The human oxidation field

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Total number of authors:
12

Published in:
Science

Link to article, DOI:
10.1126/science.abn0340

Publication date:
2022

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
Abstract:

Hydroxyl radicals (OH) are highly reactive species that can oxidize most pollutant gases. In this study, high concentrations of OH radicals were found when people were exposed to ozone in a climate-controlled chamber. OH concentrations calculated by two methods using measurements of total OH reactivity, speciated alkenes, and oxidation products were consistent with a chemically explicit model. Key to establishing this human induced oxidation field is 6-MHO, which forms when ozone reacts with the skin-oil squalene and subsequently generates OH efficiently through gas-phase reaction with ozone. A dynamic model was used to show the spatial extent of the human generated OH oxidation field and its dependency on ozone influx via ventilation. This finding has implications for the oxidation, lifetime, and perception of chemicals indoors, and ultimately human health.

One-Sentence Summary: Measurements and modeling reveal that human exposure to ozone generates a field of OH radicals indoors.
Main Text

North Americans and Europeans spend on average ~90% of their time indoors (including home, workplace and transport) (1, 2). Within this enclosed space, occupants are exposed to a multitude of chemicals from various sources, including outdoor pollutants penetrating indoors, gaseous emissions from building materials and furnishings, and products of human activities such as cooking and cleaning (3). In addition, the occupants themselves are a potent mobile source of gaseous emissions from breath and skin (human bioeffluents), as well as primary and secondary particles (4). Characterization of these indoor sources, and the main indoor removal mechanisms are key to understanding indoor air quality (5).

Chemical removal of gas-phase species in outside air during daytime is mostly initiated by hydroxyl (OH) radicals, which are formed when a short wavelength photolysis product of ozone (an excited oxygen atom, O (1D)) reacts with water. Longer wavelength photolysis of nitrous acid (HONO) and formaldehyde (HCHO) also provide small additional OH sources outside, as does the light independent ozonolysis of alkenes via Criegee intermediate formation (6). In contrast, the indoor environment is less influenced by direct sunlight, in particular UV, which is largely filtered out by glass windows, so that primary production of OH indoors via O (1D) is negligible. Although some OH can be generated by longer wavelength artificial light, by photolysis with natural light of formaldehyde and HONO if present, ozone (O3) entering the building from outside is generally considered to be the principle oxidant indoors (7). Nevertheless, previous studies have highlighted the potential importance of alkene ozonolysis (8–11) in generating OH via Criegee intermediates in indoor environments, particularly when reactive molecules such as limonene from air fresheners or cooking are abundant. Previous estimates and measurements of indoor OH concentrations have ranged between 10^5-10^7 molecules cm^{-3}, which is significantly higher than outdoor nighttime concentrations, and comparable to daytime atmospheric OH concentration levels in some regions (8–15).

None of the aforementioned model or measurement studies considered occupied indoor environments, and therefore the underlying chemical influence of human beings. Yet with every breath, humans exhale reactive alkenes such as isoprene, which can oxidize to further alkenes such as methyl vinyl ketone (MVK) and methacrolein (MACR) (16). Moreover, O3 reacting at the skin surface with the skin oil squalene (C_{30}H_{50}), a triterpene responsible for almost 50% of the unsaturated carbon atoms on human skin, releases a host of alkene containing compounds to the air, including geranyl acetone, 6-methyl-5-hepten-2-one (6-MHO), OH-6-methyl-5-hepten-2-one
(OH-6-MHO), 4-methyl-8-oxo-4-nonenal (4-MON), 4-methyl-4-octene-1,8-dial (4-MOD) and trans-2-nonenal (17). These species have the potential to react further in the gas phase, either to generate OH through reaction with O$_3$, or to deplete OH through direct reaction with the alkene. Therefore human beings have the potential to profoundly impact the oxidative environment indoors, particularly in areas of high occupancy (18), larger exposed body surface, and higher air temperature and humidity (19).

In this study, measurements were conducted in a climate controlled stainless-steel chamber (see Fig. 1) with three different groups of four adult subjects on four separate days (including two replicates from the same group) (20). The air change rate (ACR, 3.2 h$^{-1}$) and O$_3$ concentration (100 ppb at the inlet, 35 ppb indoors) used in this experiment were chosen for reproducing a realistic scenario based on the expected O$_3$ decrease due to occupancy (21). From this data, we have determined the indoor concentrations and spatial distribution of OH radicals generated by human beings upon exposure to O$_3$. This oxidative field is produced in isolation from other indoor sources or sinks of OH. A steady state approach was applied, combining measured total OH reactivity (OH loss frequency in s$^{-1}$), measured concentrations of compounds containing an alkene double bond, and available literature values of OH yields from O$_3$/alkene reactions. For comparison, the OH levels were also determined by an independent method using isoprene and its oxidation products. In the final step, the empirically derived OH levels and measurements were compared to a detailed multiphase chemical kinetic model, and these results were used to simulate high spatial and time-resolved OH distributions in a room using a computational fluid dynamics model. In order to investigate the existence and variability of spatial concentration gradients we tested four scenarios: (A) an evaluation of the experimental results using the same underfloor air distribution from a perforated floor along with intensive air mixing at the average indoor O$_3$ concentration of 35 ppb as in the experiment, (B) the same ventilation condition of the experiment without any mixing fans at the indoor O$_3$ concentration of 35 ppb to simulate a residential condition, (C) air jets supplied at ceiling height and the indoor O$_3$ concentration of 35 ppb to simulate an office condition, (D) same as (C) except the indoor O$_3$ concentration was 5 ppb.

1. Results

1.1 Total OH reactivity of human emissions
Fig. 2 shows the OH loss frequency (total OH reactivity) measured directly in the chamber. The total OH reactivity of the gas phase human bioeffluents was on average $8 \pm 4$ s$^{-1}$ in the absence of O$_3$, and $34 \pm 16$ s$^{-1}$ when O$_3$ was present (mean value ± measurement error, determined at equilibrium in the last 15 minutes before volunteers left the chamber). In the absence of O$_3$, the dominant OH sinks were reactive compounds in human breath (e.g. isoprene 64%), whereas in the presence of O$_3$, the dominant OH sinks were reactive compounds generated by O$_3$ reactions with skin lipids such as 6-MHO (31%), 4-OPA (6%) and the sum of other aldehydes (29%) (19, 22). Fig. S1 shows the fractional contributions to OH reactivity for the various measured species. A comparison between measured and calculated reactivity from the individually measured VOCs (Fig. 2) showed that the main reactive VOCs present in the chamber were quantified within the method uncertainties (total uncertainty for the measured OH reactivity = 48%; total uncertainty for the calculated OH reactivity = 30%) (19, 22). This was a prerequisite for applying the steady-state method to determine OH using total OH reactivity and the combined OH sources.

1.2 Hydroxyl radical concentration from the steady-state method

Table 1 reports the predominant alkenes of human origin measured in the presence of O$_3$, their OH production rates and resulting OH concentrations at steady state (see methods equation 5). The empirically determined OH concentration from the four experiments involving three different groups of four adult human subjects was on average $7.1 \pm 2 \times 10^5$ molecules cm$^{-3}$, while replicate experiments on the same group of subjects yielded $7.16 \pm 0.07 \times 10^5$ molecules cm$^{-3}$ (mean value±1σ). The values assume that the room is uniformly well mixed, therefore the result represents the mean OH concentration within the chamber under the prevailing conditions: ventilation rate = 3.2±0.11 h$^{-1}$, O$_3$ = 35 ppb with four people present. (Note: O$_3$ =100 ppb at inlet, and 95 ppb in chamber before people entered (20)). For one of the four experimental days, Fig. 2 shows a time series of the calculated OH concentration from the onset of its generation (when O$_3$ is introduced into the chamber) to when the human bioeffluents reached steady-state conditions. Detailed information on the measured alkene concentrations, their reaction rate coefficients and OH yields for the same experiment are provided in Table S1, while Fig. S2 shows the simplified reaction scheme of 6-MHO ozonolysis and respective products yields. The most important alkene for generating OH was found to be 6-MHO, followed by geranyl acetone, OH-6-MHO, limonene, 4-MON and 4-MOD (Fig. S3). In contrast, isoprene (OH yield 0.27), and the products resulting from isoprene reacting with OH (MVK+MACR) made a negligible contribution. Most of the
alkenes responsible for generating OH result from the ozonolysis of skin lipids. Interestingly, the same molecule, 6-MHO, is both the strongest chemical source of OH radicals (Fig. S3) and the predominant sink for OH under these conditions (Fig. S1).

1.3 Hydroxyl radical concentration from the precursor-product method

Fig. 2 also shows the concentration of OH determined via an alternative approach (see methods equation 6), namely using a precursor (isoprene) and product (m/z 71.049, here reported as m/z 71, representing the sum of the products generated from the reaction between isoprene and OH, considered here as solely methyl vinyl ketone (MVK) + methacrolein (MACR), see methods and supplement (23)). In the presence of O₃, a ~4-fold increase of the m/z 71 mixing ratio was observed (Fig. S4), which is primarily due to isoprene oxidation by OH (isoprene fractional loss=0.16%) with a small contribution from gas phase ozonolysis (isoprene fractional loss=0.012%). The mean OH concentration obtained is 1.2 ×10⁶ molecules cm⁻³, which is close to, but higher than, the value obtained from Eq. (5) (Fig. 2). The agreement between measured and calculated OH reactivity reported in Fig. 2 precludes the possibility that an unmeasured alkene is the cause. A second possibility is that the OH yields and rate coefficients used in Eq. (6), overestimate the OH radicals generated from human emissions. A sensitivity test (Table S2) was therefore conducted on the result from Eq. (6) where each input variable was varied within its confidence interval. This indicated that the variables most influencing the OH concentration are the isoprene oxidation product yields (relative change 19-31%) and the ratio between isoprene oxidation products and isoprene concentrations (relative change 19%). Therefore, any fragment interfering in the measurement of m/z 71 would result in a higher OH concentration as determined through Eq. (6). However, in a separate experiment it was noted that some m/z 71 signal was generated from the O₃ exposure of four clean shirts (without people). Detailed results on the OH reactivity of people wearing short and long clothing and solely clothing were discussed in Zannoni et al. (19). We therefore deduce that the precursor-product method overestimated the OH radical abundance due to interfering emissions of the product from the clothing. Nevertheless, it should be noted that there is broad agreement between the two OH estimates and that the values derived for human generated OH are substantial and highly significant in the indoor environment.

1.4 Modelled hydroxyl radical field in the occupied environment
The measured alkene concentrations, OH concentration and OH reactivity were simulated with the
detailed kinetic model KM-SUB-Skin-Clothing (24, 25) (Fig. S5 and Fig. S6). Outputs from the
kinetic model were then used in a computational fluid dynamics (CFD) model to simulate the
human OH radical field (26, 27). The OH radical field in the chamber due to the presence of the
people within was determined for four different conditions. The results of OH reactivity and OH
concentration under steady-state conditions with O₃ present (before the occupants left the
chambers, at 360 min elapsed time from the beginning of the experiment) are reported in Fig. 3
for all the four simulations.

