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# **Authors**

Liu, Yingjun Misztal, Pawel K Arata, Caleb <u>et al.</u>

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# **Bringing Ozone Chemistry Home**

Yingjun Liu<sup>a,b,\*</sup>, Pawel K. Misztal<sup>b,†</sup>, Caleb Arata<sup>c</sup>, Charles J. Weschler<sup>d,e</sup>, William W Nazaroff<sup>f</sup>, and Allen H. Goldstein<sup>b,f</sup>

<sup>a</sup> BIC-ESAT and SKL-ESPC, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China;

<sup>b</sup> Department of Environmental Science, Policy, and Management, University of California, Berkeley, CA 94720;

<sup>c</sup> Department of Chemistry, University of California, Berkeley, CA 94720;

<sup>d</sup> Environmental and Occupational Health Sciences Institute, Rutgers University, Piscataway, NJ 08854;

<sup>e</sup> International Centre for Indoor Environment and Energy, Technical University of Denmark,

Lyngby 2800, Denmark;

<sup>f</sup>Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720;

<sup>†</sup>Now at Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX 78712.

\*Correspondence: Yingjun Liu. E-mail: <u>yingjun.liu@pku.edu.cn</u>; Tel: 86-10-6275572.

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#### 1 Abstract

2 Outdoor ozone transported indoors initiates oxidative chemistry, forming volatile organic 3 products. The influence of ozone chemistry on indoor air composition has not been directly 4 quantified in normally occupied residences. Here, we explore indoor ozone chemistry in a house 5 in California with two adult inhabitants. We utilize space- and time-resolved measurements of 6 ozone and volatile organic compounds (VOCs) acquired over an eight-week summer campaign. 7 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 8 9 from ozone-initiated chemistry indoors. These chemicals include 6-methyl-5-hepten-2-one (6-10 MHO), 4-oxopentanal (4-OPA), nonenal, and C8-C12 saturated aldehydes, which are among the 11 commonly reported products from laboratory studies of ozone interactions with indoor surfaces 12 and with human skin lipids. These VOCs together accounted for  $\geq 12\%$  molecular yield with 13 respect to house-wide consumed ozone, with the highest net product yields for nonanal ( $\geq$ 14 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 15 16 body envelopes of the two occupants in this house are insufficient to explain the observed yields. 17 Relatedly, we observed that ozone-driven chemistry continued to produce 6-MHO and 4-OPA 18 even after the occupants had been away from the house for 5 days. These observations provide 19 evidence that skin lipids transferred to indoor surfaces made substantial contributions to ozone 20 reactivity in the studied house.

### 21 Significance Statement

22 It has been suggested that indoor exposure to ozone oxidation products contributes 23 materially to the apparent associations between outdoor ozone concentration and morbidity and 24 mortality. Our current understanding of indoor ozone chemistry derives mainly from studies 25 with test surfaces under controlled conditions. Little is known about the overall impact of ozone 26 chemistry on air composition in dynamically changing indoor residential environments. The 27 results presented here reflect the first quantitative characterization of overall indoor ozone 28 chemistry in a normally occupied home. Findings reveal a strong influence of off-body skin 29 lipids on indoor ozone chemistry. Being able to elucidate indoor air pollutants derived from 30 ozone chemistry facilitates the investigation of causal links between outdoor ozone 31 concentrations and adverse health effects.

32 Main Text

#### 33 Introduction

34 Outdoor air containing ozone  $(O_3)$  penetrates into indoor environments, including 35 residences, workplaces, and schools. Ozone undergoes fast reactions indoors; its characteristic 36 lifetime is typically a few tens of minutes (1, 2). Reactions are thought mainly to occur on the 37 large surface area in indoor environments (3), which ubiquitously contain reactive species (4, 5). 38 Indoor ozone chemistry reduces indoor ozone concentrations and forms a spectrum of oxidation 39 products, many of which are volatile (6). Emerging evidence suggests that indoor exposure to 40 the mixture of ozone and its oxidation products contributes to epidemiologically determined 41 associations between outdoor ozone concentrations and morbidity and mortality (3, 7).

