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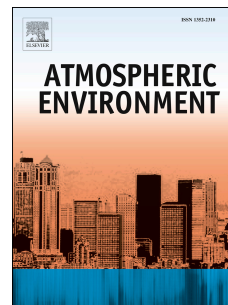
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Ozone reaction with interior building materials: influence of diurnal ozone variation, temperature and humidity

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Abstract

Elevated tropospheric ozone concentrations are associated with increased morbidity and mortality. Indoor ozone chemistry affects human exposure to ozone and reaction products that also may adversely affect health and comfort. Reactive uptake of ozone has been characterized for many building materials; however, scant information is available on how diurnal variation of ambient ozone influences ozone reaction with indoor surfaces. The primary objective of this study is to investigate ozone-surface reactions in response to a diurnally varying ozone exposure for three common building materials: ceiling tile, painted drywall, and carpet tile. A secondary objective is to examine the effects of air temperature and humidity. A third goal is to explore how conditioning of materials in an occupied office building might influence subsequent ozone-surface reactions. Experiments were performed at bench-scale with inlet ozone concentrations varied to simulate daytime (ozone elevated) and nighttime (ozone-free in these experiments) periods. To simulate office conditions, experiments were conducted at two temperatures (22 °C and 28 °C) and three relative humidity values (25%, 50%, 75%). Effects of indoor surface exposures were examined by placing material samples in an occupied office and repeating bench-scale characterization after exposure periods of 1 and 2 months. Deposition velocities were observed to be highest during the initial hour of ozone exposure with slow decrease in the subsequent hours of simulated daytime conditions. Daily-average ozone reaction probabilities for fresh materials are in the respective ranges of $(1.7-2.7) \times 10^{-5}$, $(2.8-4.7) \times 10^{-5}$, and $(3.0-4.5) \times 10^{-5}$ for ceiling tile, painted drywall, and carpet tile. The reaction probability decreases by 7% to 47% across the three test materials after two 8-h periods of ozone exposure. Measurements with the samples from an occupied office reveal that deposition velocity can decrease or increase with time. Influence of temperature and humidity on ozone-surface reactivity was not strong.

Keywords: deposition velocity, reaction probability, exposure, surface aging, regeneration

40 **1. Introduction**

41 Elevated outdoor ozone concentrations have been associated with an increased incidence of
42 adverse health effects, including premature mortality (Bell et al., 2006), asthma (Trasande and
43 Thurston, 2005), and chronic obstructive pulmonary disease (Kelly and Fussell, 2011). In most
44 epidemiological studies, outdoor ozone concentrations measured at central monitoring sites are
45 used as surrogates for human exposures. People spend the majority of their time in built
46 environments (Klepeis et al., 2001) and a substantial proportion of ozone exposure occurs
47 indoors (Weschler, 2006). Despite lower indoor concentrations, there remains the potential for
48 human health impacts at low ozone levels (Bell et al., 2006). In some guidance documents,
49 indoor levels are recommended to be reduced to “as low as reasonably achievable” (ASHRAE,
50 2011). Also, better understanding of indoor exposures for air pollutants of outdoor origin can
51 improve epidemiological estimates (Özkaynak et al., 2013). In the case of ozone, evidence
52 suggests that indoor-outdoor ozone relationships may, in part, explain variability in ozone
53 mortality coefficients across US cities (Chen et al., 2012).

54 The predominant source of indoor ozone is transport from outdoors along with ventilation air. In
55 some circumstances, indoor sources may be present including photocopiers and printers (Tuomi
56 et al., 2000), air cleaners that produce ozone as a byproduct (Waring et al., 2008), or ozone
57 generators claiming to be indoor air purifiers. Whether originating indoors or outdoors, ozone in
58 indoor environments is affected by indoor heterogeneous and homogeneous chemistry. The
59 relevant implications of indoor chemistry on human exposure to ozone are twofold. First, as
60 ozone is a reactant, indoor concentrations of ozone may be appreciably suppressed as reactions
61 proceed (Weschler, 2000). Personal monitoring studies support the notion of reduced personal
62 ozone concentrations compared with outdoor air concentrations. For example, Delfino et al.