The first condition (Fig. 3A) allows direct comparison with the measured results: air and O₃ are
supplied from a simulated perforated floor and two virtual fans mix the air inside the chamber (c.f.
Fig. 1). The maximum air velocity occurs at the chamber walls and the maximum air temperature
occurs at the human body surface, while around the subjects the air velocity and temperature are
uniformly distributed (Fig. S7). With O₃ present, the largest source of OH reactivity is the human
body surface (Fig. 3a), with O₃-squalene generated carbonyls such as 6-MHO the predominant
contributors to the OH reactivity. The maximum modelled OH reactivity is 50 s⁻¹, while the mean
chamber value is ~35 s⁻¹, in good agreement with the measured value. The spatial distribution of
the OH radicals generated by the occupants have the opposite distribution to the OH reactivity;
their concentration is highest in the room air and lowest at the body surface (Fig. 3b). The mean
OH concentration under steady-state condition is $1 \times 10^6$ molecules cm⁻³, which agrees well with
the values inferred from the two independent empirical methods described above (sections 1.2 and
1.3).

The second condition investigates the impact of the reduced air mixing by suppressing the virtual
fans and simulating a more realistic scenario of a typical residence without active mixing (Fig.
3B). A buoyancy-driven flow pattern then developed due to the low-momentum air supply from
the floor level and convective flow generated by the heat of the seated occupants. In this case, air
movement is mainly driven by temperature gradients associated with indoor heat sources as can
be seen in Fig. S9, which shows the corresponding air temperature and velocity distributions.
Without active air mixing, both air temperature and velocity have a clear vertical gradient, with
the room air temperature being highest near the chamber ceiling, and the maximum air speed
around the body surface of the occupants (Fig. S9). Therefore a strong vertical gradient of OH
reactivity is generated from the floor (low) to ceiling (high), as shown in Fig. 3C. Air temperature,
velocity and airflow pattern determine the evolution of the OH reactivity field shape, forming a
reactive cloud around and above the mouth of the occupants that prolongates above the head of the occupants (Fig. 3c) in the convectively rising air plume. Accordingly, the vertical profile of OH radical concentration is opposite to that of OH reactivity, showing a maximum at the chamber floor (Fig. 3d). The maximum modelled OH reactivity and OH concentration values were 50 s\(^{-1}\) and 2 \(\times\) 10\(^6\) molecules cm\(^{-3}\), respectively. Under such conditions, the lifetime of the OH radical is 20 ms above a person’s head, increasing to 100 ms towards the floor. The third condition investigates how the vertical gradient is affected by the location of the incoming air and O\(_3\) source. Air and O\(_3\) are supplied from a jet diffuser at ceiling height, as in a realistic scenario of a typical office. In this case the maximum OH reactivity is again reached at the body surface and above people’s heads, with minimum levels close to the air-O\(_3\) inlet (Fig. 3e). The maximum OH concentration is now displaced to the air-O\(_3\) inlet, although still caused by the interaction of O\(_3\) with 6-MHO (Fig. 3f). The fourth case investigates the spatial gradient using the conditions applied in the third case but with lower indoor O\(_3\) concentration (5 ppb). This is the median reported O\(_3\) indoor concentration from a number of residences, schools and offices during occupancy (28). As shown in Fig. 3D, the OH reactivity (Fig. 3g) and OH concentrations (Fig. 3h) are both reduced to ~20 s\(^{-1}\) and ~3 \(\times\) 10\(^4\) molecules cm\(^{-3}\), respectively, while the spatial gradients are qualitatively very similar with the original simulations with higher O\(_3\).

In summary, in all the investigated conditions, human beings exposed to O\(_3\) generated an indoor OH oxidation field around them.

2. Discussion

This study has experimentally and theoretically determined that substantial OH concentrations are generated in indoor environments due to the presence of human beings and O\(_3\), with consistent results. Using an OH production rate based on measured alkenes and simultaneous direct measurements of OH reactivity, the steady-state approach yielded OH concentrations under equilibrium conditions of 7.1 \(\pm\) 2 \(\times\) 10\(^5\) molecules cm\(^{-3}\), while the precursor-product yielded 1.2 \(\times\) 10\(^6\) molecules cm\(^{-3}\). Under the conditions of the bare chamber experiments (3.2 \(\pm\) 0.11 h\(^{-1}\)ACR, ~35 ppb O\(_3\)), the oxidation field generated by one adult is ~1.8 \(\times\) 10\(^5\) molecules cm\(^{-3}\).

These results show that human beings exposed to O\(_3\) generate a significant OH oxidizing field around them. The OH radical levels are sufficiently high to outcompete the more abundant but slower ozone reactions that are currently assumed to dominate organic compound oxidation in the
indoor environment. Isoprene, for example, under this chamber’s experimental conditions is predominately oxidized by OH.

Interestingly, the OH concentrations derived in this study are of the same order of magnitude as the OH concentrations measured or modeled in previous indoor studies (8–15) conducted without people present (Table 2). This suggests that the OH oxidizing field strength generated by human occupants is comparable to that resulting from all other indoor sources of alkenes. In this context, it is important to note that human beings are mobile, and so represent a displaceable chemical source and oxidation field indoors. Furthermore, it is shown that within indoor environments, strong spatial gradients in OH concentration can develop, the direction depending on the location of the O_3 source and ventilation. Such pronounced spatial gradients have been reported in indoor experiments previously; with OH levels varying with degree of illumination (12), trace gases showing strong gradients around the breathing zone (29) and, during cooking with, markedly different VOC levels occurring between floor and ceiling (30). Under real world conditions, the occupied space can be influenced by additional heat sources such as from incoming light or hot cooking surfaces that will further impact the spatial gradients observed. Spatial and temporal scales of indoor constituents are modulated by rates of chemical reactions, surface interactions and building ventilation; short-lived compounds including OH radicals can exhibit sharp spatial gradients, as their temporal scales are determined mainly by reaction rates and only marginally affected by deposition and ventilation rates (31).

Key to the generation of OH around human beings is the presence of reactive alkenes generated from the reaction of O_3 with various components of skin oil (e.g. squalene), in particular 6-MHO, but also geranyl acetone, OH-6-MHO, 4-MON and 4-MOD. Due to its extremely rapid reaction with OH ($k_{6-MHO+OH}=1.57\times10^{-10}$ cm$^3$molecules$^{-1}$s$^{-1}$, which is faster than isoprene) and its high measured yield of OH upon ozonolysis (0.75 (32)), 6-MHO was found to be the most important OH source and OH sink. As such, it should be included in future modeling and measurement studies of indoor environments. Previous studies have measured or estimated the indoor OH concentration based on OH generated from the ozonolysis of alkenes from non-human sources (8–10) and OH produced from nitrous acid (HONO) photolysis (12, 14). Weschler and Shields focused on the importance of terpenes from scented products to generate OH in an indoor environment (8, 9) and Carslaw calculated that typically ~ 90% of OH indoors is produced from alkene ozonolysis while only ~ 10% is generated from HONO photolysis (13). Gomez Alvarez et al. showed that when sunlight shined directly into an unoccupied classroom, HONO photolysis
was the main source of OH indoors, measuring peaks of OH up to $1.8 \times 10^6$ molecules cm$^{-3}$ during the highest photolysis period ($12$). The relative importance of these human and non-human related OH sources will depend critically on the conditions of the specific indoor environment, including lighting, outdoor and indoor sources, temperature, humidity and, as demonstrated here, people. The human induced OH field will also interact with other indoor sources and surfaces, including emissions from floors, walls, furnishings and scented products (excluded on purpose in our study). In real world environments, O$_3$ can also react with squalene in settled dust, on skin flakes, and on skin oil soiled surfaces such as clothes, generating 6-MHO and further influencing the OH oxidation field, even without people being present. Liu et al. ($18$) showed such reactions are still detectable after five days without occupancy by measuring squalene oxidation products. Zhang et al. ($33$) have estimated the “off-body” skin oil contribution from the aforementioned experiment. Collectively, squalene and three squalene-derived oxidation products (which can be a source of secondary 6-MHO) contributed 2.7 µmol of double bonds per m$^2$ of surface in this residence. Previous studies have shown that exposure to natural light indoors has a large effect on OH generation ($12$). Carslaw simulated an OH concentration of $9 \times 10^4$ molecules cm$^{-3}$ for indoor winter conditions in a home environment with artificial light ($13$), which is similar to the value obtained from our study when O$_3$ was absent. However, such levels are small in comparison to the human induced concentrations found in our study when O$_3$ was present. The indoor O$_3$ concentration is therefore a critical parameter in determining the strength of the human generated oxidation field ($8$–$10$). This in turn is dependent on the outdoor O$_3$ concentration and ventilation rates of the indoor space. Real world indoor environments including offices and homes, typically have lower ventilation rates ($21$) than that of our study. Moreover, the availability of multiple surfaces for O$_3$ reactions provided by furnishings will further lower indoor O$_3$ concentrations below those used here ($7$). At an air change rate of 3 h$^{-1}$, one would expect indoor ozone concentrations that are roughly 50% of outdoor values. At an air change rate of 1 h$^{-1}$, one would expect indoor ozone concentrations that are roughly 25% of outdoor values ($21$). Hence, while an indoor ozone level of 40 ppb is high, it does occur when outdoor levels are high and the air change rate is moderate to high. Median ozone levels for residences, offices and classrooms are circa 5 ppb ($28$), this scenario is represented by the simulation of Fig. 3g & h. Therefore, the OH concentrations associated with the human oxidation field reported from our experimental case (Fig. 3a & b) likely represent upper limits. However, even with lower O$_3$ concentrations, substantial OH fields will
establish wherever humans are exposed to \( \text{O}_3 \), which is virtually all indoor and outdoor environments.

In addition to generating OH radicals, the reaction of ozone with skin surface lipids also produces nanocluster aerosols (34).

The human OH radical oxidation field may play an important role in the detection of chemical cues since oxidation gradients near the body surface can attenuate and transform odor signals, impacting odor perception. Indeed, it was recently shown that molecules that react rapidly with the OH radical are generally more sensitively detected by the human nose (35). Growing research is reporting the role of chemical signals in human communication (36).

In indoor environments, ozone reacts primarily with organic compounds that contain carbon-carbon double bonds. This is typically about 10% of the total number of organics detected in indoor air. The hydroxyl radical is a less discriminating oxidant and reacts rapidly with almost all organics present in indoor air. A number of the measured products cannot be explained by ozone chemistry; they can only be explained by hydroxyl radical chemistry. In essence, this study reveals a cascade of oxidation pathways leading to many more oxidation products (present at higher concentrations) than would be present if ozone were the sole oxidant.

The chemistry revealed in this study has health implications. These include the acute and chronic health impacts of certain OH-oxidation products whose toxicities have been evaluated (e.g., methacrolein (37)). However, there exists a large set of reaction products with unevaluated toxicities. Knowledge about this underlying chemistry and its products can guide us towards selecting compounds for which toxicity data should be generated. This group may include compounds that adversely impact human health. The fact that products are generated in the vicinity of the breathing zone (see Fig. 3) amplifies these concerns. Over the past decade, there have been significant advances in our knowledge of the products derived from indoor ozone chemistry (38).

