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3 **Characterizing sources and emissions of volatile organic compounds in a**
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6 **northern California residence using space- and time-resolved measurements**
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INDOOR AIR

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1 **Abstract**

2 We investigate source characteristics and emission dynamics of volatile organic compounds
3 (VOCs) in a single-family house in California utilizing time- and space-resolved measurements.
4 About 200 VOC species were measured during eight weeks in summer and five in winter.
5 Spatially resolved measurements, along with tracer data, reveal that VOCs in the living space
6 were mainly emitted directly into that space, with minor contributions from the crawlspace, attic
7 or outdoors. Time-resolved measurements in the living space exhibited baseline levels far above
8 outdoor levels for most VOCs; many compounds also displayed patterns of intermittent short-
9 term enhancements (spikes) well above the indoor baseline. Compounds were categorized as
10 “high-baseline” or “spike-dominated” based on indoor-to-outdoor concentration ratio and indoor
11 mean-to-median ratio. Short-term spikes were associated with occupants and their activities,
12 especially cooking. High-baseline compounds indicate continuous indoor emissions from
13 building materials and furnishings. Indoor emission rates for high-baseline species, quantified
14 with 2-h resolution, exhibited strong temperature dependence and were affected by air-change
15 rates. Decomposition of wooden building materials is suggested as a major source for acetic
16 acid, formic acid, and methanol, which together accounted for ~75% of the total continuous
17 indoor emissions of high-baseline species.

18 **Keywords**

19 Sources; cooking; residences; occupancy; air quality; material emissions.

20 **Practical Implications**

21 This study advances knowledge about the relative contributions of three major categories of
22 indoor air sources for VOCs: building materials and furnishings, occupants and their activities,
23 and outdoor air. We find that in an 80-year old, wood-framed single-family residence in

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24 California, the building materials and furnishings dominate for most measured VOCs, with a
25 surprisingly large contribution from what appears to be wood decomposition. The building-
26 associated emission rates increase with both increasing indoor temperature and increasing air-
27 change rates. Among occupant activities, cooking is the most prominent indoor emission source.
28 Outdoor air is relatively unimportant as a contributor to indoor air VOC levels at this site.

PROOF

1. Introduction

Residential indoor air is an important contributor to pollutant exposure. The average American spends about two-thirds of their time in a residence.¹ More than half of the air breathed is residential indoor air. One major concern regarding residential indoor air quality is elevated concentrations of volatile organic compounds (VOCs). Numerous VOCs have been measured in residential indoor environments,^{2,3} and in many cases the indoor concentrations are higher than those outdoors.⁴⁻⁸ Some VOCs are known to pose health hazards, some may be important for indoor chemistry, and few have been well characterized.³ A key step towards improving knowledge about indoor VOC exposure and chemistry is to better understand the sources and their respective emission characteristics.

VOCs in residences can arise from many sources, with potentially distinctive emission characteristics. They can be emitted from various building materials, furnishings, and household products inside the living space;⁹ emitted from occupants (both endogenously and exogenously) and their regular and episodic activities (e.g., cooking and cleaning);^{10,11} produced from chemical processes taking place indoors (e.g., reaction of ozone with skin oil);^{12,13} emitted from indoor microbial communities;^{14,15} and transported from outdoors or from other connected indoor spaces (e.g., from attics, basements and crawlspaces).^{16,17} Dynamic processes affecting indoor-relevant VOC emissions have most commonly been studied in controlled laboratory settings, focusing on emissions from specific materials present indoors or from prescribed simulated activities.^{11,18} Field observations in real indoor environments under normal occupancy constitute important complements to laboratory studies. Such studies contribute information about the relative importance of various sources indoors and identify potential sources and processes that merit further investigation in the lab. However, investigating VOC sources and emissions in

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3 53 field studies has been challenging, in part because of the co-existence in indoor environments of
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5 54 many sources that emit the same VOC species. Limitations in analytical capabilities have also
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8 55 been a key fundamental restriction.
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10 56 One strategic approach to field studies characterizing VOC sources is to take advantage
11
12 57 of patterns in the spatial and temporal variability of different emission sources and the resultant
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14 58 variability of VOC concentrations. Along this line of thinking, Seifert and Ullrich proposed to
15
16 59 distinguish between continuous and intermittent sources with further subgroups of regular and
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19 60 irregular emissions.¹⁹ Considering also the spatial patterns of sources, Levin divided sources
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21 61 using a two-by-three matrix (point and distributed; constant, periodic, and episodic).²⁰ A key to
22
23 62 transform such ideas into reality is making spatially and temporally resolved VOC measurements
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26 63 in indoor field studies. The time resolution needs to be on the order of tens of minutes or better
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28 64 to capture some common sources (such as cooking) in the residential environment.¹⁹ Such a
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30 65 measurement program is demanding if undertaken using conventional VOC measurement
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32 66 techniques, i.e., taking time-integrated or snapshot samples using sorbent tubes and then carrying
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35 67 out off-line analysis of targeted compounds using gas chromatography with mass spectrometry.²¹
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38 68 Field measurements with lesser time resolution or conducted over short time spans focusing on
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40 69 targeted sources and dynamic processes have been undertaken. Examples include investigating
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42 70 the transport of VOCs from a garage or basement to the living zone using space-resolved
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44 71 measurement,^{16,17} studying the impact of renovation on indoor VOC levels by taking samples at
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46 72 daily or monthly intervals,^{22,23} and characterizing sorptive behavior of indoor VOCs using time-
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48 73 resolved measurements over periods of hours.²⁴ In addition, factor analysis has been applied to
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50 74 source-apportionment studies, utilizing time-integrated VOC measurements in numerous
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53 75 residences.^{4,25} In such investigations, attributing the statistically derived factors to different
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3 76 source classes is, however, often ambiguous and sometimes speculative, owing in part to the
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5 77 variability of VOC sources and emissions across different residences.
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8 78 Recently, online chemical ionization mass spectrometry (CIMS) has begun to be used in
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10 79 field measurements of VOCs indoors. This analytical approach can measure speciated VOCs in
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12 80 real time, with second- to minute-resolution. Time-resolved observations of speciated VOCs
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14 81 have been made in classrooms, cinemas, and football stadiums under normal occupancy, using
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16 82 proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS),^{10,26–29} as well as other
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18 83 types of CIMS instruments.³⁰ The high time resolution of this approach allows for exploring
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20 84 short-time-scale processes, which are difficult to investigate using time-integrated sampling.
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22 85 Among the important findings to emerge from such studies is the importance of human
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24 86 occupants as VOC sources in densely populated indoor environments. For example, Tang et al.
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26 87 reported that siloxanes, emitted from personal care products used by students, were among the
27
28 88 most abundant VOCs observed in a classroom.¹⁰
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33 89 Until now, measurements using CIMS-type instruments have not been reported for
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35 90 characterizing VOC concentrations and emission sources in residential environments during
36
37 91 normal occupancy. Recognizing this gap, we report here on continuous VOC observations in a
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39 92 normally occupied single-family house in northern California using PTR-ToF-MS during two
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41 93 sampling seasons. The measurement approach was designed to provide time-resolved as well as
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43 94 space-resolved information, with the latter achieved by sequentially sampling from each of six
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45 95 locations in and near the house during each 30-minute interval. Indoor VOC emission rates were
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47 96 assessed with 2-h resolution, utilizing simultaneous tracer-based determinations of air-change
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49 97 rates in the living space. Based on these VOC measurements, augmented by extensive metadata
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51 98 on environmental and operational conditions of the household, the present study aims to
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3 99 characterize general features of emissions and source attributes of VOCs in the living space of
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5 100 the studied house.
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8 9 101 **2. Methods**

10 11 102 **2.1. Observational campaign**

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13 103 Extensive observational monitoring was conducted in a single-family house (designated
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15 104 H1) in Oakland, California during two seasons. The first observational period (summer
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17 105 campaign) was eight weeks long from mid-August to early October 2016. The second period
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19 106 (winter campaign) spanned five weeks from late January to early March 2017. A detailed
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21 107 description of the studied house and of the two observational campaigns has been reported.^{31,32}
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23 108 We provide a brief recap here of aspects essential for understanding and interpreting the VOC
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25 109 data.
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29 110 The studied house is situated in the foothills of Oakland, in a lightly trafficked urban
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31 111 residential neighborhood. It was built in the 1930s of wood-frame construction. There had been
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33 112 no recent renovation or refurbishing of note. (For example, the most recent interior painting took
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35 113 place in 2011.) The house has a split-level floor plan, an unoccupied attic above, and a small
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37 114 basement and larger crawlspace below. There are three bedrooms and two bathrooms on the
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39 115 upper level (volume ~150 m³) and a kitchen, family room, and living room on the lower level
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41 116 (~200 m³). Two adult occupants (ages in the range 55-65 y) live in the house. The house is
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43 117 equipped with central heating, but no air conditioning. A decade-old natural gas-fired gravity
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45 118 furnace (buoyancy-driven, with supply registers in each room and a single, centrally located
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47 119 return register, but no fan) is situated in the crawlspace; it operated intermittently during the
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49 120 winter campaign and was off during the summer. Except for the bathrooms, the interior doors in
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51 121 the living zone were normally kept open, including at night. The entrances from the living zone
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3 122 to the substructure (basement and crawlspace) and to the attic were generally closed. The
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5 123 basement room, which was occasionally accessed, contained a washing machine, clothes dryer,
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7 124 and storage space. In addition to normal house operation (occupied periods), the occupants were
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9 125 deliberately away from the house for a few days for at least one time in each campaign. During
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11 126 these vacant periods, the house windows and doors were all closed and the furnace was off.
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14 127 Temporally and spatially resolved measurements were made for a range of gases,
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16 128 including VOCs using a PTR-ToF-MS (Ionicon Analytik GmbH, Austria, PTRTOF 8000), ozone
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18 129 (O_3), and carbon dioxide (CO_2). The gas-analysis instruments were situated in a detached garage
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20 130 about 5 m from the house. Air was continuously drawn through separate 30-meter-long 6.4-mm
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22 131 ($\frac{1}{4}$ " OD) PFA sampling tubes at a constant flow rate of ~ 2 L/min from six locations: outdoors,
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24 132 kitchen (representing the lower living zone), landing at the top of the half flight of stairs (with
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26 133 doors open to the bedrooms, representing the upper living zone), crawlspace, basement, and attic.
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28 134 A 2.0- μ m pore size PTFE filter was installed on the intake end of each sampling line to remove
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30 135 particles. The gas instruments regularly and automatically switched between subsampling from
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32 136 these lines through a 6-way manifold (NResearch, 648T091; PTFE inner contact surfaces). Two
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34 137 different sampling sequences were employed during observational monitoring. During most
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36 138 periods, data were collected with spatial resolution emphasized, switching regularly at 5-min
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38 139 intervals among each of the six inlets (i.e., 30 min for one full cycle). Two weeks in summer and
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40 140 one week in winter were used to collect data with higher temporal resolution in the living zone;
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42 141 in this case, the 30-minute cycle involved only three locations: outdoors (5 min), kitchen (20
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44 142 min) and bedroom area (5 min). In addition, to facilitate compound assignment on PTR-ToF-MS,
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46 143 short-term VOC samples were collected using sorbent tubes in the studied house and then
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3 144 analyzed using 2-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-
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5 145 ToF-MS).

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8 146 Extensive supporting data were acquired to characterize general environmental and
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10 147 operational conditions in the household. Three inert tracers were steadily released in the house
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12 148 and measured by PTR-ToF-MS.³¹ Using the tracer data, the air flow patterns between living
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14 149 space, attic and crawlspace were characterized, and the time-varying air-change rate of the living
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16 150 space was determined with 2-h time resolution.³¹ More than 50 wireless sensors were used to
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18 151 monitor time-resolved room occupancy (motion), appliance use (on/off), door/window open
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20 152 status (open/closed), and indoor temperature and humidity. Occupants also maintained daily
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22 153 presence/absence and activity logs to complement the automatically acquired metadata.
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27 154 **2.2. VOC measurement and data analysis**

28
29 155 The PTR-ToF-MS uses soft chemical ionization mass spectrometry, with hydronium ion
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31 156 (H_3O^+) serving as the primary reagent. The H_3O^+ ions can effectively protonate VOCs with
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33 157 proton affinities greater than that of water, allowing for detection of most unsaturated
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35 158 hydrocarbons, VOCs containing oxygen, nitrogen, sulfur, halogens, and silicon, among others.³³
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37 159 Due to the low exothermicity of the proton transfer reaction, the extent of product ion
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39 160 fragmentation is limited and the exact ion mass can be used as the identifier for many important
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41 161 VOCs. For some abundant VOCs that do not react with H_3O^+ , reactions with impurity reagent
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43 162 ions (i.e., O_2^+ and NO^+ ; <5%) might also produce high enough signal and thereby allow for
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45 163 detection by the instrument.³⁴
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50 164 PTR-ToF-MS spectra were collected with 2-s time resolution. The recorded spectra were
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52 165 processed using PTRwid package under IDL,³⁵ to automatically detect mass peaks, to create a
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54 166 unified peak list for each campaign, and to provide signal output in counts per second. In further
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3 167 analyzing the data, the peak signals were averaged to a time resolution of 5 min. To reduce
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5 168 possible memory effects associated with sorption in the sampling system, data for the first 2 min
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7 169 after switching from calibration to measurement or from one inlet to another inlet were excluded
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10 170 from each average.

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12 171 VOC speciation for each campaign was deciphered from the unified peak list and
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14 172 corresponding peak signals. In total, 656 mass peaks were detected in the summer campaign and
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16 173 661 in the winter campaign, using consistent signal processing criteria. The mass peaks were first
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18 174 filtered to remove background ions predominantly arising from the instrument and from tubing.
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20 175 A best-guess ion formula was then assigned to each of the remaining peaks, utilizing their exact
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22 176 masses and the correlation of their signals with other peaks. The list of ion formulas was further
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24 177 reduced by combining isotopic ions and identified fragment ions, removing interference ions,
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26 178 tracer ions, and inorganic ions, and applying an abundance threshold (inclusion criterion: average
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28 179 mixing ratio in the kitchen air > 0.005 ppb). Ion formula is a useful but by no means unique
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30 180 indicator of VOC identity (e.g., no discrimination of isomers, possibility of fragmentation).
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32 181 Some ion formulas can be confidently attributed by means of deductive reasoning to specific
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34 182 compounds or groups of compounds, such as $C_{10}H_{17}^+$ to monoterpenes, while other assignments
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36 183 are speculative or remain undetermined. In what follows, best-estimate compound assignments
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38 184 are indicated and reported together with the corresponding ion formula. In cases where the ion
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40 185 formula is uncertain, the exact ion mass is also reported. In addition to VOC ions, two inorganic
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42 186 ions, attributable to chloramine and hydrogen sulfide, are also quantified and reported.

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44 187 From the 656 ion peaks detected by PTR-ToF-MS across the summer campaign, 229
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46 188 organic ions formulas are extracted to represent measured VOC speciation. The corresponding
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48 189 procedure for the winter campaign yields 180 ion formulas from among 661 ion peaks.

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3 190 Compared with previous full-spectra VOC analysis using PTR-ToF-MS for indoor and outdoor
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5 191 air,^{26,36} here a lower fraction of ions is selected for the analysis (25-35% in this study versus >
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7 192 50% in previous studies), largely due to the extra step of combining isotopic and fragment ions.
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9 193 The reduced list of ions has minimum overlap in term of parent compounds and serves as our
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11 194 best representation of VOC speciation measured using PTR-ToF-MS.