63 (1996) report 12-h personal ozone concentrations that averaged 27% of mean outdoor ozone
64 concentrations across 12 subjects. Secondly, indoor ozone chemistry creates reaction products
65 that themselves may be reactive and/or irritating (Weschler and Shields 1996; Wolkoff et al.
66 2006). Multiple logistic regression conducted as part of the BASE study implicated indoor
67 ozone-initiated reaction products as adversely affecting occupant health (Apte et al., 2008).
68 However, evaluation of airway effects in mice exposed to model indoor air mixtures containing
69 limonene/ozone reaction products showed non-cumulative sensory irritation as a key effect, but
70 no observation of airway inflammation, the latter hypothesized to be an underlying mechanism
71 leading to adverse health effects (Wolkoff et al. 2012). Further studies of ozone-initiated
72 reaction products from building materials, including combinations of building materials at a
73 variety of conditions, are needed to elucidate the potential sensory and airway effects of ozone-
74 initiated reaction products (Carslaw et al. 2009).

75 Ozone-surface reactions are prevalent indoors and compete with air-exchange rates as prominent
76 removal mechanisms. Many studies have explored ozone reactions with building materials and
77 indoor furnishings (Lamble et al., 2011; Gall et al., 2013; Morrison and Nazaroff, 2000; Wang
78 and Morrison, 2006; Wang and Morrison, 2010; Hoang et al., 2009; Klenø et al., 2001; Grøntoft,
79 2002; Grøntoft and Raychaudhuri, 2004; Grøntoft et al., 2004; Nazaroff et al., 1993; Wechsler et
80 al., 1992; Sabersky et al., 1973; Reiss et al., 1994; Nicolas et al., 2007; Lin and Hsu, 2015).

81 These studies generally report ozone deposition velocities and reaction probabilities for different
82 building materials under various chamber or building operation conditions. Several recent studies
83 have also discussed the potential for exploiting ozone reactions on interior surfaces for low-
84 energy indoor air cleaning (Kunkel et al., 2010; Cros et al., 2012; Gall et al., 2011).

85 Researchers have examined time-averaged ozone deposition characteristics using ozone supplied
86 at a constant inlet concentration in an experimental chamber over a certain time period. Several
87 studies report time-dependent ozone deposition velocities with a constant inlet concentration and
88 find that ozone uptake diminishes over exposure periods ranging from several hours to several
89 days (Morrison and Nazaroff, 2000; Poppendieck et al., 2007). Only one study (Hoang et al.,
90 2009) has reported transient ozone deposition velocities for time-varying ambient concentrations
91 such as consecutive 48-h high ozone and 24-h zero ozone exposure. Hoang et al. (2009) reported
92 that ozone removal decreased with time during periods of continuous exposure and also observed
93 regeneration of reactivity after subsequent 24-h periods of zero ozone exposure, especially for
94 ceiling tile and sunflower board. However, there is little information available concerning how
95 the common day-and-night variation of ambient ozone concentration might influence ozone
96 reaction dynamics. An understanding of the potential impact of diurnal ozone concentration
97 variation on temporal variation of ozone uptake to building materials would permit refinement in
98 indoor air quality models of the reactive uptake of ozone on building interior surfaces.

99 Another important feature is that few studies have explored the influence of occupancy (e.g., in
100 office buildings) on ozone-surface reaction dynamics. Some studies (Wang and Morrison, 2006;
101 Wang and Morrison, 2010; Cros et al., 2012) have examined ozone deposition velocities in
102 occupied residential buildings. Nonetheless, ozone chemistry in occupied office buildings
103 warrants special attention as it can influence building-related health symptoms, comfort, and
104 productivity (Apte et al., 2008, Wargocki et al., 1999). Furthermore, occupancy patterns in
105 office buildings coincide with the daytime periods during which outdoor ozone concentrations
106 are commonly elevated.

107 Based on this background, the objectives of the present study are 1) to investigate the diurnal
108 behavior of ozone-surface reactions for three common interior finishing materials: ceiling tile,
109 painted drywall, and carpet tile; and 2) to examine the ozone-surface reaction dynamics for the
110 same materials conditioned in an occupied office building. In addition, considering the range of
111 office environmental conditions, the present study also examines the effects of air temperature
112 and humidity on ozone-surface reaction dynamics.