42 Previous studies of indoor air chemistry mainly focused on investigating ozone reactions 43 with individual indoor surfaces along with consequent release of secondary products. Studied 44 surfaces include building materials and furnishings, such as carpet, wall covering, ceiling tile, 45 wood board, and glass (8–11), as well as human skin, hair, and clothing (12–14). Observed 46 volatile products include C1-C13 carbonyls, dicarbonyls, and hydroxycarbonyls among other 47 oxygenated compounds. Product yields vary broadly, influenced by factors such as type and age 48 of surface materials (11, 15) and soiling (8, 13, 16, 17). Skin oil lipids, characterized by a high 49 proportion of squalene ( $C_{30}H_{50}$ ), are particularly important indoor ozone reactants (14). They are 50 present on skin, hair, and worn clothing of human occupants. They can also be transferred to 51 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), 6-52 53 methyl-5-hepten-2-one (6-MHO), and geranylacetone.

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

56 the contribution of ozone chemistry to the composition of dynamically changing indoor 57 environments and hence to occupants' exposure (19). First, there can be myriad sources for 58 indoor air pollutants in addition to ozone chemistry (20). Because ozone chemistry can produce 59 a particular compound does not imply that it contributes meaningfully to the indoor 60 concentration of that compound. Second, occupants might dynamically alter indoor ozone 61 reactivity via their time-dependent presence indoors as well as their intended and unintended 62 activities such as desquamation, transferring skin oils to surfaces by direct contact, cooking (e.g., 63 surface soiling by the deposition of fatty acids in cooking oils and foods), and cleaning (e.g., 64 with products that contain ozone-reactive terpenoids). Indoor studies in densely occupied spaces, 65 including in two classrooms, a simulated office, and a simulated aircraft cabin (14, 21–23), have 66 all highlighted the importance of the direct presence of human occupants for ozone chemistry. 67 For residences, which are often less densely occupied, evidence is lacking regarding the overall 68 features of indoor ozone chemistry and its impact on the indoor air composition to which 69 occupants are exposed.

70 Here, we report an investigation of indoor ozone chemistry in a normally occupied 71 residence based on temporally and spatially resolved observations of volatile organic compounds 72 (VOCs) and ozone. Data were acquired in a single-family house in Oakland, California, from an 73 extensive eight-week monitoring campaign conducted during summer 2016 (24, 25). This paper 74 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 75 76 paper, we examine the spatial and temporal distribution of ozone concentration, estimate the 77 chemical loss rate coefficient of ozone in the living space, characterize the oxidation products of 78 skin oil lipids, and undertake a non-targeted analysis to identify VOC species significantly 79 derived from ozone-initiated chemistry.

80 **Results and Discussion** 

81 **Ozone in the house.** Figure 1 (top) presents the diel variation of ozone concentration 82 measured at different locations in the house during the occupied period under the space-resolved 83 measurement scheme (cf. Materials and Methods). Mean ozone mixing ratios during the same 84 periods are reported in Table 1. The outdoor ozone level exhibited modest diel variation, with 85 the hourly median peaking at 28 ppb in the afternoon and declining to 20 ppb in the early 86 morning. The ozone level in different compartments of the house can be understood in the 87 context of the airflow patterns, i.e., with air generally flowing upwards from the crawlspace to 88 the living space and then to the attic; downwards flows were rare (25). The crawlspace air, 89 coming directly from outdoors through designed vents, exhibited consistently low ozone levels 90 (a mean value of 3.4 ppb), indicating substantial ozone loss in the crawlspace. The loss may be 91 associated with ozone titration by NO emitted from pilot lights of one or both of the natural-gas 92 furnace and water heater installed in the crawlspace; elevated NO was observed in the 93 crawlspace during wintertime monitoring in this house (26). The airflow path into the living 94 space showed a strong diel variation, with 90% of air infiltrating from the ozone-deficient 95 crawlspace at night whereas 80% directly entered from outdoors in the afternoon through opened 96 windows (Fig. 1 bottom). Correspondingly, the median indoor-to-outdoor (I/O) ratio of ozone 97 varied from 0.12 at night to  $\sim 0.27$  in the afternoon (Fig. 1 middle). As a point of comparison, 98 previously reported I/O ratios for ozone are typically in the range 0.2 - 0.7 (6). In the 99 unoccupied (and unfinished) attic, where airflow originated both from the living space and from 100 outdoors, the ozone level was similar to that in the living space, whereas in the small basement 101 room, with a constantly open window, ozone exhibited strong diel variation that was closest to 102 outdoor concentrations in the mid-afternoon.

