Title
Observing ozone chemistry in an occupied residence

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Bringing Ozone Chemistry Home

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Abstract

Outdoor ozone transported indoors initiates oxidative chemistry, forming volatile organic products. The influence of ozone chemistry on indoor air composition has not been directly quantified in normally occupied residences. Here, we explore indoor ozone chemistry in a house in California with two adult inhabitants. We utilize space- and time-resolved measurements of ozone and volatile organic compounds (VOCs) acquired over an eight-week summer campaign. Despite overall low indoor ozone concentrations (mean value of 4.3 ppb) and a relatively low indoor ozone decay constant (1.3 h^{-1}), we identified multiple VOCs exhibiting clear contributions from ozone-initiated chemistry indoors. These chemicals include 6-methyl-5-hepten-2-one (6-MHO), 4-oxopentanal (4-OPA), nonenal, and C8-C12 saturated aldehydes, which are among the commonly reported products from laboratory studies of ozone interactions with indoor surfaces and with human skin lipids. These VOCs together accounted for ≥ 12% molecular yield with respect to house-wide consumed ozone, with the highest net product yields for nonanal (⩾ 3.5%), followed by 6-MHO (2.7%) and 4-OPA (2.6%). Although 6-MHO and 4-OPA are prominent ozonolysis products of skin lipids (specifically squalene), ozone reaction with the body envelopes of the two occupants in this house are insufficient to explain the observed yields. Relatedly, we observed that ozone-driven chemistry continued to produce 6-MHO and 4-OPA even after the occupants had been away from the house for 5 days. These observations provide evidence that skin lipids transferred to indoor surfaces made substantial contributions to ozone reactivity in the studied house.

Significance Statement

It has been suggested that indoor exposure to ozone oxidation products contributes materially to the apparent associations between outdoor ozone concentration and morbidity and mortality. Our current understanding of indoor ozone chemistry derives mainly from studies with test surfaces under controlled conditions. Little is known about the overall impact of ozone chemistry on air composition in dynamically changing indoor residential environments. The results presented here reflect the first quantitative characterization of overall indoor ozone chemistry in a normally occupied home. Findings reveal a strong influence of off-body skin lipids on indoor ozone chemistry. Being able to elucidate indoor air pollutants derived from ozone chemistry facilitates the investigation of causal links between outdoor ozone concentrations and adverse health effects.

Main Text

Introduction

Outdoor air containing ozone (O_3) penetrates into indoor environments, including residences, workplaces, and schools. Ozone undergoes fast reactions indoors; its characteristic lifetime is typically a few tens of minutes (1, 2). Reactions are thought mainly to occur on the large surface area in indoor environments (3), which ubiquitously contain reactive species (4, 5). Indoor ozone chemistry reduces indoor ozone concentrations and forms a spectrum of oxidation products, many of which are volatile (6). Emerging evidence suggests that indoor exposure to the mixture of ozone and its oxidation products contributes to epidemiologically determined associations between outdoor ozone concentrations and morbidity and mortality (3, 7).

Previous studies of indoor air chemistry mainly focused on investigating ozone reactions with individual indoor surfaces along with consequent release of secondary products. Studied surfaces include building materials and furnishings, such as carpet, wall covering, ceiling tile, wood board, and glass (8–11), as well as human skin, hair, and clothing (12–14). Observed volatile products include C1-C13 carbonyls, dicarbonyls, and hydroxycarbonyls among other oxygenated compounds. Product yields vary broadly, influenced by factors such as type and age of surface materials (11, 15) and soiling (8, 13, 16, 17). Skin oil lipids, characterized by a high proportion of squalene ($C_{30}H_{50}$), are particularly important indoor ozone reactants (14). They are present on skin, hair, and worn clothing of human occupants. They can also be transferred to other surfaces such as bedding, furniture, and flooring via desquamation and by direct physical contact (18). Major volatile products of squalene ozonolysis include 4-oxopentanal (4-OPA), 6-methyl-5-hepten-2-one (6-MHO), and geranylacetone.

Past research targeting specific indoor materials and surfaces demonstrates important features of indoor surface ozone chemistry; however, these studies are insufficient for evaluating

the contribution of ozone chemistry to the composition of dynamically changing indoor environments and hence to occupants' exposure (19). First, there can be myriad sources for indoor air pollutants in addition to ozone chemistry (20). Because ozone chemistry can produce a particular compound does not imply that it contributes meaningfully to the indoor concentration of that compound. Second, occupants might dynamically alter indoor ozone reactivity via their time-dependent presence indoors as well as their intended and unintended activities such as desquamation, transferring skin oils to surfaces by direct contact, cooking (e.g., surface soiling by the deposition of fatty acids in cooking oils and foods), and cleaning (e.g., with products that contain ozone-reactive terpenoids). Indoor studies in densely occupied spaces, including in two classrooms, a simulated office, and a simulated aircraft cabin (14, 21–23), have all highlighted the importance of the direct presence of human occupants for ozone chemistry. For residences, which are often less densely occupied, evidence is lacking regarding the overall features of indoor ozone chemistry and its impact on the indoor air composition to which occupants are exposed.

Here, we report an investigation of indoor ozone chemistry in a normally occupied residence based on temporally and spatially resolved observations of volatile organic compounds (VOCs) and ozone. Data were acquired in a single-family house in Oakland, California, from an extensive eight-week monitoring campaign conducted during summer 2016 (24, 25). This paper builds on our earlier analysis of the same data set regarding ventilation and airflow patterns in the house (25), as well as concentrations and source characteristics of indoor VOCs (24). In this paper, we examine the spatial and temporal distribution of ozone concentration, estimate the chemical loss rate coefficient of ozone in the living space, characterize the oxidation products of skin oil lipids, and undertake a non-targeted analysis to identify VOC species significantly derived from ozone-initiated chemistry.

Results and Discussion

Ozone in the house. Figure 1 (top) presents the diel variation of ozone concentration measured at different locations in the house during the occupied period under the space-resolved measurement scheme (cf. Materials and Methods). Mean ozone mixing ratios during the same periods are reported in Table 1. The outdoor ozone level exhibited modest diel variation, with the hourly median peaking at 28 ppb in the afternoon and declining to 20 ppb in the early morning. The ozone level in different compartments of the house can be understood in the context of the airflow patterns, i.e., with air generally flowing upwards from the crawlspace to the living space and then to the attic; downwards flows were rare (25). The crawlspace air, coming directly from outdoors through designed vents, exhibited consistently low ozone levels (a mean value of 3.4 ppb), indicating substantial ozone loss in the crawlspace. The loss may be associated with ozone titration by NO emitted from pilot lights of one or both of the natural-gas furnace and water heater installed in the crawlspace; elevated NO was observed in the crawlspace during wintertime monitoring in this house (26). The airflow path into the living space showed a strong diel variation, with 90% of air infiltrating from the ozone-deficient crawlspace at night whereas 80% directly entered from outdoors in the afternoon through opened windows (Fig. 1 bottom). Correspondingly, the median indoor-to-outdoor (I/O) ratio of ozone varied from 0.12 at night to ~ 0.27 in the afternoon (Fig. 1 middle). As a point of comparison, previously reported I/O ratios for ozone are typically in the range 0.2 – 0.7 (6). In the unoccupied (and unfinished) attic, where airflow originated both from the living space and from outdoors, the ozone level was similar to that in the living space, whereas in the small basement room, with a constantly open window, ozone exhibited strong diel variation that was closest to outdoor concentrations in the mid-afternoon.

The following analysis mainly focuses on the living space where human exposure occurs. The mean ozone level in the living space (indoor ozone) was only 4.3 ppb, at the lower end of reported values for residences in California (27). Assuming a well-mixed living space, the indoor ozone concentration $[O_3]_{in}$ is described well by the following equation

$$\frac{d[O_3]_{in}}{dt} = (f_{crawl}[O_3]_{crawl} + f_{out}[O_3]_{out})ACR - (ACR + k_{o_3})[O_3]_{in}, \quad (1)$$

where $[O_3]_{crawl}$ and $[O_3]_{out}$ are the ozone concentrations (ppb) measured in the crawlspace and outdoors respectively; f_{crawl} and f_{out} are the fraction of airflow into the living space from the crawlspace and outdoors, respectively; ACR is the air change rate of the living space (h^{-1}), and k_{O_3} is the first-order chemical loss rate coefficient of ozone in the living space (h^{-1}). In Eq. 1, ozone loss across the building envelope through intended and unintended openings is neglected (28). Rearranging Eq. 1, we can estimate the overall chemical loss rates of ozone L_{O_3} (ppb/h) as follows:

$$L_{o_3} = k_{o_3}[O_3]_{in} = (f_{crawl}[O_3]_{crawl} + f_{out}[O_3]_{out} - [O_3]_{in})ACR - \frac{d[O_3]_{in}}{dt}. \quad (2)$$

For use of Eq. 2, ACR, f_{crawl}, and f_{out} were calculated with 2-h resolution, utilizing tracer-gas measurements to determine time-resolved air change rate (25).