113 **2. Methods**

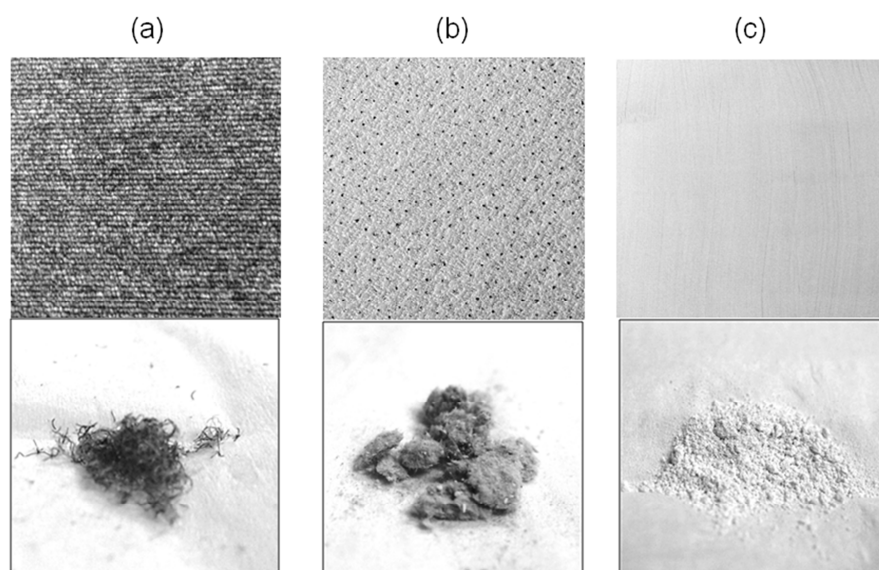
114 We measured ozone reaction rates in test chambers for three common indoor materials sourced
115 from Singapore. Rates were parameterized in terms of deposition velocities and reaction
116 probabilities. Materials were exposed under controlled conditions to a diurnally varying pattern
117 of ozone concentration. Independent variables included temperature and relative humidity. In
118 addition to measuring ozone reaction rates on new materials, we also conditioned the materials
119 by exposing samples for periods of one and two months to the air in an occupied office.

120 This section describes the detailed experimental investigation in the following order: 1) test
121 materials, 2) experimental apparatus, 3) the procedure to determine deposition velocity and
122 surface reaction probability, 4) protocols for examining ozone-surface reaction resulting from
123 material exposure in occupied indoor environments, and 5) quality assurance protocols.

124 *2.1 Selection of test materials*

125 Three types of common interior finishing materials — carpet tile, painted drywall, and ceiling
126 tile — were selected to represent 1) materials commonly installed in commercial office spaces
127 and 2) types of materials expected to comprise a large proportion of indoor surface area. The
128 carpet tile (Figure 1a) consisted of 100% bulked continuous filament synthetic fiber with PVC

129 backing (model Classic Modular Fasttrack; Weily Carpet). The thickness of carpet tile was 5.0
130 mm. The ceiling tiles (model Dune Max; Armstrong) were made of 74% recycled content and
131 were composed of a wet-formed mineral fiber and a factory-applied surface coating of latex paint
132 (Figure 1b). The ceiling tiles were marketed as qualifying for credits under the United States
133 Green Building Council LEED program. The thickness of ceiling tile was 19 mm. The drywall
134 (Figure 1c) was composed of a gypsum plaster core encased in durable, heavy-duty face and
135 backing liner (model Standard Core; Boral) with a thickness of 12.5 mm. The drywall was
136 painted with two coats of mold-guard paint (Mouldguard; Dulux) that was designed to prevent
137 mold growth on the interior surface. The paint was a blend of water, acrylic emulsion binder, and
138 non-lead pigments. The drywall was painted in two applications separated by 24 h to allow the
139 first application to dry. Painted drywall samples were then allowed to dry for 48 h and placed in
140 air-sealed plastic bags. Experiments were conducted with the painted drywall samples during the
141 subsequent 8 months. The thickness of the drywall sample was 13 mm. During experiments, all
142 material samples were placed on a foil backing to restrict ozone exposure to one primary surface.
143 The nominal material surface area exposed to bulk chamber air was 200 cm² for each tested
144 sample.



