20] Consequently, and
222 because the ventilation rate is constant when the mechanical ventilation system is operating, the
223 temporal pattern of indoor CO_2 level above the comparatively steady contribution of CO_2 from
224 supply air corresponds well with the number of occupants in each class session.
225 For VOCs primarily emitted from human metabolism, one expects a pattern similar to
226 elevated classroom CO_2. The time series for C_3H_6O (acetone) and C_5H_8 (isoprene) mixing ratios

(ppb) clearly show this pattern (second panel of Fig. 1). When the classroom was occupied, human occupants contributed the dominant proportion of the mixing ratios in indoor air for these analytes. In a review on volatile emissions from healthy humans, isoprene and acetone were identified as the two most abundant organic components from human breath,[13] and so it is expected that they would be enriched in a densely occupied indoor environment. The elevated concentrations of acetone in the early morning before the ventilation was turned on were likely caused by janitorial staff cleaning the room; similar trends were observed for other chemicals that are expected to be present in cleaning products, such as monoterpenes.

The reaction of ozone with squalene found in skin oil produces 6-methyl-5-hepten-2-one (6-MHO) and 4-oxopentanal (4-OPA) as first- and second-generation products, respectively.[29,30] These compounds have been reported in connection to ozone-initiated chemistry on the human envelope in simulated aircraft cabin,[31,32] in offices,[30,33] and in classrooms.[34] The third frame of Fig. 1 displays the time-series of 6-MHO and 4-OPA concentrations measured in this study, indicating elevated levels associated with classroom occupancy (6-MHO 0.2-0.6 ppb, and 4-OPA 0.2-0.4 ppb) consistent with the reported values in Fischer et al.[34] of 0.2-0.7 ppb, and 0.12 ppb, respectively. The elevated 4-OPA in the morning, before the start of ventilation, also behaved similarly to the last measurement in Fischer et al.,[34] when that classroom remained empty for more than 1 h at the end of the day. Indoor sources in the absence of human occupants are likely to occur from continued ozone reactions with skin oils remaining on furniture and with shed skin flakes. Desorption from surfaces where the compounds had accumulated may also have contributed. In addition to 6-MHO and 4-OPA, several other gas-phase products of ozonolysis of human skin lipids, as reported in previous studies, were detected in the classroom air at significantly lower concentrations, including geranyl acetone ($C_{13}H_{22}OH^+$), hydroxyacetone

($C_3H_6O_2H^+$, which may also be propionic acid), and 1,4-butanedial ($C_4H_6O_2H^+$), along with minor products like 5-hydroxy-4-oxopentanal ($C_5H_8O_3H^+$) and/or its isomer.[29,31,35,36] Ozone loss was observed in the classroom concurrent with increases of the ozone reaction products. Of these chemicals, 6-MHO, 4-OPA and geranyl acetone exhibited contributions from indoor sources that were much larger than from the supply air. Hydroxyacetone and 1,4-butanedial, on the other hand, had similar levels of contribution from the supply air and from indoor sources.

A few VOCs such as monoterpenes ($C_{10}H_{16}$ detected at *m*/*z* 137.132) were observed to have large episodic increases associated with occupant activity, elevated above their already consistently higher mixing ratios in the classroom than in supply air (0.1-0.3 ppb). Monoterpenes are well-known biogenic VOCs, emitted by plants and fruits[37,38] and used in fragrances in personal care and cleaning products.[39] As illustrated in the fourth panel of Fig. 1, a short-term increase was observed in monoterpene level from about 2 to 20 ppb that persisted for about 10 minutes during the class of 9:40-11:00, followed by steady decay to the normal occupied-condition concentration. The strong episodic increase corresponds to a release of ~ 70 mg of monoterpene, and must have been caused by an occupant activity, for example, peeling an orange or applying a scented personal-care product. Based on high correlation ($r > 0.96$) with *m/z* 153.13 (citral) and *m/z* 139.14 (methylisopropylcyclohexene), the ions typically found from citrus peel, and the lack of correlation with *m/z* 155.14 (linalool), frequently present in perfumed products, the fruit-associated source seems more likely. We do not have records of occupant activities to confirm the specific source, but it clearly happened when students entered the classroom at the beginning of a lecture period. In contrast, the elevated levels of monoterpenes before ventilation was turned on in the morning were smaller, and presumably associated with cleaning activities or outgassing from indoor sources overnight.