- 103 The following analysis mainly focuses on the living space where human exposure occurs. 104 The mean ozone level in the living space (indoor ozone) was only 4.3 ppb, at the lower end of 105 reported values for residences in California (27). Assuming a well-mixed living space, the
- 106 indoor ozone concentration  $[O_3]_{in}$  is described well by the following equation

107 
$$\frac{d[O_3]_{in}}{dt} = (f_{crawl}[O_3]_{crawl} + f_{out}[O_3]_{out})ACR - (ACR + k_{o_3})[O_3]_{in}, \qquad (1)$$

108 where  $[O_3]_{crawl}$  and  $[O_3]_{out}$  are the ozone concentrations (ppb) measured in the crawlspace and 109 outdoors respectively;  $f_{crawl}$  and  $f_{out}$  are the fraction of airflow into the living space from the 110 crawlspace and outdoors, respectively; ACR is the air change rate of the living space (h<sup>-1</sup>), and 111  $k_{O_3}$  is the first-order chemical loss rate coefficient of ozone in the living space (h<sup>-1</sup>). In Eq. 1, 112 ozone loss across the building envelope through intended and unintended openings is neglected 113 (28). Rearranging Eq. 1, we can estimate the overall chemical loss rates of ozone  $L_{O_3}$  (ppb/h) as 114 follows:

115 
$$L_{o_3} = k_{o_3} [O_3]_{in} = (f_{crawl} [O_3]_{crawl} + f_{out} [O_3]_{out} - [O_3]_{in}) ACR - \frac{d[O_3]_{in}}{dt}.$$
 (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 spaceresolved 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<sup>-1</sup>, and the overall best-fit  $k_{O_3}$  value is 125 1.3 h<sup>-1</sup>. These values are at the lower end of reported ozone decay rate coefficients in residences. For example, measured  $k_{O3}$  values varied from 1 h<sup>-1</sup> to 8 h<sup>-1</sup> in 43 homes in South California with 126 mean ( $\pm$  SD) of 2.8 ( $\pm$  1.3) h<sup>-1</sup> (2), and varied from 1.3 h<sup>-1</sup> to 6.0 h<sup>-1</sup> in 14 residences in China (1). 127 128 Note that our results were obtained under normal occupancy without manipulating indoor ozone, whereas the cited studies derived  $k_{O_3}$  by experimentally elevating ozone and then monitoring its 129 130 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  $C_8H_{13}^+$  ions and 4-OPA appears as the  $C_5H_9O_2^+$  ion (22). Measured signals of these ions might 138 139 also have contribution from other isomeric compounds. Below we show that the temporal pattern of indoor  $C_8H_{15}O^+$  and  $C_5H_9O_2^+$  signals is consistent with the dominant contribution 140 141 originating from 6-MHO and 4-OPA.