145

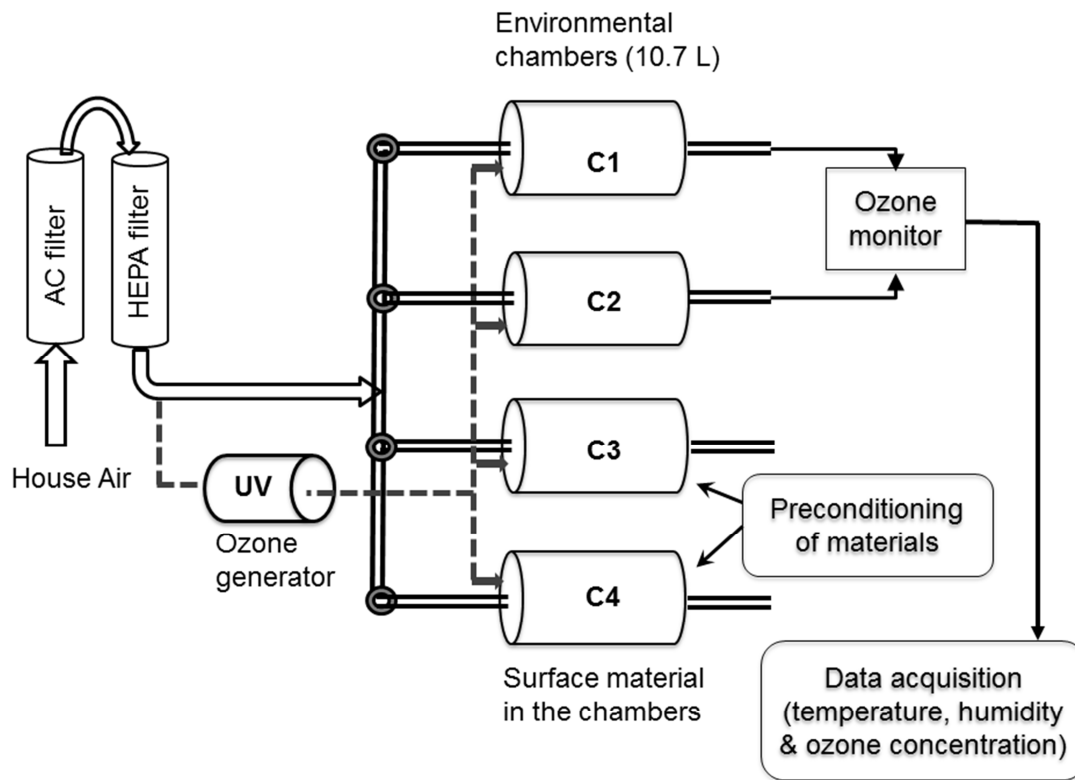
146 **Figure 1.** Three types of building materials selected as test materials for this investigation: a)
147 carpet tile, b) ceiling tile, and c) painted drywall. Upper images show the product as purchased
148 and tested. Lower images show the deconstructed material to illustrate the interior makeup of
149 each building material: a) fibers from carpet pile, b) wet-formed fiber from ceiling tile, and c)
150 crushed gypsum core.

151 2.2 Environmental chamber and test conditions

152 Figure 2 shows the experimental apparatus employed to study the ozone-material surface
153 reaction for the three test materials. The system comprised four 10.7-L (24 cm tall \times 23.8 cm
154 diameter) electropolished stainless-steel chambers housed in a constant temperature incubating
155 enclosure. Ozone reaction rates were measured at two air temperatures — 22 °C and 28 °C —
156 chosen to reflect upper and lower limits of indoor temperature during occupancy for typical air-
157 conditioned office buildings in a tropical climate. The tests were performed for both
158 temperatures at three levels of RH: 25%, 50%, and 75%. Relative humidity was measured at the
159 inlet of the chambers using an RH probe (APT system, TEC, Minneapolis, MN, USA). Note that
160 the three RH levels (25%, 50%, and 75%) correspond to absolute humidity values of 4.1, 8.3,
161 and 12.5 g/kg at 22 °C and 5.9, 11.9, and 18.0 g/kg at 28 °C. The air exchange rate of the

162 chamber was maintained at $10 \pm 0.3 \text{ h}^{-1}$ for all experiments. An exponential decay for a well-
163 mixed chamber was fit to the transient decay of ozone in the empty quenched chamber. The
164 range of decay rate estimates were from 9.18 to 11.0 h^{-1} , which are within 10% of the measured
165 air exchange rate, determined from measurements of the flow rate entering the chamber.

166 The new building materials were preserved in air-sealed bags. During each test, a material
167 sample was placed horizontally (facing upward) on a screen that was positioned slightly below
168 the middle of the chamber. Once air flow was stabilized, the sample was preconditioned for a
169 minimum of 2 days at the desired temperature and humidity without ozone exposure. Following
170 the preconditioning period, the two-day exposure experiment was initiated. Ozone was produced
171 with a UV light ozone generator (UVP model 97-0066-01, Mountain View, CA, USA). The
172 material sample was exposed to supply air containing 60-62 ppb of ozone to simulate a
173 moderately elevated yet realistic indoor ozone exposure during daytime hours with the building
174 ventilation system operating. Following each daily 8-h ozone exposure period, the ozone
175 generator was turned off and ozone-free air was supplied to the test chambers for a subsequent
176 16 h. The ozone concentration at the chamber exhaust was monitored with one-minute resolution
177 using a dual beam UV absorbance cell ozone analyzer (model 205; 2B Technologies, Boulder,
178 CO, USA). In all, 18 tests (3 materials \times 3 RH values \times 2 temperatures) were conducted for
179 characterizing ozone-surface reactions.