Products of such chemistry include short lived species such as stabilized Criegee intermediates, hydroxyl radicals, hydroperoxyl radicals, and alkylperoxy radicals, as well as more stable products such as hydrogen peroxide, organic hydroperoxides, peroxy acids, organic nitrates, and secondary organic aerosols (39–41) (see extended discussion in the supplementary information). The interactions among the human oxidation field, the convective heat transfer (thermal plume), the chemical mass transfer around a human body, and the generation of a personal reactive cloud (42), warrants further research regarding the human health implications. The different conditions simulated in this study can be particularly useful to evaluate potential mitigation strategies.
This study has shown that in the presence of O$_3$, human beings both emit and oxidize chemical compounds in their immediate environment, a process that impacts all indoor environments.

References and Notes


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**Acknowledgments:** We are thankful to Sarka Langer for measuring NO. Nico Ziersen, Thomas Klüpfel and Rolf Hofmann are acknowledged for their support. We are thankful to the volunteers for participating in the study.

**Funding:** Alfred P. Sloan Foundation grant G-2018-11233 (JW, GB, PW), G-2019-12306 (MS, DR), G-2020-13912 (MS, DR).

**Author contributions:**
- Conceptualization: JW, GB, PW, CJW, NZ
- Methodology: JW, NZ, CJW, MS, PSJL, DR, YW, GB, PW
- Investigation: NZ, JW, PSJL, MS, YW, DR, CJW, NW, LE, ML, GB, PW
- Visualization: NZ, JW, PSJL, MS, YW, DR
- Funding acquisition: JW, GB, PW, MS, DR
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- Supervision: NZ, JW, MS, DR
- Writing – original draft: NZ, JW
- Writing – review & editing: all

**Competing interests:** Authors declare that they have no competing interests.

**Data and materials availability:** All data are available in the main text or the supplementary materials

**Supplementary Materials**
- Materials and Methods
- Supplementary Text
- Figs. S1 to S9
- Tables S1 to S5
- References (1–62)
- Data S1
Table 1. Hydroxyl radical production rates of isoprene, 6-MHO, OH-6-MHO, limonene, MVK+MACR, 4-MON, 4-MOD, geranyl acetone and trans-2-nonenal (molecules×cm$^{-3}$×s$^{-1}$) and OH concentrations (molecules×cm$^{-3}$) obtained with the steady-state method from measurements of alkenes, and OH reactivity of four adult volunteers. The data reported in each column were obtained from experiments on separate days, under the same conditions, within the same campaign. A1, A2 and A3 indicate different groups of subjects. A2(1) and A2(2) were replicates of the same experiment with the same group of volunteers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>A1</th>
<th>A2(1)</th>
<th>A2(2)</th>
<th>A3</th>
</tr>
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<tbody>
<tr>
<td>Isoprene</td>
<td>3.61×10$^5$</td>
<td>3.06×10$^5$</td>
<td>3.07×10$^5$</td>
<td>4.10×10$^5$</td>
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<td>6-MHO</td>
<td>1.22×10$^7$</td>
<td>1.57×10$^7$</td>
<td>1.66×10$^7$</td>
<td>1.82×10$^7$</td>
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<tr>
<td>OH-6-MHO</td>
<td>1.67×10$^6$</td>
<td>1.72×10$^6$</td>
<td>2.35×10$^6$</td>
<td>2.72×10$^6$</td>
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<td>Limonene</td>
<td>7.52×10$^5$</td>
<td>below LoD</td>
<td>8.78×10$^5$</td>
<td>7.28×10$^5$</td>
</tr>
<tr>
<td>MVK+MACR</td>
<td>7.59×10$^3$</td>
<td>5.46×10$^3$</td>
<td>8.34×10$^3$</td>
<td>1.17×10$^4$</td>
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<tr>
<td>4-MON</td>
<td>below LoD</td>
<td>5.25×10$^4$</td>
<td>5.61×10$^5$</td>
<td>2.87×10$^5$</td>
</tr>
<tr>
<td>4-MOD</td>
<td>below LoD</td>
<td>below LoD</td>
<td>6.05×10$^5$</td>
<td>3.40×10$^5$</td>
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<td>Geranyl acetone</td>
<td>1.96×10$^6$</td>
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<td>2.44×10$^6$</td>
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<tr>
<td>Trans-2-nonenal</td>
<td>1.17×10$^5$</td>
<td>9.39×10$^4$</td>
<td>1.76×10$^5$</td>
<td>1.42×10$^5$</td>
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<tr>
<td>OH</td>
<td>4.2±1×10$^5$</td>
<td>7.2±2×10$^5$</td>
<td>7.1±2×10$^5$</td>
<td>9.7±3×10$^5$</td>
</tr>
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Fig. 1. (a) Photo-schematic of the occupied stainless steel climate chamber at the Technical University of Denmark (DTU) and (b) framework of the experiment used for the CFD modeling. Ambient air is introduced through the entire floor and exhausted via one air outlet in the ceiling.
Fig. 2. Time series of OH concentration (top), and measured OH reactivity (OHR_meas), calculated OH reactivity (OHR_calc), and ozone (bottom) for one selected experiment. OH concentration was determined with two independent methods, OH_1 (steady-state method), from the OH production rate through ozonolysis of alkenes and the measured total OH reactivity; and OH_2 (precursor-product), using the lifetime of isoprene.
Fig. 3. Spatial distribution of OH reactivity and OH concentration at elapsed time 360 min (before people left the chamber). Fig 3a & b: simulation of the experiment with two indoor mixing fans and inflow through the floor to match the experimental conditions. Fig 3c & d: simulation with no virtual mixing by fans for typical conditions. Fig 3e & f: simulation of inflow from an upper supply inlet of a wall. Fig 3g & h: simulation with lower (5 ppb) ozone from an upper supply inlet.
Table 2. Comparison between this study and previous direct and indirect measurements and estimates of OH concentration in indoor environments.

<table>
<thead>
<tr>
<th>[OH] [molecules cm(^{-3})]</th>
<th>[O(_3)]* [ppb]</th>
<th>Method</th>
<th>Notes</th>
<th>Reference</th>
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<tr>
<td>7.1±2 × 10(^5)</td>
<td>35, 100</td>
<td>Measured OH reactivity</td>
<td>Four adult occupants</td>
<td>This study</td>
</tr>
<tr>
<td>4 × 10(^5)-2 × 10(^6)</td>
<td>20, 40</td>
<td>OH direct measurements with FAGE</td>
<td>No occupants</td>
<td>Carlslaw et al., 2017 (43)</td>
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<tr>
<td>3 × 10(^5)-3.5 × 10(^6)</td>
<td>5, 180</td>
<td>OH direct measurements with FAGE</td>
<td>No occupants, cleaning while max O(_3)</td>
<td>Bloquet et al., 2016 (14)</td>
</tr>
<tr>
<td>1.8 × 10(^6)</td>
<td>5, 30</td>
<td>OH direct measurements with FAGE</td>
<td>No occupants, daytime max level</td>
<td>Gomez Alvarez et al., 2013 (12)</td>
</tr>
<tr>
<td>6.5 × 10(^4)-3.7 × 10(^5)</td>
<td>1.6, 4.8</td>
<td>Tracer decay measurement</td>
<td>No occupants</td>
<td>White et al., 2010 (15)</td>
</tr>
<tr>
<td>4.6 × 10(^5)</td>
<td>60, 120</td>
<td>Constant emission of a tracer measurement</td>
<td>No occupants, detergents present</td>
<td>Singer et al., 2006 (10)</td>
</tr>
<tr>
<td>4 × 10(^5)</td>
<td>12, 37</td>
<td>Estimate from detailed chemical model based on MCM</td>
<td>No occupants</td>
<td>Carlslaw, 2007 (13)</td>
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<tr>
<td>1.2 × 10(^5)</td>
<td>20, 200</td>
<td>Estimate based on SAPRC-99 chemistry model</td>
<td>No occupants</td>
<td>Sarwar et al., 2002 (11)</td>
</tr>
<tr>
<td>7.1±0.8 × 10(^5)</td>
<td>62, 192</td>
<td>Constant emission of a tracer measurement</td>
<td>No occupants</td>
<td>Weschler and Shields, 1997 (9)</td>
</tr>
<tr>
<td>1.7 × 10(^5)</td>
<td>20</td>
<td>Estimate based on steady-state mass-balance model</td>
<td>No occupants</td>
<td>Weschler and Shields, 1996 (8)</td>
</tr>
</tbody>
</table>

* O\(_3\): indoor, outdoor concentration
Supplementary Materials for
The Human Oxidation Field

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This PDF file includes:
- Materials and Methods
- Supplementary Text
- Figs. S1 to S11
- Tables S1 to S5
- Captions for Data S1

Other Supplementary Materials for this manuscript include the following:
- Data S1 [exp_20190415(A2), exp_20190412(A2), exp_20190426(A1), exp_20190508(A3), kinetic modeling, CFD simulation]
Materials and Methods

Chamber experiments

The experiments described in this work were conducted in a 22.5 m$^3$ stainless-steel climate chamber at the Technical University of Denmark (DTU) as part of the ICHEAR (Indoor Chemical Human Emissions and Reactivity) project (Fig.1). While human emissions were characterized under several different environmental conditions as part of the ICHEAR project (19, 20, 22), this study focuses on one benchmark condition, which was four young adult volunteers (~25 years old, body mass index 20-23.5) wearing long clothing, exposed to moderate temperature (set point 25°C) and low relative humidity (set point 30%). This condition was investigated in four experiments on separate days involving three different groups of young adult volunteers (A1, A2 and A3). Two replicate experiments were conducted on the same group of subjects A2 on separate days. The chamber was furnished with a table and four wire mesh chairs. The trace gases concentrations and OH reactivity of the unoccupied chamber were measured prior to each experiment to determine the underlying background. The chamber was ventilated with outdoor air, which was filtered to remove O$_3$ and particles and added to the chamber from a perforated floor with an air change rate (ACR) of 3.2±0.11 h$^{-1}$. Inside the chamber, air mixing was achieved by using two fans directed at the walls of the chamber. Ozone was added with the supply air with a mixing ratio at the inlet of ~100 ppb, which resulted in a chamber level of ~ 35 ppb when four people were present. The main sink for O$_3$ in the chamber was the exposed human skin. Volunteers showered the night before with provided fragrance-free liquid soap and shampoo. On the day of the experiment, they wore a set of provided identical new clothes (long sleeves shirts, trousers and socks), laundered with fragrance-free laundry detergent and tumble dried prior to the experiment. Occupants entered the O$_3$-free chamber at 9:30, left for a short lunch break (provided with bread, butter, and sliced cheese) between ~12:30-12:45, and reentered the chamber for another exposure, this time with O$_3$ present in the air, until 15:15. Ozone generation began 10 minutes after the volunteers returned into the chamber. Detailed information on the entire experimental design can be found in Bekö et al. (20).

