

MIT Open Access Articles

Indoor Air Quality Implications of Germicidal 222 nm Light

The MIT Faculty has made this article openly available. *Please share* how this access benefits you. Your story matters.

Citation: Barber, Victoria P., Goss, Matthew B., Franco Deloya, Lesly J., LeMar, Lexy N., Li, Yaowei et al. 2023. "Indoor Air Quality Implications of Germicidal 222 nm Light." Environmental Science & Technology.

As Published: 10.1021/acs.est.3c05680

Publisher: American Chemical Society (ACS)

Persistent URL: https://hdl.handle.net/1721.1/152445

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of use: Creative Commons Attribution-Noncommercial-Share Alike



1

Indoor Air Quality Implications of Germicidal 222 nm Light

Victoria Barber^{1,2§*}, Matthew B. Goss^{1§}, Lesly J. Franco Deloya⁴, Lexy N. LeMar⁵, Yaowei Li⁶, Erik Helstrom¹, Manjula Canagaratna⁷, Frank N. Keutsch^{6,8,9}, Jesse H. Kroll^{1,5*}

¹Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
 ²now at Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California, 90095
 ⁴Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United

States

⁵Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
⁶John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States
⁷Center for Aerosol and Cloud Chemistry, Aerodyne Research Incorporated, Billerica, Massachusetts 01821, United States
⁸Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States
⁹Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts 02138, United States
⁹Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts 02138, United States
⁸V.P.B. and M.B.G. contributed equally to this work *Corresponding Authors

Email: <u>vbarber@chem.ucla.edu</u> Phone: 424-259-5198 University of California, Los Angeles Department of Chemistry and Biochemistry 607 Charles E. Young Drive, East, YH3077B Los Angeles, CA 90095

Email: jhkroll@mit.edu Phone: 617-253-2409 Massachusetts Institute of Technology Department of Civil and Environmental Engineering 77 Massachusetts Avenue, 48-331 Cambridge, MA 02139

Keywords: Ultraviolet Germicidal Irradiation, Indoor Air Quality, Ozone, Photochemistry, Ventilation, Volatile Organic Compounds, Secondary Organic Aerosol

34	
35	Abstract
36 37 38 39 40 41 42 43 44 45 46 47 48 49 50	One strategy for mitigating the indoor transmission of airborne pathogens, including the SARS-CoV-2 virus, is irradiation by germicidal UV light (GUV). A particularly promising approach is 222 nm light from KrCl excimer lamps (GUV ₂₂₂); this inactivates airborne pathogens and is thought to be relatively safe for human skin and eye exposure. However, the impact of GUV ₂₂₂ on the composition of indoor air has received little experimental study. Here, we conduct laboratory experiments in a 150 L Teflon chamber to examine the formation of secondary species by GUV ₂₂₂ . We show that GUV ₂₂₂ generates ozone (O ₃) and hydroxyl radicals (OH), both of which can react with volatile organic compounds to form oxidized volatile organic compounds and secondary organic aerosol particles. Results are consistent with a box model based on known photochemistry. We use this model to simulate GUV ₂₂₂ irradiation under more realistic indoor air scenarios, and demonstrate that under some conditions, GUV ₂₂₂ irradiation can lead to levels of O ₃ , OH, and secondary organic products that are substantially elevated relative to normal indoor conditions. The results suggest that GUV ₂₂₂ should be used at low intensities and in concert with ventilation, decreasing levels of airborne pathogens while mitigating the formation of air pollutants.
51	Synopsis

52 Germicidal ultraviolet light at 222 nm (GUV₂₂₂) can inactivate airborne pathogens, but has an

53 unknown effect on indoor air quality. This study shows that GUV₂₂₂ forms ozone and hydroxyl

54 radicals, forming oxidized byproducts and fine particulate matter.

55

TOC Graphic



58 Introduction

- 59 The COVID-19 pandemic has highlighted the critical need to develop and implement strategies
- 60 to decrease the transmission of airborne pathogens. Approaches include both source control
- 61 (isolation, masking), and remediation (ventilation, air cleaning). One approach that has received
- 62 substantial attention is the use of germicidal ultraviolet (GUV) light, which inactivates airborne
- 63 pathogens. This approach goes back decades,¹ traditionally using 254 nm light from mercury
- 64 lamps. Since light of this wavelength can cause damage to skin and eyes, care must be taken to
- 65 minimize occupants' direct exposure to the GUV light.^{2,3}
- 66 A promising new approach to GUV-based air cleaning is the use of KrCl excimer lamps, which
- 67 emit at 222 nm (GUV₂₂₂).⁴ In contrast to 254 nm GUV, GUV₂₂₂ does not penetrate deeply into
- 68 biological materials. Therefore, while GUV₂₂₂ is effective at inactivating airborne viruses and
- bacteria, it is unable to penetrate the outer layer of dead skin cells or the ocular tear layer.⁵ 222
- nm light is hence less likely to reach and damage living human tissues, offering the potential for
- 71 air disinfection throughout an entire, occupied indoor space.
- 72 A risk with GUV₂₂₂-based air cleaning, as with all types of air cleaning that rely on chemical
- and/or photolytic processes, is the potential formation of unwanted secondary byproducts.^{6,7} A
- 74 particular concern with GUV₂₂₂ is the formation of ozone (O₃), a harmful air pollutant that acts
- as a strong oxidant and can lead to respiratory distress when inhaled.⁸ O₃ is formed by the UV
- 76 photodissociation of oxygen (R1-2)

77
$$O_2 + hv_{\lambda < 242 \text{ nm}} \rightarrow O + O$$
 (R1)

(R2)

$$78 \qquad O+O_2+M \rightarrow O_3+M$$

- 79 Since absorption of UV by O₂, and hence O₃ production, is strongest at short wavelengths,⁹
- 80 manufacturers of KrCl lamps have added filters to block wavelengths shorter than 222 nm. But
- since O₂ absorbs weakly even at 222 nm ($\sigma = 4.09 \times 10^{-24}$ cm² ⁹), all KrCl lamps have the potential
- 82 to generate ozone, possibly in concentrations higher than is typically found indoors.¹⁰
- 83 Ozone generated indoors, in addition to posing a direct health hazard, can set off a cascade of
- 84 chemical reactions that can also affect indoor air quality. Ozone reacts directly with alkenes,
- 85 present both in the air and on indoor surfaces, forming a range of oxidized volatile organic
- 86 compounds (OVOCs)^{11,12} and secondary organic aerosol (SOA),¹³ which may negatively impact
- 87 human health.^{14–17} O₃ chemistry can also lead to the formation of the hydroxyl radical (OH), an
- 88 even stronger oxidant. This occurs both through reactions with alkenes, which are known to form

90 Alkene +
$$O_3 \rightarrow OH$$
 + other products (R3)

91
$$O_3 + hv_{\lambda < 370 \text{ nm}} \rightarrow O_2 + O(^1D)$$
 (R4)

92
$$O(^{1}D) + H_{2}O \rightarrow 2OH$$
 (R5)

- Any increased levels of indoor O_3 from GUV_{222} would likely enhance the importance of these protections leading to higher levels of indeer OH. This includes O_2 photolysis (P4.5), which is the
- 94 reactions, leading to higher levels of indoor OH. This includes O₃ photolysis (R4-5), which is the