The ventilation system supplies outdoor air and its associated VOCs through the building ducts to the classroom. Benzene (*m*/*z* 79.053) and C8 aromatics ($C_8H_{10}H^+$, *m*/*z* 107.085) are common VOCs associated with gasoline vapors and with the exhaust of internal combustion engines. The classroom concentration of benzene and C8 aromatics clearly followed the pattern of supply air concentration, with some additional indoor source (not correlated with human occupancy) increasing the classroom-air mixing ratios in the case of benzene (lowest frame of Fig. 1.) Especially for the C8 aromatics, the time series of supply air and room air concentrations are nearly coincident after accounting for the characteristic 12-minute response time of the classroom air concentration to a change in supply air levels. (Recall that the classroom air-exchange rate is 5 h^{-1}; the characteristic response time of indoor pollutant levels to a sudden change in outdoor levels is the reciprocal, 0.2 h = 12 min.) The classroom concentration of benzene was constantly higher than the supply air level, providing evidence of a continuously emitting indoor non-occupant source (e.g., from building materials or furnishings) in addition to the supply air source.

VOC Source Rate and Its Apportionment. To quantitatively evaluate the emission sources for indoor VOCs observable by PTR-TOF-MS, we calculated the source rates of the 220 VOCs/ions for each class period during the time of stable occupancy. The median total observed source rate of VOCs to the classroom during the 18 occupied periods was 580 mg h^{-1}. Occupant related emissions were the dominant source (57%), followed by supply air (35%), and indoor non-occupant emissions (8%).

Quantitative apportionments of the three emission source categories are indicated in Fig. 2 for the 20 most abundant VOCs/ions (referred to as VOCs hereafter). Source rates for the remaining ions for which chemical formulas could be confidently assigned are summarized

296 according to chemical composition families (C_xH_y, C_xH_yO, $C_xH_yO_2$, etc.). Observed ions for
297 which empirical chemical formulas could not be confidently assigned were summed and reported
298 as "other;" these accounted for just 5% of the total mass, as shown in the pie chart. Detailed
299 results for all observed ions are summarized in Table S1 in the Supporting Information.
300 The six most abundant VOCs accounted for 62% of the total measured source rate (shown in
301 top group of Fig. 2), and the 20 most abundant VOCs accounted for 80% of the total. The label
302 cVMS represents the sum of four cyclic siloxane compounds, including D3
303 (hexamethylcyclotrisiloxane), D4 (octamethylcyclotetrasiloxane), D5
304 (decamethylcyclopentasiloxane) and D6 (dodecamethylcyclohexasiloxane), as we have
305 previously reported.[23] The dominant cVMS observed was D5.
306 Comparison of the median (shaded bars) and mean (circles) source rates is indicative of the
307 level of variance in sources during the stably occupied periods. A mean emission value higher
308 than the median indicates variability in source rates among class sessions along with positive
309 skewness. About half of the VOCs among the top 20 were observed to have highly variable
310 sources, but the sources may be variable for different reasons. Among the contributors to
311 variability are time-varying emissions from occupants (e.g., the D5 emission factor declined with
312 time of day), varying levels of urban air pollution (C8 aromatics and toluene), or variability in
313 the occurrence of specific short-term emissions events (e.g., peeling citrus fruit that releases
314 monoterpenes).
315 While indoor non-occupant emission sources made relatively small contributions to the total
316 (8%), they do provide discernible contributions to some of the top 20 VOCs, mainly among
317 organic acids (acetic acid, formic acid, acid fragment *m*/*z* 43.018), ketones (acetone), alcohols
318 (methanol, ethanol), aldehydes (acetaldehyde, hexanal), and other oxygenated VOCs

($C_9H_{10}OH^+$). Other than the observation that indoor emissions of formaldehyde were low in this classroom, these findings are consistent with the literature regarding indoor sources from building materials.[40,41] Emissions of these chemicals from non-occupant indoor sources have been extensively characterized in past studies, so we do not probe more deeply here.