Figure 3 shows a one-week time series of  $C_8H_{15}O^+$  and  $C_5H_9O_2^+$  ions, as well as time series of factors that possibly influence indoor 6-MHO and 4-OPA, including occupancy, air change rates, indoor temperature, and indoor ozone concentration. Signals of both  $C_8H_{15}O^+$  and  $C_5H_9O_2^+$  ions in the kitchen and bedroom were more than an order of magnitude higher than outdoors, indicating strong indoor sources. A key feature of the time series is that higher indoor signals were typically observed during daytime when the air change rates and indoor ozone 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 ion signals of  $C_8H_{15}O^+$  and  $C_5H_9O_2^+$  observed in these cases is consistent with theoretical 150 151 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 available for ozonolysis), elevated  $C_8H_{15}O^+$  and  $C_5H_9O_2^+$  signals were observed despite the 154 155 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.

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

173 data subject to the constraint that indoor temperature is restricted to the range 20.5-23.5 °C to 174 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 175 176 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  $C_8H_{15}O^+$ 177 from first-order ozone reaction (k), is  $0.018 \text{ h}^{-1}$ . The fitted intercept, corresponding to ozone-178 179 independent baseline emission rate  $(S_0)$ , is 0.0072 ppb/h. A striking feature in Figure 4A is that 180 the baseline emission  $S_0$  (intercept) was small compared with the range of ozone-dependent 181 production  $k[O_3]_{in}$  (e.g., an increase by 0.18 ppb/h for 10 ppb of indoor ozone). This feature 182 quantitatively demonstrates that 6-MHO production from ozone chemistry was the dominant 183 source of measured  $C_8H_{15}O^+$  signals. A similarly strong dependence of source strength on ozone 184 was also found for  $C_8H_{13}^+$  (the other product ion of 6-MHO) and  $C_5H_9O_2^+$  (4-OPA), as presented 185 in Figure S2.

186 Figure 4A also explores the role of occupancy. Since only two adults lived in the house, 187 two or fewer persons were typically present in the living space, with some exceptions due to 188 visits of guests (particularly during the party). Data for the presence of more than 4 persons are 189 labeled in Fig. 4A. Although there were only four such points, they each lie above the general 190 trend line. Such occupancy dependence is consistent with expectations for squalene ozonolysis: 191 more people present in the house would mean more squalene available for ozone reaction, 192 leading to a larger k value. The role of occupancy is also evident in the spatial distribution of 193 ozone oxidation products associated with squalene. Table 1 shows that ions associated with 6-194 MHO and 4-OPA were much higher in the routinely occupied spaces (kitchen and bedroom) than 195 in rarely occupied auxiliary spaces (crawlspace and attic). Given the regular movement of air 196 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.

202 Figure 4B explores the role of occupancy for cases with a low occupancy level by 203 analyzing a subset of data from Figure 4A with indoor ozone concentration restricted to the 204 range 2-4 ppb. This ozone range was chosen because it covered most data points during periods 205 with zero occupancy. Figure 4B plots the source strength of  $C_8H_{15}O^+$  signals as a function of 206 occupancy (left frame for 0 <occupancy  $\le 2$  persons) and then the elapsed time since the house 207 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 208 209 data. For periods with between one and two occupants, the source strength averaged 0.056 ppb/h 210 with a standard deviation of 0.014 ppb/h. However, when the house was unoccupied (right 211 frame),  $C_8H_{15}O^+$  source strength slowly decreased with the duration of vacancy. The source 212 strength was about  $0.045 \pm 0.016$  ppb/h when the house was unoccupied for less than 1 h and 213 diminished by about half, to  $0.023 \pm 0.003$  ppb/h, when the unoccupied period of time increased 214 to ~130 h. Given that the reaction between ozone and 6-MHO is fast (second-order rate coefficient of  $3.9 \times 10^{-16}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> (30)), along with the small intercept in Figure 4a (baseline 215 216 emission level of 0.007 ppb/h), it is unlikely that surface reservoirs were a substantial source of 217 6-MHO during the unoccupied period. Instead, the more probable explanation is that ozone 218 reacted with squalene in skin flakes and skin oils that had accumulated on exposed surfaces in 219 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 220

(~ 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).