- 95 main source of OH in the troposphere, but under normal conditions is negligible in indoor
- 96 environments, due to the lack of low-wavelength UV. Any OH radicals formed from R3-5 may
- 97 then oxidize a wide range of organic species and contribute further to the formation of OVOCs
- 98 and SOA.
- 99 GUV₂₂₂ therefore has the potential to dramatically affect the chemical composition of indoor air,
- 100 and may lead to the formation of chemical species that are hazardous to human health. However,
- 101 the extent and nature of this impact remains quite uncertain, even as GUV₂₂₂ is being deployed in
- 102 indoor spaces.²⁰ Two very recent experimental studies^{21,22} demonstrate O₃ production from
- 103 GUV₂₂₂, but these do not examine the overall effects on indoor air quality (including the
- 104 production of OH, OVOCs, and SOA) by GUV₂₂₂. To our knowledge the only published work
- that has is a box-modeling study by Peng et al.²³. That work predicted that 222 nm irradiation
- 106 could lead to elevated levels of O_3 and other secondary species relative to non-illuminated
- 107 conditions, especially under low-ventilation conditions.
- 108 Here we describe a series of laboratory experiments aimed at better understanding the effects of
- 109 222 nm irradiation on indoor air quality. The goal of this work is to gain process-based insight
- 110 into how such irradiation affects the chemical composition of the air; we do not examine the
- 111 effects of GUV₂₂₂ light on pathogens, indoor surfaces, or human health. These experiments,
- 112 which use a flow-through Teflon chamber coupled to a range of real-time analytical instruments,
- 113 explore the effects of several parameters relevant to indoor air processes (VOC level, ventilation,
- 114 222 nm light intensity, and humidity) on the generation of oxidants and secondary products.
- 115 Results are then used to validate a simple chemical model of GUV₂₂₂ irradiation of indoor air,
- 116 which in turn is used to examine the interplay between GUV₂₂₂ and ventilation in controlling the
- 117 levels of ozone and other chemical species in the indoor environment.

118 Materials and Methods

- 119 Experimental Methods
- 120 Experiments are carried out in a 150 L Teflon chamber, outfitted with inlet ports (for
- 121 introduction of clean air and trace species) and outlet ports (for sampling by analytical
- 122 instrumentation). Clean dry air from a zero-air generator (Aadco Model 737) is introduced into
- 123 the chamber either directly, or after passing through a bubbler filled with Milli-Q water. Mass
- 124 flow controllers are used to adjust these two flows to control chamber relative humidity. Dilution
- 125 rates are measured using acetonitrile, an inert dilution tracer $(8.0 \times 10^{-4} 9.7 \times 10^{-4} \text{ s}^{-1}, 2.9 3.5)$
- 126 ACH). Most experiments are conducted at 22°C and ~25% RH, while "higher RH" experiments
- 127 are carried out at ~45% RH.
- 128 GUV₂₂₂ light is provided by a single filtered KrCl excimer lamp (Ushio, Care222 B1 Illuminator,
- 129 peak emission at 222 nm), centered directly above the Teflon chamber. Average fluence rate
- 130 within the chamber is \sim 45 μ W/cm², estimated geometrically from the lamp intensity profile
- 131 provided by the manufacturer²⁴ (see Section S1.1). The indirect estimation of the lamp intensity
- is a limitation of this work, but the agreement between modeled and measured ozone production
- 133 (see Results and Discussion, below) indicates that it is reasonably accurate. More quantitative
- 134 estimates of UV fluence rate and its relationship to O₃ generation are available in recent work by

- 135 Peng et al.²² and Link et al.²¹ Most experiments are carried out at the full light intensity. For "low
- 136 light" experiments, the lamp emission is attenuated by several layerPs of plastic, achieving a
- 137 factor of \sim 5 reduction in intensity (determined by the reduction in the steady-state O_3
- 138 concentration which is assumed to scale linearly with average UV fluence).^{21,22} For the "O₃-
- 139 only" experiments, the light is left off, and O3 is introduced via a Pen-Ray ozone generator, with
- 140 a steady-state O₃ concentration matching that of the GUV₂₂₂ experiments (~100 ppb). Reaction
- 141 conditions for each experiment are described in detail in Table S1.
- 142 For all VOC oxidation experiments, the chamber is first allowed to reach a steady-state
- 143 concentration of O₃, either via 222 nm irradiation or direct addition. This is followed by the
- addition of 5.3 ppb of acetonitrile (the dilution tracer) (C₂H₃N, 99.8%, Sigma Aldrich), 1.2 ppb
- of 1-butan-d9-ol (intended as an OH tracer, but not used here due to the relatively low OH
- 146 levels) (C₄D₉OH, 98%, Cambridge Isotope Laboratories, Inc.), and $120 \pm 11 \ \mu g \ m^{-3}$ of
- 147 ammonium sulfate particles (to act as seed particles for any SOA production) ((NH4)₂SO4,
- 148 ≥99%, Sigma Aldrich). Finally, the relevant VOC (10 or 100 ppb) is added to chamber. VOCs
- used in this study include hexanal (C₆H₁₂O, 98%, Sigma Aldrich), cyclohexene (C₆H₁₀, 99%,
- 150 Sigma Aldrich), and (R)-(+)-limonene (C₁₀H₁₆, 97%, Sigma Aldrich). Reactant addition
- 151 procedures are described in greater detail in Section S1.2. Because the oxidants are already
- 152 present in the chamber, oxidation begins immediately, so VOC injection is taken as t = 0.
- 153 Real-time measurements of gas- and particle-phase composition in the chamber are conducted using a
- suite of analytical instruments. Ozone is measured by a UV absorption monitor (2BTech). NO_x is
- 155 monitored using a chemiluminescence NO-NO₂-NO_x analyzer (Thermo Fisher Scientific) and was below
- $156 \qquad \text{the instrument detection limit in all experiments. Reactant VOC and OVOC products are monitored}$
- using a Vocus proton transfer-reaction mass spectrometer (PTR-MS, Tofwerk, Aerodyne Research,
- 158 Inc.²⁵), and an ammonium chemical ionization mass spectrometer (NH₄⁺ CIMS, modified PTR3, see
- 159 Zaytsev et al.²⁶). Particle concentration and composition are measured using a scanning mobility particle
- 160 sizer (SMPS, TSI) and an aerosol mass spectrometer (AMS, Aerodyne Research, Inc.²⁷). Analytical
- 161 instruments are summarized in Table S2. Gas-phase mass spectrometric data is background-subtracted
- 162 and corrected for dilution. The analysis does not account for variations in detection efficiencies, which 163 may be substantial,²⁶ and we therefore report relative signals, which are unaffected by such calibration
- 164 uncertainties, rather than absolute concentrations. Particle-phase data is corrected for dilution and wall
- 165 losses by normalizing to the ammonium sulfate seed particle concentration. Data analysis and
- 166 quantification approaches are described in more detail in Section S1.3.
- 167 **Results and Discussion**

168 *Ozone production*

- 169 The production of ozone by 222 nm light is examined via the irradiation of clean chamber air.
- 170 Figure 1 shows results from four representative irradiation experiments, run at different
- 171 ventilation rates (1.3 to 3.1 air changes per hour (ACH)) and relative humidities (25%-45%). O₃
- 172 production is observed to occur immediately when the lights are turned on. O₃ levels increase
- 173 quickly at first, eventually leveling off to a steady-state value, in which photolytic production is
- balanced by removal by outflow. The O_3 production rate is measured at 324 ± 18 ppb hr⁻¹, in
- 175 reasonably good agreement with previous measurements²² when differences in average GUV_{222}

- 176 fluence rate are considered (see Section S3.1). The steady-state O₃ concentration is independent
- 177 of relative humidity, and inversely proportional to ventilation rate (Figure S3).
- 178 Dashed lines in Figure 1 denote O₃ concentrations predicted from a simple box model. This
- 179 model includes O₂ photolysis (R1-2), O_x-HO_x chemistry, and dilution (See Table S3 for rate
- 180 constants and photochemical parameters^{9–11,28–32}). Model parameters (e.g., light intensity, air-
- 181 exchange rate, and RH) are matched to each experiment. O₃ deposition, which is likely small on
- 182 Teflon surfaces, is not included. The model accurately predicts measured O₃ levels, indicating
- 183 that the processes describing ozone levels (formation from O₃ photolysis at 222 nm, loss by
- 184 outflow) are well-captured by the simple model.





agree well with the predictions from the simple box model (dashed lines) across a range of

188 ventilation rates and relative humidities. Measurements shown in red are taken at 25% RH.