The contributions from supply air were a typical mixture of outdoor air VOCs expected to be found in urban areas such as acetone, acetic acid, methanol, acetaldehyde, monoterpenes, organic acids, isoprene, ethanol, and components of gasoline, such as benzene, toluene, and C8 aromatics, etc.[42,43] In this study, the mean contributions of these outdoor air VOCs to classroom air was 35% of the total. That level of contribution could vary substantially in other areas, depending on the level of outdoor air pollution and the building ventilation rates. A more detailed analysis of the composition and source characteristics of outdoor air in this study would not provide general results relevant to predicting indoor air concentrations elsewhere.

A noteworthy result from this study is that human occupant emissions were the dominant source of VOC during classroom-occupied periods, contributing 58% of the total mass of quantified sources. Of the top 20 VOC, all but three (C8 aromatics, toluene, and C_4H_6O) had substantial contributions from human occupants. Three cVMS (primarily D5, along with D4 and D6) together comprised ~1/3 of the total indoor VOC mass concentration in the classroom and were predominantly associated with occupant emissions.[23] Other prominent VOCs whose source was ~1/3 or more from human occupants included acetone, isoprene, acetic acid, methanol, acetaldehyde, monoterpenes, organic acids (formic, acid fragments), ethanol, hexanal, (iso) butyl and (iso) propyl fragments, hydroxyacetone, and the products of ozone reactions with skin oil, i.e., 4-OPA and 6-MHO. Hundreds of organic acids have been previously detected in volatiles from human skin secretions,[13,44,45] including acetic and formic acid. Previous studies using PTR-

342 TOF-MS to analyze human breath show most of the same dominant 15 compounds including
343 acetone, methanol, acetaldehyde, ethanol, formic acid, (iso) butyl fragment ($C_4H_8H^+$), and
344 isoprene.[46] One significant difference worth noting is that Herbig et al. reported *m*/*z* 71.049
345 ($C_4H_6OH^+$) in breath, but we observed no occupancy-related source and instead observed indoor
346 non-occupant sources of this ion to be dominant. The $C_4H_6OH^+$ ion could be from methyl vinyl
347 ketone or from methacrolein,[47] which are products of the atmospheric oxidation of isoprene.
348 Observed occupant emissions included N- and S-containing VOCs. Volatile sulfur
349 compounds, which are the main cause for oral malodor,[48-50] and which contribute to underarm
350 odors, [44] were detected in classroom air. Examples include methanethiol (*m*/*z* 49.013, CH_4SH^+)
351 and dimethyl sulfide (*m*/*z* 63.025, $C_2H_6SH^+$). A large number of nitrogen-containing compounds
352 have also been identified as volatiles from human body, mostly in human breath,[13] consistent
353 with our observations in classroom air.
354 **Emission Factors for Human-Emitted Compounds.** As might be expected, we found that
355 the occupant-averaged CO_2 generation rate was relatively stable across all class periods,
356 indicating similar average metabolic activity levels among occupants. Analogous
357 characterization of the spectrum of occupant-emitted VOCs was conducted by calculating the
358 per-person emission factors (EFs, $\mu g\ p^{-1}\ h^{-1}$), as listed in Figure 3, with a pie chart indicating
359 percent mass contributions for each species to the total human occupant emission rates.
360 The cVMS had the highest EF among all occupancy-associated VOC emissions.[23] The next
361 highest EF values were for acetone, acetic acid, monoterpenes, isoprene, methanol, acetaldehyde,
362 ethanol, formic and other acid fragments. Wang [21] reported subject-weighted emission factors in
363 a university classroom for some of the same organic compounds that we observed. The EFs
364 reported by Wang for chemicals known to be major metabolic products in human breath,