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14 195 Airborne concentrations (in part per billion by volume, ppb) of parent VOCs were
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16 196 estimated from measured signals of individual ions by first adjusting for ion transmission and
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18 197 then applying a sensitivity factor. Mass-dependent ion transmission relative to H_3O^+ and its drift
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20 198 over each multiweek observational period was corrected utilizing calibrations obtained daily by
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22 199 sampling from a multicomponent VOC gas standard mixture.³⁷ For some major ions (such as
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24 200 acetic acid, formic acid, furfural, and siloxane [D5]), the corresponding sensitivity factors were
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26 201 obtained from calibrations using authentic standard compounds during or after the campaign.
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28 202 For other ions, a default sensitivity factor was applied, assuming a constant rate coefficient at
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30 203 $2.5 \times 10^9 \text{ cm}^3 \text{ s}^{-1}$ for the reactions of parent VOCs with H_3O^+ and with the water cluster
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32 204 $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$. This assumption typically has an uncertainty of $\pm 50\%$ in estimated parent compound
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34 205 concentrations.³⁸

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36 206 A range of statistical parameters of measured VOC concentrations was calculated. Mean
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38 207 and median concentrations (C_{Avg} and C_{Med}) were determined for each VOC ion in each space for
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40 208 vacant and occupied periods in each campaign, serving as the basis of calculating more digested
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42 209 parameters. The C_{Avg} and C_{Med} values in the occupied periods were calculated based on
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44 210 measurements taken during space-resolved sampling to guarantee equivalent comparison across
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46 211 spaces. The C_{Avg} and C_{Med} in the vacant period were calculated only using measurements during
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48 212 the longer vacant periods (> 2 days; in the beginning of winter campaign and at the end of
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3 213 summer campaign, respectively). In the event that calculated C_{Avg} or C_{Med} of an ion in a space
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5 214 was below the detection limit of that ion, half of the detection limit was used instead. More
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7 215 digested parameters calculated using mean and median concentrations include indoor-to-outdoor
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9 216 (I/O) ratio of mean concentration for each indoor space, as well as mean-to-median concentration
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11 217 ratio in the kitchen, $(C_{Avg}/C_{Med})_{kitchen}$. In addition, the I/O ratio was calculated for the overall
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13 218 living zone; here, the indoor concentration was taken as the volume-weighted mean of the
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15 219 average concentration measured in the kitchen and bedroom area. Note: in contrast to absolute
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17 220 concentration, the ratios are not subject to uncertainties associated with instrument calibration.
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21 221 Peak analysis was applied to concentration time series measured in the kitchen for each
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23 222 ion. The measured time series during the whole campaign was first normalized to 30-min
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25 223 resolution. Peak position of each spike was automatically identified on the times series using an
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27 224 optimized peak-detection algorithm. A manual check across a large range of ions indicated that
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29 225 this algorithm had high fidelity, with few false identifications. Nevertheless, some small spikes
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31 226 might not have been detected owing to fast temporal variation in baseline concentrations, e.g.,
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33 227 associated with window opening (particularly during the summer). The total number of ions
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35 228 which spiked within each hour (h^{-1}) was counted and used in some analyses.
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41 229 **2.3. Determining indoor emission rates**

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43 230 Time-resolved emission rates in the living zone were determined for VOC ions using
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45 231 indoor air-change rates determined with 2-h resolution.³¹ Key approximations made in this
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47 232 calculation are (1) that the occupied internal volume of the house can be effectively considered
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49 233 as well-mixed; and (2) that only indoor emissions and air change between indoor and outdoor air
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51 234 influence indoor-air concentrations. These approximations are supported by three important
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53 235 observations: (1) tracer results showed that air in the upper and lower living spaces mixed fairly
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236 well;³¹ (2) the crawlspace and attic generally served as one-way paths for airflow into and out of
 237 living zone, respectively;³¹ and (3) VOC composition in the crawlspace was similar to that
 238 outdoors (cf. Section 3.2). Under this approximation, the mass balance of a VOC in the living
 239 zone is given by the following equation:

$$240 \quad \frac{dC_{\text{in}}}{dt} V = \frac{E}{\rho} - A \cdot (C_{\text{in}} - C_{\text{out}}) \cdot V, \quad (1)$$

241 where $C_{\text{in}} = C_{\text{in}}(t)$ and $C_{\text{out}} = C_{\text{out}}(t)$ are the concentrations in the living zone and outdoors (ppb;
 242 part per billion by volume); V is the volume of the living zone (m^3); $E = E(t)$ is the emission rate
 243 in the living zone (mg h^{-1}), ρ is the gas density for the compound (mg mm^{-3}), and $A = A(t)$ is the
 244 living-space air-change rate (h^{-1}). Treating $A(t)$ and $E(t)$ as constant over each interval of $\Delta t [t, t$
 245 $+ \Delta t]$, we obtain the following approximation of $E(t)$ by integrating equation (1):

$$246 \quad E = \rho V \left(\frac{C_{\text{in}}(t + \Delta t) - C_{\text{in}}(t)}{\Delta t} + A \cdot (\overline{C_{\text{in}}} - \overline{C_{\text{out}}}) \right), \quad (2)$$

247 where $\overline{C_{\text{in}}}$ and $\overline{C_{\text{out}}}$ are the averages over $[t, t + \Delta t]$ of C_{in} and C_{out} , respectively. In application, ρ
 248 is calculated based on molar mass of the compound (ion) at 20 °C, V is the measured living-
 249 space volume (350 m^3), and Δt is 2 h. The time-dependent outdoor concentration, C_{out} , is
 250 directly measured. The time-dependent indoor concentration, C_{in} , is approximated as the
 251 weighted mean of VOC concentrations measured in the kitchen and bedroom area. Values of
 252 $C_{\text{in}}(t + \Delta t) - C_{\text{in}}(t)$, $\overline{C_{\text{in}}}$, and $\overline{C_{\text{out}}}$ are derived using the same procedure as when determining air-
 253 change rate using measured tracer concentrations.³¹

254 3. Results and Discussion

255 Figure 1 presents an overview of the measurement results, displaying a full time series of
 256 the sum of measured VOC concentration ($\sum \text{VOCs}$) at each of the six measurement locations in
 257 the summer (Fig. 1A, for 8 weeks) and winter (Fig. 1B, for 5 weeks) campaigns. Two prominent

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3 258 features of the time series are highlighted. First, \sum VOCs in the living zone (bedroom and
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5 259 kitchen) and in the attic were of similar scale, and were an order of magnitude higher than those
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7 260 in subfloor spaces (basement and crawlspace) which were close to the outdoor level. This
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9 261 feature was exhibited consistently for both occupied and vacant periods in both seasons.
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11 262 Secondly, for \sum VOCs measured in the living zone, the vacant periods were characterized by
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13 263 consistently high background levels while the occupied periods displayed frequent short-term
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15 264 increases on top of these levels. The implication of this observation is that occupants and their
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17 265 activities influenced the temporal pattern of VOC concentrations. Utilizing the observed spatial
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19 266 and temporal variation in VOC concentrations, the following analysis aims to characterize
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21 267 generic features of indoor VOC emissions and sources, in particular focusing on VOCs measured
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23 268 in the living zone where human exposure occurs.

29 269 **3.1. VOC composition in the living zone**

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32 270 Figure 2A presents the average VOC mass spectrum measured by PTR-ToF-MS for
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34 271 kitchen air. Mass-to-charge ratio of detected ions (m/z , with implicit units of the atomic mass
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36 272 unit normalized by the charge number), which is a proxy of molecular mass ($m/z = m + 1$ in
37
38 273 typical case of proton transfer reaction) of the corresponding compound, ranged from 25 to 450.
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40 274 Most ions (176) were detected in both campaigns. Some were detected only in summer (53) and
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42 275 a few only in winter (4). Table S1 presents the complete list of detected ions, along with the
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44 276 respective compound assignments and key measurement parameters in each season. For more
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46 277 than half of the ions only detected in the summer, the mass-to-charge ratios were greater than
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48 278 120 and the signals were just above the respective detection limits. The lower prevalence of
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50 279 these ions in the winter campaign might be attributed to the lower wintertime indoor air
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52 280 temperature (16-18 °C) than in the summer (20-23 °C), driving more massive (and usually less
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3 281 volatile) organic molecules to partition more onto surfaces than into the air. As shown in Figure
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5 282 2A, the measured average concentrations of individual VOCs spanned over four orders of
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7 283 magnitude from 0.005 ppb to 100 ppb, exhibiting a generally decreasing trend with increasing
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9 284 ion mass. A noteworthy exception of this trend was high ion signals of cyclic siloxanes (D4, D5,
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11 285 and D6) at $m/z > 290$, attributable to their exceptionally high volatilities relative to their
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13 286 molecular masses and widespread use in consumer products.¹⁰
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17 287 Figure 2B presents scatter plots of averaged concentrations in kitchen air of the 176 ions
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19 288 detected in the two seasons, colored according to ion mass. In general, the data points cluster
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21 289 close to the 1:1 line, suggesting an overall similarity of VOC composition in the two seasons.
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23 290 Ions corresponding to small alcohols, carboxylic acids, and carbonyls were among the most
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25 291 abundant observed across the two seasons. Examples include (ordered by the abundance) ethanol
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27 292 ($C_2H_7O^+$), acetic acid ($C_2H_5O_2^+$), methanol (CH_5O^+), formic acid ($CH_3O_2^+$), acetone + propanal
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29 293 ($C_3H_7O^+$), and acetaldehyde ($C_2H_5O^+$).
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33 294 Despite overall similarity, Figure 2B also shows some clear seasonal differences in the
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35 295 VOC composition. For ions at higher masses, the concentrations were generally higher in the
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37 296 summer than in the winter (just above the 1:1 line), which might be an effect of temperature and
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39 297 volatility. In addition, clear exceptions to the near 1:1 relationship are evident and are generally
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41 298 attributable to variation in occupant activities. For example, the winter concentration of ions
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43 299 from siloxane D5 and monoterpenes were more than 5 times higher than those in the summer.
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45 300 Their enhancements in winter were associated with increases in the use of skin care products and
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47 301 in the consumption of wintertime citrus fruits (such as oranges), respectively.
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3.2. Spatial distribution of VOC emission sources

In theory, VOCs in the living-zone air could be transported from outdoors, transported from coupled spaces (attic, crawlspace, and basement), or emitted directly into the living zone itself. Space-resolved VOC measurements, combined with the house airflow pattern as characterized using tracers, is used herein to evaluate the relative importance of each of these possible pathways. Tracer release observations demonstrated there were substantial *upward* interzonal airflows with negligible *downward* airflows among the living zone, attic, and crawlspace in the studied house.³¹ The implication is that VOC emissions in the crawlspace, if present, could influence concentrations in the living zone. Conversely, emissions into the attic could not materially contribute to living zone concentrations.

Figure 3 presents histograms of the indoor-to-outdoor concentration ratios (I/O) of measured VOC ions for each indoor space in each season. As described in Section 2.2, the I/O ratios of individual VOC ions were calculated using the mean concentration in each space. An underlying assumption of space-resolved analysis herein, including I/O ratios, is that the same compound assignment can hold for an ion measured in different spaces. The I/O ratios for the crawlspace had a narrow distribution of values centered around 1 in both seasons, indicating that VOC composition in the crawlspace was close to that outdoors. By comparison, the distributions of I/O ratios measured in the living zone, including both the kitchen and bedroom area, were broader with many substantially higher values. For >75% of ions, the average living-zone concentrations were more than 5 times higher than outdoors ($I/O > 5$). For about half of the ions, the difference was at least one order of magnitude ($I/O > 10$). These results demonstrate that for most VOCs measured in the living zone neither outdoor air nor the crawlspace was a major source.

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3 325 For a few VOCs observed in the living zone, transport from outdoors or from the
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5 326 crawlspace did, however, make considerable and even dominant contributions. For example, a
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7 327 few halogen-containing ions, including CCl_3^+ (likely from CHCl_3 based on GC×GC-ToF-MS
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9 328 analysis of VOC samples), CCl_2F^+ (only detected in summer), and $\text{C}_7\text{H}_4\text{F}_2\text{Cl}^+$ (likely from
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11 329 parachlorobenzotrifluoride $\text{C}_7\text{H}_4\text{F}_3\text{Cl}$ based on GC×GC-ToF-MS), had I/O ratios close to 1 in all
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13 330 the measured indoor spaces, suggesting a dominant contribution from outdoors. The C_2H_4^+ ion
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15 331 exhibited a consistently high I/O ratio (18) in the crawlspace in both seasons and lower ratios in
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17 332 the living zone (11 in summer and 15 in winter). This ion is possibly a product of natural gas
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19 333 leakage from the furnace or water heater in the crawlspace, detected via reactions other than
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21 334 proton transfer. The ratio of I/O values of C_2H_4^+ ion in the two indoor spaces is consistent with
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23 335 the fraction of air entering into the living zone from the crawlspace (i.e., on average ~60% in
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25 336 summer and ~80% in winter), suggesting that the C_2H_4^+ signal observed in the living zone was
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27 337 predominantly attributable to transport from the crawlspace.
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33 338 Contributions from the attic and basement to the living zone also appear to be minor
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35 339 overall. Although high I/O ratios were observed in the attic for many VOCs ions, air rarely
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37 340 flowed downwards from the attic to the living zone.³¹ To the contrary, some of the high I/O
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39 341 ratios in the attic can, at least in part, be due to upward transport from the living zone. The
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41 342 distribution of I/O ratios in the basement was similar to that in the crawlspace and values were
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43 343 much lower than in the living zone. No single ion exhibited higher I/O ratios in the basement
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45 344 than in the living zone, suggesting that emissions into the basement did not make important
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47 345 contributions for any VOC ions observed in the living zone. For example, the highest I/O ratio
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49 346 observed in the basement (28) was for $\text{C}_{10}\text{H}_{21}\text{O}^+$, but the corresponding I/O ratios in the kitchen
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51 347 and bedroom area were much higher (> 80).
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3 348 Since transport from outdoors and from coupled spaces in the house cannot explain the
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5 349 concentration levels observed in the living zone for most VOCs ions, the clear implication is that
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8 350 the major sources of VOCs in the living zone were emissions directly into the living zone. Such
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10 351 emissions can originate from the building envelope, from the static contents (such as furniture)
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12 352 inside the space, from bioeffluents of the human occupants, and from occupants' activities. The
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14 353 next two sections will discuss features regarding occupant-related emissions and building-related
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16 354 emissions (including furnishings and household products), respectively, as interpreted from time-
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18 355 resolved measurements.
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22 356 **3.3. Intermittent emissions from occupants and their activities**