224 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 225 226 any source-strength dependence on occupancy level under the normally low occupancy (Fig. 4B 227 Left). That is, the off-body squalene contributes substantially to the total squalene-associated 228 ozone reactivity when the house is normally occupied by 2 (or fewer) occupants, such that the 229 influence of occupancy changes is attenuated. With this interpretation, the contribution of on-230 body squalene became substantial only in the rare presence (during this monitoring campaign) of 231 multiple guests.

232 The large contribution of off-body skin oils is also consistent with high effective yields of 233 6-MHO and 4-OPA in this study. The effective yields of 6-MHO and 4-OPA (Table 1) were 234 estimated by taking the ratio of (a) the total production rate coefficient  $\sum k_i$  of corresponding 235 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 236 237 the total ozone loss in the house on a molecular basis and provide overall characterization of 238 indoor ozone chemistry without differentiating among organic/inorganic precursors, 239 primary/secondary reactions, or heterogeneous/gas-phase reactions. That said, we expect most 240 surfaces to be covered with thin films that result from the accumulation over time of semivolatile 241 organic compounds and airborne particles (4, 31, 32). The house where the sampling occurred 242 was built in the 1930s and there had been no recent renovation or refurnishing of note. As has 243 been demonstrated for freshly cleaned windows (33) and vertically positioned glass capillary 244 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<sup>3</sup> (floor area  $\sim$  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 is as high as that reported for a simulated aircraft cabin of 28.4 m<sup>3</sup> in the presence of 16 subjects 248 249 (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 examination the result seems reasonable. Two humans in  $350 \text{ m}^3$  of living space are estimated to 257 remove ozone with a first-order rate constants of ~  $0.2 \text{ h}^{-1}$  (18), which accounted for about one-258 sixth the central tendency for  $k_{O_3}$  in Figure 2 (1.3 h<sup>-1</sup>). While we do not know the contribution to 259  $k_{O3}$  of skin flakes and skin oils accumulated on "off-body" surfaces, circumstantial evidence 260 261 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  $32 \mu g/g$  (35). Squalene is semivolatile, with a vapor pressure of  $3.7 \times 10^{-7}$  Pa at 25 °C (37), and so sorption to indoor 264 265 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

269 on various indoor surfaces in a classroom and proposed that human skin lipids could be a major 270 source (4). Based on decrease of 6-MHO source strength during the vacant period, we roughly 271 estimated the lifetime of off-body squalene was ~400 h and the total amount of off-body 272 squalene present was ~0.36 mmol (equal to 150 mg) (SI Appendix). The associated surface C=C 273 concentration would be ~ 2  $\mu$ mol/m<sup>2</sup>, largely consistent with the observations of Deming and 274 Ziemann (4).

275 Previous indoor studies in simulated microenvironments as well as a classroom have 276 highlighted the importance of ozone reactions with on-body squalene (14, 21, 22). The current 277 finding identifies a substantial contribution of off-body skin lipids to ozone chemistry in a 278 normally occupied residence. The new information about factors that can materially influence 279 exposure to ozone and its byproducts merits further investigation. Contributions of off-body skin 280 oils might also influence densely occupied environments, in addition to residences. For example, 281 Tang et al. estimated occupant and non-occupant VOC source strengths in a university classroom 282 in California (38). Their results indicated a non-occupant source strength of about 25% of the 283 occupant source for 6-MHO, and about 80% for 4-OPA. It is plausible that these contributions 284 resulted from ozonolysis of off-body squalene that originated from skin oils and skin flakes of 285 classroom occupants. Additionally, our results call for caution in extrapolating simulated 286 scenarios of ozone chemistry in test houses or chambers. That is, because such facilities are not 287 routinely occupied, they lack an important element of real-world settings - soiling of indoor 288 surfaces by the skin oil and skin flakes of occupants.