365 including acetone, acetaldehyde, acetic acid, methanol, and ethanol, were all within a factor of
366 two of our measured EFs. This agreement is good for studies using completely independent
367 populations, measurement techniques, standards, and undertaken four decades apart. However,
368 surprisingly, the EFs Wang reported for toluene and phenol were one to two orders of magnitude
369 higher than the values we obtained (308 and 396 $\mu g\ p^{-1}\ h^{-1}$ versus 6 and 12 $\mu g\ p^{-1}\ h^{-1}$,
370 respectively). Human exposure to toluene in many urban areas has been dramatically reduced
371 over the past 40 years as a result of improved emission controls for outdoor air pollutants. We
372 might also speculate about another potential factor contributing to the differences observed: a
373 reduction over time in the use of aromatic compounds, which have been gradually withdrawn
374 from consumer products and from other items that would be carried to class by students.
375 The total average VOC emission factor for human occupants that we have obtained, 6.3 mg
376 h^{-1} $person^{-1}$, is only partly accounted for by the VOCs reported in past studies. As shown in Fig.
377 3, cVMS accounted for 44%, acetone for 16%, the sum of identified acids, acid fragments,
378 methanol, ethanol, isoprene, and monoterpenes accounted for another ~20%, and the remaining
379 ~20% consisted of a large array of VOCs with small but measurable EFs summed into classes of
380 chemicals by their elemental composition (C_xH_y, C_xH_yO, $C_xH_yO_2$, $C_xH_yO_3$, N-containing, S-
381 containing). (See Table S2 for a list of VOCs for which the occupancy-associated emissions
382 were greater than 25% of the total source strength.) Only a few percent of the total observed EF
383 are unidentified by chemical formula owing to a lack of any definitive match to the observed
384 exact ion mass. While some of the most abundant chemicals had been previously reported, the
385 full range of reported species and the time resolution of our measurements provide novel
386 contributions to knowledge regarding human influence on the composition of indoor air. The
387 specific population studied here (engineering students in a university classroom in northern

California), cannot be assumed to be representative of the broader human population. Additional research focusing on emissions from different groups of people in different indoor spaces are likely to reveal important variability in occupant emission rates due to age, activity, health status, emotional state[19] or other factors.

In this study, we have examined the full spectrum of VOCs emitted indoors in a university classroom and found that human occupants were the major contributor to the mass of indoor VOCs, exceeding contributions from supply air and from indoor non-occupant sources. The per-person emission factors for human-emitted chemicals have rarely been reported in previous studies. Our findings improve knowledge of human emissions influencing the chemistry of indoor environments, including chemically speciated per-capita emission factors that can be used for modeling indoor air quality.

Supporting Information

Integral Material Balance for Evaluating VOC Source Rates and its Apportionment

PTR-TOF-MS VOC Measurement Details

Table S1. Source rates (mg h^{-1}) for 220 ions measured in all stable class periods during 5 sampling days.

Table S2. Emission factor (μg h^{-1} p^{-1}) for VOCs with occupant-source contributing > 25% of the total median source rates.