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25 357 The time series of observed VOCs in the living zone was generally characterized by clear
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27 358 short-term enhancements (spikes) on top of more slowly variable baseline levels. For some
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29 359 compounds, the baseline level was relatively low, and the presence of strong spikes was the
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31 360 major feature of the concentration time series. The spikes for some compounds were episodic;
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34 361 for others, the pattern was more nearly periodic. Ethanol, the most abundant VOC observed in
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36 362 the living zone, is an example of a species whose time-pattern is dominated by spiky behavior.
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38 363 (The summer time series for ethanol is shown in Figure S1A). In contrast, for some other
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41 364 compounds, such as acetic acid (the second most abundant VOC observed; Figure S1B), the
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43 365 most prominent feature of the time series is a consistently elevated baseline concentration. There
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45 366 were some spikes in acetic acid concentration above the baseline, but their contribution to the
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47 367 average concentration over the whole campaign was small. Other compounds fell in between
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50 368 such that their concentration time series showed considerable influence from both spikes and the
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52 369 high baseline level. (One example is acetaldehyde as displayed in Figure S1C). These distinct
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3 370 features serve as the basis of analysis in this and the following sections to distinguish intermittent
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5 371 occupant-related emissions from continuous building-related emissions.
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8 372 Figure 4 shows the time series of kitchen concentrations for selected compounds on one
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10 373 particular day along with recorded occupant activities. When the occupants were asleep (0-6
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12 374 AM), concentrations of all the compounds were relatively steady. At breakfast time, pyridine
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14 375 concentration ($C_5H_6N^+$) spiked from 0.06 ppb to 1.7 ppb and ethanol concentration increased
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16 376 from 80 ppb to 420 ppb, attributable to making coffee and toasting bread (which, as a fermented
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18 377 product, contains ethanol), respectively. In the morning when occupants did some house
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20 378 cleaning, concentrations of solvents, such as ethanol and acetone, increased by factors of 6-7. In
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22 379 the afternoon, when occupants prepared ratatouille using a frying pan at high temperature,
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24 380 concentrations of many compounds became elevated. Some were elevated persistently (e.g.,
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26 381 $C_2H_7S^+$ attributable to ethanethiol and dimethyl sulfide)¹¹ and others were elevated only for a
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28 382 short period (e.g., $C_5H_9^+$ likely attributable to isoprene). A party was hosted in the evening with
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30 383 about a dozen guests. Ethanol concentration rose strongly to 4.3 ppm (50 times higher than the
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32 384 overnight level). Elevated concentrations were also observed for ethanethiol + dimethyl sulfide
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34 385 from ratatouille being reheated and served, for isoprene mainly attributable to human breath, and
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36 386 for D5 from personal care products such as antiperspirants. After the party, another large ethanol
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38 387 spike was observed, coincident with a spike of chloramine (H_3NCl^+ ; inorganic compound;
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40 388 disinfectant in tap water), likely associated with cleaning up after the party. At the end of the
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42 389 day, occupants left the kitchen with the dishwasher running, and another spike of chloramine was
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44 390 observed attributable to dishwasher operation. The examples displayed in Figure 4 illustrate that
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46 391 occupants and their activities can emit many VOCs and greatly enhance their indoor
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48 392 concentrations in a temporally specific manner. The effect is seen in the concentration time
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3 393 series as short-term elevations (spikes) above the respective baseline concentrations. In the next
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5 394 few paragraphs, we describe how we utilize the spikiness feature of the time series to gain more
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8 395 in-depth understanding of occupant-related emissions.
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10 396 No ions were observed to spike during vacant periods in either campaign, but spikes
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12 397 frequently occurred during periods when occupants were home and awake. We used spike
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14 398 statistics to identify prominent VOC-emitting activities. Spikes (corresponding peak time points)
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17 399 were automatically identified in the times series of individual VOC ions using a customized peak
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19 400 detection algorithm. Figure 5 shows averaged hourly occurrence of the number of spiked VOC
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21 401 ions (h^{-1}) in the summer and winter occupied periods. Diel variation in the number of spiked
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23 402 ions peaked at breakfast and at dinner time. The diel pattern of spikiness in VOC abundance
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26 403 resembles remarkably the variation in the frequency of stove burner use, which serves as a proxy
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28 404 indicator for cooking activities. This spike analysis strongly suggests that cooking activities
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30 405 were the dominant contributor to occupant-associated intermittent VOC emissions. As a
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33 406 reference point, some recent laboratory studies demonstrate that cooking can emit a large variety
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35 407 of VOCs.^{11,39}
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38 408 As shown in Figure 4, VOC spikes in the concentration time series were asymmetric,
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40 409 with a rapid rise and a more gradual decline. Declines often extended for hours or even days
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42 410 (e.g. Figure S1A) after the corresponding emission events. Evidence supports an interpretation
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44 411 that this gradual decline feature was influenced not only by air change but also by sorptive
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46 412 interactions with indoor surfaces. To illustrate, Figure S2 displays a snapshot time series of the
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48 413 concentration of pyridine ($\text{C}_5\text{H}_6\text{N}^+$; emitted from making drip coffee), as well as its indoor
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50 414 emission rate. The indoor emission rate was quantified with 2-h time resolution, using measured
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53 415 indoor and outdoor concentrations and air-change rates. The quantified emission rate was a net
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3 416 effect considering all sources and sinks indoors, but without specific accounting for sorptive
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5 417 interactions. Figure S2 also shows the predicted decline from the peak pyridine concentration
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7 418 assuming that only air change contributes to removal. When pyridine concentration increased to
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9 419 its peak concentration, the emission rate sharply increased as expected. Immediately after the
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11 420 peak concentration, a steep decline of modeled emission rates was observed, often to a negative
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13 421 value, whereas the pyridine concentration was still elevated above the baseline level. The
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15 422 negative emission rate occurred when the pyridine concentrations in the indoor air declined more
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17 423 rapidly than expected by air change alone, indicating a net uptake of airborne pyridine by indoor
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19 424 surfaces. After the steep drop, modeled emission rates of pyridine rebounded to above zero and
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21 425 subsequently slowly declined, suggesting that pyridine taken up by the surfaces was slowly
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23 426 released back to the indoor air. The implication of these results is that pulsed emissions from
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25 427 occupants' activities can have longer-lasting effects on indoor VOC concentrations owing to
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27 428 reversible interactions with indoor surfaces. This effect has been studied in controlled
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29 429 experiments conducted in chambers⁴⁰ and in controlled field assessments;²⁴ however, it has not
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31 430 been reported previously for an observational investigation of an ordinarily occupied residence.

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33 431 The presence of spikes in a concentration time series can increase the mean concentration
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35 432 across the whole observational period, but will have less effect on the median. Herein we used
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37 433 the mean-to-median concentration ratio ($C_{\text{Avg}}/C_{\text{Med}}$) as a quantitative indicator of the relative
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39 434 importance of occupant-related emissions. Figure 6 presents histograms of $C_{\text{Avg}}/C_{\text{Med}}$ for all
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41 435 organic ions during the occupied and vacant periods in each season, respectively. For vacant
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43 436 periods, values of $C_{\text{Avg}}/C_{\text{Med}}$ tightly clustered around 1.0 and rarely went above 1.1, with mean
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45 437 values of 1.02 in the summer and 1.01 in the winter. For occupied periods, the $C_{\text{Avg}}/C_{\text{Med}}$
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47 438 distribution broadened and extended more toward higher values. For ethanol, acetic acid, and
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3 439 acetaldehyde (Figure S1), the summer $C_{\text{Avg}}/C_{\text{Med}}$ ratios were 2.3, 1.0, and 1.3, respectively. In
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5 440 total, there were 8 ions in the summer and 6 in the winter with $C_{\text{Avg}}/C_{\text{Med}} > 1.5$. For $C_{\text{Avg}}/C_{\text{Med}} >$
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7 441 1.1, the respective numbers of ions were 55 for summer and 24 for winter.

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10 442 Table 1 lists a subset of 12 ions for which the $C_{\text{Avg}}/C_{\text{Med}}$ values were greater than 1.5
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12 443 during at least one season; these represent compounds with major (dominant) contributions from
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14 444 occupant-related emissions. Emission sources of the individual compounds were further
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16 445 constrained by associating the respective spikes with event records. Emissions of the siloxanes
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18 446 D5 and D6 can be attributed to the use of personal care products (for both species) and cleaning
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20 447 products (for D6). Each of the other occupancy-dominated species were predominantly
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22 448 associated with cooking. For example, ions $\text{C}_5\text{H}_6\text{N}^+$ (pyridine) and $\text{C}_5\text{H}_5\text{O}^+$ (likely a fragment
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24 449 ion) typically spiked when making coffee. Ion $\text{C}_9\text{H}_9\text{O}^+$ (cinnamaldehyde) was particularly
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26 450 abundant when making applesauce (a frequent activity during summer but not done in winter).
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28 451 Large spikes of $\text{C}_6\text{H}_9\text{O}_4^+$ ion (tentatively attributed to 3-deoxyglucosone; see Table 1 notation)
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30 452 occurred when baking granola. Spikes of $\text{C}_2\text{H}_3\text{O}_4^+$ (likely attributable to oxalic acid) were
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32 453 observed during some occasions of sautéing in the summer. A few other ions spiked during a
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34 454 wider variety of cooking events, including $\text{C}_2\text{H}_7\text{O}^+$ (ethanol), $\text{C}_4\text{H}_6\text{N}^+$ (pyrrole), and $\text{C}_{10}\text{H}_{17}^+$
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36 455 (monoterpenes; consumption of citrus fruits led to a particularly high $C_{\text{Avg}}/C_{\text{Med}}$ in winter). In
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38 456 addition, two inorganic ions, attributable to chloramine and H_2S , also had high $C_{\text{Avg}}/C_{\text{Med}}$ values
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40 457 associated with use of tap water and cooking (especially melting butter), respectively.

41 458 **3.4. Continuous building-related emissions**

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43 459 Figure 6 shows that, for the majority of VOCs, intermittent event emissions were not
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45 460 their major source, with $(C_{\text{Avg}}/C_{\text{Med}})_{\text{kitchen}}$ less than 1.06 for 58% of measured ions in summer and
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47 461 for 74% in winter. A few additional criteria were applied to further select ions whose time series

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3 462 were characterized by elevated baseline levels in the living zone, indicating that the dominant
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5 463 sources were continuous building-material and furnishing-associated emissions into the living
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8 464 space. These specific selection criteria were applied: $(I/O)_{\text{kitchen}} > 10$, $(C_{\text{Avg}}/C_{\text{Med}})_{\text{kitchen}} < 1.06$,
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10 465 and $(I/O)_{\text{kitchen}} > 2 (I/O)_{\text{crawlspac}}$ during both monitoring campaigns. This selection process
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12 466 yielded 56 organic ions. The analysis in this section focuses on indoor emissions of these 56
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15 467 ions.

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17 468 Figure 7A shows a pie chart of mean indoor emission rates of the 56 organic ions for the
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19 469 summer occupied period. The mean summed emission rate of the 56 ions was 37.4 mg h^{-1} during
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21 470 summer (average temperature $22 \text{ }^{\circ}\text{C}$), as compared to 23.3 mg h^{-1} during winter (average
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23 471 temperature $17 \text{ }^{\circ}\text{C}$). The top six most highly emitted VOCs/ions were acetic acid, methanol,
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25 472 formic acid, formaldehyde, $\text{C}_6\text{H}_{11}^+$ (likely an alcohol fragment, such as *cis*-3-hexen-1-ol),⁴¹ and
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27 473 furfural. Acetic acid alone accounted for half of the summed VOC emission rate; methanol and
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29 474 formic acid together accounted for a quarter. In addition, ions attributable to a homologue of
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31 475 saturated carbonyls ($\text{C}_6\text{-C}_{12}$) and saturated fatty acids ($\text{C}_6\text{-C}_8$) accounted for 10% and 12% of the
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33 476 emissions, respectively. The remaining ions, for which a chemical formula could be confidently
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35 477 assigned, were summarized according to ion formula family (C_xH_y^+ , $\text{C}_x\text{H}_y\text{O}^+$, and $\text{C}_x\text{H}_y\text{O}_2^+$).
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37 478 Ions for which empirical ion formulas could not be confidently assigned were summed and
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39 479 reported as “others”; these account for $<0.5\%$ of the building-associated emissions. The full list
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41 480 of 56 ions and their respective average emission rates in each season are reported in Table S1.
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47 481 A key feature of the VOC species that are dominated by building-related emissions is a
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49 482 strong temperature dependence. Figure 7B illustrates this point, displaying the dependence of
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51 483 indoor emission rates on indoor temperature. In this analysis, the determined 2-h average
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53 484 emission rates were sorted according to indoor temperature, binned with $1 \text{ }^{\circ}\text{C}$ resolution. The
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3 485 mean was taken for each one-degree temperature interval containing at least 50 data points.
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5 486 Indoor temperature was primarily 16-18 °C in winter and 20-23 °C in summer. As shown in
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7 487 Figure 7B, summed emission rates increased with temperature in each season as well as across
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9 488 the two seasons. For temperatures spanning 16 to 23 °C, an overall doubling of building-
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11 489 associated VOC emission rate was observed. Similar trends were evident for most individual
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13 490 ions/groups of ions, such as acetic acid (Figure 7B).
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17 491 The temperature dependence of indoor concentration of these continuously emitted VOCs
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19 492 is observed to be less pronounced. As shown in Figure 8A, the summed concentration of 56 ions
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21 493 did increase with temperature in the winter as the corresponding emission rates increased. The
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23 494 increase of concentration with temperature was modest in the summer (Figure 8A), despite the
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25 495 strong dependence of emission rates on temperature. These features can be resolved when taking
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27 496 account of temperature-dependent air-change rates in this naturally ventilated house. In the
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29 497 summer, occupants used window opening as a means to adjust indoor temperature. A higher air-
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31 498 change rate was generally observed at higher temperatures, with a 50% increase from 20 to
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33 499 23 °C (Figure 8B). The observation of a smaller temperature effect on VOC concentrations in
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35 500 summer is hence associated with the combination of enhanced emissions at higher indoor
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37 501 temperature and enhanced removal via elevated air change. The implication is that higher indoor
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39 502 emission rates do not always lead to higher indoor concentration levels, since the concentrations
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41 503 and therefore exposures are also modulated by air change.
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47 504 We also infer from the observations that variation in air-change rate affects VOC
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49 505 emission rates by altering indoor concentrations. From a mass-transfer perspective, the VOC
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51 506 emission rate from indoor materials varies with the difference between the airborne VOC
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53 507 concentration near material surfaces and the concentration in the core indoor space. The gas-
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3 508 phase VOC concentration near the material surface is regulated by the air-material partition
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5 509 coefficient, which is a function of temperature.⁴² For the selected 56 ions, the observed relations
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7 510 of emission rate, concentration, and temperature were generally in line with theory (i.e., at fixed
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9 511 indoor concentration the emission rate was higher at higher temperature and at a fixed
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11 512 temperature it was higher when the measured concentration was lower). Figure S3 shows the
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13 513 data (after filtering spikes) for acetic acid as an example. An increase in air-change rate lowers
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15 514 the corresponding indoor VOC concentration, making the concentration gradient larger than it
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17 515 would be otherwise, and thereby enhancing the emission rate. For this particular house, the
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19 516 apparent temperature dependence of VOC emissions (Figure 7B) is a combined effect of more
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21 517 partitioning into the air at higher temperature and a larger concentration gradient associated with
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23 518 enhanced air change at higher temperatures. In particular, the stronger dependence of emission
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25 519 rates on temperature in the summer than in the winter, as shown in Figure 7B, can result from
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27 520 larger increase of air-change rates with higher temperatures in the summer (Figure 8B).
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33 521 We also used the empirical evidence in this study to seek out clues about the major
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35 522 building-associated VOC emission sources. One set of clues emerges from measured VOC
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37 523 concentrations in the attic. Figure 9 plots the I/O ratio in the attic versus that in the living zone
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39 524 for all the VOC ions measured during the summer campaign. The size and color of each data
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41 525 point is respectively scaled by C_{Avg} and C_{Avg}/C_{Med} of the corresponding ion measured in the
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43 526 kitchen. The dashed line represents the lower limit of attic I/O ratio predicted solely by transport
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45 527 from the living zone and from outdoors, as given by this expression:
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$$49 \quad 528 \quad (I/O)_{attic, predicted} = (1 - \chi) + (I/O)_{living} \chi, \quad (3)$$

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52 529 where χ is the fraction of air entering attic from living zone, estimated to be 0.22 using the attic-
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54 530 to-living-zone ratio of average concentration of the tracer released in the living zone; $(1 - \chi)$ is the
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3 531 fraction of air entering attic directly from outdoors, assuming that the air transported directly
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5 532 from the crawlspace to the attic is negligible.³¹ The light grey band in Figure 9 represents the
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8 533 confidence interval for estimated attic I/O ratio, assuming a 40% uncertainty for χ .
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10 534 As shown in Figure 9, some data points lie within the grey band, indicating that the attic
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12 535 concentrations of the corresponding compounds could be primarily a consequence of transport
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14 536 from the living zone and from outdoors. For these compounds, direct emissions into the attic
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17 537 appear relatively unimportant as a source. Most species/ions with dominant emissions from
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19 538 occupant-associated activity in the living zone (in red), such as ethanol, pyridine, D5, and D6,
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21 539 belong to this category. By contrast, the attic I/O ratio of some ions can be 4-10 times higher
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24 540 than the transport-focused predictions of equation (3), suggesting strong direct emission sources
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26 541 into the attic for these species. These species/ions include small carboxylic acids, aldehydes and
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28 542 alcohols (e.g., acetic acid, formic acid, methanol, acetaldehyde), some furanoids (e.g., furfural
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31 543 and dimethylfuran), and some aromatics ($C_7H_9O^+$, $C_9H_{11}O^+$, and $C_8H_{11}^+$).
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33 544 The unoccupied and unfinished attic is framed with redwood lumber (~ 80 years old) and
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35 545 also has exposed plywood sheathing from reroofing that was completed more than a decade
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38 546 before the measurement campaign. The attic contains fiberglass insulation, decades old, above
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40 547 the ceiling of the living zone. It also contains some stored personal items of the occupants, such
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42 548 as cardboard boxes with books, seasonal decorations, children's playthings, and luggage. These
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45 549 contents, present at much lower densities than in the living zone, did not appear to be prominent
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47 550 VOC sources based on a focused "sniffing" experiment using the PTR-ToF-MS with a moveable
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49 551 sampling probe. It seems likely, therefore, that the direct VOC emissions into the attic are
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51 552 largely attributable to emissions from wooden building materials. Since the same wooden
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54 553 building materials also envelop the living space, emissions from wood is also likely an important
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3 554 VOC source for the living zone. Consistent with this hypothesis, the VOCs exhibiting the
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5 555 strongest building-associated emissions into the living space (large purple points in Figure 9; e.g.
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7 556 acetic acid, formic acid, and methanol) are among those exhibiting the strongest emissions into
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10 557 the attic (i.e. points well above the grey band).