Volatile organic compounds and hydroxyl radical reactivity measurements

Volatile organic compounds (VOCs) were measured using a proton transfer reaction-time of flight-mass spectrometer (PTR-ToF-MS 8000, Ionicon Analytik GmbH, Austria, (44)) and a custom built fast gas chromatography-mass spectrometry instrument (GC-MS). The PTR-ToF-MS was
operated under standard conditions \((P_{\text{drift}}=2.2 \text{ mbar}, T_{\text{inlet}}=60^\circ \text{C} \text{ and } E/N=137 \text{ Td})\) with a mass resolution 4000 at 96 amu, a time resolution of 20 s, and an uncertainty between 10-50\%. The instrument was calibrated with a certified gas standard mixture (Apel-Riemer Environmental Inc., USA) containing 14 compounds (methanol, acetonitrile, acetaldehyde, acetone, dimethyl sulfide, isoprene, methyl vinyl ketone, methacrolein, methyl ethyl ketone, benzene, toluene, xylene, 1,3,5-trimethylbenzene and \(\alpha\)-pinene), while a theoretical method was applied to determine the mixing ratios of the masses of the compounds not included in the gas standard. The fast GC-MS was operated with an \(O_3\) scrubber at the inlet and a cryogenic preconcentrator in which a sampling volume of 20-40 mL of air was collected. A certified gravimetrically determined gas standard mixture including isoprene and propanal (Apel-Riemer Environmental Inc., USA) was used to calibrate the fast GC-MS during the campaign. The time resolution of the fast GC-MS measured VOCs is 3 minutes with an uncertainty of 10\%.

Total OH reactivity was measured using a custom-built comparative reactivity method instrument (CRM, (45)) which consists of a glass flow reactor coupled to a proton transfer reaction-quadrupole-mass spectrometer (PTR-QMS, Ionicon Analytik GmbH, Austria (44)) to monitor the concentration of a reference molecule competing with trace gas molecules in air for reaction with in situ-generated OH. Pyrrole \((C_4H_5N)\) was used as the reference molecule because it is normally not found in ambient air, its reaction rate with OH is known and fast (46), and its concentration can be unambiguously detected by PTR-MS \((C_4H_5NH^+, m/z \ 68)\). Hydroxyl radicals are generated inside the reactor from the photolysis of water vapor, which is achieved by using a Hg UV lamp (emitting at 184.9 nm) and wet \(N_2\). Pyrrole (Westfalen AG, Germany) is measured in clean air and dry \(N_2\) after photolysis (concentration \(C_1\)), in the presence of OH (\(C_2\)), and in ambient air (\(C_3\)). The PTR-MS was operated at standard conditions \((P_{\text{drift}} = 2.2 \text{ mbar}, E/N = 130 \text{ Td}, T_{\text{inlet}} = 60 \ ^\circ \text{C})\) to monitor \(m/z \ 68\) with a dwell time of 20s. Assuming pseudo first order kinetics inside the reactor ([pyrrole]>>[OH]), the OH reactivity is obtained from pyrrole concentrations \(C_1, C_2, C_3\) with the following Eq. (1):

\[
R_{\text{air}} = \frac{(C_3-C_2)}{(C_1-C_3)} \times k_{\text{pyrrole+OH}} \times C_1
\]

where, \(k_{\text{pyrrole+OH}}\) is the rate constant of the reaction between pyrrole and OH \((1.20 \pm 0.16) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) (46). The PTR-MS was operated at standard conditions \((P_{\text{drift}} = 2.2 \text{ mbar}, E/N = 130 \text{ Td}, T_{\text{inlet}} = 60 \ ^\circ \text{C})\), \(C_1\) was quantified by using an OH scavenger and switches between \(C_2\)
and C3 were programmed to occur every 5 minutes. The data workflow includes PTR-MS calibration with pyrrole at different levels of humidity, humidity correction on C2 to correct for OH recycling when humidity changes, reactivity calibration for deviation from pseudo-first order kinetics with test gases i having different \( k_{i+OH} \), and dilution of the sampling flow into the flow reactor. All correction factors were determined experimentally and test gases included isoprene, acetaldehyde, propane and propene. The resolution of the OH reactivity measurement was 1-10 minutes, the limit of detection (1σ) is \( \sim 5s^{-1} \) and the quantified total uncertainty is \( \sim 48\% \). Detailed information on the measurements can be found in Zannoni et al. (19) and Wang et al. (22), and references therein.

A common inlet of fluorinated ethylene propylene (FEP, OD \( \frac{1}{2}'' \), length 5m) was used to draw the air (sampling flow \( \sim 7 \text{ L min}^{-1} \)) from the chamber outlet to the VOCs and OH reactivity instruments. Additional data used in this study include \( \text{O}_3 \), temperature and humidity that were all measured through separate inlets. Ozone was monitored with a 2B Technologies Model 205 \( \text{O}_3 \) monitor (2B Technologies, USA) with a time resolution of 10 seconds (accuracy: 1.0 ppb or 2% of reading). Air temperature and RH were monitored with a Vaisala GMW90 (accuracy: temperature \( \pm 0.5 \) °C, RH \( \pm 2.5\% \) below 60%, \( \text{CO}_2 \) \( \pm 30 \) ppm + 2 % of reading; Vaisala Corporation, Finland) connected to a HOBO® UX120-006M 4-channel analog data logger (Onset Computer Corporation, USA) with a time resolution of 1 minute.

**Inferred hydroxyl radical concentration**

The hydroxyl radical (OH) concentration was determined with two independent methods. The first method, referred to here as the “steady-state method”, assumes that the production rate and loss rate of the OH radicals are in balance, which is a reasonable assumption for such a short-lived species. Direct measurements of individual VOCs and total OH reactivity from the four separate experiments described above were used to determine the OH production and loss rates, respectively. One experiment (from the two replicates) was selected to further investigate the inferred OH concentration with an independent method, and model the spatial distribution of the OH field in the occupied environment.

The mechanism of the gas-phase reaction of an alkene with \( \text{O}_3 \) proceeds via \( \text{O}_3 \) addition to the \( \text{C}≡\text{C} \) double bond to form an energy rich ozonide, which dissociates into Criegee biradicals and carbonyl compounds. The Criegee biradicals can stabilize with molecular collisions or decompose
and yield OH \((47, 48)\). The OH radical formation resulting from the decomposition of the Criegee biradicals at atmospheric conditions depends on the number, configuration and identity of the alkyl substituents around the C=C bond \((47)\).

The mean OH chamber concentration is derived via the steady-state assumption and a production and a loss term, showed in Eq. (2) and (3), respectively:

\[
\frac{d[OH]}{dt} = \sum_i \text{yield}_i \times k_{i+O_3} \times [VOC_{O_3,i}] \times [O_3] \quad (2)
\]

where, \(VOC_{O_3,i}\) stands for all VOCs reactive to \(O_3\) and here specifically refers to the measured hydrocarbons with unsaturated (C=C) bonds, since only these are relevant given the ventilation time scales of the experiment; \(O_3\), is the measured \(O_3\) concentration; \(k_{i+O_3}\), is the rate constant of the reaction between alkenes and \(O_3\), and \(\text{yield}_i\) is the fractional OH yield from the ozonolysis reaction between compound \(i\) and \(O_3\).

\[-\frac{d[OH]}{dt} = -\sum_i k_{i+OH} \times [VOC_{OH,i}] \quad (3)
\]

Where, \(VOC_{OH,i}\) stands for all VOCs reactive to OH, and \(k_{i+OH}\), is the rate constant for the reaction between the \(i\)th VOC and OH.

Combining Eq. (2) and (3) we obtain Eq. (4):

\[
\frac{d[OH]}{dt} = \sum_i \text{yield}_i \times k_{i+O_3} \times [VOC_{O_3,i}] \times [O_3] - \sum_i k_{i+OH} \times [VOC_{OH,i}] \quad (4)
\]

When Eq. (4) equals zero, the OH concentration is in approximate steady state, therefore the following Eq. (5) is valid:

\[
[OH]_{ss} = \frac{\sum_i \text{yield}_i \times k_{i+O_3} \times [VOC_{O_3,i}] \times [O_3]}{\sum_i k_{i+OH} \times [VOC_{OH,i}]} \quad (5)
\]

The term in the numerator represents the total OH production rate from alkene ozonolysis reactions and the term in the denominator represents the total OH loss rate, which we have determined directly as the total OH reactivity. The alkenes whose measured concentrations were considered in Eq. (2, 4 and 5) were: isoprene, limonene, 6-methyl-5-hepten-2-one (6-MHO), OH-6-methyl-5-hepten-2-one (OH-6-MHO), geranyl acetone, methyl vinyl ketone (MVK), methacrolein (MACR), 4-methyl-8-oxo-4-nonenal (4-MON), 4-methyl-4-oc-tene-1,8-dial (4-MOD) and trans-2-nonenal.
Rate coefficients for the ozonolysis reactions were taken from the published literature (8, 47, 48), while alkene OH yields were either found in the literature (8, 9, 47–49) or estimated (47) (see Table S1).

The second approach, referred as the precursor-product method, uses isoprene as a reference molecule. Isoprene is known to be emitted by human breath and was monitored throughout the campaign without any interferences. Reaction with OH is the dominant sink for isoprene, and its rates of reaction with O₃ and OH are well established (50). In environments with low NO, isoprene reaction with OH yields methyl vinyl ketone (MVK), methacrolein (MACR), and isoprene peroxides (ISOPOOHs). However, for NO concentrations ~1ppb, as measured in the chamber during the experiment, formation of ISOPOOHs is negligible (23), therefore, the isoprene oxidation reaction with OH can be simplified as follows:

\[
\text{ISOPRENE} + OH \rightarrow a\text{MVK} + b\text{MACR} \quad (k_1)
\]

\[
\text{MVK} + OH \rightarrow \text{products} \quad (k_2)
\]

\[
\text{MACR} + OH \rightarrow \text{products} \quad (k_3)
\]

where MVK and MACR are detected together at m/z 71 by the PTR-ToF-MS. Hence, we have used an average rate coefficient (\(k_{\text{avg}} = 2.44 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}\)) based on \(k_2\) and \(k_3\), for reaction of OH with those products (23). Similarly, an average yield (\(x\)) is considered based on the individual product yields \(a\) and \(b\) (23). We can derive [OH] based on \(k_1\), \(k_{\text{avg}}\), and \(x\) using Eq.(6) (51), where \(t\) is the chamber flushing time:

\[
\frac{m/z \text{ 71}}{\text{isoprene}} = \left( \frac{x \times k_1}{k_{\text{avg}} - k_1} \right) \times \left( 1 - e^{(k_1 - k_{\text{avg}})\left[\text{OH}\right]t} \right)
\]

It should be noted that breath emissions of isoprene are also sensitive to physiological parameters, possibly resulting in small variations in the measured concentration due to altered metabolism after the lunch break. We applied the precursor-product method to one experiment from the four reported here where isoprene concentration in the afternoon was lower than in the morning. A separate experiment conducted in the same chamber with four cleaned shirts, identical to those used by the volunteers, was used to assess any possible interference with the concentrations of isoprene and the compounds with m/z 71. It was found that these cleaned shirts, in the presence of O₃, also emit small concentrations of m/z 71 (0.02 ppb/m²). The value measured from the shirt...
experiment was used to estimate the emission of \( m/z \) 71 per m\(^2\) of clothing worn by the volunteers (shirts and pants), and this estimated value was subtracted from the calculations described above (0.22 ppb). Furthermore, in a dedicated sensitivity study (Table S2) we examined the sensitivity of the calculated OH concentration to changes in the “ratio of the compounds with \( m/z \) 71 to isoprene” arising from the potential interferences described above.