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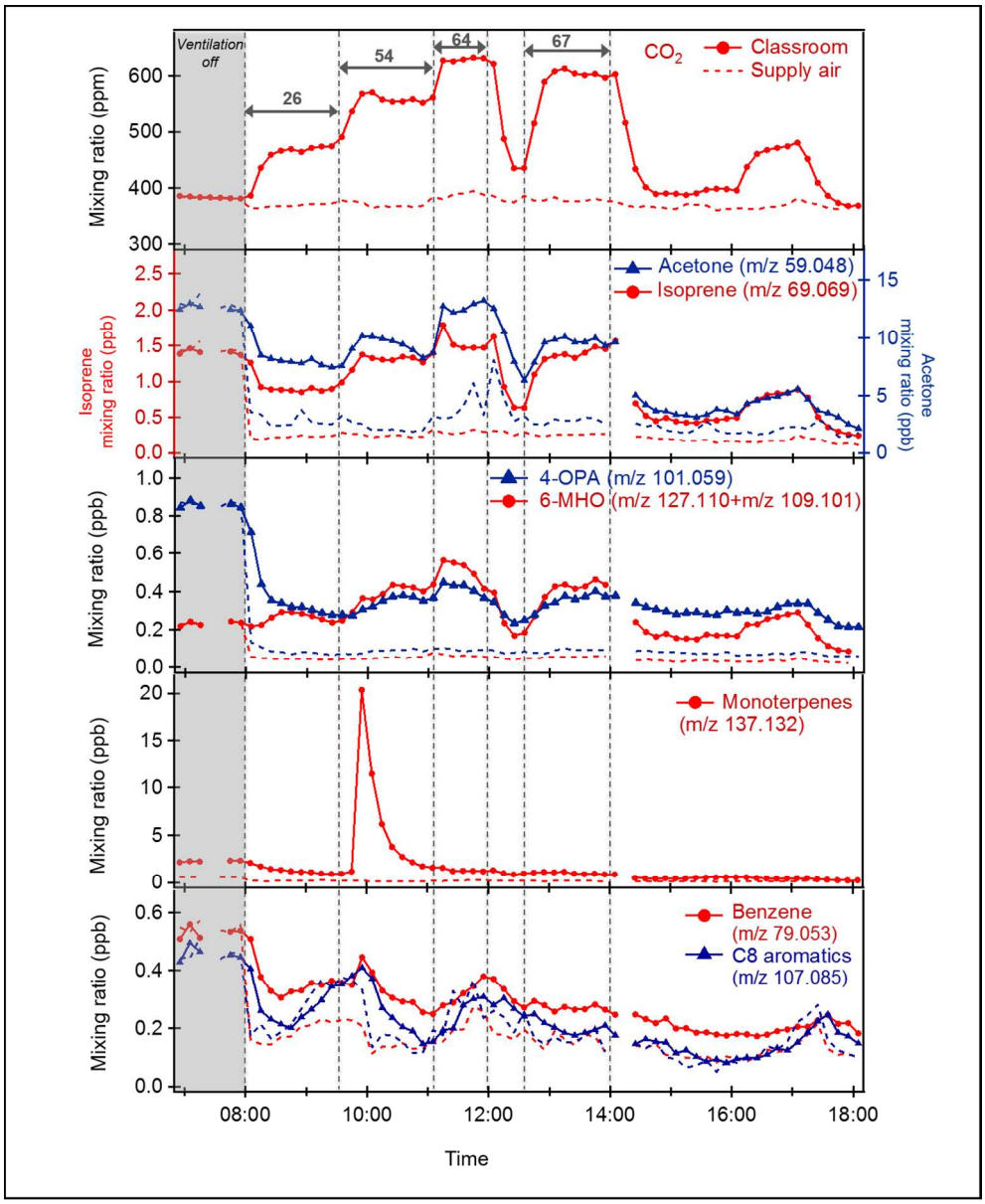

Figure 1. Time series of mixing ratios in the classroom (solid line with markers) and supply air (dashed line) for CO2 and some representative VOCs. Vertical dashed lines define the duration of each class period on 13 November 2014; the average number of occupants in each class is noted above the arrows in the top panel.

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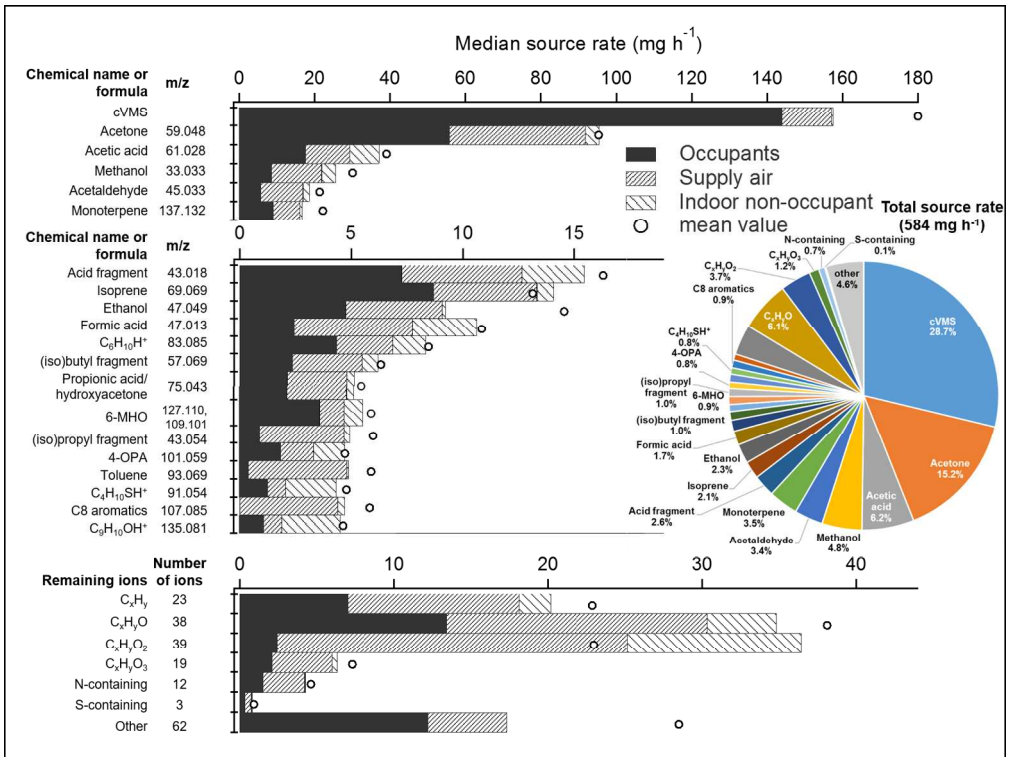