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12 558 Detailed mechanisms resulting in emissions of the small-molecule organic compounds
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14 559 from the wooden building materials of this 80-year-old house remain to be better understood.
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16 560 One plausible hypothesis is decomposition of wood, which is mainly composed of celluloses,
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18 561 hemicelluloses, and lignin. The suite of organic compounds elevated in the attic closely
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20 562 resembles the volatile degradation products of heat-treated wood as reported in laboratory-based
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22 563 measurements.^{43,44} With heat treatment, the reactions are believed to start with deacetylation of
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24 564 hemicelluloses, and the released acetic acid further catalyzes the decomposition of
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26 565 polysaccharides and reduces their degree of polymerization.^{45,46} Commonly reported volatile
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28 566 products are acetic acid and furfural;^{43,44,47-49} the latter compound is a degradation product of
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30 567 some pentoses.⁴⁶ Production of formic acid, methanol, small aldehydes, other furanoids, and
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32 568 some phenolic compounds (lignin decomposition products) are also reported.⁴³ The timber used
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34 569 to build this house was unlikely heat treated prior to construction, based on the wood color and
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36 570 building age. We suspect that similar degradation processes might have taken place over the
37
38 571 near century time scale since house construction. High abundance of acetic acid and furfural in
39
40 572 both the attic and in the living zone, along with high abundance of other compounds associated
41
42 573 with wood degradation, are consistent with the hypothesis of wood decomposition being their
43
44 574 major source.

45
46 575 As a further note, the high detection frequency and high abundance of acetic acid, formic
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48 576 acid, and furfural have been reported for residential air in places where wood-framed houses are

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2
3 577 common. Mixing ratios of acetic acid and formic acid were measured in residences in New
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5 578 Jersey and in the greater Boston area at levels comparable to the current study and also more
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8 579 than an order of magnitude higher than outdoors.^{50,51} An indoor air survey of ~3800 homes in
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10 580 Canada showed that furfural was detected in 98% of homes (acetic acid was not a target
11
12 581 compound in that study).² Another study in Finland showed that furfural was detected in 21 out
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14 582 of 26 houses.⁵² Although further investigation is warranted, emissions from wood construction
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16 583 materials might have been important sources of these VOCs among others for the residences in
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18
19 584 previous studies.

21
22 585 Emissions from the wooden building envelope are prominent in this studied house. Yet,
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24 586 the building envelope cannot explain the whole story of material-associated emissions into the
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26 587 living zone. As shown in Figure 9, for some VOCs such as nonanal, phenol, and decanal, high
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28 588 I/O ratios were observed in the living zone, but their attic I/O ratios were just slightly above what
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30
31 589 is predicted by transport. For these VOCs, continuous emission sources other than the wood
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33 590 building envelope were present in the living zone. Specific sources for these compounds were
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35 591 not isolated. While there are multiple possible sources, we suspect phenol could have been
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38 592 emitted from plastic products, and nonanal and decanal could be emitted from ozone reactions
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40 593 with various indoor surfaces (e.g., with surface oil films originating from cooking).^{13,53}

43 594 **4. Conclusion**

45 595 We have characterized the general features of sources and emissions of VOCs in the
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47 596 living space of a normally occupied single-family house in northern California. The analysis is
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50 597 based on space- and time-resolved measurement of a full spectrum of VOCs observable by PTR-
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52 598 ToF-MS throughout two multiweek, continuous monitoring campaigns. In total, about 200 VOC
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55 599 ions (species) were measured. For the studied house, most VOCs observed in the living space

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3 600 were primarily emitted from sources directly into the living space. Transport from outdoors and
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5 601 from coupled spaces such as the crawlspace, basement, and attic were overall minor for a large
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7 602 majority of VOCs. For many VOCs observed in the living space, continuous temperature-
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9 603 dependent emissions were prominent, characterized in the time series by indoor concentrations
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11 604 consistently elevated above outdoor levels. These emissions come from building materials,
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13 605 furnishings, and other static contents of the household. In particular, slow decomposition of the
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15 606 wooden building envelope is suggested as a major source for acetic acid, formic acid, and
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17 607 methanol, which together accounted for approximately 75% of the total continuous indoor
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19 608 emission, as well as for some other abundant VOCs. Intermittent emissions from occupants and
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21 609 their activities produced short-term enhancements (spikes) in the VOC concentration time series.
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23 610 The diel pattern of the number of spiked ions indicates that cooking activities were the major
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25 611 occupancy-associated VOC emission sources. The influence of activity emissions on indoor
26
27 612 concentrations of emitted VOCs can extend beyond the period of source activity, exhibit as a
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29 613 slow decline in the concentration time series following spikes. The persistence is most likely due
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31 614 to reversible sorptive interactions of the VOCs with interior surfaces.
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37
38 615 Much of the concern about indoor air VOCs in the past has focused on primary emissions
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40 616 from new building materials and furnishings. There is ample evidence that these emissions
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42 617 decline over time.^{22,23} To our surprise, notwithstanding that the residence studied here is old and
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44 618 has not been remodeled or refurbished recently, the overall spectrum of VOCs measured is still
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46 619 dominated by continuous emissions from the building and its contents. The distinction is that the
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48 620 emissions in this house seem to be largely secondary. The dominance of small oxygenated
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50 621 compounds (small carboxylic acids, alcohols, and carbonyls) in the spectrum of measured VOCs
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52 622 and the continuous emission pattern for many of them indicate they likely result from ongoing
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3 623 chemical processes, such as decomposition and oxidation. Slow decomposition of wooden
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5 624 building materials is suggested as a potentially important pathway, but other unidentified
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8 625 chemical pathways might also exist. These results call attention to the possible importance of
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10 626 indoor chemistry as a source for indoor VOCs, even in older structures.

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12 627 Our team's first indoor study using PTR-ToF-MS revealed that in a university classroom
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14 628 the occupants themselves were the primary source of indoor VOCs, including the noteworthy
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16 629 prominence of cyclic siloxanes from personal care products.^{10,26} Relative to a classroom, the
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18
19 630 typical single-family dwelling in the United States has more ventilation per person, more high-
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21 631 emitting activities (such as cooking), and more emissions from objects in the building materials
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23 632 and furnishings. In both the university classroom setting and in the residential environment we
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25
26 633 found the contribution of outdoor air to indoor VOC levels to be modest. The combination of
27
28 634 much higher VOC levels indoors than outside and the high proportion of time spent indoors,
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30
31 635 especially in residences, points to the need for a shift in overall air quality research emphasis
32
33 636 toward the indoor environment to more thoroughly understand the species and concentrations of
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35 637 VOCs that dominate indoor chemistry and human exposure.

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37
38 638 From a technical perspective, this study demonstrates how continuous time- and space-
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40 639 resolved VOC observations can contribute toward understanding the source characteristics and
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42 640 emission dynamics of VOCs in occupied buildings. Space-resolved measurements in this 80-
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44 641 year-old wood-framed house have led to the discovery of a previously unreported major VOC
45
46 642 source, slow decomposition of aged wooden building materials. Looking to the future, similar
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49 643 measurements in other types of residences might help identify additional interesting and
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51 644 important VOC sources that are currently not well understood or potentially not recognized. The
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54 645 use of time-resolved measurements in an occupied residence allowed identification of cooking as

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3 646 the major source coming directly from occupants and their activities. Even though the two
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5 647 occupants had relatively simple indoor lifestyles (e.g., rarely cooking meat, having no evident
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7 648 emissions-associated hobbies, and spare use of personal care or commercial cleaning products)
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10 649 in this moderately large house, emissions from occupants and their activities still made
11
12 650 considerable contributions to tens of indoor VOC ions. In residences with higher occupant
13
14 651 density and more VOC-emitting activities, occupants' contribution could be even more
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16
17 652 important.
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21
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27
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29
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31
32 under a protocol approved in advance by the Committee for Protection of Human Subjects for
33
34 the University of California, Berkeley (Protocol #2016-04-8656).
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Table 1. List of ions with dominant contributions from occupants and their activities.^a

Ions (species) ^b	Summer ^c		Winter ^c			Major intermittent sources	
	C_{Avg} (ppb)	I/O	C_{Avg}/C_{Med}	C_{Avg} (ppb)	I/O		C_{Avg}/C_{Med}
$C_{10}H_{17}^+$ (monoterpenes)	1.5	13	1.4	13	100	2.3	citrus fruits (winter), cooking, cleaning
$C_2H_7O^+$ (ethanol)	130	44	2.3	150	63	1.9	beer and wine, toasting bread, other cooking, cleaning
$C_5H_5O^+$ (unknown ^d)	0.24	22	1.4	0.56	80	1.6	coffee
$C_9H_9O^+$ (cinnamaldehyde)	0.24	21	1.6	0.062	25	1.07	making applesauce (summer), other cooking
$C_2H_3O_4^+$ (oxalic acid)	0.016	2.3	1.8	NA ^e	NA	NA	sautéing certain vegetables
$C_6H_9O_4^+$ (3DG ^f)	0.015	2.5	2.5	0.012	10	1.3	baking granola, other cooking
$C_4H_6N^+$ (pyrrole)	0.10	100	2.6	0.070	35	1.6	sautéing (sometimes), coffee, other cooking
$C_5H_6N^+$ (pyridine)	0.10	10	1.8	0.070	6.4	1.3	coffee
$C_{10}H_{31}O_5Si_5^+$ (D5)	0.87	34	2.0	20	280	6.0	use of personal care products
$C_{12}H_{37}O_6Si_6^+$ (D6)	0.13	130	1.6	0.05	67	1.5	use of personal care and cleaning products
H_3NCl^+ (chloramine)	0.088	13	1.5	0.031	14	2.6	use of tap water
H_3S^+ (hydrogen sulfide)	0.007	2.0	1.7	0.012	3.3	1.6	cooking (esp. melting butter)

^a Selection criteria: $(C_{Avg}/C_{Med})_{kitchen}$ greater than 1.5 in at least one season, where C_{Avg} is the mean concentration and C_{Med} is the median.

^b Ions are sorted by formula family ($C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_z^+$, $C_xH_yN_z^+$, siloxane ions, inorganic ions)

^c Presented indoor data are for measurements in the kitchen during occupied periods.

^d $C_5H_5O^+$ might be is a fragment of certain furanoids.⁵⁴

^e Ion was not detected in winter.

^f Tentative assignment to 3-deoxyglucosone (3DG; $C_6H_{10}O_5$), a dicarbonyl sugar that is synthesized through the Maillard reaction; $C_6H_9O_4^+$ can be a dehydrated ion of $C_6H_{10}O_5$.

Figures

Fig. 1. Time series of summed VOC concentration ($\sum\text{VOCs}$) during (A) summer and (B) winter campaigns. The grey shaded region represents the longer vacant periods (≥ 2 days) in each campaign. Traces in purple, green, orange, blue, cyan, and red represent measurements in the attic, bedroom area, kitchen, basement, crawlspace, and outdoors, respectively.

Fig. 2. VOC composition in the kitchen air measured using PTR-ToF-MS under normal occupancy: (A) averaged VOC mass spectrum and (B) scatter plot of averaged concentrations (C_{Avg}) of VOC ions in the summer against those in the winter. In panel (A), the dark grey vertical lines represent C_{Avg} of individual ions which are detected in both seasons. The red and blue lines represent ions detected only in the summer and only in the winter, respectively, with C_{Avg} shown for only that season. The mass spectrum has been filtered to remove internal, isotopic, and fragment ions. In Panel (B), the data are shown for ions detected in both seasons, colored by ion masses. For some prominent ions, parent VOC compounds or ion formulas are labeled. The solid grey line denotes a 1:1 relationship.

Fig. 3. Histogram of the indoor-to-outdoor ratios (I/O) of averaged concentrations (C_{Avg}) of the VOC ions for each indoor space. Data are presented from the top to bottom for the attic, bedroom area, kitchen, basement, and crawlspace, in summer (left) and winter (right) campaigns, respectively. Dotted lines indicate equal indoor and outdoor concentrations (I/O = 1). Number of ions with I/O > 10 is listed for each indoor space. Data are not shown for I/O > 50.

Fig. 4. Time series on a selected day (22 September 2016) of (top) activities recorded by sensors and occupants and (bottom) kitchen concentrations of selected compounds. Selected compounds (associated major ions) include pyridine ($\text{C}_5\text{H}_6\text{N}^+$), ethanol ($\text{C}_2\text{H}_7\text{O}^+$), acetone ($\text{C}_3\text{H}_7\text{O}^+$), ethanethiol + dimethyl sulfide (DMS; $\text{C}_2\text{H}_7\text{S}^+$), isoprene (C_5H_9^+), methylsiloxane D5 ($\text{C}_{10}\text{H}_{31}\text{O}_5\text{Si}_5^+$), and chloramine (H_3NCl^+). *Background and peak concentrations (in ppb) of each compound are noted. **Peak value out of plot range.