The indoor ozone chemical loss rate, L_{O_3}, with 2-h resolution, was obtained for all space-resolved measurement periods. Figure 2 shows the scatter plot of L_{O_3} versus the ozone concentration $[O_3]_{in}$ in the living space. Given the low ozone level in the crawlspace, data are only shown for $f_{out} > 0.6$ to exclude low-signal values with correspondingly high uncertainty, and thus emphasizing daytime data. In Fig. 2, the slope from any data point to zero would correspond to its k_{O_3} value ($k_{O_3} = L_{O_3} / [O_3]_{in}$). As shown in Fig. 2, k_{O_3} values of most data points lie within lines corresponding to the range 0.8-2.0 h^{-1}, and the overall best-fit k_{O_3} value is

125 1.3 h^{-1}. These values are at the lower end of reported ozone decay rate coefficients in residences.
126 For example, measured k_{O_3} values varied from 1 h^{-1} to 8 h^{-1} in 43 homes in South California with
127 mean (± SD) of 2.8 (± 1.3) h^{-1} (2), and varied from 1.3 h^{-1} to 6.0 h^{-1} in 14 residences in China (1).
128 Note that our results were obtained under normal occupancy without manipulating indoor ozone,
129 whereas the cited studies derived k_{O_3} by experimentally elevating ozone and then monitoring its
130 decay under house-closed condition in the absence of occupants. The sustained long-term
131 average ozone loss rate (as measured in our work) might be lower than the short-term loss rate
132 associated with a sudden ozone enhancement (as reported in prior literature).

133 **Ozonolysis products from squalene.** Next, we explore the VOC data for products
134 arising from indoor ozonolysis. VOC signals were measured using a proton-transfer-reaction
135 time-of-flight mass spectrometer (PTR-ToF-MS; see Materials and Methods). Our analysis
136 starts by focusing on the unique and most abundant volatile products of squalene ozonolysis: 6-
137 MHO ($C_8H_{14}O$) and 4-OPA ($C_5H_8O_2$). In PTR-MS analysis, 6-MHO is detected as $C_8H_{15}O^+$ and
138 $C_8H_{13}^+$ ions and 4-OPA appears as the $C_5H_9O_2^+$ ion (22). Measured signals of these ions might
139 also have contribution from other isomeric compounds. Below we show that the temporal
140 pattern of indoor $C_8H_{15}O^+$ and $C_5H_9O_2^+$ signals is consistent with the dominant contribution
141 originating from 6-MHO and 4-OPA.

142 Figure 3 shows a one-week time series of $C_8H_{15}O^+$ and $C_5H_9O_2^+$ ions, as well as time
143 series of factors that possibly influence indoor 6-MHO and 4-OPA, including occupancy, air
144 change rates, indoor temperature, and indoor ozone concentration. Signals of both $C_8H_{15}O^+$ and
145 $C_5H_9O_2^+$ ions in the kitchen and bedroom were more than an order of magnitude higher than
146 outdoors, indicating strong indoor sources. A key feature of the time series is that higher indoor
147 signals were typically observed during daytime when the air change rates and indoor ozone
148 concentrations were higher (e.g., September 20-24). Higher air change rate alone is normally

149 expected to reduce indoor concentration of species with a dominant indoor source. The higher
150 ion signals of $C_8H_{15}O^+$ and $C_5H_9O_2^+$ observed in these cases is consistent with theoretical
151 predictions that 6-MHO and 4-OPA production from squalene ozonolysis can outweigh removal
152 by ventilation (29). In particular, when the occupants hosted a party on the evening of 22
153 September, with 17 persons present in the house (and, therefore, substantially more squalene
154 available for ozonolysis), elevated $C_8H_{15}O^+$ and $C_5H_9O_2^+$ signals were observed despite the
155 higher ventilation rate during that event. Additionally, signals of the two ions exhibited sporadic
156 and brief spikes, likely associated with sources other than squalene ozonolysis or other
157 compounds (SI Appendix). However, these spikes only represent minor contributions to overall
158 ion signals.

159 Further analysis is based on net indoor source strengths (S) of VOC signals instead of
160 their concentrations. Utilizing a mass-balance equation, indoor source strengths of VOC signals
161 (ppb/h) have been determined with 2-h resolution from simultaneously measured air change rates
162 and indoor and outdoor concentrations (24). If the indoor source strength (S_i) of a VOC i is
163 contributed by production (P_i) from ozone chemistry, in addition to direct emission, one can
164 represent the total production rate as $S_i = S_{i,0} + P_i = S_{i,0} + k_i\,[O_3]_{in}$, where $S_{i,0}$ is the ozone-
165 independent emission rate of i (ppb/h); and k_i is an effective first-order production rate
166 coefficient of i from ozone reaction (h^{-1}). In the case that squalene ozonolysis is the dominant
167 reaction to produce i, k_i would be proportional to the amount of squalene indoors available for
168 reaction. Note that this equation is a simplified representation; the determined S_i is a net value,
169 incorporating not only indoor emission and chemical production, but also indoor wall interaction
170 and possible indoor loss from chemical reaction.

171 Figure 4A shows the dependence of source strength of the $C_8H_{15}O^+$ ion on indoor ozone
172 concentration $[O_3]_{in}$ with data points colored by occupancy. Figure 4A includes all available

data subject to the constraint that indoor temperature is restricted to the range 20.5-23.5 °C to minimize possible confounding effects of temperature (Fig. S1). As shown in Fig. 4A, $C_8H_{15}O^+$ source strength exhibits close correlation with indoor ozone. The R^2 of a linear fit of the data set after excluding two outliers (source strength greater than upper quartile plus 3× interquartile range) is 0.66. The fitted slope, corresponding to the production rate coefficient of $C_8H_{15}O^+$ from first-order ozone reaction (k), is 0.018 h^{-1}. The fitted intercept, corresponding to ozone-independent baseline emission rate (S_0), is 0.0072 ppb/h. A striking feature in Figure 4A is that the baseline emission S_0 (intercept) was small compared with the range of ozone-dependent production $k[O_3]_{in}$ (e.g., an increase by 0.18 ppb/h for 10 ppb of indoor ozone). This feature quantitatively demonstrates that 6-MHO production from ozone chemistry was the dominant source of measured $C_8H_{15}O^+$ signals. A similarly strong dependence of source strength on ozone was also found for $C_8H_{13}^+$ (the other product ion of 6-MHO) and $C_5H_9O_2^+$ (4-OPA), as presented in Figure S2.

Figure 4A also explores the role of occupancy. Since only two adults lived in the house, two or fewer persons were typically present in the living space, with some exceptions due to visits of guests (particularly during the party). Data for the presence of more than 4 persons are labeled in Fig. 4A. Although there were only four such points, they each lie above the general trend line. Such occupancy dependence is consistent with expectations for squalene ozonolysis: more people present in the house would mean more squalene available for ozone reaction, leading to a larger k value. The role of occupancy is also evident in the spatial distribution of ozone oxidation products associated with squalene. Table 1 shows that ions associated with 6-MHO and 4-OPA were much higher in the routinely occupied spaces (kitchen and bedroom) than in rarely occupied auxiliary spaces (crawlspace and attic). Given the regular movement of air from the kitchen and bedroom to attic, it is reasonable that the concentrations in the attic were

higher than those in the crawlspace. A comparison of basement and crawlspace levels is also informative. The basement exhibited the highest level of ozone (Fig. 1) and also was a site for a clothes washer and soiled laundry; the crawlspace was never occupied and did not contain clothing or other objects associated with occupant contact. The $C_8H_{15}O^+$ signal was much higher in the basement than in the crawlspace.

Figure 4B explores the role of occupancy for cases with a low occupancy level by analyzing a subset of data from Figure 4A with indoor ozone concentration restricted to the range 2-4 ppb. This ozone range was chosen because it covered most data points during periods with zero occupancy. Figure 4B plots the source strength of $C_8H_{15}O^+$ signals as a function of occupancy (left frame for $0 <$ occupancy ≤ 2 persons) and then the elapsed time since the house was last occupied (right frame for occupancy = 0). From the left frame, one cannot clearly discern how $C_8H_{15}O^+$ source strength changed with occupancy level given the variability of the data. For periods with between one and two occupants, the source strength averaged 0.056 ppb/h with a standard deviation of 0.014 ppb/h. However, when the house was unoccupied (right frame), $C_8H_{15}O^+$ source strength slowly decreased with the duration of vacancy. The source strength was about 0.045 ± 0.016 ppb/h when the house was unoccupied for less than 1 h and diminished by about half, to 0.023 ± 0.003 ppb/h, when the unoccupied period of time increased to ~130 h. Given that the reaction between ozone and 6-MHO is fast (second-order rate coefficient of 3.9×10^{-16} cm^3 mol^{-1} s^{-1} (30)), along with the small intercept in Figure 4a (baseline emission level of 0.007 ppb/h), it is unlikely that surface reservoirs were a substantial source of 6-MHO during the unoccupied period. Instead, the more probable explanation is that ozone reacted with squalene in skin flakes and skin oils that had accumulated on exposed surfaces in the home. Assuming that this interpretation is correct, we can further infer that during normal occupancy (Fig. 4B Left) the contribution of off-body skin oil/flakes to $C_8H_{15}O^+$ source strength

(~ 0.045 ppb/h, estimated as the level during initial unoccupied period) was substantially larger than the contribution from the body envelopes of the occupants (~ 0.011 ppb/h, estimated as the difference of 0.056 ppb/h and 0.045 ppb/h).