189

190 Decay of VOCs upon 222 nm irradiation.

191 In a second set of experiments (Table S1), VOCs are added to the irradiated chamber after O3

192 levels reach steady state. Experiments center on two VOCs: hexanal, a C6 compound that reacts

only with OH, and cyclohexene, a C6 compound that reacts with both OH and O₃. VOC decays

are shown in Figure 2. Negligible change in O_3 concentration is observed upon introduction of

10 ppb of VOC; when 100 ppb of cyclohexene is introduced, a small O₃ depletion (~4.3 ppb) is
observed.



198

Figure 2: Normalized decays of two VOCs (hexanal and cyclohexene) after introduction to the GUV₂₂₂-irradiated chamber (see also Figure S4). Time = 0 refers to when the VOC was injected into the chamber. Traces are background- and dilution-corrected, so observed decays are from oxidative loss only. Details of each experimental condition (base, O₃ only, low light) are given in the text and Table S1. Solid black lines denote single-exponential fits to the observed decays; dashed black lines show the expected decay of cyclohexene from reaction with O₃ only.²⁸

206 Under "base conditions" (10 ppb VOC precursor, 222 nm light, ~25% RH) (Figure 2AB), the

207 concentrations of both hexanal and cyclohexene decrease after being introduced to the irradiated

208 chamber. Concentrations are corrected for dilution; losses by direct photolysis and uptake to

209 surfaces are expected to be minimal (see Section S3.2). Therefore, decays indicate oxidative loss

210 only. This oxidation cannot be explained by O₃ alone. Hexanal does not react with O₃ – a very

- small decay of hexanal is attributed to minor, non-oxidative loss pathways (see SI). While
- 212 cyclohexene does react with O₃, its decay is far faster than what can be attributed to the O₃
- reaction (dashed line). Indeed, for experiments in which the GUV₂₂₂ light is off and VOCs are
- exposed to the same levels of O_3 as in the irradiated case (Figure 2CD), the hexanal does not decrease at all, and cyclohexene decays far less than in the irradiation case, at a rate consistent
- with reaction with O₃ (plus a small contribution from OH generated by the ozonolysis reaction,
- reaction R3). This observed "excess reactivity" (the difference in observed decays and decays
- expected from O_3 reaction alone) indicates that GUV_{222} irradiation generates not only O_3 but
- 219 other oxidants as well.

- 220 Additional experiments carried out under a range of reaction conditions provide evidence that
- these additional oxidants are OH radicals, formed from reactions 3-5. For example, experiments
- with the 222 nm fluence rate attenuated substantially (~ 9 μ W cm⁻², Figure 2EF) exhibit VOC
- decay rates that are much slower compared to those under base conditions. This attenuation is
- assumed to decrease steady-state O₃ concentrations proportionally. However, the observed
- excess reactivity disproportionately decreases, by approximately an order of magnitude. This is consistent with OH formation, which depends on the photolysis of both O₂ and O₃, as well as (in
- 226 consistent with OH formation, which depends on the photolysis of both O₂ and O₃, as well as (in 227 the case of cyclohexene) the ozonolysis reactions. The dependence of decays on other
- experimental parameters, such as VOC concentration and relative humidity, are also consistent
- with OH production from GUV₂₂₂ lights; this is discussed in detail in Section S3.3.
- 230 We estimate average OH levels in all experiments using an exponential fit to the VOC timeseries
- and known OH rate constants.^{29,30} For cyclohexene experiments, average measured [O₃] and the
- O_3 + cyclohexene rate constant are included in the fit to account for excess reactivity. The range
- of [OH] measured in each experiment is calculated by applying the same exponential fits to a
- rolling 15-minute window (see Section S3.4 for more details). We also calculate OH levels using
- 235 our simple box model by including a highly simplified oxidation scheme (Table S3) for each
- 236 injected VOC. Reaction rates of the VOC with OH and O₃ are taken from the literature, and
- 237 oxidation products are assumed to have the same OH reactivities as their precursors. Measured
- and modeled average [OH] agree well (Figure 3), providing strong evidence that GUV₂₂₂
- produces not only O₃ (R1-2) but also OH (R3-5), and that oxidation by both O₃ and OH can take
- 240 place upon irradiation with 222 nm light.





- 242 Figure 3: Experimentally-derived average OH concentration vs. average OH concentration
- 243 predicted by the box model, for all cyclohexene and hexanal experiments (see Section S3.4).

Note the break in the x-axis. Error bars represent the range of values observed throughout the experiment.

- 246 Formation of gas-phase oxidation products
- 247 The formation of oxidized gas-phase products is observed in all experiments in which VOC
- 248 oxidation occurs. Product distributions for three cyclohexene experiments (base conditions, O₃
- only, and low light) are shown in Figure 4. Additional product distributions and time-series
- 250 results (including for the hexanal experiments) are provided in Figures S5 and S6.



251

252 *Figure 4*: Gas-phase products from cyclohexene experiments. Panel A: Normalized mass

- 253 spectrometric signal of products formed for the GUV₂₂₂ irradiation (base conditions), O₃-only,
- and low-light experiments (see Section S3.5 for calculations and Figure S5 for other
- experimental conditions). Signals are integrated from t = 250 s to 2500 s, normalized to total
- integrated ion signal and grouped by carbon number (nC). In all cases products are dominated by
- 257 $C_{6}H_{10}O_{2}$ (the major cyclohexene + OH reaction product) and $C_{6}H_{10}O_{3}$, (the major cyclohexene +
- 258 O_3 product). Panel B: The ratio of the C₆H₁₀O₂-to-C₆H₁₀O₃ signals vs. the ratio of the rates of 259 OH and O₃ oxidation, for all cyclohexene experiments. Concentrations of OH are determined
- from the fits in Figure 2, while concentrations of O₃ are measured directly. The dashed line is a
- 261 linear fit to the data; since the two products have differing sensitivities in the instrument, this
- differs from the 1:1 line. Error bars represent the range of values observed throughout the
- 263 experiment.
- 264 Measured products are dominated by C6 and C5 compounds, as expected given that cyclohexene
- is a C6 species. The two products with the largest mass spectrometric signals, C₆H₁₀O₂ and
- $266 \quad C_6H_{10}O_3$, are the major products of the OH and O₃ initiated oxidation of cyclohexene,
- 267 respectively^{33,34} (see Scheme S1) (Products are detected as the analyte-NH4⁺ adduct, and reported

- as the analyte formula.) The ratios of the signals from the two products vary among experiments,
- 269 indicating differences in the relative concentrations of OH and O₃. In Figure 4b, the ratio of the
- 270 mass spectrometric signals of these two products is shown vs. the relative OH-to-O₃ oxidation
- 271 rate ratios (calculated from the experimentally-determined values of [OH] and [O₃]) for each
- 272 cyclohexene experiment. A strong correlation ($R^2 = 0.98$) is found between the two ratios,
- 273 providing further support for OH-initiated oxidation, and more generally for OH radical
- production from irradiation by 222 nm light. The products formed in the 222 nm irradiation of
- hexanal are also broadly consistent with OH-initiated oxidation (see Scheme S2).³⁵
- 276 Secondary organic aerosol formation
- 277 In all experiments, dry ammonium sulfate seed particles are added to the chamber, providing
- surface area onto which low-volatility species may condense, and enabling the assessment of
- 279 potential SOA formation. SOA formation is observed in a number of experiments (Table S1 and
- 280 Figure S7). SOA formation is generally modest for most hexanal and cyclohexene experiments,
- 281 likely due to the relatively small size (C6) and low concentrations (10 ppb) of those species.
- Higher concentrations of SOA are observed for experiments with high initial concentrations (100
- 283 ppb) of hexanal or cyclohexane, and for those using limonene ($C_{10}H_{16}$, a monoterpene commonly
- found in fragrances and cleaning products). In fact, the GUV₂₂₂ irradiation of 100 ppb limonene
- 285 (a level that can be found in indoor environments immediately after cleaning events^{36,37}) results
- in exceedingly high SOA loadings, on the order of $400 \pm 80 \ \mu g \ m^{-3}$. Additionally, the formation
- of new particles is observed upon 222 nm irradiation under some conditions (Section S3.6 and
- Figure S8). This effect is not observed when O₃ is added without 222 nm irradiation. GUV₂₂₂-
- 289 induced nucleation occurs even when no VOCs are added, and so may result from
- 290 photochemistry of organic species on the chamber surfaces, or even of the surface materials
- themselves. Whether this is a general feature of the irradiation of organics on indoor surfaces is
- unclear from the present experiments, but it does suggest that 222 nm irradiation may induce
- 293 new particle formation in some environments.