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3 **Fig. 5.** Hourly variation in the average number of spiked VOC ions measured in the kitchen
4 (grey bars; left axis) and burner uses (orange lines; right axis) in (A) summer and (B)
5 winter campaigns during normal occupancy.
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8 **Fig. 6.** Histogram of kitchen mean-to-median concentration ratios (C_{Avg}/C_{Med}) for organic ions in
9 (A) summer and (B) winter campaigns. Data are presented for vacant and occupied
10 periods in grey and red colors, respectively. Ion count is listed for $C_{Avg}/C_{Med} > 1.5$, > 1.1
11 and < 1.06 , respectively, for the occupied periods.
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16 **Fig. 7.** Indoor emission rates for VOC ions that are dominated by continuous indoor emissions:
17 (A) pie chart of averaged emission rate in summer and (B) stacked bar chart of emission
18 rates by indoor temperature across two seasons. Selection criteria for included ions are
19 provided in the text. Both pie and bars are colored by VOC speciation. Emission rates in
20 mg h^{-1} were determined for each ion with 2-h resolution. In panel (B), an average is
21 shown for each integer temperature at which more than 50 emission rates were measured.
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26 **Fig. 8.** Variation with indoor temperature: (A) stacked concentration for VOCs that have a
27 dominant source of indoor continuous emissions and (B) air-change rate. Data are shown
28 for each integer temperature bin for which more than 50 measurements were recorded. In
29 Panel (A), stacked bars represent averaged summed concentrations in ppb at individual
30 integer temperature, colored by VOC speciation. The color code is the same as the pie
31 chart in Fig. 7A. In Panel (B), vertical lines, horizontal lines, and points represent
32 interquartile ranges, medians, and means of measured air-change rates within 1°C
33 temperature intervals.
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40 **Fig. 9.** Scatter plot of indoor-to-outdoor (I/O) ratios in the attic versus those in the living zone
41 for all the organic ions observed in the summer campaign. The size and color of each
42 data point is respectively scaled by average concentration (C_{Avg}) and mean-to-median
43 concentration ratio (C_{Avg}/C_{Med}) measured in the kitchen. The dashed grey line represents
44 the predicted lower limit of attic I/O ratios, assuming that the attic concentration is solely
45 determined by transport from the living zone and from outdoors. The light grey band
46 shows uncertainty of the prediction. Ion and compound assignments are noted for some
47 prominent species.
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Figure 1