This evidence contains a clue to help reconcile the apparent contradiction between the elevation of $C_8H_{15}O^+$ source strength in the presence of > 4 persons (Fig. 4A) and the absence of any source-strength dependence on occupancy level under the normally low occupancy (Fig. 4B Left). That is, the off-body squalene contributes substantially to the total squalene-associated ozone reactivity when the house is normally occupied by 2 (or fewer) occupants, such that the influence of occupancy changes is attenuated. With this interpretation, the contribution of on-body squalene became substantial only in the rare presence (during this monitoring campaign) of multiple guests.

The large contribution of off-body skin oils is also consistent with high effective yields of 6-MHO and 4-OPA in this study. The effective yields of 6-MHO and 4-OPA (Table 1) were estimated by taking the ratio of (a) the total production rate coefficient $\sum k_i$ of corresponding identified VOC signals (slope in Fig. 4A and Fig. S2) to the chemical loss-rate coefficient of ozone, k_{O_3} (Fig. 2), i.e., $y_i = \sum k_i / k_{O_3}$. By definition, the obtained effective yields are relative to the total ozone loss in the house on a molecular basis and provide overall characterization of indoor ozone chemistry without differentiating among organic/inorganic precursors, primary/secondary reactions, or heterogeneous/gas-phase reactions. That said, we expect most surfaces to be covered with thin films that result from the accumulation over time of semivolatile organic compounds and airborne particles (4, 31, 32). The house where the sampling occurred was built in the 1930s and there had been no recent renovation or refurnishing of note. As has been demonstrated for freshly cleaned windows (33) and vertically positioned glass capillary tubes (34), organic surface films with thickness on the order of 10 to 20 nm accumulate over

245 months in typical indoor environments. In the studied house of volume 350 m^3 (floor area ~ 140
246 m^2) normally occupied by two adults, the combined effective yield of 6-MHO and 4-OPA was
247 5.2% per consumed ozone, on a molecule-by-molecule basis. Remarkably, this combined yield
248 is as high as that reported for a simulated aircraft cabin of 28.4 m^3 in the presence of 16 subjects
249 (22). The simulated aircraft was only occupied during the experiments and was unlikely to have
250 been widely soiled with skin flakes and skin oils to the extent that an occupied home would be.
251 Although other factors might also come into play, substantial soiling by skin flakes and skin oil
252 could help reconcile the observed high yield of squalene oxidation products despite the low
253 occupant density in this study.
254 A contribution to ozone reactivity from off-body skin flakes/oil has been anticipated (18,
255 35) and is supported by recent studies (4, 32). The magnitude of this contribution compared to
256 that of on-body squalene revealed herein is potentially surprising. However, upon closer
257 examination the result seems reasonable. Two humans in 350 m^3 of living space are estimated to
258 remove ozone with a first-order rate constants of ~ 0.2 h^{-1} (18), which accounted for about one-
259 sixth the central tendency for k_{O_3} in Figure 2 (1.3 h^{-1}). While we do not know the contribution to
260 k_{O_3} of skin flakes and skin oils accumulated on "off-body" surfaces, circumstantial evidence
261 indicates that it is significant. Humans shed their entire outer layer of skin every 2–4 weeks (36).
262 In dust samples collected from 500 children's bedrooms in Odense, Denmark, squalene was the
263 third most abundant identified organic, with a median mass fraction of 32 μg/g (35). Squalene is
264 semivolatile, with a vapor pressure of 3.7×10^{-7} Pa at 25 °C (37), and so sorption to indoor
265 surfaces via gas-phase transport may also occur. Furthermore, the low level of indoor ozone at
266 the residence that we studied might contribute to the accumulation of off-body squalene since the
267 persistence time scale of squalene should be longer with slower ozonolysis. As a related point,
268 Deming and Ziemann recently reported an observation of ubiquitous C=C bonds in surface films

on various indoor surfaces in a classroom and proposed that human skin lipids could be a major source (4). Based on decrease of 6-MHO source strength during the vacant period, we roughly estimated the lifetime of off-body squalene was ~400 h and the total amount of off-body squalene present was ~0.36 mmol (equal to 150 mg) (SI Appendix). The associated surface C=C concentration would be ~ 2 μmol/m^2, largely consistent with the observations of Deming and Ziemann (4).

Previous indoor studies in simulated microenvironments as well as a classroom have highlighted the importance of ozone reactions with on-body squalene (14, 21, 22). The current finding identifies a substantial contribution of off-body skin lipids to ozone chemistry in a normally occupied residence. The new information about factors that can materially influence exposure to ozone and its byproducts merits further investigation. Contributions of off-body skin oils might also influence densely occupied environments, in addition to residences. For example, Tang et al. estimated occupant and non-occupant VOC source strengths in a university classroom in California (38). Their results indicated a non-occupant source strength of about 25% of the occupant source for 6-MHO, and about 80% for 4-OPA. It is plausible that these contributions resulted from ozonolysis of off-body squalene that originated from skin oils and skin flakes of classroom occupants. Additionally, our results call for caution in extrapolating simulated scenarios of ozone chemistry in test houses or chambers. That is, because such facilities are not routinely occupied, they lack an important element of real-world settings – soiling of indoor surfaces by the skin oil and skin flakes of occupants.

Non-targeted analysis of ozonolysis products. To explore whether other indoor VOCs might be substantially associated with ozonolysis, we developed and applied a systematic screening approach. As a screening index, we computed a dimensionless source strength ratio, defined as the increase in source strength for a fixed increment (10 ppb) of ozone concentration

($\Delta S_{10\ ppb\ O_3}$) divided by the baseline source strength (S_0). A higher value of $\Delta S_{10\ ppb\ O_3} / S_0$ indicates a larger contribution of ozone chemistry to the overall VOC signal. As illustrated in Fig. 4A, this index can be obtained from the linear fit of indoor source strength of a VOC signal versus indoor ozone over a restricted indoor temperature range (20.5-23.5 °C) and after removing extreme outliers, where S_0 corresponds to the fitted intercept and $\Delta S_{10\ ppb\ O_3}$ is extracted from the fitted slope.

A confounding factor in the evaluation of this index is ventilation. Due to effects of indoor surface reservoirs, an increase of ventilation rate was associated with a less-than-anticipated decrease of indoor VOC signals (39, 40), and, hence, an apparent increase of net source strength (Fig. S3). Considering that indoor ozone levels tended to be higher with higher ventilation rates (Fig. 3), this effect can create a correlation between indoor source strength and ozone, even for compounds whose constituents do not have oxygen and therefore clearly did not arise directly from ozonolysis (Fig. S3). To compensate, we compute a supplementary index, the concentration ratio of a species at two air change rates — 1 h^{-1} and 0.25 h^{-1} ($C_{1\ h^{-1}} / C_{0.25\ h^{-1}}$) — which is an indicator of the surface-reservoir effect. Values of this index for VOC signals were obtained from linear fits of indoor-outdoor concentration difference versus air change rate at 20.5-23.5 °C, after removing outliers.

Figure 5 shows a scatter plot of $\Delta S_{10\ ppb\ O_3} / S_0$ versus $C_{1\ h^{-1}} / C_{0.25\ h^{-1}}$ for 61 VOC signals that feature continuous indoor sources. These signals were selected based on the same criteria as in our previous paper, excluding those that have either strong influence from intermittent emissions (such as cooking) or considerable contributions from outdoors or crawlspace air (24). Each data point represents a VOC signal. The color indicates the R^2 of the linear fit of its source strength versus indoor ozone. The point size scales with the fitted slope. Values of $C_{1\ h^{-1}} / C_{0.25\ h^{-1}}$ ranged from 0.45 to 1.37, much higher than the value of 0.25 that would be expected for a

317 constant source strength case, with no wall effects, and for steady-state conditions. Values of
318 $\Delta S_{10\ ppb\ O_3} / S_0$ ranged from 0.6 to 26.

319 Most data points in Fig. 5 are distributed along a line with a positive slope; other points
320 lie above the line. The line represents a lower bound of $\Delta S_{10\ ppb\ O_3} / S_0$ for a given $C_{1\ h^{-1}} / C_{0.25\ h^{-1}}$,
321 likely corresponding to the extent of $\Delta S_{10\ ppb\ O_3} / S_0$ that can be explained by surface reservoir
322 effects. This interpretation is supported by two observations. Firstly, the data points generally
323 are aligned with expected stickiness of parent compounds. Specifically, the lowest five points
324 correspond to relatively high volatility species — $C_3H_4N^+$, $C_5H_5O_2^+$, $C_3H_5O^+$, CH_3O^+, and
325 CH_5O^+ — whereas the highest five are for species with lower volatility — $C_{15}H_{27}N_2^+$, $C_9H_{15}O_2^+$,
326 $C_7H_{11}O^+$, $C_{15}H_{23}^+$, and $C_8H_{17}O_2^+$. Secondly, all values of $C_{1\ h^{-1}} / C_{0.25\ h^{-1}}$ on the line are less than
327 1.0 (solid line), consistent with expectation from a surface reservoir effect, which can make
328 indoor species concentration at the higher air change rate close to, but no more than (dotted line),
329 that at the lower air change rate.