Figure 2. Median (shaded bars) and mean (circles) values of the VOC source rate (mg h^{-1}) measured in 18 class sessions. The mass-to-charge ratio (m/z) and assigned chemical formulas or names for the 20 most abundant ion/VOC groups are listed on the left of the graph. Of the remaining ions, those with known formulas are grouped by chemical composition and plotted at the bottom of the graph. The contribution of these top 20 individual ions and ion groups to the total source rate (mean value of 18 class periods) is shown in the pie chart on the right; ions with no empirical formula are summed and reported as "other".

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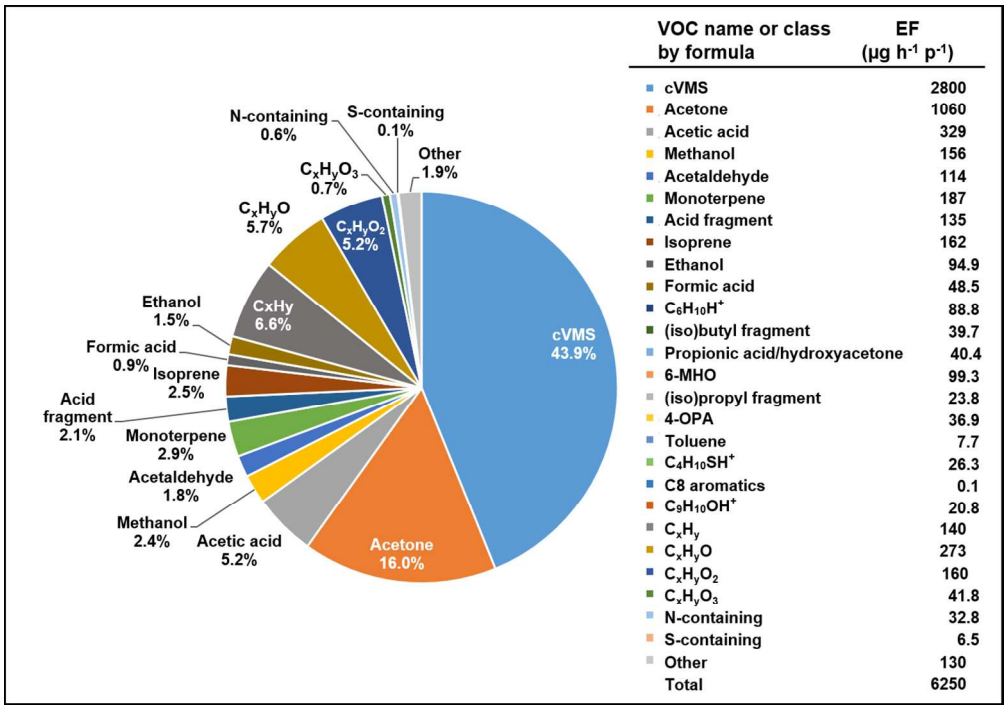

Figure 3. Human occupant emission factors (EF, μg p^{-1} h^{-1}) for chemical species shown as relative contributions to the total (pie chart). The 20 most emitted compounds are specifically labeled, 62 (28% of total 220 ions) ions with no assigned formulas are grouped as "other" and the remaining ions are categorized by number of oxygen and containing of nitrogen or sulfur in the molecule as C_xH_y, $_xH_yO$, $C_xH_yO_2$, $C_xH_yO_3$, N-containing and S-containing. The values of EF for the listed compounds and ion groups are shown on the right.

376x263mm (96 x 96 DPI)