289 Non-targeted analysis of ozonolysis products. To explore whether other indoor VOCs 290 might be substantially associated with ozonolysis, we developed and applied a systematic 291 screening approach. As a screening index, we computed a dimensionless source strength ratio, 292 defined as the increase in source strength for a fixed increment (10 ppb) of ozone concentration

293  $(\Delta S_{10 \text{ ppb } O_3})$  divided by the baseline source strength (S<sub>0</sub>). A higher value of  $\Delta S_{10 \text{ ppb } O_3} / S_0$ 

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  $\Delta S_{10 \text{ ppb } O_3}$  is extracted from the fitted slope.

299 A confounding factor in the evaluation of this index is ventilation. Due to effects of 300 indoor surface reservoirs, an increase of ventilation rate was associated with a less-than-301 anticipated decrease of indoor VOC signals (39, 40), and, hence, an apparent increase of net 302 source strength (Fig. S3). Considering that indoor ozone levels tended to be higher with higher 303 ventilation rates (Fig. 3), this effect can create a correlation between indoor source strength and 304 ozone, even for compounds whose constituents do not have oxygen and therefore clearly did not 305 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<sup>-1</sup> and 0.25 h<sup>-1</sup> ( $C_{1 h^{-1}} / C_{0.25 h^{-1}}$ ) — 306 307 which is an indicator of the surface-reservoir effect. Values of this index for VOC signals were 308 obtained from linear fits of indoor-outdoor concentration difference versus air change rate at 309 20.5-23.5 °C, after removing outliers.

Figure 5 shows a scatter plot of  $\Delta S_{10 \text{ ppb } O_3} / S_0$  versus  $C_{1 \text{ h}^{-1}} / C_{0.25 \text{ h}^{-1}}$  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  $C_{1 \text{ h}^{-1}} / C_{0.25 \text{ h}^{-1}}$ 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  $\Delta S_{10 \text{ ppb } O_3} / S_0$  ranged from 0.6 to 26.

319 Most data points in Fig. 5 are distributed along a line with a positive slope; other points lie above the line. The line represents a lower bound of  $\Delta S_{10 \text{ ppb } O_2} / S_0$  for a given  $C_{1 \text{ h}^{-1}} / C_{0.25 \text{ h}^{-1}}$ , 320 321 likely corresponding to the extent of  $\Delta S_{10 \text{ ppb } O_2}$  /  $S_0$  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 correspond to relatively high volatility species  $-C_3H_4N^+$ ,  $C_5H_5O_2^+$ ,  $C_3H_5O^+$ ,  $CH_3O^+$ , and 324  $CH_5O^+$  — whereas the highest five are for species with lower volatility —  $C_{15}H_{27}N_2^+$ ,  $C_9H_{15}O_2^+$ , 325  $C_7H_{11}O^+$ ,  $C_{15}H_{23}^+$ , and  $C_8H_{17}O_2^+$ . Secondly, all values of  $C_{1h^{-1}}/C_{0.25h^{-1}}$  on the line are less than 326 327 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 signals,  $C_8H_{15}O^+$  and  $C_8H_{13}^+$  attributed to 6-MHO exhibited a notably high  $\Delta S_{10 \text{ ppb } O_3}/S_0$  value 332 above 20. Other VOC signals well above the line (i.e., above the grey region) include  $C_5H_9O_2^+$ 333 attributable to 4-OPA,  $C_9H_{17}O^+$  and  $C_9H_{15}^+$  attributable to nonenal, and ions attributable to the 334  $C_8$ - $C_{12}$  saturated aldehdyes. As presented in Table 1, the total effective yield for all identified 335 336 compounds is at least 12%. The effective yield of nonanal was the highest ( $\geq 3.5\%$ ), followed by 337 6-MHO (2.7%), 4-OPA (2.6%), decanal ( $\geq 1.3\%$ ), and nonenal ( $\geq 1.0\%$ ). 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

of oxygenated VOCs in this house, which was several hundred ppb (24). However, certain
products may contribute even at low abundances to odors (e.g., nonenal (41)) or irritation (e.g.,
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):≥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