330 Based on the above analysis, we can consider that the VOC signals for points situated
331 well above the line in Fig. 5 are strongly produced by ozone chemistry. Among these VOC
332 signals, $C_8H_{15}O^+$ and $C_8H_{13}^+$ attributed to 6-MHO exhibited a notably high $\Delta S_{10\ ppb\ O_3} / S_0$ value
333 above 20. Other VOC signals well above the line (i.e., above the grey region) include $C_5H_9O_2^+$
334 attributable to 4-OPA, $C_9H_{17}O^+$ and $C_9H_{15}^+$ attributable to nonenal, and ions attributable to the
335 C_8-C_{12} saturated aldehdyes. As presented in Table 1, the total effective yield for all identified
336 compounds is at least 12%. The effective yield of nonanal was the highest (≥ 3.5%), followed by
337 6-MHO (2.7%), 4-OPA (2.6%), decanal (≥ 1.3%), and nonenal (≥ 1.0%). Note that, except for
338 6-MHO and 4-OPA, the estimated yields represent lower limits, since our analysis might have
339 missed some smaller fragment ions of these aldehydes (SI Appendix). The identified compounds,
340 with summed indoor concentration of several ppb, contribute only marginally to the total loading

341 of oxygenated VOCs in this house, which was several hundred ppb (24). However, certain
342 products may contribute even at low abundances to odors (e.g., nonenal (41)) or irritation (e.g.,
343 4-OPA (42)).

344 Volatile products identified through this non-target analysis are among the most
345 commonly reported products from ozone interaction with indoor surfaces and human skin oil.
346 The C8-C10 aldehydes, particularly nonanal, have been reported as key products of ozonolysis
347 for many indoor building and furnishing materials (9–11, 15). Surface soiling by oleic
348 acids/esters from cooking oil might lead to additional nonanal production, as suggested by field
349 measurements (8, 16), as well as by lab tests of building materials placed in real indoor
350 environments (17). Notably, Wang and Morrison found that nonanal was the most prominent
351 secondary aldehyde emitted from almost all the tested surfaces in residences they studied (8, 16);
352 the product yield varied in the range 0-34% across the surfaces sampled. Their observation is
353 consistent with our finding that nonanal exhibited the highest effective yield of $\geq$ 3.5% among all
354 identified products. For ozone interaction with skin lipids, decanal is another key oxidation
355 product in addition to 6-MHO and 4-OPA, specifically from ozonolysis of some abundant
356 unsaturated fatty acids such as cis-hexadec-6-enoic acid (5-6% of skin surface lipids by weight)
357 (18). In terms of relative ratios, yields of the three compounds quantified herein (2.7% (6-
358 MHO):2.6% (4-OPA):$\geqslant$1.3% (decanal)), were comparable with those reported in a simulated
359 office experiment for skin oil ozonolysis with two occupants (14.4% (6-MHO):12.5% (4-
360 OPA):6.3% (decanal)) (14). Octanal, undecanal, and dodecanal were also detected in skin oil
361 ozonolysis experiments, but their fatty acid precursors are less abundant (14).

362 The unsaturated aldehyde nonenal has been previously identified as an oxidation product
363 of new carpets (2-nonenal) (11, 16), certain skin surface lipids (3-nonenal) (18), omega-7
364 unsaturated fatty acids (2-nonenal) (43), and linoleic acid (2- and 4- nonenal) (44), a common

365 constituent of linseed oil and certain cooking oils. In the house we studied, there were older area
366 carpets in several rooms, and cooking activities occurred frequently. We cannot glean from the
367 evidence which precursor(s) contributed to the secondary production of nonenal. Worth noting
368 is that nonenal was not detected in previous field measurements on kitchen countertops where
369 nonanal was prominent (8, 16). However, we suspect that result might be a technical artifact
370 arising from the off-line analysis method used in those studies. That is, nonenal, which contains
371 a C=C bond, might have been consumed by ozone reaction after collection on Tenax tubes,
372 considering the use of a high level of ozone (40-120 ppb) and the absence of an ozone scrubber
373 during sampling. In any case, given the high yield of nonenal observed here, in combination
374 with the particularly low odor threshold for this compound (41), further investigation of nonenal
375 from indoor ozonolysis reactions is warranted.

376 It should be noted that some frequently reported ozonolysis products in previous studies
377 of indoor surfaces or skin oil, including formaldehyde, acetone, hexanal, and geranylacetone, did
378 not emerge as apparent ozone byproducts in our analysis (Fig. 5). Ions corresponding to
379 formaldehyde (CH_3O^+) and hexanal ($C_6H_{13}O^+$) lie near the baseline in Fig. 5, suggesting no more
380 than a marginal contribution of ozone chemistry to indoor formaldehyde and hexanal generation.
381 Major indoor sources of formaldehyde include urea-formaldehyde-bonded composite wood
382 products (45). Continuous indoor sources of hexanal are uncertain, but may be related to certain
383 wood materials (46, 47). Acetone was excluded from the analysis in Figure 5, because of strong
384 contributions from intermittent sources as indicated by a high mean-to-median concentration
385 ratio (24). Sources of acetone include human breath and household cleaning agents. The yield of
386 acetone has been reported to be about 2 times higher than 6-MHO for skin oil ozonolysis (14),
387 but the measured indoor concentration of acetone in the present study was 50 times higher than
388 of 6-MHO, suggesting that the contribution of ozone chemistry for acetone at this site was

relatively small. Geranylacetone was also excluded in Figure 5, because its indoor-to-outdoor ratio (indicator for strong indoor source) and mean-to-median ratio did not reach the selection criteria. Even if we relax the data constraint to include the product ion of geranylacetone in the analysis (Figure S4), the ion lies in the grey region and is characterized by a high value of $C_{1\ h^{-1}}$ / $C_{0.25\ h^{-1}}$. A probable interpretation is that the stickiness of geranylacetone to indoor surfaces strongly interferes with our ability to discern its relationship to ozone-initiated chemistry using our approach. Given the presence of these and other compounds which can be contributed by ozone chemistry but did not emerge as apparent ozone byproducts, the actual total yield of volatile organic products from ozone chemistry in the house can be several times higher than the summed effective yield of all identified compounds reported here.

To summarize, the results presented in this paper represent the first quantitative characterization of ozone-initiated chemistry in a normally occupied residence. We identified a range of VOCs that had strong contributions from indoor ozone chemistry (Fig. 5), even though the house we studied had both low indoor ozone concentrations (Fig. 1) and a low indoor ozone loss rate (Fig. 2). Being able to elucidate how residential VOC composition is altered by ozone-initiated chemistry substantiates prior laboratory-based investigations. It is important to recognize that the health effects associated with ambient ozone might be materially influenced by the products of indoor ozone chemistry. Of concern in this regard are not only those species characterized here, but also other potentially toxic products known to be a consequence of ozonolysis, but which our instrumentation is incapable of detecting, such as secondary ozonides, hydroperoxides, and epoxides (48, 49).

Materials and Methods

412 The studied house, built in the 1930s of wood-frame construction, has a split-level living
413 zone, an unoccupied attic above, and a small basement and larger crawlspace below. Two adult
414 occupants (male and female, aged 60-65 y) live in the house. In addition to normal house
415 operation conditions (occupied periods), the occupants were deliberately away on a few
416 occasions for one or more days during the monitoring period. During the vacant periods, the
417 house windows and exterior doors were closed. Other than a request to maintain interior doors
418 open (to facilitate interzonal transport and mixing), occupants were instructed to live as they
419 normally would, including normal use of window opening to maintain thermal comfort. The
420 occupants gave informed consent for this study, which was approved by the Committee for
421 Protection of Human Subjects for the University of California, Berkeley (Protocol #2016-04-
422 8656).
423 Ozone and VOCs were measured using a UV-absorption based ozone monitor (Thermal
424 49i) and a PTR-ToF-MS, respectively. Both instruments were situated in a detached garage and
425 sub-sampled via shared continuous-operating equal length 30-meter PFA sampling lines from the
426 kitchen, bedroom, crawlspace, basement, attic, and outdoors. During vacant periods, sampling
427 was conducted using a spaced-resolved scheme (sampling from each of the 6 locations for 5
428 mins in a twice-per-hour cycle). During occupied periods, sampling was conducted using the
429 space-resolved measurement scheme for ~ 5 weeks and using a time-resolved scheme (outdoor 5
430 mins, kitchen 20 mins, and bedroom 5 mins, twice per hour) for ~ 2 weeks. SI Appendix
431 provides a detailed description of the sampling system, associated data trimming protocols, as
432 well as an evaluation of the influence of the sampling system on instrument response.
433 For PTR-ToF-MS, the primary reagent is the hydronium ion (H_3O^+), which can
434 effectively protonate most oxygenated VOCs. Resultant product ions were measured, often in
435 the form of $VOCH^+$, but fragmentation can also occur. In total, 218 VOC signals (organic ion

formulas after combining isotopic ions and some known fragment ions) were extracted to represent measured VOC speciation across the campaign (24). Depending on sample air composition, a VOC signal might be dominantly attributed to one VOC species, and might be contributed by a few species. Airborne concentrations (in part per trillion/billion by volume, ppt/ppb) were estimated for individual VOC signals as described in SI Appendix.