**Kinetic modeling**

We applied the KM-SUB-Skin-Clothing model to reproduce experimental measurements of VOCs and OH reactivity. The model has previously been described in detail (24, 25) and is summarized below. It includes reactions and diffusion in the gas-phase, boundary layer, clothing, gap between the clothing and skin and all layers of the skin. Parameters relevant to skin oil, such as diffusion and partitioning coefficients, were updated from the original publication to recent values estimated from molecular dynamic simulations. Unknown parameters were varied until the outputted kinetic model lines reproduced the measured concentrations of the different species reasonably well (Fig. S5-S6) and the model was subsequently used to calculate uptake coefficients, yields and emission rates which were provided as inputs to the CFD simulations (Table S5). Products resulting from squalene ozonolysis in clothing and skin oil (acetone, 6-MHO, geranyl acetone, 4-OPA, 4-MON, 4-MOD and 1,4-butanedial) had previously been included in the model. Trans-2-nonenal, nonanal, propanal and acetaldehyde were added as other skin lipid ozonolysis products, each with a specific yield in this version of the model (Table S4). Acetone, isoprene, and methanol from breath as well as ammonia from skin were treated using emission rates (Table S5). All other measured skin and breath species were lumped together into two groups and treated using emission rates and average weighted rate coefficients (Table S3 and S5). Gas-phase reactions of \( O_3 \) with alkenes forming OH and the reactions of OH with all species were included in the kinetic model (Table S3). Once the kinetic model had reproduced the measured concentrations of the different species (Fig. S5-S6), uptake coefficients, yields and emission rates were determined and provided as inputs to the CFD simulations (Table S5).

**Computational fluid dynamic modeling**

The transient computational fluid dynamic (CFD) model (26) was designed based on the experimental conditions, considering room geometry, the number of occupants, air flow rates, mixing fan settings, \( O_3 \) concentrations, and surface conditions (Fig. S7-S8). Four benchmark-
computerized manikins along with ventilation airflow from the perforated floor were simulated in the 3-D CFD model (Fig. 1). The model simulated turbulent indoor airflow associated with the rising thermal plume and air mixing fans using the Menter k-ω shear stress transport turbulence model. The CFD model simulated 24 chemical reactions including O₃ reactions with skin oils and OH reactions with VOCs in the chamber (Table S3). Surface depositions of O₃ and geranyl acetone as well as yields of ozonolysis products at the occupant surfaces were inputted based on the kinetic model (Table S5). The CFD model results were evaluated by comparison with concentrations of chemical species and OH reactivities observed in the experiments (Fig. S9). Four CFD models were analyzed: (A) the first one with the mixing fans and air with O₃ supplied from a simulated perforated floor (reproducing the exact experimental conditions), (B) as the first one but without the mixing fans, (C) a third one without the mixing fans and with ventilation air containing O₃ supplied from a point source near the ceiling, (D) a fourth with lower indoor O₃ concentration (5 ppb) but otherwise identical to the third. The four different simulations aim to investigate the impact of the indoor flow pattern, the location of the O₃ source, and the indoor O₃ concentration on the OH spatial distribution.

**Supplementary Text**

**Hydroxyl radical loss rate of human emissions**

Fig. S1 shows the total OH reactivity partitioned into the calculated OH reactivity from the measured volatile organic compounds. We used different colored fills for the most reactive compounds (i.e., 6-methyl-5-hepten-2-one (6-MHO), 4-oxopentanal (4-OPA), isoprene, m/z 137.132 (assumed to be entirely limonene), geranyl acetone, sum of aldehydes excluding 4-OPA, and “other measured compounds”). “Other measured compounds” includes ketones apart from 6-MHO and geranyl acetone, carboxylic acids, alcohols, aromatic compounds, and nitrogen and sulfur containing compounds. The full list of measured compounds used to calculate the OH reactivity is reported in Zannoni et al. (19) and Wang et al. (22).

**Hydroxyl radical concentration from the steady-state method**

The mechanism of the gas-phase reaction of an alkene with O₃ proceeds via O₃ addition to the C=C double bond to form an energy rich ozonide which dissociates into Criegee biradicals and carbonyl compounds. The Criegee biradicals can stabilize with molecular collisions or decompose
and yield OH. In the case of 6-MHO reacting with O$_3$, it was shown that the ozonide decomposes
to yield either acetone and a Criegee biradical (Fig.S2, panel A, reaction 1a) or 4-oxopentanal (4-OPA) and a different Criegee biradical (Fig.S2, panel A, reaction 1b) ($^{32,52}$). Previous studies indicate that the latter is the dominant pathway; the yield for the formation of acetone from reaction 1a was found to be 0.30, while the yield for the formation of 4-OPA from reaction 1b was found to be 0.82 ($^{32,52}$). As shown in Fig. S2 panel A, the resultant Criegee biradical isomerizes to yield a hydroperoxide, which further decomposes to yield OH. Additional contribution to OH formation comes from the biradical formed through reaction 1a. The formed hydroxyl radical can compete with O$_3$ for reacting with 6-MHO. Indeed, the rate coefficient of the reaction of 6-MHO with OH is six orders of magnitude faster than the one for 6-MHO with O$_3$ ($k_{6\text{-MHO}+\text{OH}} = 1.57 \times 10^{-10}$ cm$^3$ x molecules$^{-1}$ x s$^{-1}$, $k_{6\text{-MHO}+\text{O}_3} = 3.94 \times 10^{-16}$ cm$^3$ x molecules$^{-1}$ x s$^{-1}$). However, the indoor O$_3$ concentration is more than six orders of magnitude larger than the estimated OH concentration. Reaction of 6-MHO with OH yields acetone (0.71) and 4-OPA (0.59) ($^{32}$). Total yields of acetone and 4-OPA from 6-MHO reacting with O$_3$ and OH are reported in Fig.S2 panels B and C. In the case of acetone, reactions from 6-MHO with O$_3$ and OH explain about 6% of its measured concentration, consistent with acetone being a common byproduct to many reactions involving squalene and other skin oil constituents. In contrast, 6-MHO is a dominant precursor of 4-OPA, as reactions of 6-MHO with O$_3$ and OH can explain ~40% of 4-OPA’s observed concentration.

Hydroxyl radical concentration from precursor-product method

Fig. S4 shows the observed concentration of isoprene, $m/z$ 71 and $m/z$ 71/isoprene used to infer the OH concentration from the precursor-product method. $m/z$ 71 represents the sum of isoprene oxidation products, methyl vinyl ketone (MVK), methacrolein (MACR) and isoprene peroxides (ISOPOOHs) ($^{23}$). However, formation of ISOPOOHs is observed only under low NO regime. In the chamber, NO concentration was ~1 ppb most of the time. In such a chemical regime, ISOPOOHs concentration is negligible (ISOPOOHs/(MVK+MACR) < 0.1) and for this reason it was not accounted in the OH calculation.

Oxidation of isoprene to MVK+MACR, dominated by OH, is observed after O$_3$ addition to the chamber (Fig. S3). Results from a sensitivity study conducted on the OH concentration determined from the precursor-product method based on isoprene’s lifetime are reported in Table S2. Each parameter involved in the calculation of OH was varied in its possible confidence interval. Particularly, the
rate coefficient of the reaction of isoprene with OH was varied within 10% (53), the average rate coefficient of MVK and MACR with OH was varied within 16% (53), the products yield of the reaction of isoprene with OH was varied within 25% (assumed from (49)), the chamber flush time was varied within 0.02% (20), the m/z 71/isoprene was varied within 10%, which is the stated uncertainty on the calibration factors of the fast GC-MS and PTR-Tof-MS measuring the concentrations of the compounds, and within 20% as an upper limit accounting for fragmentation of other molecules on m/z 71 in the PTR-Tof-MS and possible changes in isoprene concentration due to occupants’ metabolism after the lunch break (20, 22). Results are mostly sensitive to the average formation yield of the isoprene oxidation products from the reaction with OH (relative change 19-31%) and to the ratio m/z71/isoprene (relative change 19%).

We also considered the case that the instrument measuring NO concentration was not sensitive enough to detect small mixing ratios (below 1 ppb) of NO. It is possible that the NO mixing ratio reached extremely low values after O₃ addition to the chamber air. In such chemical regime, isoprene oxidation by OH yields MVK, MACR and ISOPOOHs. In this case, Eq. (6) should consider as \( k_{\text{avg}} \) the average of the rate coefficients of the OH reactions with MVK, MACR and ISOPOOHs, and as \( x \) the average of the individual oxidation product (MVK, MACR, ISOPOOHs) yields (23). Such possibility is not affecting the final result of OH inferred with the precursor-product method (difference in concentrations of 3%).

**KM-SUB-Skin-Clothing and CFD model**

The transient computational fluid dynamics (CFD) model was designed to simulate O₃ reactions with human surfaces and subsequent OH reactions with ozonolysis products. The CFD domain was modeled by mimicking experimental conditions, including room geometry, occupancy, O₃ concentrations from supply inlets, airflow rates, and air mixing rates (Fig. S7, S9-S10 and Table S5). In the model, the volume of the chamber was 22.5 m³, and four manikins (54) were seated around a square table facing each other. The air with O₃ was supplied from the five floor inlets to simulate supply air from the perforated floor inlet, and exhausted through the outlet in the ceiling. Mimicking the experimental condition, two indoor fans with an air speed of 1 m/s were facing two side walls to mix the indoor air. The surface temperature of manikins was set to 35°C, while the room air temperature was 25°C. Due to the temperature difference between the human surface and ambient air, convective thermal plumes were generated around the occupant body. In the simulation, ammonia and other species (a lump sum of other species emitted from the skin) were
released from the human surface, and occupants exhaled various chemicals (i.e., isoprene, acetone, methanol, and other species) with a constant mass flow rate (Table S5). The average room concentrations maintained were 40 ppb for ammonia, 13 ppb for other species from the skin, 5 ppb for isoprene, 25 ppb for acetone, 6 ppb for methanol, and 1 ppb for other species from the breath under the steady-state condition.