295 Extrapolation to indoor environments

- 296 The above laboratory experiments demonstrate that GUV₂₂₂ irradiation forms ozone, OH, and a
- range of oxidation products; measured ozone and inferred OH agree broadly with predictions by
- a photochemical box model. However, real-world indoor environments are substantially different
- than our simple laboratory system: they involve a large number of organic compounds,
- 300 depositional loss of ozone and other species, infiltration of outdoor pollutants, a wide range of
- 301 possible ventilation rates, and typically much lower average UV fluence rates. Here we extend
- 302 our photochemical model to a more realistic indoor air scenario, with the goal of understanding
- how GUV₂₂₂ may impact indoor air quality under a range of ventilation and irradiation
- 304 conditions.
- 305 For simulations of chemistry in a more realistic indoor environment, two "lumped" VOCs are
- 306 included in the model: one (VOC1) that reacts with OH but not with O₃, and another (VOC2)
- 307 that reacts with both OH and O₃. Rate constants for VOC1 are chosen based on typical values for
- 308 indoor VOCs (Section S2.1 and Tables S3 and S4); rate constants for VOC2 are assumed to be
- 309 equal to those of limonene. OH yields from $O_3 + VOC2$ are assumed to by 0.86, equal to that of
- 310 limonene.¹¹ All oxidation reactions form lumped organic products that can also react with OH.
- 311 VOC emission rates (84 ppb hr⁻¹ and 4.2 ppb hr⁻¹ for VOC1 and VOC2, respectively) are
- 312 determined from previous measurements of OH and O₃ reactivities in indoor environments;^{38,39}
- details of these calculations are given in Section S2.1. The model is run at 298 K, 1 atm, and
- 314 30% RH. We also include a background concentration of O₃ in the ventilation air (40 ppb,
- 315 consistent with typical outdoor O₃ concentrations), a 25% loss of O₃ to the ventilation system,
- 316 and an O₃ deposition constant of 3 hr^{-1} ^{10,31}.
- 317 The range of light fluence rates chosen covers US and international guidelines on 222 nm
- 318 exposure limits (ranging from 0.8 to 16 μ W/cm² assuming a continuous 8-hour exposure^{40,41}) as
- 319 well as the values in previous studies used for pathogen deactivation (average irradiance of up to
- 320 2.73 μ W/cm² at 1.7 m above the ground from Eadie et al.⁴² and 3.5 μ W/cm² from Peng et al.²³).
- 321 The range used in our model extends higher to take into account proposals for the use of
- 322 significantly higher light fluence rates, 4^{3} and include the fluence rates in our experiments (~45
- 323 μ W/cm²). Ventilation rates span a range of typical indoor values, and include the minimum
- 324 American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE)
- recommendations for homes (0.35 ACH), offices (~2-3 ACH), and health care settings (10
- 326 ACH).⁴⁴

	A. Effective air changes per hour (eACH)								B. Steady-state ozone (ppb)							
	50	589	589	589	590	591	594	599	50	116	112	106	97	79	64	51
${ m iUV}_{222}$ fluence rate (${ m \mu W}~{ m cm}^{-2}$	25	294	295	295	295	297	299	304	25	58	57	55	52	46	41	37
	10	118	118	118	119	120	123	128	10	23	24	24	25	27	28	29
	5	59	59	59	60	61	64	69	5	12	13	14	16	20	23	26
	2.5	30	30	30	30	32	34	39	2.5	6.2	7.5	9.2	12	17	21	24
	1	12	12	12	13	14	17	22	1	2.9	4.3	6.2	9.2	15	20	24
	0.5	6	6.1	6.4	6.9	8.4	11	16	0.5	1.8	3.2	5.1	8.3	14	19	23
0	0	0.1	0.25	0.5	1	2.5	5	10	0	0.81	2.1	4.1	7.4	14	19	23
		0.1	0.25	0.5	1	2.5	5	10		0.1	0.25	0.5	1	2.5	5	10
C. Steady-state OH (molec. $\text{cm}^{-3} \times 10^{-6}$) D. Steady-state oxidation produced														ducts	(ppb)	
-	50	0.25	0.54	0.9	1.4	2.2	2.8	3.8	50	96	35	15	6.3	1.7	0.58	0.2
cm ⁻²	25	0.14	0.28	0.43	0.61	0.86	1.1	1.6	25	72	25	10	3.8	0.92	0.29	0.096
Μη)	10	0.091	0.16	0.22	0.28	0.38	0.49	0.68	10	56	17	6.5	2.3	0.52	0.16	0.052
rate	5	0.067	0.1	0.14	0.18	0.26	0.35	0.47	5	46	13	4.7	1.6	0.39	0.13	0.04
snce	2.5	0.046	0.07	0.096	0.13	0.21	0.28	0.37	2.5	36	9.7	3.5	1.3	0.33	0.11	0.035
22 flue	1	0.027	0.045	0.068	0.11	0.18	0.25	0.32	1	24	6.7	2.6	1	0.29	0.1	0.032
SUV _{2:}	0.5	0.019	0.035	0.058	0.096	0.17	0.24	0.3	0.5	17	5.4	2.3	0.95	0.28	0.098	0.031
0	0	0.009	0.025	0.048	0.086	0.16	0.23	0.28	0	9.3	3.9	1.9	0.86	0.26	0.094	0.03
		0.1	0.25 Ve	0.5 entilati	1 on rate	2.5 e (ACI	0.1 0.25 0.5 1 2.5 5 10 ventilation rate (ACH)									

328 Figure 5: Effects of ventilation and GUV₂₂₂ fluence rate on modeled GUV efficacy and indoor 329 air quality (see also Figures S9-S12). Panel A: effective air changes per hour (eACH) for indoor pathogens, based on the previously reported inactivation rate of SARS-CoV-2 at 222 nm⁴⁵ 330 331 (Section S4.2). Panels B-D: steady-state concentrations of (B) O₃, (C) OH, and (D) organic 332 oxidation products, respectively, as predicted by the photochemical box model. Panel D 333 calculations assume unit yields, and do not account for VOC production from surfaces (see 334 Figure S11) or recycling by NO_x-HO_x interactions (Figure S12), so likely represent lower limits. Lighter colors represent larger values; note that the logarithmic color scaling is different for each 335 336 panel. Additional model results are given in Figures S9 and S10.