Data associated with this paper is provided in Dataset S1.

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Author contribution. A.G., W.N., Y.L., P.M., and C.A. designed the field campaign, Y.L., P.M., and C.A. collected the PTR-ToF-MS and ozone data, Y.L., C.W., W.N., and A.G. analyzed the data, Y.L. wrote the manuscript, and all authors edited the manuscript and provided comments.

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References

1. M. Yao, B. Zhao, Surface removal rate of ozone in residences in China. *Build. Environ.* **142**, 101–106 (2018).
2. K. Lee, J. Vallarino, T. Dumyahn, H. Özkaynak, J. D. Spengler, Ozone decay rates in residences. *J. Air Waste Manage. Assoc.* **49**, 1238–1244 (1999).
3. C. J. Weschler, Ozone's impact on public health: contributions from indoor exposures to ozone and products of ozone-Initiated chemistry. *Environ. Health Perspect.* **114**, 1489–1496 (2006).
4. B. L. Deming, P. J. Ziemann, Quantification of alkenes on indoor surfaces and implications for chemical sources and sinks. *Indoor Air* **30**, 914–924 (2020).
5. J. Shen, Z. Gao, Ozone removal on building material surface: A literature review. *Build. Environ.* **134**, 205–217 (2018).
6. C. J. Weschler, Ozone in indoor environments: Concentration and chemistry. *Indoor Air* **10**, 269–288 (2000).
7. C. Chen, B. Zhao, C. J. Weschler, Assessing the influence of indoor exposure to "outdoor ozone" on the relationship between ozone and short-term mortality in U.S. communities. *Environ. Health Perspect.* **120**, 235–240 (2012).
8. H. Wang, G. Morrison, Ozone-surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends. *Indoor Air* **20**, 224–234 (2010).
9. M. Nicolas, O. Ramalho, F. Maupetit, Reactions between ozone and building products: Impact on primary and secondary emissions. *Atmos. Environ.* **41**, 3129–3138 (2007).

10. S. P. Lamble, R. L. Corsi, G. C. Morrison, Ozone deposition velocities, reaction probabilities and product yields for green building materials. *Atmos. Environ.* **45**, 6965–6972 (2011).

11. G. C. Morrison, W. W. Nazaroff, Ozone interactions with carpet: Secondary emissions of aldehydes. *Environ. Sci. Technol.* **36**, 2185–2192 (2002).

12. L. S. Pandrangi, G. C. Morrison, Ozone interactions with human hair: Ozone uptake rates and product formation. *Atmos. Environ.* **42**, 5079–5089 (2008).

13. B. K. Coleman, H. Destaillats, A. T. Hodgson, W. W. Nazaroff, Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. *Atmos. Environ.* **42**, 642–654 (2008).

14. A. Wisthaler, C. J. Weschler, Reactions of ozone with human skin lipids: Sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. *Proc. Natl. Acad. Sci.* **107**, 6568–6575 (2010).

15. O. A. Abbass, D. J. Sailor, E. T. Gall, Effect of fiber material on ozone removal and carbonyl production from carpets. *Atmos. Environ.* **148**, 42–48 (2017).

16. H. Wang, G. C. Morrison, Ozone-initiated secondary emission rates of aldehydes from indoor surfaces in four homes. *Environ. Sci. Technol.* **40**, 5263–5268 (2006).

17. C. J. Cros, G. C. Morrison, J. A. Siegel, R. L. Corsi, Long-term performance of passive materials for removal of ozone from indoor air. *Indoor Air* **22**, 43–53 (2012).

18. C. J. Weschler, Roles of the human occupant in indoor chemistry. *Indoor Air* **26**, 6–24 (2016).

19. M. Kruza, A. C. Lewis, G. C. Morrison, N. Carslaw, Impact of surface ozone interactions on indoor air chemistry: A modeling study. *Indoor Air* **27**, 1001–1011 (2017).

20. P. Wolkoff, Volatile organic compounds - Sources, measurements, emissions, and the impact on indoor air quality. *Indoor Air* **5 (Suppl. 3)**, 9–73 (1995).

21. J. Xiong, Z. He, X. Tang, P. K. Misztal, A. H. Goldstein, Modeling the time-dependent concentrations of primary and secondary reaction products of ozone with squalene in a university classroom. *Environ. Sci. Technol.* **53**, 8262–8270 (2019).

22. C. J. Weschler, *et al.*, Ozone-initiated chemistry in an occupied simulated aircraft cabin. *Environ. Sci. Technol.* **41**, 6177–6184 (2007).

23. A. Fischer, E. Ljungström, S. Langer, Ozone removal by occupants in a classroom. *Atmos. Environ.* **81**, 11–17 (2013).

24. Y. Liu, *et al.*, Characterizing sources and emissions of volatile organic compounds in a northern California residence using space- and time-resolved measurements. *Indoor Air* **29**, 630–644 (2019).

25. Y. Liu, *et al.*, Detailed investigation of ventilation rates and airflow patterns in a northern California residence. *Indoor Air* **28**, 572–584 (2018).

26. C. Arata, *et al.*, Measurement of NO_3 and N_2O_5 in a residential kitchen. *Environ. Sci. Technol. Lett.* **5**, 595–599 (2018).

27. K. Lee, *et al.*, Nitrous acid, nitrogen dioxide, and ozone concentrations in residential environments. *Environ. Health Perspect.* **110**, 145–149 (2002).

28. H. Zhao, B. Stephens, A method to measure the ozone penetration factor in residences under infiltration conditions: application in a multifamily apartment unit. *Indoor Air* **26**, 571–581 (2016).

29. C. M. Salvador, *et al.*, Indoor ozone/human chemistry and ventilation strategies. *Indoor Air* **29**, 913–925 (2019).

30. E. Grosjean, D. Grosjean, J. H. Seinfeld, Gas-phase reaction of ozone with trans-2-hexenal, trans-2-hexenyl acetate, ethylvinyl ketone, and 6-methyl-5-hepten-2-one. *Int. J. Chem. Kinet.* **28**, 373–382 (1996).

31. C. J. Weschler, W. W. Nazaroff, Growth of organic films on indoor surfaces. *Indoor Air* **27**, 1101–1112 (2017).

32. E. T. Gall, D. Rim, Mass accretion and ozone reactivity of idealized indoor surfaces in mechanically or naturally ventilated indoor environments. *Build. Environ.* **138**, 89–97 (2018).

33. C.-Y. Huo, *et al.*, Phthalate esters in indoor window films in a northeastern Chinese urban center: Film growth and implications for human exposure. *Environ. Sci. Technol.* **50**, 7743–7751 (2016).

34. C. Y. Lim, J. P. Abbatt, Chemical composition, spatial homogeneity, and growth of indoor surface films. *Environ. Sci. Technol.* **54**, 14372–14379 (2020).

35. C. J. Weschler, *et al.*, Squalene and cholesterol in dust from Danish homes and daycare centers. *Environ. Sci. Technol.* **45**, 3872–3879 (2011).

36. H. Baker, A. M. Kligman, Technique for estimating turnover time of human stratum corneum. *Arch. Dermatol.* **95**, 408–411 (1967).

37. A. Zafar, J. Chickos, The vapor pressure and vaporization enthalpy of squalene and squalane by correlation gas chromatography. *J. Chem. Thermodyn.* **135**, 192–197 (2019).

38. X. Tang, P. K. Misztal, W. W. Nazaroff, A. H. Goldstein, Volatile organic compound emissions from humans indoors. *Environ. Sci. Technol.* **50**, 12686–12694 (2016).

39. C. Fortenberry, *et al.*, Analysis of indoor particles and gases and their evolution with natural ventilation. *Indoor Air* **29**, 761–779 (2019).

40. C. Wang, *et al.*, Surface reservoirs dominate dynamic gas-surface partitioning of many indoor air constituents. *Sci. Adv.* **6**, eaay8973 (2020).

41. D. G. Guadagni, R. G. Buttery, S. Okano, Odour thresholds of some organic compounds associated with food flavours. *J. Sci. Food Agric.* **14**, 761–765 (1963).

42. S. E. Anderson, *et al.*, Irritancy and allergic responses induced by exposure to the indoor air chemical 4-oxopentanal. *Toxicol. Sci.* **127**, 371–381 (2012).