A total of 24 chemical reactions were simulated (Table S3) in the CFD model. As O₃ reacted with human occupants, primary and secondary ozonolysis products (6-MHO, 4-OPA, acetone, geranyl acetone, 4-MON, 4-MOD, and 1,4 butanediol) were produced from the human surfaces. Some of the primary products reacted with O₃ again, producing secondary products in the ambient air (R1-R4). Isoprene and trans-2-nonenal from the occupants reacted with O₃ (R5-R6). OH radicals from the O₃ reactions in R1-R6 reacted with ozonolysis products and other species emitted from occupants in R7 – R22. In R23 and R24, O₃ and geranyl acetone were deposited on the indoor surfaces.

The KM-SUB-Skin-Clothing model provided uptake coefficients of O₃ and geranyl acetone and yields of ozonolysis products on the human surface (Table S5). Based on these values, deposition rates of O₃ to the human surface and geranyl acetone to indoor surface and emission rates of squalene ozonolysis products were calculated as shown below (27, 55, 56).

$$E_o = \frac{\gamma <W>}{4} C_o \quad (7)$$

where $E_o$ is deposition flux, $\gamma$ is the uptake coefficient, $< W >$ is Boltzmann’s velocity, and $C_o$ is the surface concentration of O₃.

$$E_i = Y_i C_o \quad (8)$$

where $E_i$ is emission rates of ozonolysis product $i$ and $Y_i$ is yield of product $i$.

To simulate the turbulent air flow due to thermal plumes and momentum air flow from the mixing fans, the CFD model used the Menter k-ω shear stress transport turbulence model (27, 57); where $k$ represents kinetic energy and $\omega$ is specific dissipation. The model results were validated by comparing time-varying concentrations of species and OH reactivities from the experiment. In Fig. S11, blue dots represent the CFD model results, and black dots are the experimental values. The CFD model reproduced the time-varying concentrations of the primary and secondary product (6-MHO), the secondary product (4-OPA), and isoprene with reasonable accuracy. Also, the OH reactivity estimates from the CFD model agree well with the values calculated from the experiment. Ozone and OH concentrations of the CFD model follow the trend of the experimental
condition, showing a coefficient of determination ($R^2$) of 95%. Using the validated CFD model, two parametric studies were performed. In these analyses (Fig. S9-S10), all conditions are the same as the experimental condition except for the mixing fans being off (Fig. S9-S10) and the air with $O_3$ is supplied from a point source near the ceiling (Fig. S10).

Health Impact of Secondary Species

Numerous primary and secondary oxidation products are formed when ozone and hydroxyl radicals react with the constituents of skin surface lipids. In the case of ozone, such reactions are limited to those lipids with unsaturated carbon bonds, including squalene and the unsaturated acyl groups of tri-, di- and monoacylglycerols, wax esters, and fatty acids. In contrast, the hydroxyl radical reacts with all skin oil constituents, either via addition reactions at carbon-carbon double bonds (faster) or via H-atom abstraction at other sites (slower). Hydroxyl radical addition reactions at double bonds commonly produce many of the same products generated when ozone reacts with the double bonds. Some of these oxidation products may adversely impact human health. Stable products of concern include hydrogen peroxide and organic peroxides, unsaturated aldehydes and dicarbonyls (17), oxoacids; organic nitrates (17), nanocluster aerosols (34), secondary organic aerosols (58) and aged secondary organic aerosols. Short-lived and/or highly reactive products, themselves capable of driving further oxidation, include stabilized Criegee intermediates, hydroperoxo ($HO_2$) and alkylperoxy radicals (RO$_2$), secondary ozonides, and peroxy acids and hydroperoxides. The latter three classes are thermally stable but rapidly decompose in the presence of water.

Toxicity information is available for only a few of the products within the classes listed above. For example, a number of dicarbonyls are known to be bioactive. 4-Oxopentanal (4-OPA) is an airway irritant (59) and has been shown to reduce the viability of human bronchial epithelial cells (60).

Another dicarbonyl product, 1,4-butanedial quickly converts to 2,5-dihydroxytetrahydrofuran in aqueous solutions. Unfortunately, toxicity information is missing for the vast majority of these products, and, at present, we must use in silico approaches to evaluate potential toxicity (e.g., US EPA’s ToxCast, https://www.epa.gov/chemical-research/toxicity-forecasting). Certain products generated when inhaled ozone reacts with species in the respiratory tract are known to cause oxidative stress and are also generated exogenously via ozone or hydroxyl radical reactions with skin lipids. An open question is the extent to which exogenous production of such products,
followed by inhalation, results in health damage comparable to that which occurs with endogenous production of these oxidation products. In summary, there is reason to suspect that a number of the oxidation products generated by ozone and hydroxyl radicals adversely impact human health at elevated concentrations. The fact that these products are generated in the vicinity of the breathing zone, as shown in the modeling in the present paper, amplifies this concern.

If we accept that some of these products are a health concern, how do different ventilation strategies impact inhalation intake and perhaps dermal absorption of the products of concern? In general, higher air change rates reduce the time available for secondary gas-phase reactions but have a much smaller impact on secondary surface chemistry. More specifically, the four ventilation conditions modeled using CFD (Fig. 3a-3h) partially illustrate how different degrees of mixing, flow patterns, air supply locations and indoor O$_3$ concentration resulting from outdoor O$_3$ inflow impact OH spatial distribution and the concentration of OH in the breathing zone. Such simulations can be used to evaluate potential mitigation strategies.
Fig. S1.
Total OH reactivity partitioned into the calculated OH reactivity of the measured VOCs. Four people entered the chamber at 49 min and left for a short break at ~230-240 min. Ozone was added to the chamber at 253 min. People left the chamber at 390 min. Background measurements of chamber supply air were performed at ~150 min and at ~330 min. “Others” include measured ketones (6-MHO and geranyl acetone excluded), carboxylic acids, alcohols, aromatic compounds, nitrogen and sulfur containing compounds.
Fig. S2.