- 338 Key model results are provided in Figure 5. Figure 5A shows the effective air change rate
- 339 (eACH) across a wide range of GUV₂₂₂ fluence and ventilation rates; even modest irradiation
- levels lead to substantial increases in eACH (see also Figure S9A). Figures 5B, C, and D show
- 341 the steady-state indoor concentrations of O₃, OH, and total oxidation products (assuming unit
- 342 yield), respectively.
- 343 Steady-state ozone levels (Figure 5B) are higher with 222 nm irradiation than without. Sources
- of O₃ include photochemistry (R1-2) and infiltration of outdoor air, while sinks include
- 345 deposition, ventilation, and chemical reaction (rates and contributions of individual processes are
- 346 given in Figures S9B-E). With low irradiation, O₃ levels are governed mainly by infiltration of
- outdoor air, and O₃ increases are modest. Under the highest fluence rates (>25 μ W/cm²), and
- especially under low ventilation rates (<1 ACH), indoor O_3 can reach levels exceeding that of the outdoors, and can even exceed the OSHA indoor limit of 100 ppb. However, even a small
- 349 outdoors, and can even exceed the OSHA indoor mint of 100 ppb. However, even a sman
 350 change in indoor O₃ levels can have a dramatic effect on people's total ozone exposure,⁴⁶ given
- the large fraction of time people spend indoors. In most cases, deposition represents the
- 252 deminent sink of spans (Figure SOD)
- dominant sink of ozone (Figure S9D).
- 353 Figure 5C shows steady-state levels of OH as a function of ventilation and 222 nm light
- 354 intensity. Sources of OH include O3-alkene reactions (R3) and photochemistry (R4-5), while
- 355 sinks are dominated by reactive losses (see also Figures S9F-G). In the absence of GUV₂₂₂
- irradiation, modeled OH is from alkene ozonolysis only, with predicted levels ($\sim 10^5$ molec cm⁻³)
- 357 overlapping but falling on the low end of measured and modeled OH in indoor spaces (which
- range from $6x10^4$ -1. $6x10^6$ molec cm⁻³);^{47–56} this underestimate may arise from the omission of
- 359 photolysis of trace species such as nitrous acid (HONO) or aldehydes, which may be important
- 360 in some environments.⁵⁷ As with O_3 , GUV_{222} irradiation leads to increases in indoor levels of
- 361 OH. At low to moderate irradiation levels, this increase in OH is mostly due to the alkene 362 ozonolysis reaction, while at higher levels, ozone photolysis plays a larger role (Figure S9G).
- 363 OH increases with increasing photochemistry (higher GUV₂₂₂ fluence rates and ozone
- 364 concentrations), but is substantially modulated by losses from reaction with VOCs. VOC
- 365 concentrations are higher at low ventilation rates (see Figure S9H), due to the buildup of emitted
- 366 VOCs, which suppresses OH concentrations. At high light intensities, steady-state OH levels can
- 367 approach outdoor levels, matching or exceeding indoor OH measurements during transient
- 368 events such as cleaning or cooking activities.^{58,59}
- 369 The production of O₃ and OH by GUV₂₂₂-driven chemistry and their subsequent reactions with
- 370 VOCs leads to an increase in organic oxidation products (OVOCs and SOA). Steady-state levels
- 371 and production rates of such products (assuming unit yields) are shown in Figures 5D and S9I.
- 372 Concentrations increase with increased light intensity, and are especially high at low ventilation
- 373 rates. Since more than one product molecule may be formed per oxidation reaction, and OVOCs
- 374 may also be formed by surface reactions of O₃ or OH, these numbers likely represent lower
- 375 limits. Of particular concern is the production of hazardous air pollutants (HAPs, such as CH₂O)
- and SOA, both of which may represent health hazards in the indoor environment. Concentrations
- 377 of SOA are challenging to predict, as SOA production depends on the amounts and identity of
- 378 the indoor VOCs, as well as on a host of reaction conditions. However, SOA levels on the order

- of a few μ g/m³ might occur (Figure S10); the production of SOA from 222 nm irradiation in
- 380 realistic indoor settings is an important area of future research.
- 381 The simplicity of the model neglects some additional secondary effects, which are highly
- 382 uncertain. For example, volatile secondary organic products stemming from reactive surface
- 383 losses of O₃ (e.g., to paint, textiles, skin)^{12,60} could represent an additional secondary effect of
- 384 GUV₂₂₂ on indoor air quality. Preliminary modeling suggests that this may increase OVOC
- concentrations by as much as a factor of 100 (Figure S11). Similarly, indoor environments
 contain NO_X, which can affect the levels and fates of oxidants. While NO_X chemistry is not
- 387 modeled explicitly here, due in part to uncertainties in NOx photolysis processes, we have
- 388 carried out additional simulations to estimate the role of HOx-NO_x cycling. As shown in Section
- 389 S4.1 and Figure S12, such cycling increases OH concentrations and OVOC product formation
- 390 substantially. We do not examine the role of HONO, which can be present in high (ppb) levels
- indoors⁵⁵ and absorbs strongly at 222 nm ($\sigma = 1.35 \times 10^{-18} \text{ cm}^{2.9}$); HONO photolysis may lead to
- 392 even higher OH levels than predicted here. All of these effects have the potential to increase
- 393 OVOC formation, suggesting that the OVOC concentrations presented in Figure 5 are best
- understood as a lower limit and that the indoor air quality impacts of 222 nm irradiation could be
- 395 more severe than predicted here.

396 Implications

- 397 Our laboratory studies demonstrate that GUV₂₂₂ light leads to the production of (1) ozone, (2)
- 398 OH radicals, and (3) secondary organic species (OVOCs and SOA); these are in broad agreement
- 399 with prior model predictions.²³ The resulting concentrations of such secondary species can be
- 400 substantially higher than are normally found in indoor environments; in extreme cases, these
- 401 increases can be dramatic, leading to oxidation conditions similar to those found in outdoor
- 402 environments. The negative health impacts associated with the unavoidable generation of these
 403 secondary species most importantly O₃, fine particular matter, and HAPs thus need to be
- taken into account (and ideally mitigated) when considering the use of 222 nm disinfection in
- 405 indoor spaces.
- 406 While a detailed analysis of the health impacts of GUV₂₂₂ use (both the benefits from
- 407 inactivation of airborne pathogens and the drawbacks from secondary pollutant formation) is
- 408 beyond the scope of this work, our results offer some broad guidance as to the optimal use of
- 409 GUV₂₂₂ in indoor environments. Most importantly, GUV₂₂₂ disinfection alone is not a safe
- 410 substitute for ventilation as a means to control levels of indoor airborne pathogens, as it can lead
- 411 to the buildup of indoor ozone and other pollutants to dangerous levels (Figure 5). However,
- 412 GUV₂₂₂ may be effectively used in conjunction with ventilation: relatively modest irradiation
- 413 levels combined with carefully chosen ventilation conditions can greatly enhance the effective
- 414 air change rate (Figure 5A), while limiting the levels of secondary pollutants (Figures 5B-D).
- 415 Moreover, due to the unavoidable formation of secondary pollutants, GUV₂₂₂ lights should be
- 416 run at the lowest effective levels whenever possible. Further, the combination of GUV₂₂₂
- 417 irradiation with air-cleaning technologies (e.g., sorbents for ozone and OVOCs, filters for
- 418 particulate matter) may serve to minimize indoor secondary pollutant levels, potentially enabling

- 419 safer use of GUV₂₂₂ under poorly-ventilated environments. Quantifying the benefits and
- 420 tradeoffs of these combined approaches (ventilation, GUV₂₂₂ irradiation, and/or air cleaning) in
- 421 terms of pathogen transmission, air pollutant levels, human health, and cost-effectiveness, is a
- 422 critical next step toward ensuring healthier indoor environments.

423 Supporting Information

- 424 Experimental conditions and methods, additional modeling methods, additional results and
- 425 discussion (incl. ozone steady-state calculations, discussion of VOC loss pathways, discussion of
- 426 elevated VOC and RH experiments, more complete product distribution figures, reaction
- 427 schemes, and SMPS data), model results (incl. additional model output figures and calculation of
- 428 effective air changes per hour) (PDF)

429 Acknowledgements and Funding Sources

- 430 This work is supported by the U.S. National Science Foundation under grants ECS-2108811 and
- 431 AGS-2129835 and the Harvard Global Institute. The authors thank Bella Nesti (Harvard
- 432 University) for assisting with the initial phases of data analysis, and Jose Jimenez (University of
- 433 Colorado Boulder) for helpful discussions.