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<sub>3</sub>O<sup>+</sup>) and hexanal (C<sub>6</sub>H<sub>13</sub>O<sup>+</sup>) 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

389 relatively small. Geranylacetone was also excluded in Figure 5, because its indoor-to-outdoor 390 ratio (indicator for strong indoor source) and mean-to-median ratio did not reach the selection 391 criteria. Even if we relax the data constraint to include the product ion of geranylacetone in the 392 analysis (Figure S4), the ion lies in the grey region and is characterized by a high value of  $C_{1h^{-1}}/$ 393  $C_{0.25 \text{ h}^{-1}}$ . A probable interpretation is that the stickiness of geranylacetone to indoor surfaces 394 strongly interferes with our ability to discern its relationship to ozone-initiated chemistry using 395 our approach. Given the presence of these and other compounds which can be contributed by 396 ozone chemistry but did not emerge as apparent ozone byproducts, the actual total yield of 397 volatile organic products from ozone chemistry in the house can be several times higher than the 398 summed effective yield of all identified compounds reported here. 399 To summarize, the results presented in this paper represent the first quantitative 400 characterization of ozone-initiated chemistry in a normally occupied residence. We identified a 401 range of VOCs that had strong contributions from indoor ozone chemistry (Fig. 5), even though 402 the house we studied had both low indoor ozone concentrations (Fig. 1) and a low indoor ozone 403 loss rate (Fig. 2). Being able to elucidate how residential VOC composition is altered by ozone-404 initiated chemistry substantiates prior laboratory-based investigations. It is important to 405 recognize that the health effects associated with ambient ozone might be materially influenced 406 by the products of indoor ozone chemistry. Of concern in this regard are not only those species 407 characterized here, but also other potentially toxic products known to be a consequence of 408 ozonolysis, but which our instrumentation is incapable of detecting, such as secondary ozonides, 409 hydroperoxides, and epoxides (48, 49).

410

## 411 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 occupants gave informed consent for this study, which was approved by the Committee for 420 421 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  $\sim 5$  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<sup>+</sup>, but fragmentation can also occur. In total, 218 VOC signals (organic ion

- 436 formulas after combining isotopic ions and some known fragment ions) were extracted to
- 437 represent measured VOC speciation across the campaign (24). Depending on sample air
- 438 composition, a VOC signal might be dominantly attributed to one VOC species, and might be
- 439 contributed by a few species. Airborne concentrations (in part per trillion/billion by volume,
- 440 ppt/ppb) were estimated for individual VOC signals as described in SI Appendix.
- 441 Data associated with this paper is provided in Dataset S1.

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### ORCID

Yingjun Liu https://orcid.org/0000-0001-6659-3660 Pawel K. Misztal https://orcid.org/0000-0003-1060-1750 Caleb Arata https://orcid.org/0000-0002-0170-8794 Charles J. Weschler https://orcid.org/0000-0002-9097-5850 William W. Nazaroff https://orcid.org/0000-0001-5645-3357 Allen H. Goldstein https://orcid.org/0000-0003-4014-4896

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### **List of Figures**

Figure 1. Diel variation of (top) ozone concentrations in various locations of the studied house, (middle) indoor ozone concentration in the living space normalized by outdoor concentration (I/O), and (bottom) apportionment of air flowing into the living space, between directly from outdoors and via the crawlspace. Data are shown for normally occupied period averaged during the five-week-long space-resolved measurement mode. The solid lines, respectively, represent medians; the shaded regions represent the corresponding interquartile ranges.