43. S. Haze, *et al.*, 2-Nonenal newly found in human body odor tends to increase with aging. *J. Invest. Dermatol.* **116**, 520–524 (2001).

44. T. Moise, Y. Rudich, Reactive uptake of ozone by aerosol-associated unsaturated fatty acids: Kinetics, mechanism, and products. *J. Phys. Chem. A* **106**, 6469–6476 (2002).

45. T. Salthammer, S. Mentese, R. Marutzky, Formaldehyde in the indoor environment. *Chem. Rev.* **110**, 2536–2572 (2010).

46. A.-M. Manninen, P. Pasanen, J. K. Holopainen, Comparing the VOC emissions between air-dried and heat-treated Scots pine wood. *Atmos. Environ.* **36**, 1763–1768 (2002).

47. A. T. Hodgson, A. F. Rudd, D. Beal, S. Chandra, Volatile organic compound concentrations and emission rates in new manufactured and site-built houses. *Indoor Air* **10**, 178–192 (2000).

48. S. Zhou, M. W. Forbes, J. P. D. Abbatt, Kinetics and products from heterogeneous oxidation of squalene with ozone. *Environ. Sci. Technol.* **50**, 11688–11697 (2016).

49. M. Yao, C. J. Weschler, B. Zhao, L. Zhang, R. Ma, Breathing-rate adjusted population exposure to ozone and its oxidation products in 333 cities in China. *Environ. Int.* **138**, 105617 (2020).