434 **References**

- 435 (1) Wells, W. F.; Wells, M. W.; Wilder, T. S. The Environmental Control of Epidemic
 436 Contagion: I. An Epidemiologic Study of Radiant Disinfection of Air in Day Schools.
 437 American Journal of Epidemiology 1942, 35 (1), 97–121.
 428 https://doi.org/10.1002/outparticeumals.gip.el18780
- 438 https://doi.org/10.1093/oxfordjournals.aje.a118789.
- 439 (2) Nardell, E. A. Air Disinfection for Airborne Infection Control with a Focus on COVID-19:
 440 Why Germicidal UV Is Essential[†]. *Photochemistry and Photobiology* 2021, 97 (3), 493–
 441 497. https://doi.org/10.1111/php.13421.
- 442 (3) Centers for Disease Control and Prevention. Upper Room Ultraviolet Germicidal
 443 Irradiation (UVGI). https://www.cdc.gov/coronavirus/2019444 ncov/community/ventilation/uvgi.html (accessed 2023-05-17).
- 445 (4) Blatchley, E. R.; Brenner, D.; Claus, H.; Cowan, T. E.; Linden, K.; Liu, Y.; Mao, T.; Park,
 446 S.-J.; Simons, R.; Sliney, D. *Far UV-C Radiation: Current State-of Knowledge*; White
 447 paper; International Ultraviolet Association Task Force.
- 448 (5) Buonanno, M.; Welch, D.; Shuryak, I.; Brenner, D. J. Far-UVC Light (222 Nm) Efficiently
 449 and Safely Inactivates Airborne Human Coronaviruses. *Sci Rep* 2020, *10* (1), 10285.
 450 https://doi.org/10.1038/s41598-020-67211-2.
- 451 (6) Collins, D. B.; Farmer, D. K. Unintended Consequences of Air Cleaning Chemistry.
 452 *Environ. Sci. Technol.* 2021, 55 (18), 12172–12179.
 453 https://doi.org/10.1021/acs.est.1c02582.
- (7) Ye, Q.; Krechmer, J. E.; Shutter, J. D.; Barber, V. P.; Li, Y.; Helstrom, E.; Franco, L. J.;
 Cox, J. L.; Hrdina, A. I. H.; Goss, M. B.; Tahsini, N.; Canagaratna, M.; Keutsch, F. N.;
- 456 Kroll, J. H. Real-Time Laboratory Measurements of VOC Emissions, Removal Rates, and
- 457 Byproduct Formation from Consumer-Grade Oxidation-Based Air Cleaners. *Environ. Sci.*
- 458 *Technol. Lett.* **2021**, *8* (12), 1020–1025. https://doi.org/10.1021/acs.estlett.1c00773.
- 459 (8) Turner, M. C.; Jerrett, M.; Pope, C. A.; Krewski, D.; Gapstur, S. M.; Diver, W. R.;
- 460 Beckerman, B. S.; Marshall, J. D.; Su, J.; Crouse, D. L.; Burnett, R. T. Long-Term Ozone

- 461 Exposure and Mortality in a Large Prospective Study. *Am J Respir Crit Care Med* **2016**,
- 462 *193* (10), 1134–1142. https://doi.org/10.1164/rccm.201508-1633OC.
- 463 (9) Burkholder, J.; Sander, S. P.; Abbatt, J. P. D.; Barker, J. R.; Cappa, C.; Crounse, J. D.;
 464 Dibble, T. S.; Huie, R. E.; Kolb, C. E.; Kurylo, M. J.; Orkin, V. L.; Percival, C. J.;
 465 Wilmouth, D. M.; Wine, P. H. *Chemical Kinetics and Photochemical Data for Use in*466 *Atmospheric Studies*; 19–5; NASA Jet Propulsion Laboratory, 2020.
- 467 (10) Nazaroff, W. W.; Weschler, C. J. Indoor Ozone: Concentrations and Influencing Factors.
 468 *Indoor Air* 2022, *32* (1). https://doi.org/10.1111/ina.12942.
- (11) Calvert, J. G. *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University
 Press, 2000.
- 471 (12) Wisthaler, A.; Weschler, C. J. Reactions of Ozone with Human Skin Lipids: Sources of
 472 Carbonyls, Dicarbonyls, and Hydroxycarbonyls in Indoor Air. *Proceedings of the National*473 *Academy of Sciences* 2010, 107 (15), 6568–6575. https://doi.org/10.1073/pnas.0904498106.
- 474 (13) Kroll, J. H.; Seinfeld, J. H. Chemistry of Secondary Organic Aerosol: Formation and
 475 Evolution of Low-Volatility Organics in the Atmosphere. *Atmospheric Environment* 2008,
 476 42 (16), 3593–3624. https://doi.org/10.1016/j.atmosenv.2008.01.003.
- 477 (14) US EPA. Dose-Response Assessment for Assessing Health Risks Associated with Exposure
 478 to Hazardous Air Pollutants. https://www.epa.gov/fera/dose-response-assessment-
- 479 assessing-health-risks-associated-exposure-hazardous-air-pollutants (accessed 2023-05-02).
- (15) Dockery, D. W.; Pope, C. A.; Xu, X.; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, B. G.;
 Speizer, F. E. An Association between Air Pollution and Mortality in Six U.S. Cities. *New England Journal of Medicine* 1993, *329* (24), 1753–1759.
 https://doi.org/10.1056/NEJM199312093292401.
- (16) Burnett, R.; Chen, H.; Szyszkowicz, M.; Fann, N.; Hubbell, B.; Pope, C. A.; Apte, J. S.;
 Brauer, M.; Cohen, A.; Weichenthal, S.; Coggins, J.; Di, Q.; Brunekreef, B.; Frostad, J.;
- 486 Lim, S. S.; Kan, H.; Walker, K. D.; Thurston, G. D.; Hayes, R. B.; Lim, C. C.; Turner, M.
- C.; Jerrett, M.; Krewski, D.; Gapstur, S. M.; Diver, W. R.; Ostro, B.; Goldberg, D.; Crouse,
 D. L.; Martin, R. V.; Peters, P.; Pinault, L.; Tjepkema, M.; van Donkelaar, A.; Villeneuve,
- 488 D. L., Martin, K. V., Peters, F., Pinautt, L., Tjepkenia, M., Van Donkenaar, A., Vineneuve, 489 P. J.; Miller, A. B.; Yin, P.; Zhou, M.; Wang, L.; Janssen, N. A. H.; Marra, M.; Atkinson,
- 490 R. W.; Tsang, H.; Quoc Thach, T.; Cannon, J. B.; Allen, R. T.; Hart, J. E.; Laden, F.;
- 491 Cesaroni, G.; Forastiere, F.; Weinmayr, G.; Jaensch, A.; Nagel, G.; Concin, H.; Spadaro, J.
- V. Global Estimates of Mortality Associated with Long-Term Exposure to Outdoor Fine
 Particulate Matter. *Proceedings of the National Academy of Sciences* 2018, *115* (38), 9592–
- 494 9597. https://doi.org/10.1073/pnas.1803222115.
- 495 (17) Pye, H. O. T.; Ward-Caviness, C. K.; Murphy, B. N.; Appel, K. W.; Seltzer, K. M.
 496 Secondary Organic Aerosol Association with Cardiorespiratory Disease Mortality in the
 497 United States. *Nat Commun* 2021, *12* (1), 7215. https://doi.org/10.1038/s41467-021-27484498 1.
- (18) Donahue, N. M.; Drozd, G. T.; Epstein, S. A.; Presto, A. A.; Kroll, J. H. Adventures in
 Ozoneland: Down the Rabbit-Hole. *Phys. Chem. Chem. Phys.* 2011, *13* (23), 10848–10857.
 https://doi.org/10.1039/C0CP02564J.
- 502 (19) Levy, H. Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted.
 503 Science 1971, 173 (3992), 141–143. https://doi.org/10.1126/science.173.3992.141.
- 504 (20) Bender, E. Disinfecting the Air with Far-Ultraviolet Light. *Nature* 2022, *610* (7933), S46–
 505 S47. https://doi.org/10.1038/d41586-022-03360-w.