**Figure 2.** Scatter plot of the indoor chemical loss rates of ozone  $L_{O_3}$  (ppb/h) versus the livingspace ozone concentration  $[O_3]_{in}$  (ppb). The loss rate,  $L_{O_3}$ , was calculated using Eq. 2 based on the mass balance of ozone in the living space with 2-h resolution. Data are shown for times when the outdoor fraction of total airflow into the living space ( $f_{out}$ ) is greater than 0.6. The solid orange line represents the best linear fit to the data. Dashed orange lines have slopes of 0.8 and 2.0 h<sup>-1</sup>, respectively.

- **Figure 3.** Time series of VOC signals that might be attributed to products from squalene ozonolysis and possible influencing factors. Panels from top to bottom show occupancy (number of persons present indoors), air change rate (ACR; h<sup>-1</sup>), indoor temperature (T; °C), ozone concentration (ppb),  $C_8H_{15}O^+$  signal (ppb), and  $C_5H_9O_2^+$  signal (ppb).  $C_8H_{15}O^+$  and  $C_5H_9O_2^+$  ions correspond to the pronated ions of 6-MHO ( $C_8H_{14}O$ ) and 4-OPA ( $C_5H_8O_2$ ) without fragmentation, respectively.
- Figure 4. Dependence of  $C_8H_{15}O^+$  (6-MHO) source strength on (A) indoor ozone concentration and (B) occupancy. Panel A shows all available data using 2-h resolution and restricted to an indoor temperature range of 20.5-23.5 °C. Panel B uses a subset of

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  $2 \ge \text{occupancy} > 0$  (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 ( $\Delta S_{10 \text{ ppb } \text{O}_3}/S_0$ ); and the *x* axis is an indoor concentration ratio, defined as concentration at an air change rate of 1 h<sup>-1</sup> divided by that at 0.25 h<sup>-1</sup> ( $C_{1 \text{ h}^{-1}}/C_{0.25 \text{ h}^{-1}}$ ). 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.











	VOC signals		Mean mixing ratio d (ozone in ppb; VOC signals in ppt)						Derived parameters <sup>e</sup>			
	lonª	Species <sup>b</sup>	Outdoor	Kitchen	Bedroom	Crawlspace	Basement	Attic	<i>k</i> (h <sup>-1</sup> )	$\Delta S_{10 \text{ ppb } O_3} / S_0$	$C_{1 h^{-1}}/C_{0.25 h^{-1}}$	Yield <sup>f</sup>
Ozone			23	4.6	3.8	3.4	9.9	4.5				
PTR	C₅H9O2⁺	4-OPA	39	400	420	56	190	240	0.034	10	1.04	2.6%
	C <sub>8</sub> H <sub>15</sub> O⁺	6-MHO	6	180	190	17	58	94	0.018	26	1.21	2.7%
	C <sub>8</sub> H <sub>13</sub> +	6-MHO ∘	7	160	170	19	59	100	0.016	23	1.29	
	C <sub>8</sub> H <sub>17</sub> O⁺	Octanal	4	120	130	12	31	77	0.008	3.6	0.72	≥0.6%
	C9H17O+	Nonenal	4	82	85	9	24	44	0.007	10	1.10	≥1.0%
	$C_9H_{15}$ +	Nonenal °	5	71	65	9	25	30	0.006	13	1.37	
	C9H19O⁺	Nonanal	3	370	370	21	98	160	0.033	10	1.03	≥3.5%
	$C_9H_{17}$ +	Nonanal °	5	150	150	17	71	67	0.012	7.1	0.97	
	$C_{10}H_{21}O^{\scriptscriptstyle +}$	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%

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

<sup>a</sup> The PTR ions presented here are those well above the baseline in Fig. 5.

<sup>b</sup> 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.

<sup>c</sup> 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.

<sup>d</sup> Mean mixing ratio during occupied period when in space-resolved measurement mode.

<sup>e</sup> See detailed description of the parameters in the main text.

<sup>f</sup> 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).