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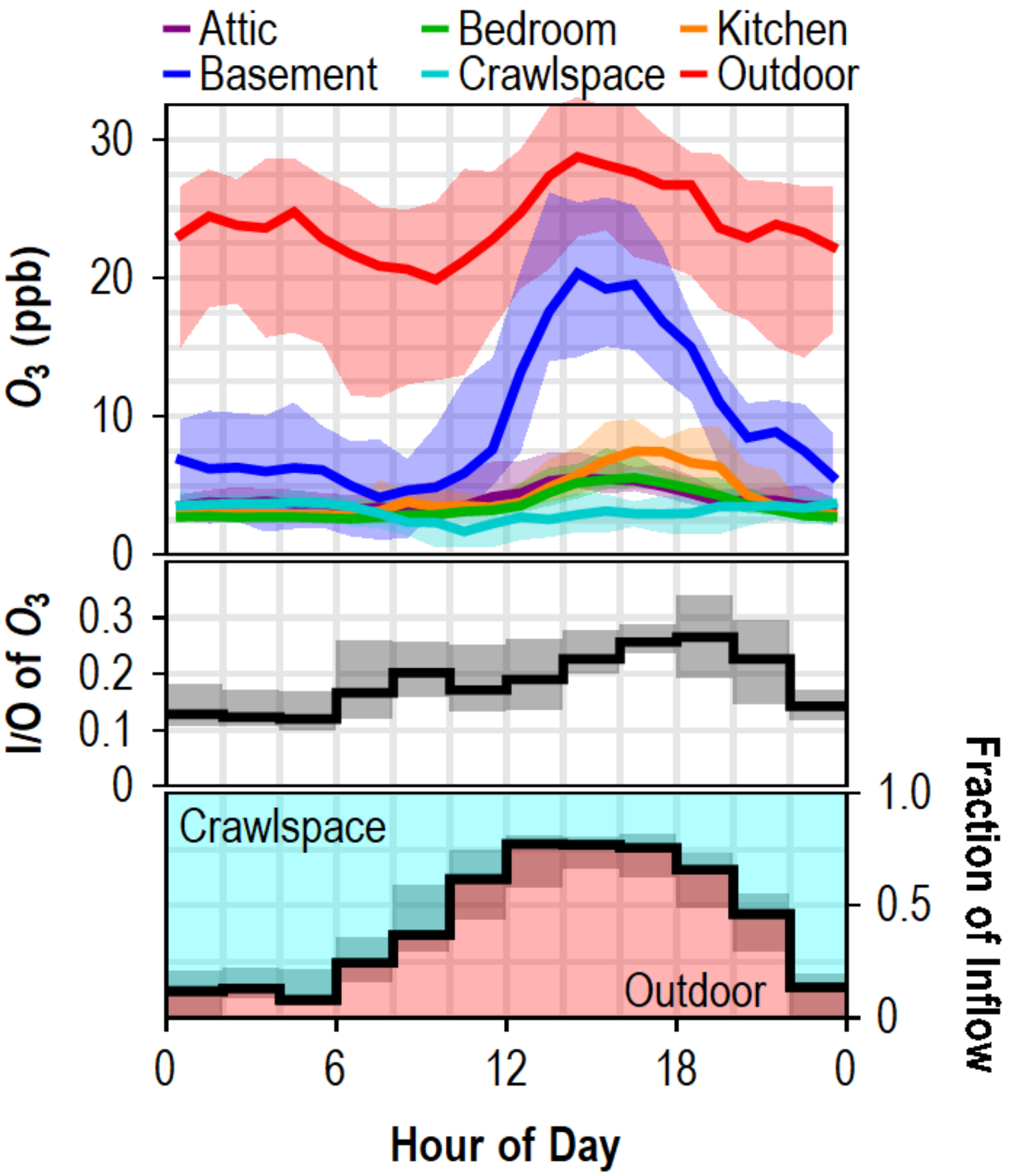
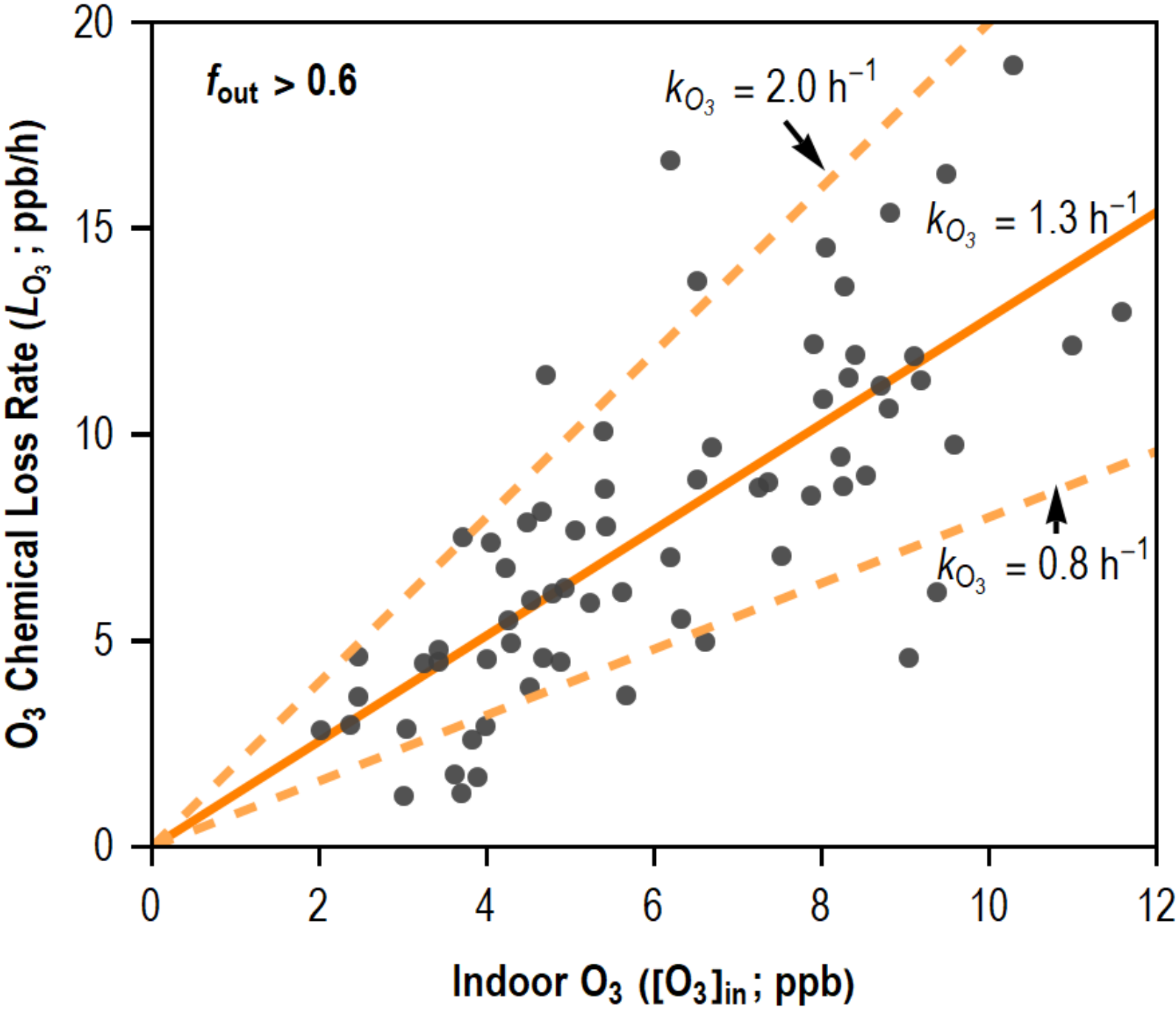
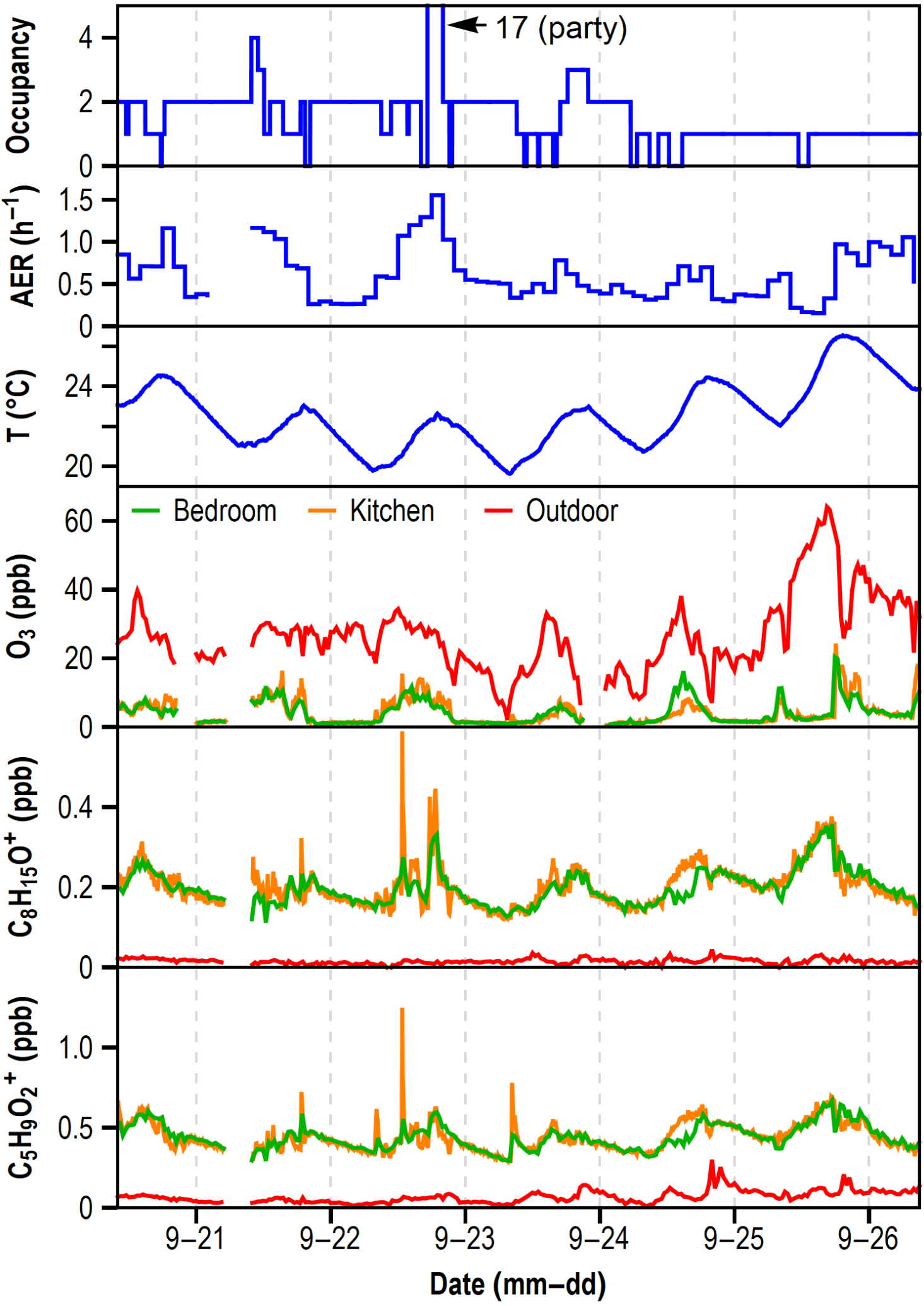
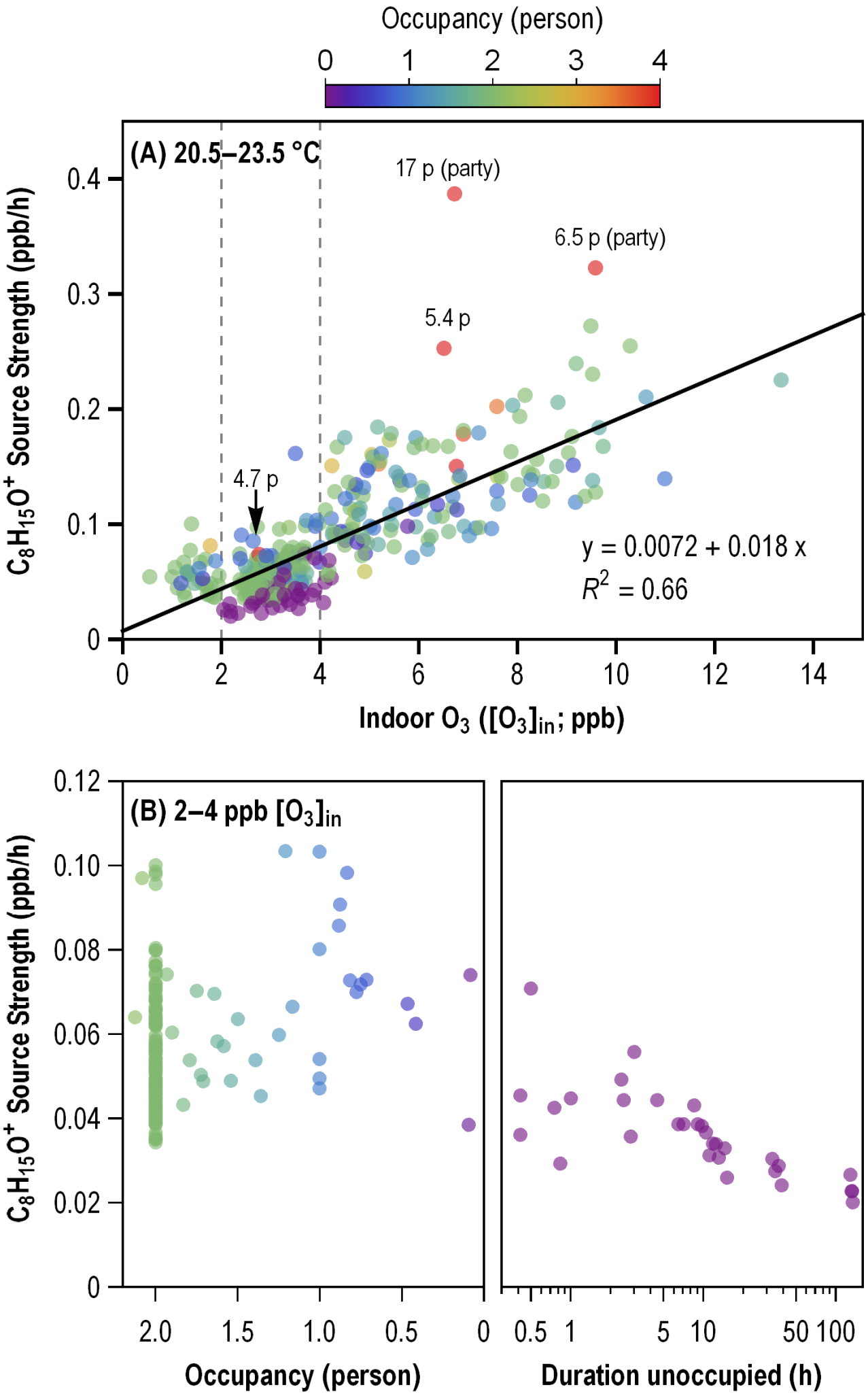
data in panel A (bounded by dashed lines, with indoor ozone of 2-4 ppb) and plots $C_8H_{15}O^+$ source strength versus occupancy for 2 ≥ occupancy > 0 (left side) and versus unoccupied time duration for occupancy = 0 (right side), respectively. Data points are colored to indicate occupancy level. In Panel A, the black line shows a linear fit of data after excluding outliers of $C_8H_{15}O^+$ source strength (UQ + 3 IQR); exact occupancy level was labeled for occupancy > 4. Occupancy level represents the average for the 2-h integration period, and so can be a non-integer value when occupants are present for only part of the interval.

Figure 5. VOC signals for continuously emitted species mapped into a 2-dimensional plot to identify compounds with pronounced production from indoor ozone chemistry. The *y* axis is indoor source strength ratio, defined as change of source strength associated with a 10-ppb increase of ozone, normalized by the ozone-independent source strength ($\Delta S_{10\ ppb\ O_3}/S_0$); and the *x* axis is an indoor concentration ratio, defined as concentration at an air change rate of 1 h^{-1} divided by that at 0.25 h^{-1} ($C_{1\ h^{-1}}/\ C_{0.25\ h^{-1}}$). Each data point is colored by R^2 of the linear fit of indoor source strength versus indoor ozone, and the point size is scaled to the corresponding slope (*k*). The grey line represents a fit to the baseline. Emissions for chemicals along this line are ozone independent. The light grey region represents an approximate uncertainty band, plotted as the line value ± 1.