- 506 (21) Link, M. F.; Shore, A.; Hamadani, B. H.; Poppendieck, D. Ozone Generation from a
 507 Germicidal Ultraviolet Lamp with Peak Emission at 222 Nm. *Environ. Sci. Technol. Lett.*508 2023, 10 (8), 675–679. https://doi.org/10.1021/acs.estlett.3c00318.
- (22) Peng, Z.; Day, D. A.; Symonds, G. A.; Jenks, O. J.; Stark, H.; Handschy, A. V.; de Gouw,
 J. A.; Jimenez, J. L. Significant Production of Ozone from Germicidal UV Lights at 222
 Nm. *Environ. Sci. Technol. Lett.* 2023, *10* (8), 668–674.
- 512 https://doi.org/10.1021/acs.estlett.3c00314.
- (23) Peng, Z.; Miller, S. L.; Jimenez, J. L. Model Evaluation of Secondary Chemistry Due to
 Disinfection of Indoor Air with Germicidal Ultraviolet Lamps. *Environ. Sci. Technol. Lett.*2023, 10 (1), 6–13. https://doi.org/10.1021/acs.estlett.2c00599.
- 516 (24) Ushio, Inc. Care222 Technical Specification Sheet.
 517 https://www.ushio.com/files/specifications/care222-filtered-far-uv-c-excimer-lamp-module 518 technical-data-sheet.pdf (accessed 2023-05-03).
- 519 (25) Krechmer, J.; Lopez-Hilfiker, F.; Koss, A.; Hutterli, M.; Stoermer, C.; Deming, B.;
- Kimmel, J.; Warneke, C.; Holzinger, R.; Jayne, J.; Worsnop, D.; Fuhrer, K.; Gonin, M.; de
 Gouw, J. Evaluation of a New Reagent-Ion Source and Focusing Ion–Molecule Reactor for
 Use in Proton-Transfer-Reaction Mass Spectrometry. *Anal. Chem.* 2018, *90* (20), 12011–
 12018. https://doi.org/10.1021/acs.analchem.8b02641.
- (26) Zaytsev, A.; Breitenlechner, M.; Koss, A. R.; Lim, C. Y.; Rowe, J. C.; Kroll, J. H.;
 Keutsch, F. N. Using Collision-Induced Dissociation to Constrain Sensitivity of Ammonia Chemical Ionization Mass Spectrometry (NH4+ CIMS) to Oxygenated Volatile Organic Compounds. *Atmos. Meas. Tech.* 2019, *12* (3), 1861–1870. https://doi.org/10.5194/amt-12-1861-2019.
- (27) DeCarlo, P. F.; Kimmel, J. R.; Trimborn, A.; Northway, M. J.; Jayne, J. T.; Aiken, A. C.;
 Gonin, M.; Fuhrer, K.; Horvath, T.; Docherty, K. S.; Worsnop, D. R.; Jimenez, J. L. FieldDeployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer. *Anal. Chem.*2006, 78 (24), 8281–8289. https://doi.org/10.1021/ac061249n.
- (28) Stewart, D. J.; Almabrok, S. H.; Lockhart, J. P.; Mohamed, O. M.; Nutt, D. R.; Pfrang, C.;
 Marston, G. The Kinetics of the Gas-Phase Reactions of Selected Monoterpenes and CycloAlkenes with Ozone and the NO3 Radical. *Atmospheric Environment* 2013, *70*, 227–235.
 https://doi.org/10.1016/j.atmosenv.2013.01.036.
- (29) Aschmann, S. M.; Arey, J.; Atkinson, R. Kinetics and Products of the Reactions of OH
 Radicals with Cyclohexene, 1-Methyl-1-Cyclohexene, *Cis* -Cyclooctene, and *Cis* Cyclodecene. J. Phys. Chem. A 2012, 116 (38), 9507–9515.
- 540 https://doi.org/10.1021/jp307217m.
- (30) D'Anna, B.; Andresen, Ø.; Gefen, Z.; J. Nielsen, C. Kinetic Study of OH and NO 3 Radical
 Reactions with 14 Aliphatic Aldehydes. *Physical Chemistry Chemical Physics* 2001, *3* (15),
 3057–3063. https://doi.org/10.1039/B103623H.
- (31) Grøntoft, T.; Raychaudhuri, M. R. Compilation of Tables of Surface Deposition Velocities
 for O3, NO2 and SO2 to a Range of Indoor Surfaces. *Atmospheric Environment* 2004, *38*(4), 533–544. https://doi.org/10.1016/j.atmosenv.2003.10.010.
- 547 (32) Saunders, S. M.; Jenkin, M. E.; Derwent, R. G.; Pilling, M. J. Protocol for the Development
 548 of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric Degradation of Non-
- 549 Aromatic Volatile Organic Compounds. *Atmospheric Chemistry and Physics* **2003**, *3* (1),
- 550 161–180. https://doi.org/10.5194/acp-3-161-2003.