Simplified reaction scheme of 6-MHO ozonolysis, once formed from squalene ozonolysis, to yield acetone, 4-OPA and OH (panel A). Acetone concentrations resulting from 6-MHO reactions with ozone and OH are represented by the red and blue areas in panel B. 4-oxopentanal (4-OPA) concentrations resulting from 6-MHO reactions with ozone and OH are represented by the red and blue areas in panel C. For reference, the measured concentrations of 6-MHO, acetone and 4-OPA are reported in the two panels. The values reported in the panels are the net values obtained after subtracting the concentrations of the three compounds measured while the chamber was empty, and while the chamber was occupied by four people without ozone being present. Hence, the values are representative of mostly skin oil chemistry.
Fig. S3.
OH concentration estimated with the steady-state method fractionally attributed to the relative contributions from ozonolysis of the measured alkenes.
**Fig. S4.**
Time series of isoprene, m/z 71 (MVK+MACR) volume mixing ratios (VMR) and their ratio m/z 71/ isoprene.
**Fig. S5.**
Modeled time series of OH concentration and OH reactivity with KM-SUB-Skin-Clothing kinetics model. The left panel shows the OH concentration resulting from two different rate coefficients of the reaction 6-MHO + O$_3$. The method used for calculating the OH concentration is the steady-state approach.
Fig. S6.
Measurements and KM-SUB-Skin-Clothing model simulations of ozone, products derived from ozone reactions with human skin oil, and species emitted from skin and breath.
**Fig. S7.**
Simulated air velocity (a, b) and air temperature (c) distribution inside the chamber as calculated using CFD modeling. The simulation reproduces the experiment with air and O$_3$ supplied from a simulated perforated floor and two fans facing the walls operating inside the chamber (condition A described in Section 1.4).
Fig. S8. OH reactivity (a&c) and OH concentration (b&d) temporal and spatial distribution at elapsed time of 253 min (beginning of ozone generation, panels a&b) and at elapsed time of 360 min (before people left the chamber, panels c&d). The simulations reflect air and O$_3$ supplied from a perforated floor and two mixing fans operating inside the chamber. These were the actual experimental conditions (condition A described in Section 1.4).
Fig. S9.
Simulated air velocity (a, b) and air temperature (c) distribution inside the chamber with CFD modeling. Air and O₃ are supplied from a simulated perforated floor and mixing fans are absent (condition B described in Section 1.4).
Fig. S10.
Simulated air velocity (a, b) and air temperature (c) distribution inside the chamber with CFD modeling. Air and O$_3$ are supplied from a point source near the ceiling and mixing fans are absent (condition C described in Section 1.4).
Fig. S11. CFD model values compared with measurements (except for OH concentration that was calculated); a) Ozone concentration, b) 6-MHO concentration, c) 4-OPA concentration, d) isoprene concentration, e) OH concentration calculated with the steady-state approach, and f) OH reactivity.
Table S1.
Hydroxyl radical production rates from the predominant alkenes for the experiment selected for the KM-SUB-Skin-Clothing and CFD simulations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>Steady state Concentration [molecules cm(^{-3})]</th>
<th>(K_{\text{i}+\text{O}_3}) [cm(^3) molecules(^{-1}) s(^{-1})]</th>
<th>OH yield</th>
<th>OH production rate [molecules cm(^3) s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>C(_5)H(_8)</td>
<td>1.03×10(^{11})</td>
<td>1.28×10(^{17})</td>
<td>0.27</td>
<td>3.07×10(^{5})</td>
</tr>
<tr>
<td>6-MHO</td>
<td>C(<em>8)H(</em>{14})O</td>
<td>6.5×10(^{10})</td>
<td>3.94×10(^{-10})</td>
<td>0.75</td>
<td>1.66×10(^{7})</td>
</tr>
<tr>
<td>OH-6-MHO</td>
<td>C(<em>8)H(</em>{15})O(_2)</td>
<td>7.15×10(^9)</td>
<td>3.80×10(^{-10})</td>
<td>1</td>
<td>2.35×10(^6)</td>
</tr>
<tr>
<td>Limonene</td>
<td>C(<em>{10})H(</em>{16})</td>
<td>5.4×10(^9)</td>
<td>2.20×10(^{-10})</td>
<td>0.86</td>
<td>8.78×10(^5)</td>
</tr>
<tr>
<td>MVK+MACR</td>
<td>C(_8)H(_6)O</td>
<td>1.68×10(^{10})</td>
<td>3.20×10(^{-10})</td>
<td>0.18</td>
<td>8.34×10(^5)</td>
</tr>
<tr>
<td>4-MON</td>
<td>C(<em>{10})H(</em>{16})O(_2)</td>
<td>1.64×10(^9)</td>
<td>4.30×10(^{-10})</td>
<td>0.92</td>
<td>5.61×10(^5)</td>
</tr>
<tr>
<td>4-MOD</td>
<td>C(<em>9)H(</em>{14})O(_2)</td>
<td>1.77×10(^9)</td>
<td>4.30×10(^{-10})</td>
<td>0.92</td>
<td>6.05×10(^5)</td>
</tr>
<tr>
<td>Geranyl acetone</td>
<td>C(<em>{13})H(</em>{22})O</td>
<td>3.28×10(^7)</td>
<td>8.60×10(^{-10})</td>
<td>1</td>
<td>2.44×10(^5)</td>
</tr>
<tr>
<td>Trans-2-nonenal</td>
<td>C(<em>9)H(</em>{16})O</td>
<td>1.57×10(^{10})</td>
<td>1.30×10(^{-17})</td>
<td>1</td>
<td>1.76×10(^5)</td>
</tr>
</tbody>
</table>
Table S2.
Sensitivity study on the OH concentration determined from the precursor-product method. Input variables as expressed in Eq. (6) are reported in the first column, where $k_1$ refers to the rate constant of the reaction between isoprene and OH, $k_{avg}$ refers to the rate constant of the reaction between isoprene oxidation products and OH and $x$ refers to the average of the products yields from isoprene oxidation reaction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base value</th>
<th>Perturbation</th>
<th>OH concentration [molecules × cm$^{-3}$]</th>
<th>Relative change [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>1.2×10^6</td>
<td>+10%</td>
<td>1.2×10^6</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>1.3×10^6</td>
<td>11</td>
</tr>
<tr>
<td>$k_1$</td>
<td>1×10^-10</td>
<td>+16%</td>
<td>1.2×10^6</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>-16%</td>
<td>1.2×10^6</td>
<td>0.25</td>
</tr>
<tr>
<td>$k_{avg}$</td>
<td>2.44×10^-11 cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>+25%</td>
<td>9.3×10^5</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-25%</td>
<td>1.5×10^6</td>
<td>31</td>
</tr>
<tr>
<td>$x$</td>
<td>0.34</td>
<td>+10%</td>
<td>1.3×10^6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>1.0×10^6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+20%</td>
<td>1.4×10^6</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-20%</td>
<td>9.3×10^5</td>
<td>19</td>
</tr>
<tr>
<td>Flush time</td>
<td>1161 s</td>
<td>+0.02%</td>
<td>1.2×10^6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.02%</td>
<td>1.2×10^6</td>
<td>10</td>
</tr>
<tr>
<td>$m/z$71/isoprene</td>
<td>0.05</td>
<td>+10%</td>
<td>1.3×10^6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>1.0×10^6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+20%</td>
<td>1.4×10^6</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-20%</td>
<td>9.3×10^5</td>
<td>19</td>
</tr>
</tbody>
</table>
Table S3.
Gas-phase reactions, rate coefficients and yields included in KM-SUB-Skin Clothing and the CFD simulations.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficients (cm³ s⁻¹ or s⁻¹) and yields</th>
<th>Reference and notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + 6-MHO → 4-OPA + Acetone + Y₁ OH</td>
<td>( k_2 = 4.3 \times 10^{-6} ), ( Y_2 = 1 )</td>
<td>Rates from EPIWEB v4.1.</td>
</tr>
<tr>
<td>O₂ + Geranyl acetone → 0.5 4-OPA + 0.5 4-MON + 0.5 Acetone + 0.5 6-MHO + Y₁ OH</td>
<td>( k_2 = 8.6 \times 10^{-6} ), ( Y_2 = 1 )</td>
<td>Yields were estimated from (S, 47).</td>
</tr>
<tr>
<td>O₂ + 4-MON → 2 4-OPA + Y₁ OH</td>
<td>( k_3 = 4.3 \times 10^{-6} ), ( Y_3 = 0.92 )</td>
<td>Rates previously summarized in (22).</td>
</tr>
<tr>
<td>O₂ + 4-MOD → 4-OPA + 1,4 butanediol + Y₂ OH</td>
<td>( k_8 = 4.3 \times 10^{-6} ), ( Y_8 = 0.92 )</td>
<td>Rates ( k_{19} ) and ( k_{22} ) are average weighted rate coefficients for species that are not being treated individually.</td>
</tr>
<tr>
<td>O₂ + Isoprene → Product + Y₂ OH</td>
<td>( k_5 = 1.3 \times 10^{-10} ), ( Y_5 = 0.27 )</td>
<td></td>
</tr>
<tr>
<td>O₂ + Trans-2-nonenal → Product + Y₆ OH</td>
<td>( k_6 = 1.3 \times 10^{-11} ) - 4.3 ( Y_6 = 1 )</td>
<td></td>
</tr>
<tr>
<td>Acetone + OH → Product</td>
<td>( k_6 = 1.8 \times 10^{-13} )</td>
<td></td>
</tr>
<tr>
<td>6-MHO + OH → Product</td>
<td>( k_7 = 1.6 \times 10^{-10} )</td>
<td></td>
</tr>
<tr>
<td>Geranyl acetone + OH → Product</td>
<td>( k_9 = 1.6 \times 10^{-10} )</td>
<td></td>
</tr>
<tr>
<td>4-OPA + OH → Product</td>
<td>( k_{10} = 2.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>4-MON + OH → Product</td>
<td>( k_{11} = 1.6 \times 10^{-10} )</td>
<td></td>
</tr>
<tr>
<td>4-MOD + OH → Product</td>
<td>( k_{12} = 1.6 \times 10^{-10} )</td>
<td></td>
</tr>
<tr>
<td>1,4 butanediol + OH → Product</td>
<td>( k_{13} = 5.7 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>Propanal + OH → Product</td>
<td>( k_{14} = 2.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>Nonanal + OH → Product</td>
<td>( k_{15} = 3.6 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>Trans-2-nonenal + OH → Product</td>
<td>( k_{16} = 4.4 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde + OH → Product</td>
<td>( k_{17} = 1.5 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>Ammonia + OH → Product</td>
<td>( k_{18} = 1.6 \times 10^{-13} )</td>
<td></td>
</tr>
<tr>
<td>Other species emitted from skin + OH → Product</td>
<td>( k_{19} = 1.2 \times 10^{-11} ) (before people enter, no O₃), ( 1.4 \times 10^{-11} ) (4 people in the chamber, no O₃), ( 1.4 \times 10^{-11} ) (4 people exited the chamber, no O₃), ( 1.5 \times 10^{-11} ) (4 people re-entered, no O₃), ( 1.5 \times 10^{-11} ) (4 people in the chamber, O₃ present), ( 1.3 \times 10^{-11} ) (No people, O₃ present)</td>
<td></td>
</tr>
<tr>
<td>Isoprene + OH → Product</td>
<td>( k_{20} = 1.0 \times 10^{-10} )</td>
<td></td>
</tr>
<tr>
<td>Methanol + OH → Product</td>
<td>( k_{21} = 9.0 \times 10^{-13} )</td>
<td></td>
</tr>
<tr>
<td>Other species emitted from breath + OH → Product</td>
<td>( k_{22} = 6.7 \times 10^{-12} ) (before people enter, no O₃), ( 6.6 \times 10^{-12} ) (4 people in the chamber, no O₃), ( 6.9 \times 10^{-12} ) (4 people exited the chamber, no O₃), ( 7.0 \times 10^{-12} ) (4 people re-entered, no O₃), ( 1.1 \times 10^{-13} ) (4 people in the chamber, O₃ present), ( 1.1 \times 10^{-13} ) (No people, O₃ present)</td>
<td></td>
</tr>
<tr>
<td>Geranyl acetone (+ surfaces) → Product</td>
<td>( k_{23} = 1.0 \times 10^{-4} )</td>
<td>Fitted to the data. Geranyl acetone is known to be sticky and O₃ is known to react with indoor surfaces.</td>
</tr>
<tr>
<td>O₂ (+ surfaces) → Product</td>
<td>( k_{24} = 4.5 \times 10^{-5} )</td>
<td></td>
</tr>
</tbody>
</table>