Attic
Bedroom
Kitchen
Basement
Crawlspace
Outdoor
30
20
10
0
O_3 (ppb)
0.3
0.2
0.1
0
I/O of O_3
Crawlspace
Outdoor
1.0
0.5
0
Fraction of Inflow
0
6
12
18
0
Hour of Day


f_{out} > 0.6
k_{O_3} = 2.0 h^{-1}
k_{O_3} = 1.3 h^{-1}
k_{O_3} = 0.8 h^{-1}
O_3 Chemical Loss Rate (L_{O_3}; ppb/h)
Indoor O_3 ($[O_3]_{in}$; ppb)
0
5
10
15
20
0
2
4
6
8
10
12


Occupancy
4
2
0
17 (party)
AER (h^{-1})
1.5
1.0
0.5
0
T (°C)
24
20
Bedroom
Kitchen
Outdoor
O_3 (ppb)
60
40
20
0
$C_8H_{15}O^+$ (ppb)
0.4
0.2
0
$C_5H_9O_2^+$ (ppb)
1.0
0.5
0
9–21
9–22
9–23
9–24
9–25
9–26
Date (mm–dd)


Occupancy (person)
0
1
2
3
4
(A) 20.5–23.5 °C
17 p (party)
6.5 p (party)
5.4 p
4.7 p
y = 0.0072 + 0.018 x
R^2 = 0.66
$C_8H_{15}O^+$ Source Strength (ppb/h)
Indoor O_3 ($[O_3]_{in}$; ppb)
(B) 2–4 ppb $[O_3]_{in}$
Occupancy (person)
Duration unoccupied (h)

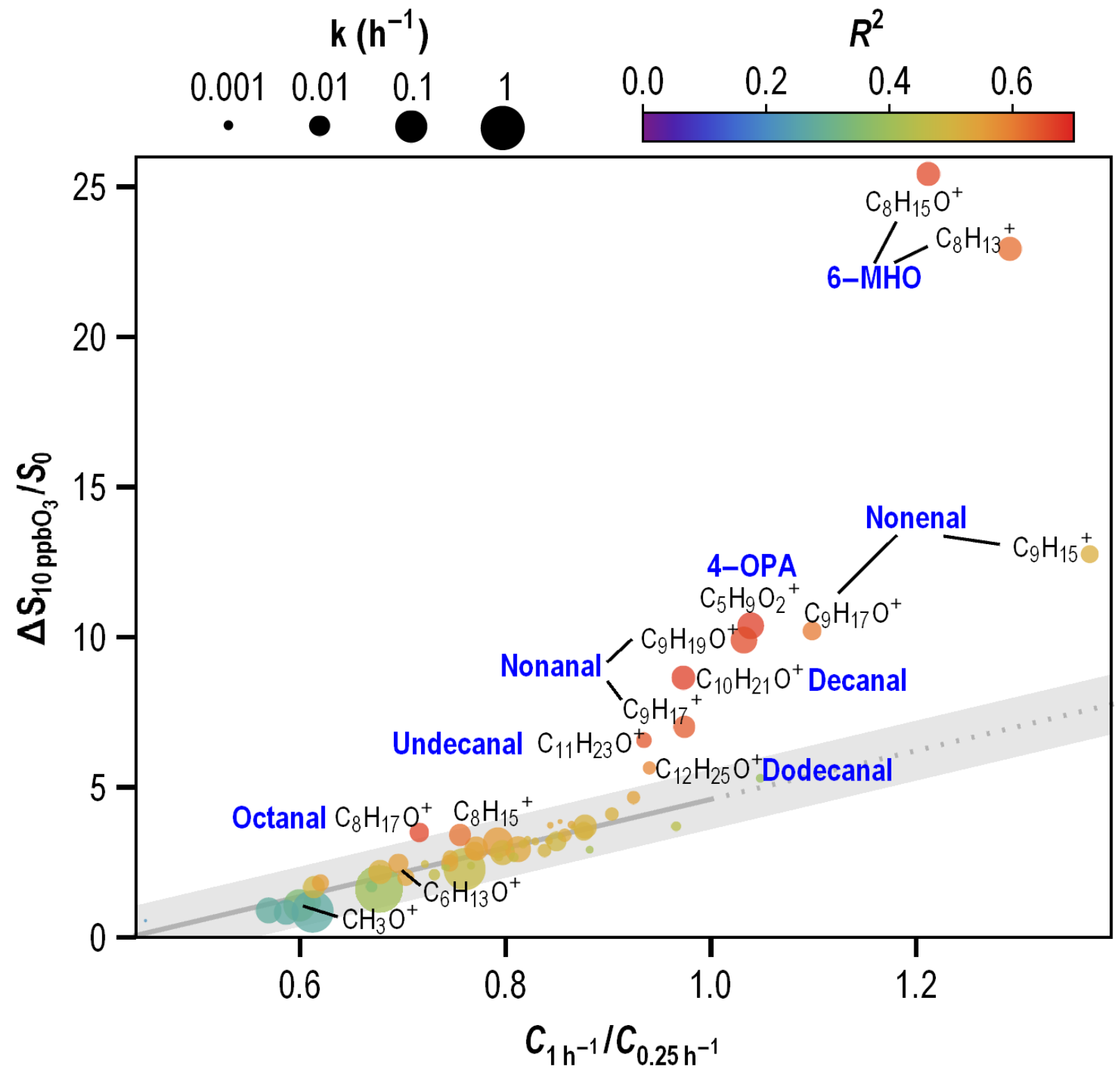

k (h−1)
0.001
0.01
0.1
1
R2
0.0
0.2
0.4
0.6
25
20
15
10
5
0
ΔS10 ppbO3/S0
0.6
0.8
1.0
1.2
C1 h−1/C0.25 h−1
C8H15O+
C8H13+
6–MHO
Nonenal
C9H15+
4–OPA
C5H9O2+
C9H17O+
C9H19O+
Nonanal
C10H21O+
Decanal
C9H17+
Undecanal
C11H23O+
C12H25O+
Dodecanal
Octanal
C8H17O+
C8H15+
C6H13O+
CH3O+

Table 1 Summary for ozone concentration and VOC signals identified as having a major origin from indoor ozone chemistry.

	VOC signals		Mean mixing ratio [d] (ozone in ppb; VOC signals in ppt)						Derived parameters [e]			
	Ion[a]	Species [b]	Outdoor	Kitchen	Bedroom	Crawlspace	Basement	Attic	k (h^{-1})	$\Delta S_{10\ ppb\ O_3}/S_0$	$C_{1\ h^{-1}}/C_{0.25\ h^{-1}}$	Yield [f]
Ozone			23	4.6	3.8	3.4	9.9	4.5				
PTR	$C_5H_9O_2^+$	4-OPA	39	400	420	56	190	240	0.034	10	1.04	2.6%
	$C_8H_{15}O^+$	6-MHO	6	180	190	17	58	94	0.018	26	1.21	2.7%
	$C_8H_{13}^+$	6-MHO [c]	7	160	170	19	59	100	0.016	23	1.29	
	$C_8H_{17}O^+$	Octanal	4	120	130	12	31	77	0.008	3.6	0.72	≥0.6%
	$C_9H_{17}O^+$	Nonenal	4	82	85	9	24	44	0.007	10	1.10	≥1.0%
	$C_9H_{15}^+$	Nonenal [c]	5	71	65	9	25	30	0.006	13	1.37	
	$C_9H_{19}O^+$	Nonanal	3	370	370	21	98	160	0.033	10	1.03	≥3.5%
	$C_9H_{17}^+$	Nonanal [c]	5	150	150	17	71	67	0.012	7.1	0.97	
	$C_{10}H_{21}O^+$	Decanal	6	200	230	17	87	90	0.018	8.7	0.97	≥1.3%
	$C_{11}H_{23}O^+$	Undecanal	3	45	52	6	20	26	0.004	6.6	0.93	≥0.3%
	$C_{12}H_{25}O^+$	Dodecanal	2	28	32	5	13	15	0.002	5.7	0.94	≥0.2%

[a] The PTR ions presented here are those well above the baseline in Fig. 5.

[b] Species are attributed by matching identified ion formulas with known indoor ozonolysis products. These species probably make a dominant contribution to corresponding ion signals in the living space but may or may not in other spaces.

[c] Ratios of two VOC signals attributed to the same species might be slightly different in kitchen and bedroom due to the presence of other minor contributing species.

[d] Mean mixing ratio during occupied period when in space-resolved measurement mode.

[e] See detailed description of the parameters in the main text.

[f] Yield for identified VOC species, estimated as the sum of yields for respective identified product ions. For some species, the sum only represents a lower limit due to the possible presence of unidentified fragment ions (cf. SI Appendix).