- (33) Hansel, A.; Scholz, W.; Mentler, B.; Fischer, L.; Berndt, T. Detection of RO2 Radicals and
 Other Products from Cyclohexene Ozonolysis with NH4+ and Acetate Chemical Ionization
 Mass Spectrometry. *Atmospheric Environment* 2018, *186*, 248–255.
 https://doi.org/10.1016/j.atmosenv.2018.04.023.
- (34) Aschmann, S. M.; Tuazon, E. C.; Arey, J.; Atkinson, R. Products of the Gas-Phase Reaction
 of O3 with Cyclohexene. J. Phys. Chem. A 2003, 107 (13), 2247–2255.
 https://doi.org/10.1021/jp022122e.
- (35) Barua, S.; Iyer, S.; Kumar, A.; Seal, P.; Rissanen, M. An Aldehyde as a Rapid Source of
 Secondary Aerosol Precursors: Theoretical and Experimental Study of Hexanal
 Autoxidation. EGUsphere 2023, 1–24. https://doi.org/10.5194/egusphere-2023-128.
- (36) Singer, B. C.; Coleman, B. K.; Destaillats, H.; Hodgson, A. T.; Lunden, M. M.; Weschler,
 C. J.; Nazaroff, W. W. Indoor Secondary Pollutants from Cleaning Product and Air
 Freshener Use in the Presence of Ozone. *Atmospheric Environment* 2006, 40 (35), 6696–
 6710. https://doi.org/10.1016/j.atmosenv.2006.06.005.
- (37) Wainman, T.; Zhang, J.; Weschler, C. J.; Lioy, P. J. Ozone and Limonene in Indoor Air: A
 Source of Submicron Particle Exposure. *Environmental Health Perspectives* 2000, *108*(12), 1139–1145. https://doi.org/10.1289/ehp.001081139.
- (38) Price, D. J.; Day, D. A.; Pagonis, D.; Stark, H.; Algrim, L. B.; Handschy, A. V.; Liu, S.;
 Krechmer, J. E.; Miller, S. L.; Hunter, J. F.; de Gouw, J. A.; Ziemann, P. J.; Jimenez, J. L.
 Budgets of Organic Carbon Composition and Oxidation in Indoor Air. *Environ. Sci. Technol.* 2019, *53* (22), 13053–13063. https://doi.org/10.1021/acs.est.9b04689.
- (39) Mattila, J. M.; Arata, C.; Abeleira, A.; Zhou, Y.; Wang, C.; Katz, E. F.; Goldstein, A. H.;
 Abbatt, J. P. D.; DeCarlo, P. F.; Vance, M. E.; Farmer, D. K. Contrasting Chemical
 Complexity and the Reactive Organic Carbon Budget of Indoor and Outdoor Air. *Environ. Sci. Technol.* 2022, *56* (1), 109–118. https://doi.org/10.1021/acs.est.1c03915.
- (40) International Commission on Non-Ionizing Radiation Protection (ICNIRP). Guidelines on
 Limits of Exposure to Ultraviolet Radiation of Wavelengths between 180 Nm and 400 Nm
 (Incoherent Optical Radiation). *Health Phys* 2004, 87 (2), 171–186.
 https://doi.org/10.1097/00004032-200408000-00006.
- (41) American Conference of Governmental Industrial Hygienists. 2023 Threshold Limit Values
 (TLVs) and Biological Exposure Indices (BEIs); 2023.
- 582 (42) Eadie, E.; Hiwar, W.; Fletcher, L.; Tidswell, E.; O'Mahoney, P.; Buonanno, M.; Welch, D.;
 583 Adamson, C. S.; Brenner, D. J.; Noakes, C.; Wood, K. Far-UVC (222 Nm) Efficiently
 584 Inactivates an Airborne Pathogen in a Room-Sized Chamber. *Sci Rep* 2022, *12* (1), 4373.
 585 https://doi.org/10.1038/s41598-022-08462-z.
- 586 (43) Esvelt, K. M. Delay, Detect, Defend: Preparing for a Future in Which Thousands Can
 587 Release New Pandemics. *The Geneva Centre for Security and Policy*. November 2022.
- 588 (44) ASHRAE/ANSI Standard 62.1-2022. Ventilation and Acceptable Indoor Air Quality, 2022.
- (45) Ma, B.; Linden, Y. S.; Gundy, P. M.; Gerba, C. P.; Sobsey, M. D.; Linden, K. G.
 Inactivation of Coronaviruses and Phage Phi6 from Irradiation across UVC Wavelengths. *Environ. Sci. Technol. Lett.* 2021, 8 (5), 425–430.
- 592 https://doi.org/10.1021/acs.estlett.1c00178.
- 593 (46) Weschler, C. J. Ozone's Impact on Public Health: Contributions from Indoor Exposures to
- 594 Ozone and Products of Ozone-Initiated Chemistry. *Environ Health Perspect* 2006, *114*
- 595 (10), 1489–1496. https://doi.org/10.1289/ehp.9256.

- 596 (47) Weschler, C. J.; Shields, H. C. Production of the Hydroxyl Radical in Indoor Air. *Environ*.
- 597 Sci. Technol. **1996**, 30 (11), 3250–3258. https://doi.org/10.1021/es960032f.
- (48) Weschler, C. J.; Shields, H. C. Measurements of the Hydroxyl Radical in a Manipulated but Realistic Indoor Environment. *Environ. Sci. Technol.* 1997, *31* (12), 3719–3722.
 https://doi.org/10.1021/es970669e.
- (49) Carslaw, N. A New Detailed Chemical Model for Indoor Air Pollution. *Atmospheric Environment* 2007, *41* (6), 1164–1179. https://doi.org/10.1016/j.atmosenv.2006.09.038.
- (50) Waring, M. S.; Wells, J. R. Volatile Organic Compound Conversion by Ozone, Hydroxyl Radicals, and Nitrate Radicals in Residential Indoor Air: Magnitudes and Impacts of Oxidant Sources. *Atmospheric Environment* 2015, *106*, 382–391. https://doi.org/10.1016/j.atmosenv.2014.06.062.
- (51) Carslaw, N.; Fletcher, L.; Heard, D.; Ingham, T.; Walker, H. Significant OH Production
 under Surface Cleaning and Air Cleaning Conditions: Impact on Indoor Air Quality. *Indoor Air* 2017, 27 (6), 1091–1100. https://doi.org/10.1111/ina.12394.
- 610 (52) Gligorovski, S.; Weschler, C. J. The Oxidative Capacity of Indoor Atmospheres. *Environ.*611 *Sci. Technol.* 2013, 47 (24), 13905–13906. https://doi.org/10.1021/es404928t.
- (53) Fiorentino, E.-A.; Chen, H.; Gandolfo, A.; Lannuque, V.; Sartelet, K.; Wortham, H.
 Measurements and Modelling of OH and Peroxy Radicals in an Indoor Environment Under
 Different Light Conditions and VOC Levels. *Atmospheric Environment* 2023, 292, 119398.
 https://doi.org/10.1016/j.atmosenv.2022.119398.
- (54) Mendez, M.; Amedro, D.; Blond, N.; Hauglustaine, D. A.; Blondeau, P.; Afif, C.; Fittschen,
 C.; Schoemaecker, C. Identification of the Major HOx Radical Pathways in an Indoor Air
 Environment. *Indoor Air* 2017, 27 (2), 434–442. https://doi.org/10.1111/ina.12316.
- 619 (55) Gómez Alvarez, E.; Amedro, D.; Afif, C.; Gligorovski, S.; Schoemaecker, C.; Fittschen, C.;
 620 Doussin, J.-F.; Wortham, H. Unexpectedly High Indoor Hydroxyl Radical Concentrations
 621 Associated with Nitrous Acid. *Proceedings of the National Academy of Sciences* 2013, *110*622 (33), 13294–13299. https://doi.org/10.1073/pnas.1308310110.
- (56) Zannoni, N.; Lakey, P. S. J.; Won, Y.; Shiraiwa, M.; Rim, D.; Weschler, C. J.; Wang, N.;
 Ernle, L.; Li, M.; Bekö, G.; Wargocki, P.; Williams, J. The Human Oxidation Field. *Science* 2022, *377* (6610), 1071–1077. https://doi.org/10.1126/science.abn0340.
- (57) Kowal, S. F.; Allen, S. R.; Kahan, T. F. Wavelength-Resolved Photon Fluxes of Indoor
 Light Sources: Implications for HOx Production. *Environ. Sci. Technol.* 2017, *51* (18),
 10423–10430. https://doi.org/10.1021/acs.est.7b02015.
- (58) Rosales, C. M. F.; Jiang, J.; Lahib, A.; Bottorff, B. P.; Reidy, E. K.; Kumar, V.; Tasoglou,
 A.; Huber, H.; Dusanter, S.; Tomas, A.; Boor, B. E.; Stevens, P. S. Chemistry and Human
 Exposure Implications of Secondary Organic Aerosol Production from Indoor Terpene
- 632 Ozonolysis. *Science Advances* **2022**, *8* (8), eabj9156.
- 633 https://doi.org/10.1126/sciadv.abj9156.
- 634 (59) Reidy, E.; Bottorff, B. P.; Rosales, C. M. F.; Cardoso-Saldaña, F. J.; Arata, C.; Zhou, S.;
 635 Wang, C.; Abeleira, A.; Hildebrandt Ruiz, L.; Goldstein, A. H.; Novoselac, A.; Kahan, T.
- 636 F.; Abbatt, J. P. D.; Vance, M. E.; Farmer, D. K.; Stevens, P. S. Measurements of Hydroxyl
- 637 Radical Concentrations during Indoor Cooking Events: Evidence of an Unmeasured
- 638 Photolytic Source of Radicals. *Environ. Sci. Technol.* **2023**, *57* (2), 896–908.
- 639 https://doi.org/10.1021/acs.est.2c05756.

- 640 (60) Wang, H.; Morrison, G. Ozone-Surface Reactions in Five Homes: Surface Reaction
- 641 Probabilities, Aldehyde Yields, and Trends. *Indoor Air* **2010**, *20* (3), 224–234.
- 642 https://doi.org/10.1111/j.1600-0668.2010.00648.x.