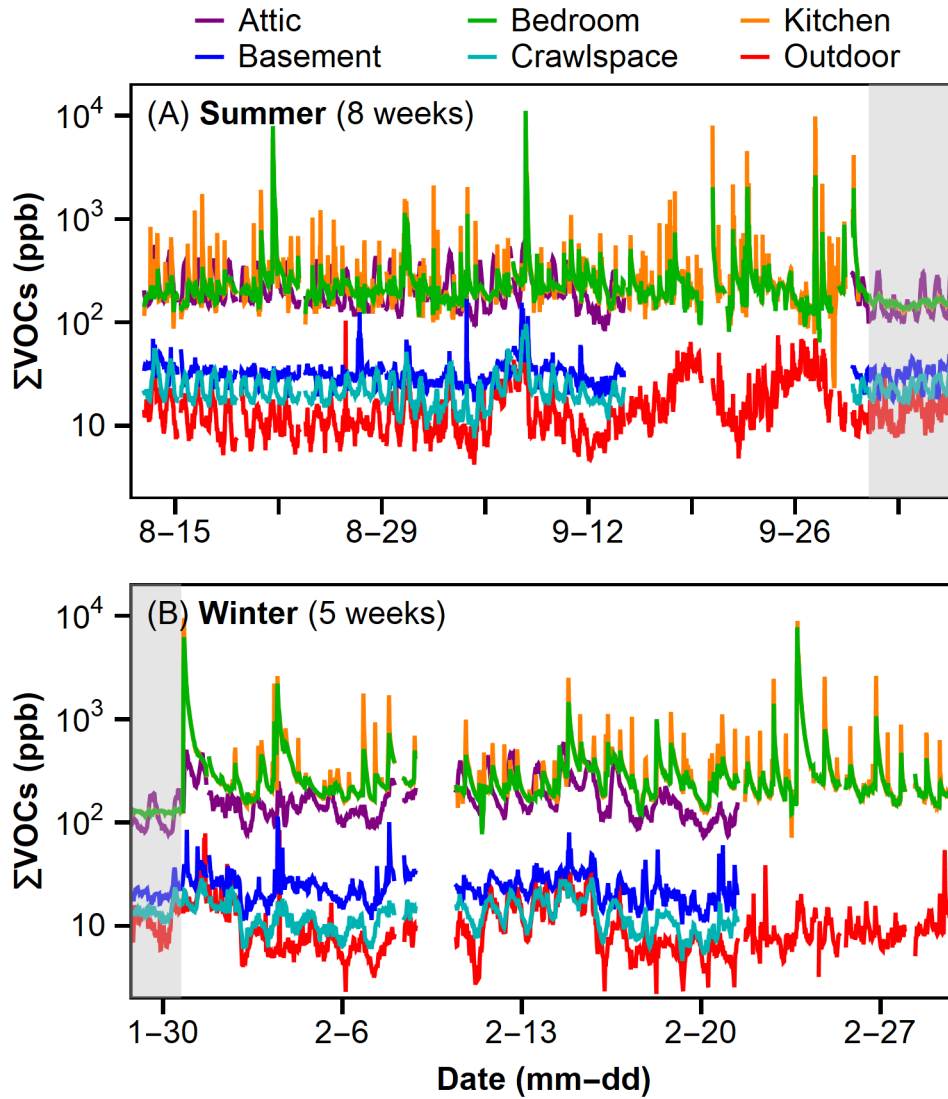


Figure 2

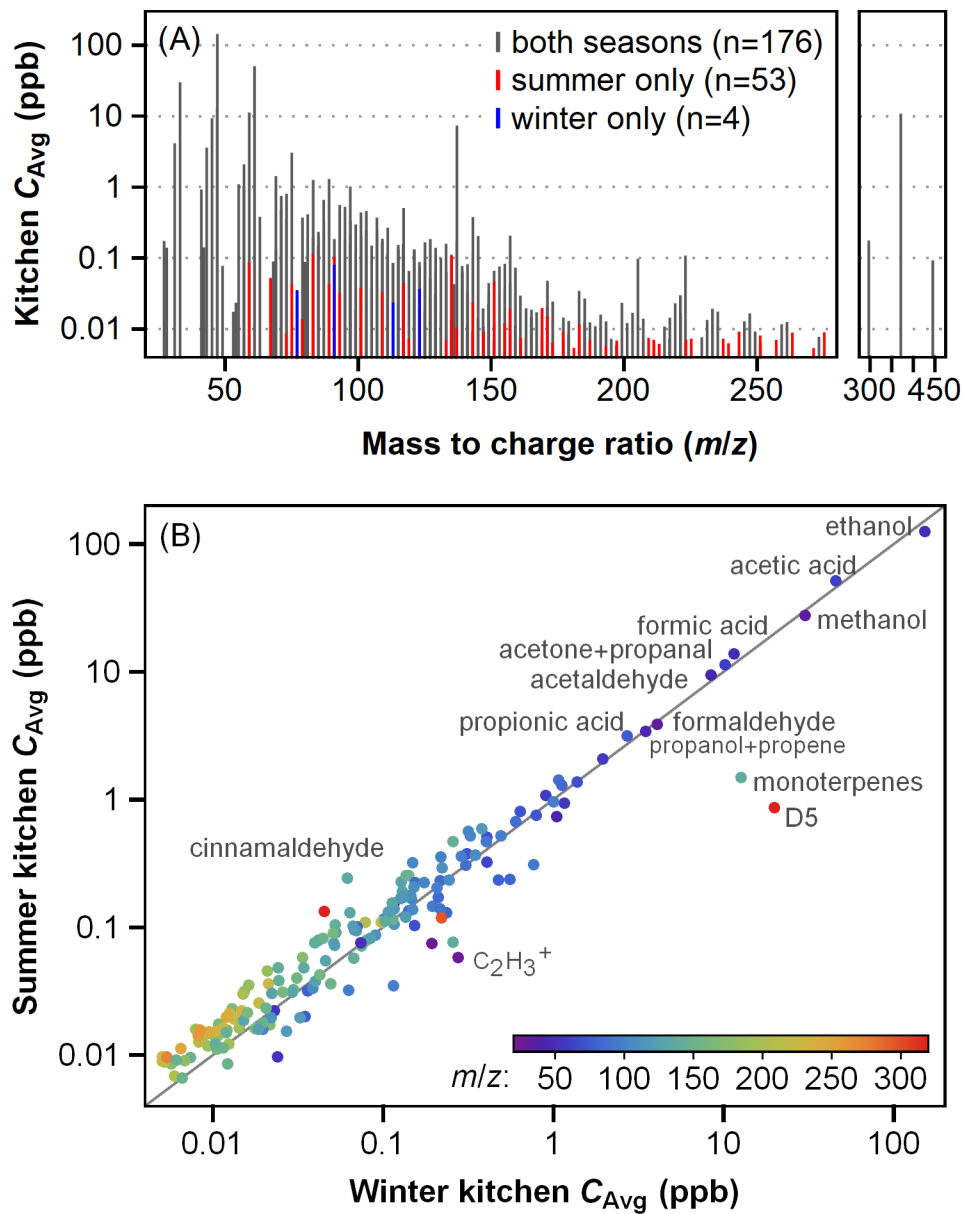


Figure 3

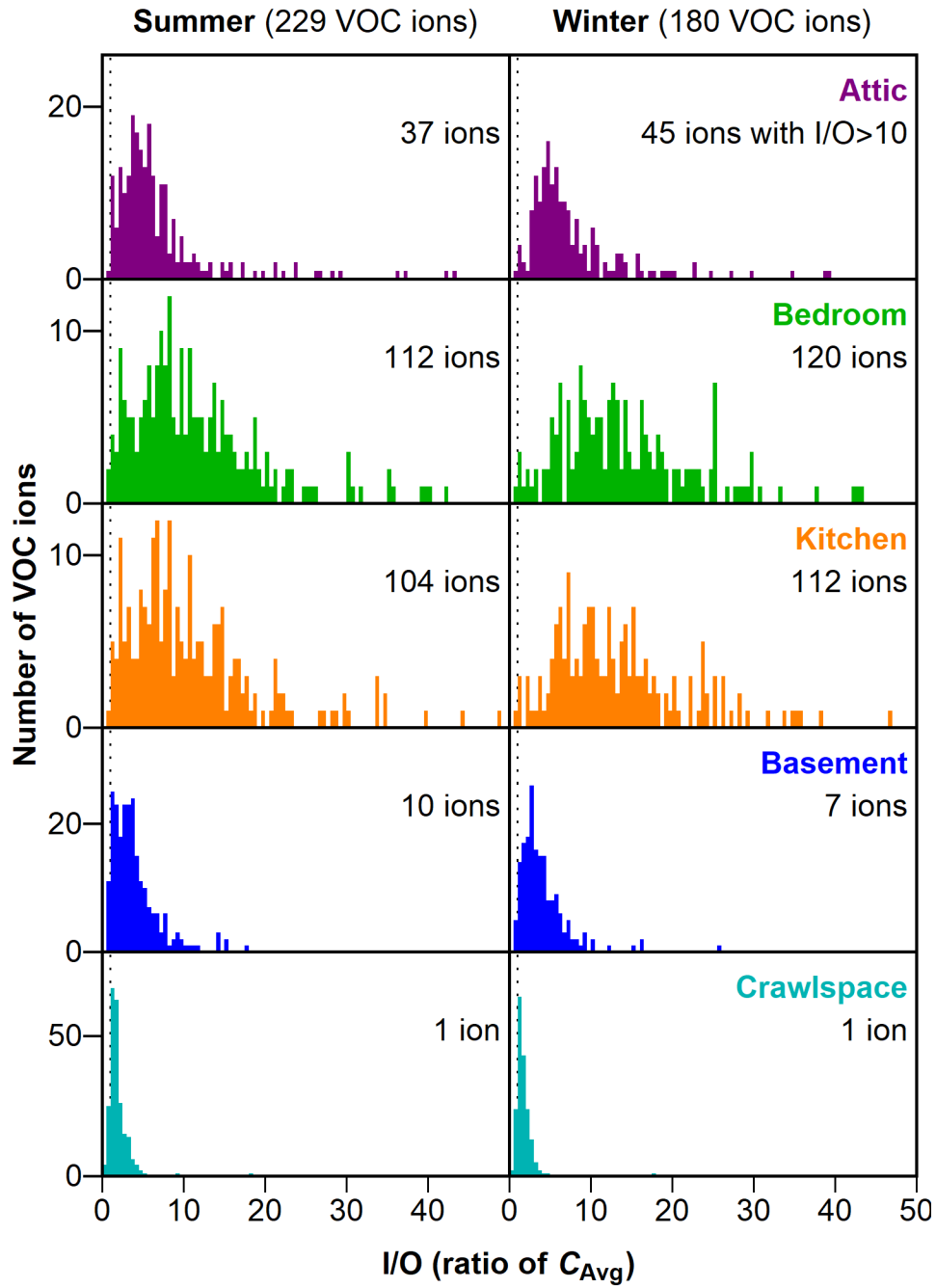


Figure 4

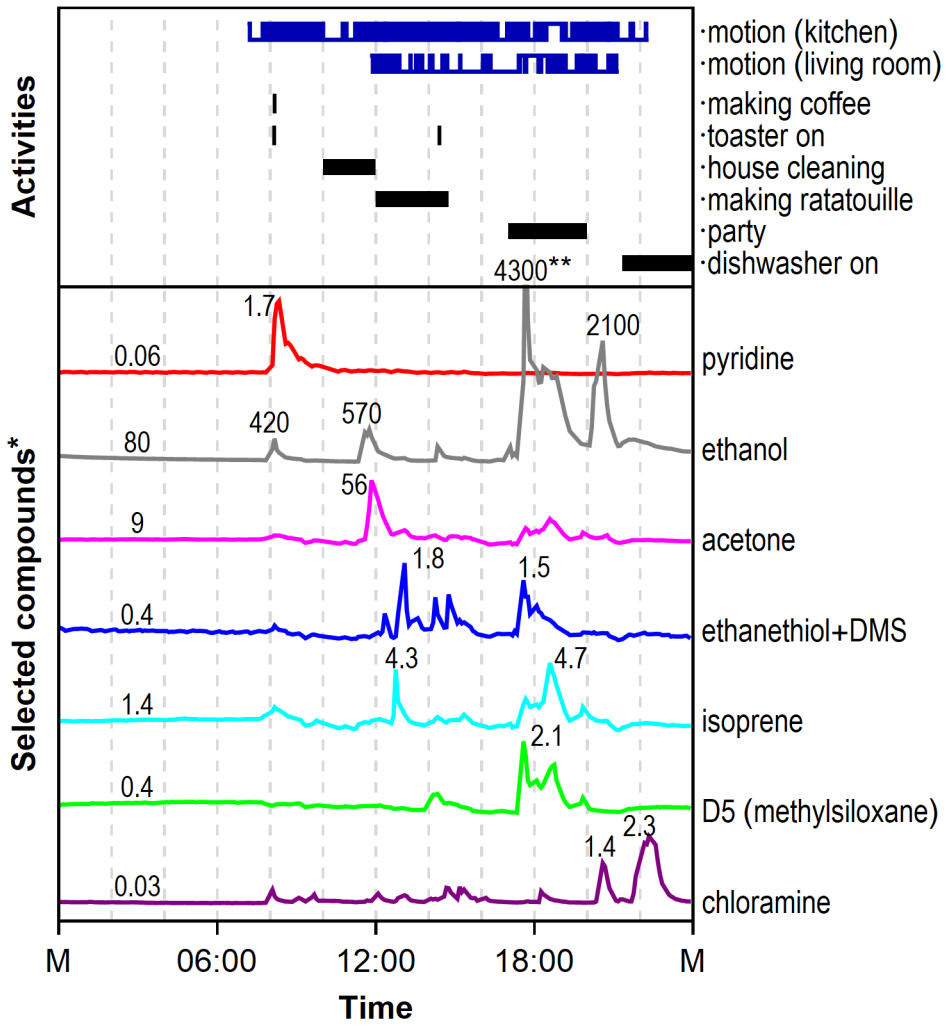


Figure 5

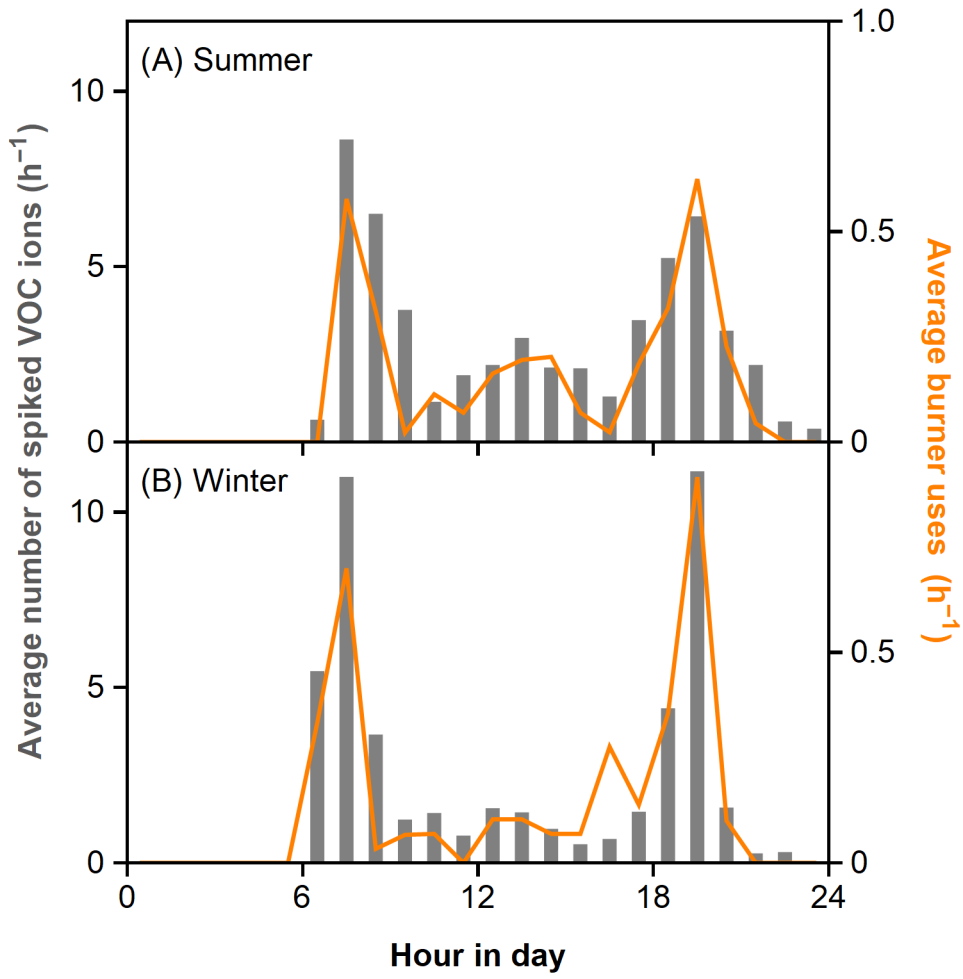


Figure 6

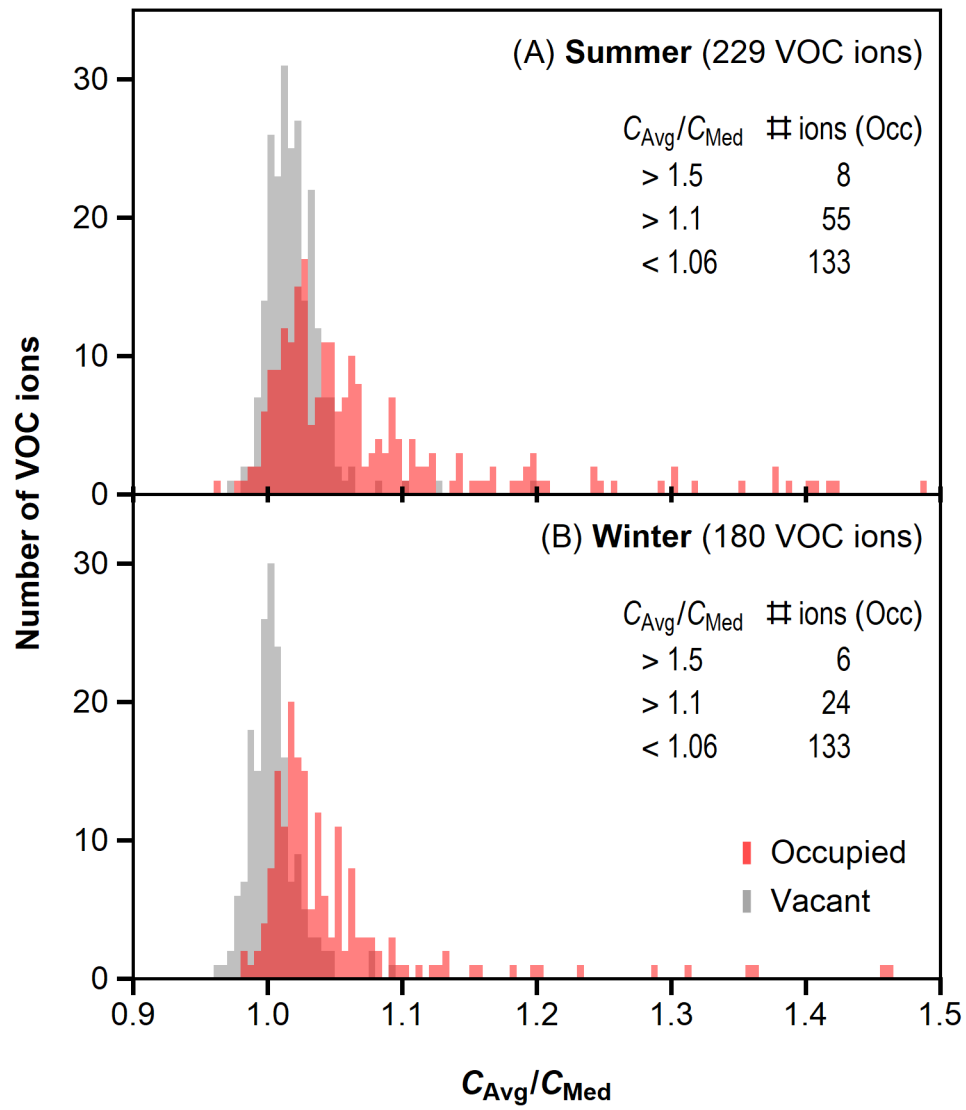


Figure 7

(A) Total indoor emission rate of 37.4 mg h^{-1} (summer) for 56 ions dominated by indoor continuous emission

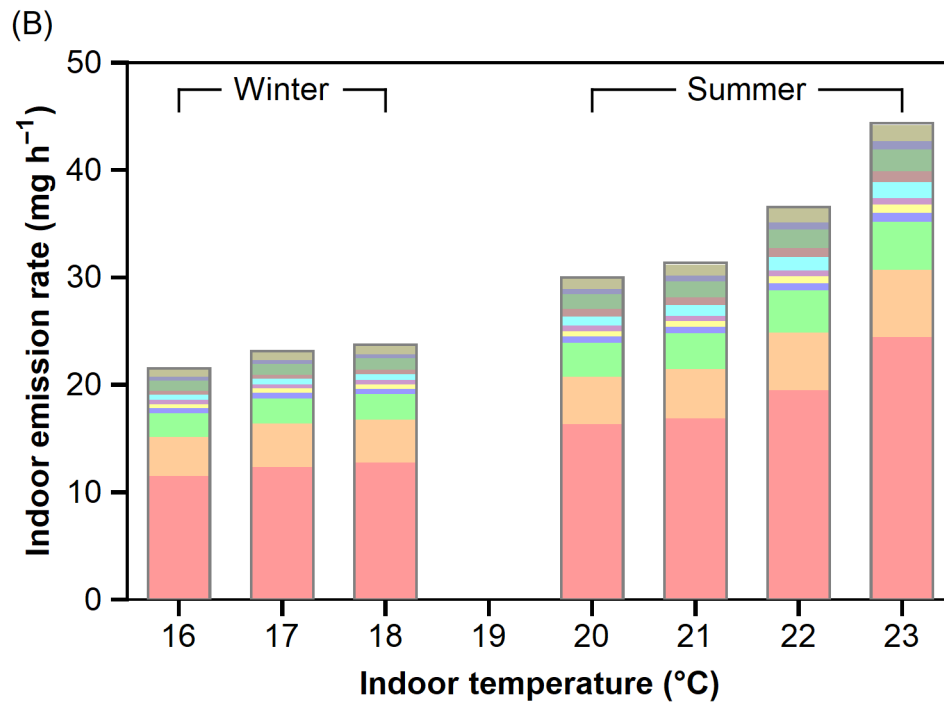
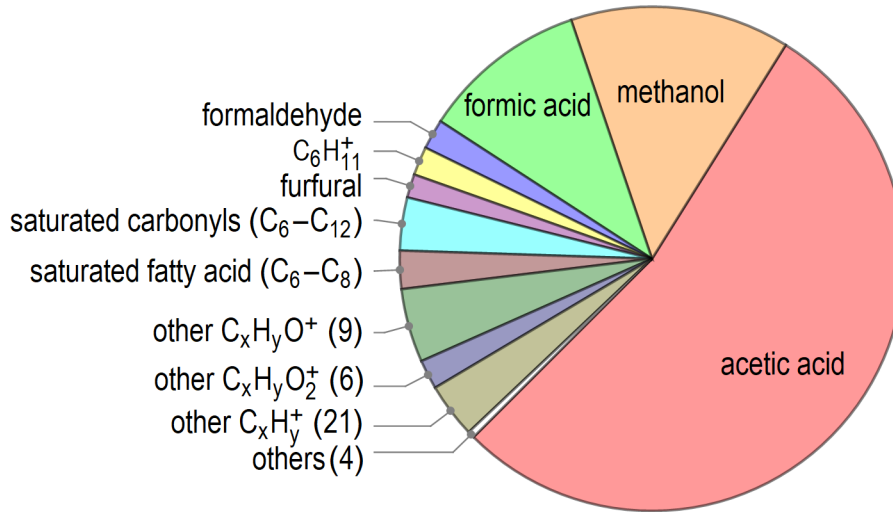


Figure 8

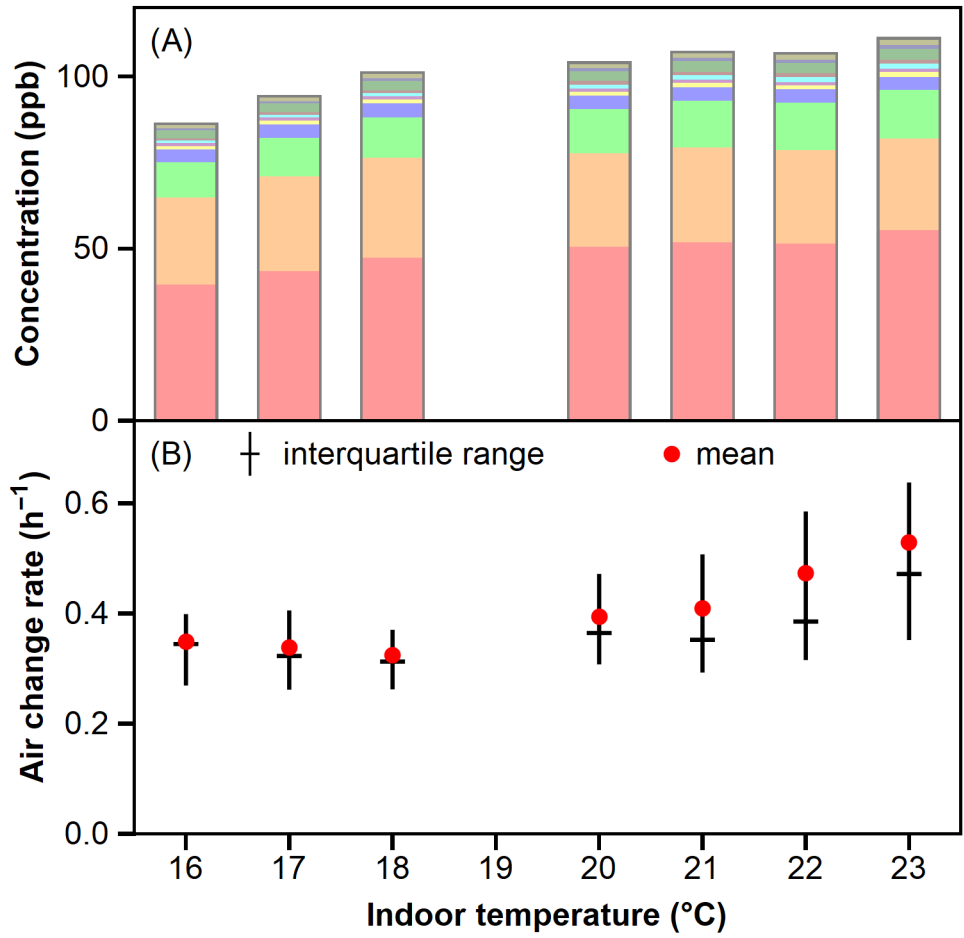
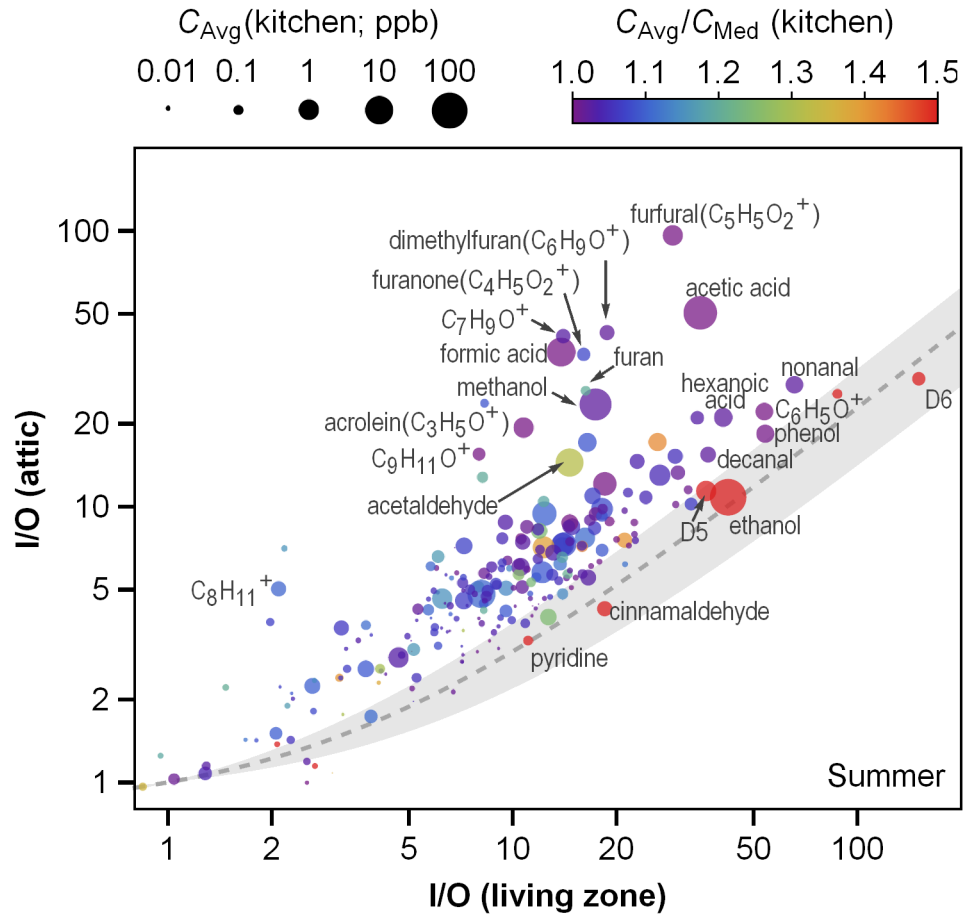


Figure 9



Supplementary Materials

for

Characterizing sources and emissions of volatile organic compounds in a northern California residence using space- and time-resolved measurements

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INDOOR AIR

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Table S1: Full list of organic ions detected in the current study and key measurement data in each season.