Submitted Manuscript: Confidential
Template revised February 2021
Table S4.
New and updated parameters included in KM-SUB-Skin-Clothing. Note that other parameters can be found in previous publications (24, 25).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room size (m$^3$)</td>
<td>22.5</td>
<td>From measurements</td>
</tr>
<tr>
<td>Air exchange rate (h$^{-1}$)</td>
<td>3.1</td>
<td>From measurements</td>
</tr>
<tr>
<td>Surface area of the 4 people (m$^2$)</td>
<td>6.8 m$^2$</td>
<td>Assuming a surface area of 1.7 m$^2$ for each person</td>
</tr>
<tr>
<td>Volume taken up by the 4 people (m$^3$)</td>
<td>0.28 m$^3$</td>
<td>Assuming a volume of 0.07 m$^3$ for each person</td>
</tr>
<tr>
<td>Ozone production rate (molecule cm$^{-3}$ s$^{-1}$)</td>
<td>$2.12 \times 10^9$</td>
<td>Calculated as 100ppb $\times$ AER. Maintains a concentration of 100ppb in the chamber in the absence of people and wall losses.</td>
</tr>
<tr>
<td>Boundary layer next to the clothing (cm)</td>
<td>0.3</td>
<td>Small boundary layer is consistent with relatively turbulent air (fans were switched on in the chamber)</td>
</tr>
<tr>
<td>Volume percentage of skin oil and other substances in clothing (%)</td>
<td>1</td>
<td>Within the range used in the KM-SUB-Skin-Clothing paper (25)</td>
</tr>
<tr>
<td>Effective squalene conc. in the clothing skin oil and other substances (cm$^3$)</td>
<td>$3.8 \times 10^{12}$</td>
<td>Effective concentration of squalene is low compared to values previously used to model studies in the KM-SUB-Skin clothing paper as clothing was not worn overnight unlike those studies. Effective concentration of skin oil reactive species is within the range previously used in the KM-SUB-Skin-Clothing paper (25)</td>
</tr>
<tr>
<td>Effective conc. of other skin oil reactive species in the clothing skin oil and other substances (cm$^3$)</td>
<td>$2.2 \times 10^{14}$</td>
<td></td>
</tr>
<tr>
<td>Effective conc. of laundering species 1 in the clothing skin oil and other substances (cm$^3$)</td>
<td>$2.8 \times 10^{18}$</td>
<td>Within the range used in the KM-SUB-Skin-Clothing paper (25)</td>
</tr>
<tr>
<td>Effective conc. of laundering species 1 in the clothing skin oil and other substances (cm$^3$)</td>
<td>$1.4 \times 10^{19}$</td>
<td>Within the range used in the KM-SUB-Skin-Clothing paper (25)</td>
</tr>
<tr>
<td>Diffusion coefficient of propanal in the stratum corneum (cm$^2$ s$^{-1}$)</td>
<td>$1.33 \times 10^{10}$</td>
<td>Calculated using the equations of (61)</td>
</tr>
<tr>
<td>Diffusion coefficient of nonanal in the stratum corneum (cm$^2$ s$^{-1}$)</td>
<td>$2.14 \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of trans-2-nonenal in the stratum corneum (cm$^2$ s$^{-1}$)</td>
<td>$1.89 \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of acetaldehyde in the stratum corneum (cm$^2$ s$^{-1}$)</td>
<td>$7.57 \times 10^{11}$</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of propanal in the viable epidermis (cm$^2$ s$^{-1}$)</td>
<td>$3.09 \times 10^{6}$</td>
<td>Calculated using the equations of (62)</td>
</tr>
<tr>
<td>Diffusion coefficient of nonanal in the viable epidermis (cm$^2$ s$^{-1}$)</td>
<td>$3.11 \times 10^{7}$</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of trans-2-nonenal in the viable epidermis (cm$^2$ s$^{-1}$)</td>
<td>$3.75 \times 10^{7}$</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of acetaldehyde in the viable epidermis (cm$^2$ s$^{-1}$)</td>
<td>$4.76 \times 10^{6}$</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of propanal and acetaldehyde in skin oil (cm$^2$ s$^{-1}$)</td>
<td>$2 \times 10^{6}$</td>
<td>Estimated based on values for similar molecules</td>
</tr>
<tr>
<td>Diffusion coefficient of trans-2-nonenal and nonanal in skin oil (cm$^2$ s$^{-1}$)</td>
<td>$1 \times 10^{6}$</td>
<td></td>
</tr>
<tr>
<td>Initial concentration of geranyl acetone in the clothing skin oil and other substances (cm$^3$)</td>
<td>$8.1 \times 10^{16}$</td>
<td>These species are semi-volatile and may therefore may be present from reactions occurring before the people enter the chamber</td>
</tr>
<tr>
<td>Initial concentration of 6-MHO in the clothing skin oil and other substances (cm$^3$)</td>
<td>$6.7 \times 10^{17}$</td>
<td></td>
</tr>
</tbody>
</table>
Initial concentration of 4-MON in the clothing skin oil and other substances (cm\(^{-3}\)) & 1.6 \times 10^{16} \\
Initial concentration of 4-MOD in the clothing skin oil and other substances (cm\(^{-3}\)) & 1.0 \times 10^{16} \\
Initial concentration of trans-2-nonenal in the clothing skin oil and other substances (cm\(^{-3}\)) & 1.9 \times 10^{15} \\
Initial concentration of nonanal in the clothing skin oil and other substances (cm\(^{-3}\)) & 4.1 \times 10^{15} \\
Initial concentration of propanal in the clothing skin oil and other substances (cm\(^{-3}\)) & 1.7 \times 10^{15} \\
Initial concentration of acetaldehyde in the clothing skin oil and other substances (cm\(^{-3}\)) & 1.1 \times 10^{15} \\
Initial concentration of 1,4 butanedral in the clothing skin oil and other substances (cm\(^{-3}\)) & 1.1 \times 10^{15} \\
Partitioning coefficient of 6-MHO for clothing (mol cm\(^{-3}\) atm\(^{-1}\)) & 15.5 \\
& A factor of 3 larger than used in the KM-SUB-Skin-Clothing paper (25) \\
Partitioning coefficient of Geranyl acetone for clothing (mol cm\(^{-3}\) atm\(^{-1}\)) & 968 \\
& A factor of 6.7 larger than used in the KM-SUB-Skin-Clothing paper (25) \\
Partitioning coefficient of propanal and acetaldehyde for clothing (mol cm\(^{-3}\) atm\(^{-1}\)) & 0.0014 \\
& Assumed to be the same value as used in the model for acetone \\
Partitioning coefficient of trans-2-nonenal and nonanal for clothing (mol cm\(^{-3}\) atm\(^{-1}\)) & 15.5 \\
& Assumed to be the same value as used in the model for 6-MHO \\
Partitioning coefficient of 4-MON for clothing (mol cm\(^{-3}\) atm\(^{-1}\)) & 558 \\
& A factor of 2.1 larger than used in the KM-SUB-Skin-Clothing paper (25) \\
Partitioning coefficient of 4-MOD for clothing (mol cm\(^{-3}\) atm\(^{-1}\)) & 266 \\
& A factor of 2 larger than used in the KM-SUB-Skin-Clothing paper (25) \\
Partitioning coefficient of propanal and acetaldehyde for skin oil (mol cm\(^{-3}\) atm\(^{-1}\)) & 0.00054 \\
& Assumed to be the same value as used in the model for acetone \\
Partitioning coefficient of trans-2-nonenal and nonanal for skin oil (mol cm\(^{-3}\) atm\(^{-1}\)) & 0.083 \\
& Assumed to be the same value as used in the model for 6-MHO \\
Yield of propanal from the reaction of other skin oil reactive species with ozone & 0.095 \\
& Values were obtained by fitting to the data. However, these may be somewhat codependent on the concentration of the skin oil reactive species used in the model. \\
Yield of nonanal from the reaction of other skin oil reactive species with ozone & 0.11 \\
Yield of trans-2-nonenal from the reaction of other skin oil reactive species with ozone & 0.07 \\
Yield of acetaldehyde from the reaction of other skin oil reactive species with ozone & 0.11 \\
6-MHO production rate in clothing skin oil and other substances when ozone was absent in the chamber (molecule cm\(^{-3}\) s\(^{-1}\)) & 1.7 \times 10^{12} \\
& Needed to explain the increase and then steady concentration in the presence of people and with no ozone. May be due to previous reactions occurring before the people enter the chamber and the molecules already being present on their skin and hair. Possibly a constant production over the experimental time scale is due to transport from the skin oil or due to reactions of long-lived intermediates. \\
4-OPA production rate in clothing skin oil and other substances without ozone reactions (molecule cm\(^{-3}\) s\(^{-1}\)) & 2.5 \times 10^{12} \\
Geranyl acetone production rate in clothing skin oil and other substances without ozone reactions (molecule cm\(^{-3}\) s\(^{-1}\)) & 1.7 \times 10^{12} \\
4-MON production rate in clothing skin oil and other substances without ozone reactions (molecule cm\(^{-3}\) s\(^{-1}\)) & 3.9 \times 10^{11} \\
4-MOD production rate in clothing skin oil and other substances without ozone reactions (molecule cm\(^{-3}\) s\(^{-1}\)) & 2.6 \times 10^{11} \\
Trans-2-nonenal production rate in clothing skin oil and other substances without ozone reactions (molecule cm\(^{-3}\) s\(^{-1}\)) & 4.6 \times 10^{11}
<table>
<thead>
<tr>
<th>Substance</th>
<th>Production Rate (molecule cm$^{-3}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonanal production rate in clothing skin oil and other substances without ozone reactions</td>
<td>$6.9 \times 10^{11}$</td>
</tr>
<tr>
<td>Propanal production rate in clothing skin oil and other substances without ozone reactions</td>
<td>$8.4 \times 10^{11}$</td>
</tr>
<tr>
<td>Acetaldehyde production rate in clothing skin oil and other substances without ozone reactions</td>
<td>$3.8 \times 10^{12}$</td>
</tr>
<tr>
<td>1,4 butanedial production rate in clothing skin oil and other substances without ozone reactions</td>
<td>$8.3 \times 10^{11}$</td>
</tr>
<tr>
<td><strong>Background, skin and breathing emission rates</strong></td>
<td><strong>See table S3</strong></td>
</tr>
<tr>
<td><strong>Determined by fitting to the data</strong></td>
<td></td>
</tr>
</tbody>
</table>
Table S5.
Parameters determined by KM-SUB-Skin-Clothing and provided as inputs to the CFD simulations. The uptake coefficient of O$_3$ and the product yields were calculated for the time point just before the people left the chamber for the second time.

<table>
<thead>
<tr>
<th>Species</th>
<th>Uptake coefficient of O$_3$ or yield of products outputted from KM-SUB-Skin-Clothing</th>
<th>Emission rate to the gas-phase used in KM-SUB-Skin-Clothing (molecule cm$^{-3}$ s$^{-1}$) ***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>$2.55 \times 10^{-4}$ **</td>
<td>N/A</td>
</tr>
<tr>
<td>Acetone</td>
<td>$9.06 \times 10^{-2}$ **</td>
<td>$3.8 \times 10^5$ (breath)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4.2 \times 10^7$ (background)</td>
</tr>
<tr>
<td>6-MHO</td>
<td>$8.24 \times 10^{-1}$ **</td>
<td>N/A</td>
</tr>
<tr>
<td>Geranyl acetone</td>
<td>$5.12 \times 10^{-1}$ **</td>
<td>N/A</td>
</tr>
<tr>
<td>4-OPA</td>
<td>$4.56 \times 10^{-2}$ **</td>
<td>N/A</td>
</tr>
<tr>
<td>4-MON</td>
<td>$1.86 \times 10^{-3}$ **</td>
<td>$2.1 \times 10^5$ (background)</td>
</tr>
<tr>
<td>4-MOD</td>
<td>$3.12 \times 10^{-3}$ **</td>
<td>$3.2 \times 10^7$ (background)</td>
</tr>
<tr>
<td>1,4 butanedio</td>
<td>$1.29 \times 10^{-2}$ **</td>
<td>$5.9 \times 10^5$ (background)</td>
</tr>
<tr>
<td>Propanal</td>
<td>$2.55 \times 10^{-2}$ **</td>
<td>N/A</td>
</tr>
<tr>
<td>Nonanal</td>
<td>$2.53 \times 10^{-2}$ **</td>
<td>$1.1 \times 10^5$ (background)</td>
</tr>
<tr>
<td>Trans-2-nonenal</td>
<td>$1.76 \times 10^{-2}$ **</td>
<td>$1.1 \times 10^5$ (background)</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>$3.64 \times 10^{-2}$ **</td>
<td>$3.4 \times 10^5$ (background)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>N/A</td>
<td>$8.7 \times 10^8$ (skin)</td>
</tr>
<tr>
<td>Other species emitted from skin</td>
<td>N/A</td>
<td>$1.7 \times 10^8$ (background) and $3.1 \times 10^8$ (skin)</td>
</tr>
<tr>
<td>Isoprene</td>
<td>N/A</td>
<td>$1 \times 10^6$ (breath)</td>
</tr>
<tr>
<td>Methanol</td>
<td>N/A</td>
<td>$8.5 \times 10^7$ (background) and $1.2 \times 10^9$ (breath)</td>
</tr>
<tr>
<td>Other species emitted from breath</td>
<td>N/A</td>
<td>$1.1 \times 10^7$ (background) and $2.3 \times 10^7$ (breath)</td>
</tr>
</tbody>
</table>

* Calculated using the near surface gas-phase concentration

** Calculated as (Flux of VOC out of the clothing - flux of VOC into the clothing)/(Flux of ozone into the clothing-flux of O$_3$ out of the clothing) using the near surface gas phase conc.

*** Emission rates were applied to the whole room volume. Note that the emission rates from breath were set to $2.6 \times 10^8$, $1.4 \times 10^8$ and $1.5 \times 10^7$ molecule cm$^{-3}$ s$^{-1}$ when fitting the morning data for acetone, methanol and other species emitted from breath, respectively. Ammonia skin emissions were set to $5.8 \times 10^8$ molecule cm$^{-3}$ s$^{-1}$ in the morning and other species emitted from skin had an emission rate of $7.7 \times 10^7$ molecule cm$^{-3}$ s$^{-1}$ in the absence of ozone.
Data S1. (separate file)

Measured concentrations at steady state and OH production rates for isoprene, 6-MHO, OH-6-MHO, limonene, MVK+MACR, 4-MON, 4-MOD, geranyl acetone, and trans-2-nonenal. Measurements of the benchmark condition were conducted with three different groups of adult subjects (A1, A2, A3) on four separate days (20190412 and 20190415 are replicates of the same condition with the same group of subjects). Modeled concentrations at steady state with the kinetic model and the CFD model.