C ^a	U ^b	m/z	Ion formula	Compound assignment ^c	Summer			Winter		
					C _{avg} ^d (ppb)	I/O ^d	E ^e (mg h ⁻¹)	C _{avg} ^d (ppb)	I/O ^d	E ^e (mg h ⁻¹)
		27.024	C2H3+	alkyl fragment	0.058	15	0.009	0.276	14	0.10
		28.030	C2H4+	alkyl fragment	0.075	11	^f	0.194	14	^f
*		31.018	CH3O+	formaldehyde	3.88	19	0.72	4.07	18	0.53
*		33.033	CH5O+	methanol	27.6	18	5.3	30.1	24	4.1
		41.038	C3H5+	alkyl fragment	0.738	14	0.18	1.04	12	0.55
		42.034	C2H4N+	acetonitrile	0.155	1.3	0.010	0.116	1.4	0.010
		43.054	C3H7+	propanol fragment (-H2O) + propene	3.41	14	0.87	3.49	12	2.7
		45.034	C2H5O+	acetaldehyde	9.42	15	2.7	8.44	13	1.6
*		47.012	CH3O2+	formic acid	13.8	14	4.0	11.6	15	2.3
		47.049	C2H7O+	ethanol	126	44	40	152	63	31
		49.016	CH5S+	methanethiol	0.075	8.5	0.020	0.074	14	0.015
		53.038	C4H5+	alkyl fragment	0.010	6.2	0.003	0.024	10	0.005
		54.033	C3H4N+	acrylonitrile**	0.022	11	0.007	0.023	9.9	0.005
		56.056	C4H7+ ^g	alkyl fragment	0.942	4.7	0.27	1.17	7.1	0.25
*		57.034	C3H5O+	acrolein + propionic acid fragment	1.07	11	0.36	0.902	14	0.21
		57.069	C4H9+	butanol fragment (-H2O) + butene	2.08	14	0.72	1.95	12	0.48
*		59.011	C2H3O2+	glyoxal**	0.084	7.9	0.025			
		59.048	C3H7O+	C3 saturated carbonyl (propanal + acetone)	11.4	7.9	3.6	10.2	9.7	2.6
*		61.028	C2H5O2+	acetic acid	51.5	35	20	45.7	34	12
		63.027	C2H7S+	dimethyl sulfur + ethanethiol	0.324	3.0	0.12	0.408	20	0.11
		67.054	C5H7+	alkyl fragment	0.050	12	0.022			
		68.049	C4H6N+	pyrrole	0.101	99	0.042	0.070	35	0.017
		69.033	C4H5O+	furan	0.104	17	0.041	0.153	14	0.043
		69.069	C5H9+	isoprene	1.36	12	0.56	1.38	29	0.42
		71.048	C4H7O+	unsaturated carbonyl (e.g., methyl vinyl ketone)	0.508	7.2	0.21	0.409	10	0.12
		71.085	C5H11+	pentanol fragment (-H2O) + pentene	0.808	17	0.35	0.638	14	0.20
		72.994	C2HO3+		0.008	5.5	0.003			
		73.028	C3H5O2+	acrylic acid**	0.375	7.1	0.16	0.312	6.4	0.083
		73.064	C4H9O+	C4 saturated carbonyl (butanal + others)	0.752	6.3	0.29	0.796	5.1	0.20
*		75.005	C2H3O3+		0.041	15	0.022			
		75.043	C3H7O2+	propionic acid	3.13	12	1.4	2.71	12	0.86
*	*	77.003	C2H5OS+	mercaptoacetaldehyde**	0.020	13	0.009	0.035	26	0.013
		77.022	C2H5O3+	glycolic acid**	0.032	2.1	0.007	0.036	11	0.012

		77.039	C6H5+	aromatic fragment				0.034	5.7	0.010
		78.994	C2H4OCl+		0.013	5.9	0.006			
		79.052	C6H7+	benzene	0.235	3.1	0.084	0.477	3.6	0.12
		80.048	C5H6N+	pyridine	0.101	10	0.048	0.070	6.4	0.026
		80.990	C2H3ClF+		0.130	4.1	0.045	0.237	9.7	0.074
		81.034	C5H5O+	fragment of furanoid compound	0.237	22	0.11	0.558	81	0.20
		82.944	CHCl2+		0.111	16	0.058			
		83.012	C4H3O2+		0.012	4.3	0.005			
		83.049	C5H7O+	furan	0.173	17	0.076	0.211	17	0.075
*		83.085	C6H11+	cis-3-hexen-1-ol + others	1.30	27	0.69	1.12	28	0.41
		85.029	C4H5O2+	furanone	0.135	16	0.075	0.141	8.7	0.049
		85.064	C5H9O+	cyclopentanone + others	0.233	9.4	0.11	0.217	11	0.078
		85.100	C6H13+	hexanol fragment (-H2O) + hexene	0.224	9.6	0.12	0.154	8.4	0.057
		87.043	C4H7O2+	diacetyl + others	0.669	16	0.35	0.602	17	0.23
		87.079	C5H11O+	C5 saturated carbonyl (pentanal + others)	0.307	12	0.14	0.307	11	0.11
*		89.026	C3H5O3+		0.041	5.1	0.022			
		89.059	C4H9O2+	butyric acid	1.43	19	0.78	1.07	19	0.45
*		90.998	C2H3O4+		0.016	2.3	0.005			
		91.022	C2H7O2Si+	dimethoxysilane				0.078	26	0.029
		91.040	C3H7O3+		0.101	15	0.055			
		91.051	C7H7+	1,3,5-norcaratriene or aromatic fragment	0.139	13	0.084	0.218	16	0.088
		93.008	C3H6OCl+		0.031	5.7	0.016			
*		93.036	C6H5O+	aromatic fragment	0.468	49	0.29	0.405	36	0.19
		93.069	C7H9+	toluene	0.309	2.5	0.15	0.770	5.9	0.27
		94.998	C2H7S2+	dimethyl disulfide	0.032	15	0.018	0.063	27	0.027
*	*	95.017	C2H7O2S+	dimethyl sulfone**	0.146	16	0.090	0.195	52	0.088
*		95.048	C6H7O+	phenol	0.519	56	0.32	0.493	47	0.21
		96.960	C2H3Cl2+		0.168	6.0	0.077	0.146	7.1	0.051
		96.996	CH5O3S+	methanesulfonic acid	0.035	8.3	0.018	0.115	20	0.049
*		97.028	C5H5O2+	furfural	0.954	29	0.56	0.999	23	0.41
*		97.063	C6H9O+	dimethyl furan	0.203	19	0.12	0.207	16	0.084
*		97.100	C7H13+		0.360	15	0.22	0.289	15	0.12
*		99.007	C4H3O3+		0.016	1.0	<0.001	0.020	1.4	0.002
		99.043	C5H7O2+	furfuranol	0.116	6.2	0.065	0.101	6.2	0.036
		99.079	C6H11O+	cis-3-hexenal and others	0.353	17	0.22	0.218	14	0.093
		100.937	CCl2F+		0.037	1.3	0.005			
*		101.059	C5H9O2+	acetylpropionyl + others	0.518	10	0.35	0.326	12	0.14
*		101.093	C6H13O+	C6 saturated carbonyl (butanal + others)	0.224	11	0.13	0.175	12	0.070
		103.039	C4H7O3+	acetate anhydrate**	0.322	11	0.19	0.149	9.5	0.074
		103.074	C5H11O2+	valeric acid	0.566	27	0.34	0.318	16	0.22

1	*	*	105.034	C4H9OS+	methional**	0.033	12	0.027	0.039	14	0.019
2											
3											
4	*		105.069	C8H9+	styrene	0.138	11	0.086	0.150	11	0.068
5											
6	*		107.049	C7H7O+	benzaldehyde	0.366	14	0.24	0.349	15	0.16
7			107.085	C8H11+	C8 aromatics	0.236	2.0	0.090	0.245	2.2	0.073
8											
9			109.028	C6H5O2+		0.032	1.9	0.012			
10			109.065	C7H9O+	cresol	0.179	14	0.13	0.145	9.5	0.070
11	*		109.100	C8H13+		0.207	23	0.16	0.152	18	0.079
12			111.044	C6H7O2+	benzenediol	0.106	13	0.067	0.116	14	0.052
13											
14	*		111.080	C7H11O+		0.086	12	0.060	0.090	12	0.042
15	*		111.116	C8H15+	1-octen-3-ol fragment (-H2O) + others	0.294	13	0.21	0.222	20	0.11
16											
17			113.023	C5H5O3+		0.020	1.5	0.002	0.022	2.1	0.006
18			113.059	C6H9O2+		0.094	8.3	0.062	0.070	8.5	0.033
19			113.094	C7H13O+		0.096	9.2	0.064	0.068	9.8	0.032
20											
21			113.130	C8H17+	octanol fragment (-H2O) + others				0.023	17	0.012
22			115.037	C5H7O3+		0.015	2.3	0.006	0.027	4.8	0.011
23											
24			115.075	C6H11O2+		0.168	8.1	0.11	0.126	9.1	0.063
25	*		115.108	C7H15O+	C7 saturated carbonyl	0.139	11	0.094	0.116	12	0.055
26			116.906	CCl3+	CHCl3 (GC×GC)	0.172	1.0	0.004	0.132	1.1	0.003
27			117.055	C5H9O3+		0.043	8.2	0.029			
28											
29	*		117.091	C6H13O2+	hexanoic acid	0.594	40	0.48	0.382	26	0.23
30			119.033	C4H7O4+		0.007	2.2	0.003			
31			119.086	C9H11+		0.075	7.9	0.055	0.052	6.9	0.027
32			121.029	C7H5O2+		0.020	2.3	0.012	0.032	10	0.018
33											
34			121.065	C8H9O+	anisaldehyde + others	0.132	16	0.11	0.107	24	0.064
35			121.100	C9H13+		0.119	2.1	0.051	0.135	2.3	0.046
36	*		123.044	C7H7O2+	benzoic acid + others	0.103	13	0.10	0.067	13	0.041
37			123.080	C8H11O+					0.035	10	0.020
38	*		123.116	C9H15+		0.091	13	0.073	0.053	10	0.029
39											
40			125.024	C6H5O3+	furandicarbaldehyde	0.016	2.2	0.010	0.019	2.9	0.007
41			125.059	C7H9O2+		0.038	5.9	0.026	0.040	5.3	0.019
42	*		125.096	C8H13O+		0.082	16	0.065	0.085	22	0.050
43	*		125.131	C9H17+	hydrindane + others	0.191	30	0.17	0.130	24	0.074
44			127.038	C6H7O3+		0.031	3.1	0.024	0.022	5.2	0.010
45											
46			127.075	C7H11O2+		0.055	7.3	0.041	0.046	9.2	0.026
47	*		127.111	C8H15O+	oct-1-en-3-one + others	0.227	29	0.21	0.128	24	0.077
48											
49			129.058	C6H9O3+		0.031	3.2	0.020	0.029	4.0	0.014
50			129.089	C7H13O2+		0.073	5.1	0.051	0.052	6.5	0.029
51	*		129.126	C8H17O+	C8 saturated carbonyl + 1-octen-3-ol	0.154	33	0.13	0.113	22	0.064
52			131.070	C6H11O3+		0.019	8.8	0.016	0.015	9.5	0.010
53	*		131.106	C7H15O2+	heptanoic acid	0.130	23	0.13	0.064	15	0.045
54		*	133.021	C8H5O2+		0.007	3.4	0.005			

		133.065	C9H9O+	cinnamaldehyde	0.244	21	0.28	0.062	25	0.037
		133.098	C10H13+		0.080	11	0.077	0.042	7.9	0.024
		135.043	C8H7O2+		0.013	3.5	0.009			
		135.081	C9H11O+		0.112	7.7	0.090	0.103	6.1	0.059
		135.113	C10H15+		0.102	3.8	0.067			
		136.024	C7H6NS+	benzothiazole	0.048	9.0	0.042	0.034	10	0.024
	*	137.003	C7H5OS+		0.010	6.7	0.008			
		137.060	C8H9O2+	4-anisaldehyde + others	0.077	9.6	0.077	0.257	35	0.16
		137.133	C10H17+	monoterpenes	1.48	13	1.3	12.7	100	7.2
		139.039	C7H7O3+		0.048	3.0	0.071	0.024	6.2	0.017
		139.071	C8H11O2+		0.075	12	0.085	0.040	12	0.030
		139.110	C9H15O+		0.073	8.5	0.059	0.075	24	0.049
	*	139.143	C10H19+		0.057	12	0.050	0.067	13	0.047
		141.052	C7H9O3+		0.012	2.7	0.007	0.010	6.5	0.006
		141.091	C8H13O2+		0.038	8.6	0.034	0.024	9.3	0.016
	*	141.126	C9H17O+	nonenal + others	0.105	21	0.10	0.052	15	0.035
		143.032	C6H7O4+		0.009	1.7	0.005			
		143.070	C7H11O3+		0.023	4.6	0.019			
	*	143.107	C8H15O2+		0.115	14	0.11	0.114	16	0.076
	*	143.142	C9H19O+	C9 saturated carbonyl	0.468	66	0.49	0.258	57	0.17
		145.049	C6H9O4+	3-deoxyglucosone**	0.015	2.5	0.013	0.012	10	0.005
	*	145.123	C8H17O2+	octanoic acid	0.255	15	0.30	0.137	14	0.11
		146.977	C6H5Cl2+		0.018	5.2	0.014	0.020	5.2	0.012
		147.043	C9H7O2+		0.009	4.1	0.007	0.006	6.8	0.004
		147.079	C10H11O+		0.010	6.8	0.009	0.007	6.3	0.005
		147.114	C11H15+		0.009	4.9	0.007	0.012	5.7	0.008
	*	147.130	C8H19O2+		0.009	6.7	0.009			
		149.025	C8H5O3+		0.023	2.8	0.013	0.021	3.4	0.010
		149.097	C10H13O+		0.036	9.3	0.039	0.049	16	0.035
		149.128	C11H17+		0.032	6.3	0.028	0.030	6.7	0.018
		151.037	C8H7O3+		0.007	2.1	0.004	0.007	4.3	0.004
		151.073	C9H11O2+		0.011	6.7	0.009	0.012	5.7	0.008
		151.112	C10H15O+		0.082	14	0.066	0.045	7.1	0.036
		151.145	C11H19+		0.045	12	0.037			
		153.126	C10H17O+		0.071	7.0	0.064	0.075	5.6	0.047
		155.068	C8H11O3+		0.012	6.5	0.011			
	*	155.107	C9H15O2+		0.040	18	0.045	0.031	15	0.026
		155.140	C10H19O+	monoterpene alcohols	0.080	18	0.082	0.080	38	0.071
		157.087	C8H13O3+		0.019	8.2	0.018			
	*	157.121	C9H17O2+		0.043	11	0.047	0.043	15	0.033
	*	157.158	C10H21O+	C10 saturated carbonyl	0.254	35	0.30	0.142	80	0.11
		159.068	C7H11O4+		0.011	3.0	0.009	0.011	9.5	0.008

		159.138	C9H19O2+	nonanoic acid	0.090	8.2	0.12	0.051	12	0.043
		160.999	C7H4ClF2+	parachlorobenzotrifluoride	0.031	0.8	<0.001	0.026	0.9	<0.001
		161.093	C11H13O+		0.007	3.6	0.007			
		163.072	C10H11O2+		0.010	2.1	0.007	0.005	4.7	0.004
		163.131	C8H19O3+		0.022	8.7	0.022	0.016	8.5	0.012
		165.091	C10H13O2+		0.018	9.6	0.019	0.011	9.3	0.008
		165.163	C12H21+		0.023	8.3	0.021	0.013	7.8	0.010
		167.105	C10H15O2+		0.021	6.2	0.021	0.013	7.2	0.010
		169.084	C9H13O3+		0.007	5.1	0.007			
		169.120	C10H17O2+	pinonaldehyde + others	0.016	4.6	0.017	0.018	7.6	0.014
		169.153	C11H21O+		0.019	6.9	0.021			
		171.104	C9H15O3+		0.015	9.6	0.017			
	*	171.132	C13H15+		0.017	7.4	0.020	0.022	13	0.018
	*	171.172	C11H23O+	C11 saturated carbonyl	0.058	17	0.072	0.034	32	0.030
		173.082	C8H13O4+		0.006	3.9	0.006			
		173.154	C10H21O2+	decanoic acid	0.032	9.5	0.046	0.015	12	0.014
		177.054	C10H9O3+		0.009	1.5	0.006			
		177.125	C12H17O+		0.009	6.4	0.010	0.006	7.4	0.005
		177.160	C13H21+		0.016	11	0.018	0.012	13	0.011
		179.093	C7H15O5+		0.009	3.1	0.009	0.007	3.7	0.005
		179.178	C13H23+		0.014	6.7	0.015	0.011	8.5	0.009
		181.118	C11H17O2+		0.005	4.9	0.006			
		183.083	C13H11O+		0.046	9.1	0.069	0.021	7.2	0.021
		183.171	C12H23O+		0.011	5.2	0.013			
		185.136	C14H17+		0.014	7.9	0.017	0.010	8.0	0.009
	*	185.188	C12H25O+	C12 saturated carbonyl	0.035	14	0.047	0.016	16	0.017
		187.135	C10H19O3+		0.007	9.1	0.009			
	*	187.166	C11H23O2+	undecanoic acid	0.016	22	0.024	0.008	14	0.007
	*	189.157	C14H21+		0.012	12	0.015	0.009	17	0.009
		191.177	C14H23+		0.016	7.9	0.019	0.014	17	0.013
		193.154	C13H21O+		0.005	6.4	0.007			
	*	193.192	C14H25+		0.012	11	0.015	0.012	15	0.012
		195.171	C13H23O+		0.009	6.5	0.011	0.005	7.4	0.006
		197.136	C15H17+		0.006	5.9	0.008			
		197.216	C14H29+		0.007	6.0	0.008			
		199.170	C12H23O2+		0.030	5.0	0.047	0.015	7.1	0.017
	*	* 201.181	C15H21+		0.014	12	0.023	0.009	11	0.009
	*	203.179	C15H23+		0.018	21	0.025	0.015	25	0.014
		205.197	C15H25+	sesquiterpenes	0.109	34	0.15	0.079	25	0.073
		207.176	C14H23O+		0.007	6.9	0.009	0.006	11	0.006
	*	207.206	C15H27+		0.015	15	0.019	0.012	23	0.012
		209.218	C15H29+		0.007	7.7	0.010			

		211.144	C16H19+		0.007	5.8	0.010			
		211.232	C15H31+		0.006	5.9	0.009			
		213.162	C16H21+		0.006	6.1	0.008			
		213.218	C14H29O+	C14 saturated carbonyl	0.006	5.0	0.010			
		215.172	C16H23+		0.013	4.9	0.016	0.008	8.4	0.009
		217.109	C17H13+		0.009	2.2	0.019	0.005	5.9	0.006
	*	217.180	C16H25+		0.016	8.2	0.027	0.012	17	0.013
	*	219.210	C16H27+	C16 aromatics + others	0.026	22	0.036	0.019	28	0.020
	*	221.156	C14H21O2+	chromanol + others	0.036	30	0.058	0.021	18	0.027
	*	221.220	C16H29+		0.019	20	0.027	0.013	24	0.015
		223.070	C6H19O3Si3+	siloxane D3	0.110	8.1	0.13	0.098	19	0.098
		223.238	C16H31+		0.007	9.9	0.010			
		225.252	C16H33+		0.007	6.9	0.010			
		229.200	C17H25+		0.010	6.8	0.016	0.005	7.4	0.006
	*	231.211	C17H27+		0.015	21	0.024	0.010	20	0.012
	*	233.227	C17H29+	C17 aromatics + others	0.022	30	0.034	0.015	24	0.017
	* *	235.222	C15H27N2+	sparteine**	0.021	21	0.036	0.013	18	0.016
		237.253	C17H33+		0.007	11	0.012			
		239.269	C17H35+		0.006	6.8	0.010			
		243.215	C18H27+		0.009	8.5	0.015			
	*	245.226	C18H29+		0.015	17	0.025	0.010	18	0.012
	*	247.243	C18H31+	C18 aromatics + others	0.020	22	0.033	0.012	21	0.015
	*	249.255	C18H33+		0.011	14	0.019	0.007	12	0.008
		251.164	C15H23O3+		0.008	2.1	0.025			
		251.267	C18H35+		0.006	8.0	0.011			
		257.229	C19H29+		0.007	7.3	0.012			
	*	259.242	C19H31+		0.014	16	0.026	0.008	15	0.011
	*	261.258	C19H33+		0.016	14	0.028	0.008	15	0.011
		263.271	C19H35+		0.009	11	0.015			
		271.248	C20H31+		0.005	4.4	0.011			
		273.258	C20H33+		0.010	10	0.018	0.005	9.7	0.008
		275.273	C20H35+		0.009	10	0.017			
		297.080	C8H25O4Si4+	siloxane D4	0.118	4.7	0.16	0.221	210	0.31
		371.094	C10H31O5Si5+	siloxane D5	0.868	34	1.9	19.9	280	24
		445.090	C12H37O6Si6+	siloxane D6	0.133	130	0.35	0.045	67	0.12

^a An asterisk indicates an ion characterized by continuous emissions. The selection criteria include $(I/O)_{\text{kitchen}} > 10$, $(C_{\text{Avg}}/C_{\text{Med}})_{\text{kitchen}} < 1.06$, and $(I/O)_{\text{kitchen}} > 2 (I/O)_{\text{crawl space}}$

^b An asterisk indicates an ion with uncertain ion formula assignment.

^c A double asterisk indicates a tentative compound assignment.

^d Kitchen data are reported. The values of C_{Avg} are reported with maximum of 3 significant numbers and precision down to 0.001 ppb. The values of I/O are reported with maximum of 2 significant numbers. Entry is blank if the ion is not detected in a specific season.

1
2
3 ^e Indoor emission rate E is reported. The values of E are reported with maximum of 2 significant number and
4 precision down to 0.001 mg h^{-1} . Entry is blank if the ion is not detected in a specific season, unless indicated
5 otherwise.

6 ^f For C_2H_4^+ ion, emission mainly comes from the crawlspace (see the main text). Indoor emission rate is
7 deliberately blank because of this.

8
9 ^g The signal of C_4H_7^+ ion (m/z 55.0547) was overshadowed by the signal of water cluster ion H_7O_3^+ (m/z 55.039).
10 The isotopic ion $\text{C}_3(^{13}\text{C})\text{H}_7^+$ (m/z 56.0576) was used for the quantification instead.
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PROOF

List of Supplement Figures

- Fig. S1.** Concentration time series of (A) ethanol, (B) acetic acid, and (C) acetaldehyde in the living zone during the summer campaign. Kitchen and bedroom concentrations are plotted in green and orange, respectively. Vacant periods are indicated with grey background. The black and red dashed lines represent mean and median concentrations during the occupied period, respectively.
- Fig. S2.** Time series of (A) concentration and (B) emission rates of $C_5H_6N^+$ ion (pyridine). In panel (A), the green and orange solid lines represent measured kitchen and bedroom concentrations (30-min resolution), respectively. The dashed grey lines represent the predicted decay of the living-zone concentration with removal driven solely by air change (i.e., neglecting sorptive interactions of pyridine with indoor surfaces). In panel (B), effective emission rates into the living zone are plotted with 2-h resolution.
- Fig. S3.** Scatter plot of indoor emission rate versus indoor concentration of acetic acid. Data are presented with 2-h resolution, filtered to remove occupancy-associated emission spikes, and include both summer and winter occupied periods. Data points are colored by the corresponding indoor temperature. The inset figure shows a subset of the data with indoor temperatures of 22-23 °C. The grey line is a linear fit of emission rate versus concentration considering just the subset data. The figure shows higher emission rates at higher temperatures for fixed indoor concentrations. Also, emission rates were lower at higher concentrations if attention is restricted to a narrow temperature band which covers a wide concentration range (e.g., 22-23 °C).

Figure S1

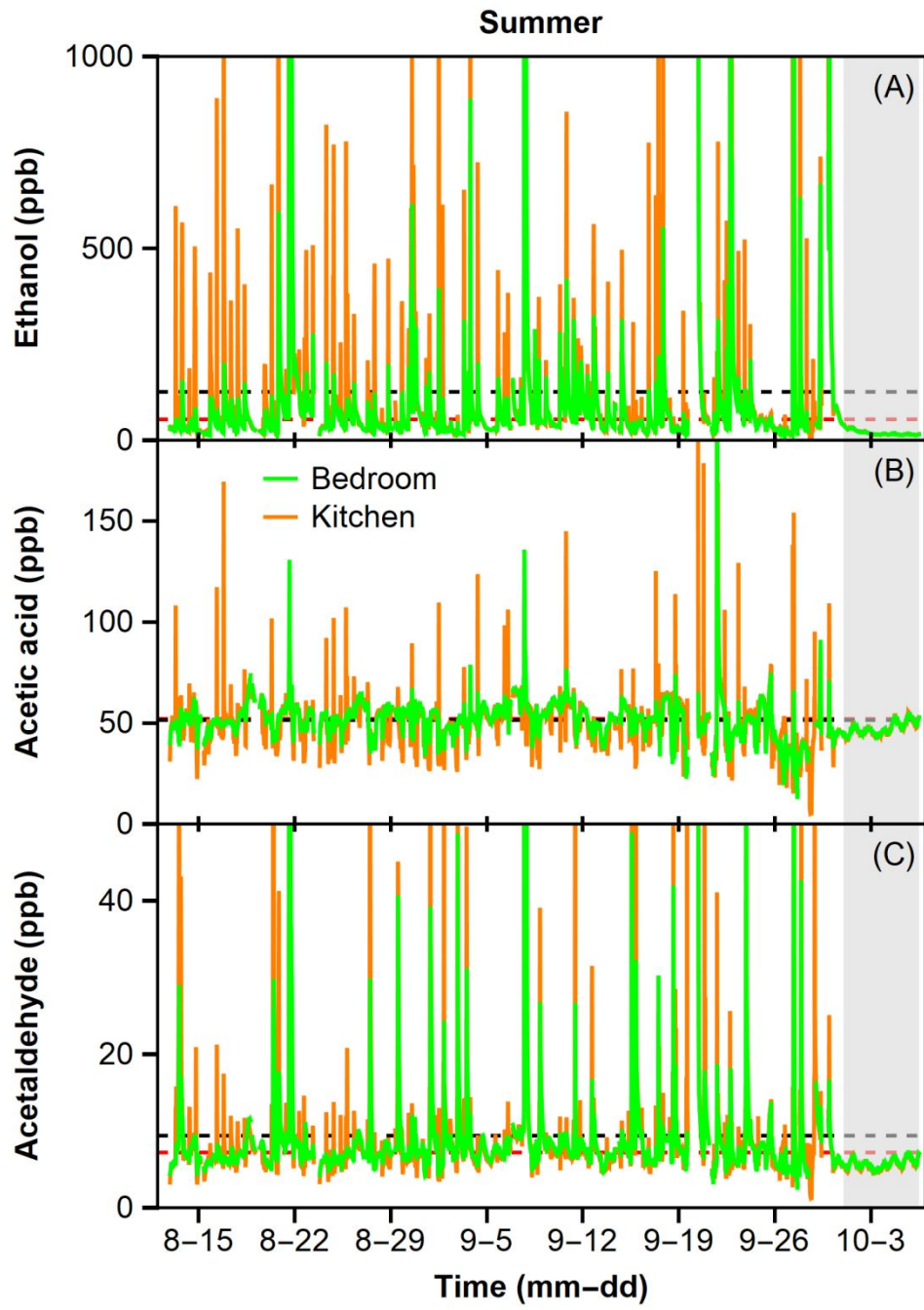


Figure S2

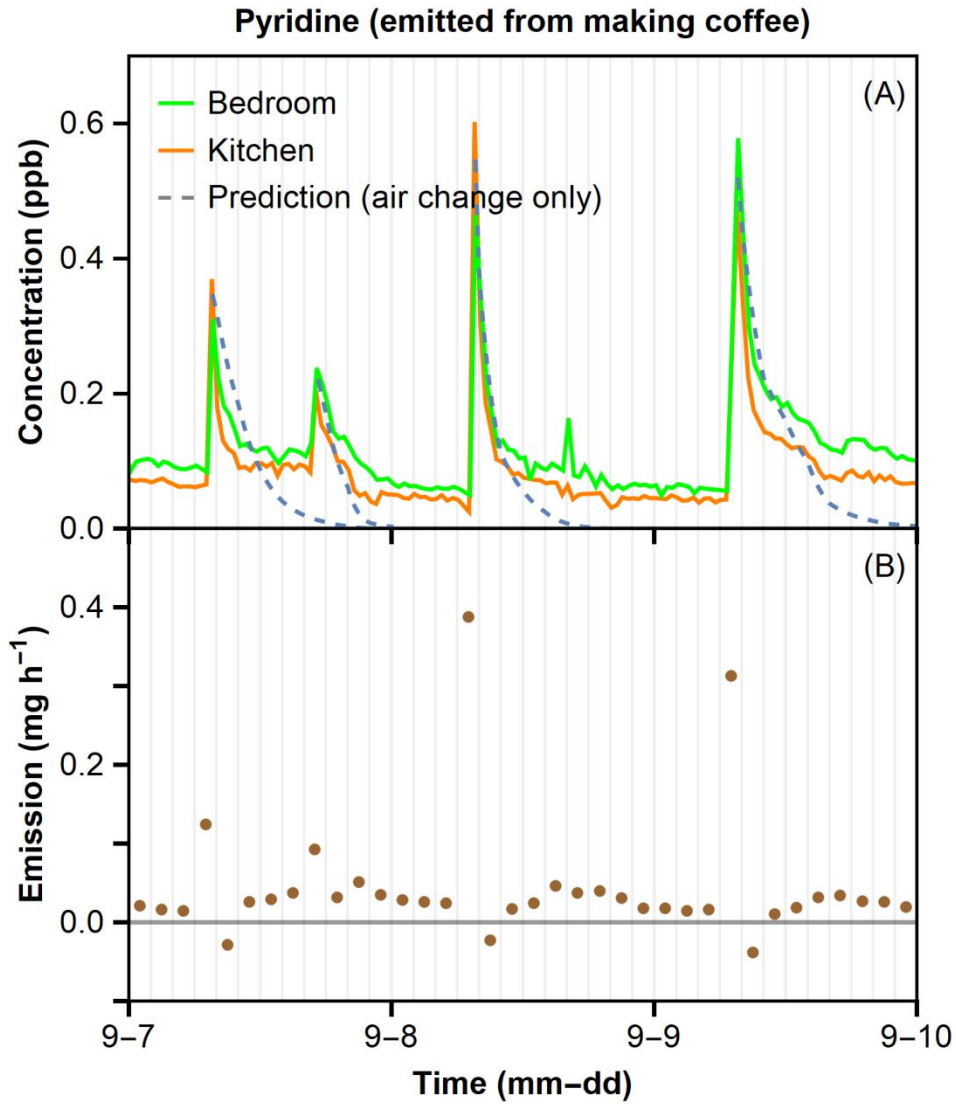


Figure S3