180

181

Figure 2. Schematic diagram of experimental apparatus.

182 2.3 Parameterizing ozone reaction rates on test materials

183 The measured ozone concentrations were used along with material surface area, chamber volume,
 184 and air exchange rate to determine the ozone deposition velocity. Ozone deposition velocities to
 185 each material were calculated by applying a time-dependent material balance for ozone in
 186 chamber air, shown in eq 1:

$$187 \quad \frac{dC(t)}{dt} = a(C_{supply} - C(t)) - v_d(t) \frac{S}{V} C(t) \quad (1)$$

188 In eq 1, $C(t)$ = ozone concentration in the chamber (ppb), C_{supply} = supply ozone concentration
 189 (ppb), S = surface area of the material sample (cm^2), $v_d(t)$ = deposition velocity (cm s^{-1}), V =
 190 chamber volume (cm^3), and a = air exchange rate (s^{-1}).

191 This equation is derived assuming that homogeneous reactions of ozone with chemicals emitted
 192 from materials are negligible. The surface-to-volume ratio (S/V) ratio used in this study was
 193 about 2 m^{-1} based on surface samples of 200 cm^2 and a chamber volume of $10,700 \text{ cm}^3$.
 194 Previous researchers (Singer et al. 2007; Lee et al. 2009) have reported S/V ratios ranging from
 195 1.2 to 4.6 m^{-1} for residential indoor environments. The S/V ratio varies with indoor dimensions,
 196 surface type, and furnishings. The materials tested in this study contribute large fractional
 197 coverage in an office; therefore S/V ratio of 2 m^{-1} is deemed appropriate.

198 The ozone deposition velocity was determined by means of discretizing eq 1 explicitly with
 199 respect to time and solving for the ozone deposition velocity, as shown in eq 2:

$$200 \quad v_d(t) = \frac{V}{S \cdot C(t)} \left\{ [a(C_{supply} - C(t))] - \frac{C(t+1) - C(t)}{\Delta t} \right\} \quad (2)$$

201 Eq 2 was solved using time-varying measured ozone concentrations with 5-min time steps ($\Delta t =$
 202 300 s).

203 The deposition velocity was further parameterized through resistance-uptake theory that models
 204 ozone uptake to a surface as the sum of serial resistances describing two governing processes:
 205 transport to the surface and surface reaction kinetics, as shown in eq 3 (Cano-Ruiz et al., 1993).

$$206 \quad \frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v \rangle} \quad (3)$$

207 In eq 3, v_t is the transport-limited deposition velocity (cm/s), γ is the reaction probability (-), and
 208 $\langle v \rangle$ is the Boltzmann velocity for ozone ($3.61 \times 10^4 \text{ cm/s}$ and $3.64 \times 10^4 \text{ cm/s}$ for $22 \text{ }^\circ\text{C}$ and $28 \text{ }^\circ\text{C}$,
 209 respectively).

210 In this study, the transport-limited deposition velocity (v_t) was evaluated for the experimental
211 apparatus and environmental conditions by deploying a polybutadiene-coated glass surface in the
212 chamber. Ozone reacts rapidly and irreversibly with the numerous double C=C bonds in
213 polybutadiene (Black et al., 2000). We supplied polybutadiene coating in the form of a viscous
214 liquid consisting of 80% 1-4 addition and 20% 1-2 addition polymers. Earlier laboratory studies
215 have shown that the mass of the polybutadiene coating increases with ozone reaction with
216 surface and the uptake of ozone by the polybutadiene coating is not limited by reaction rate, but
217 is instead controlled by the rate of external mass-transfer (Fog 1985; Black et al. 2000). Based on
218 these results, the measured deposition velocity of ozone to a polybutadiene surface (v_d) can be
219 equated to the transport-limited deposition velocity for the chamber apparatus (v_t). As would be
220 expected, v_t was observed to not vary significantly with temperature. Accordingly, the deposition
221 velocity measured to the test materials (eq 2) varied mainly due to the change in the surface
222 reaction probability, γ . This reaction probability is defined as the fractional likelihood of a
223 reaction given a collision between a surface and reactive pollutant in air. It should be noted that
224 the polybutadiene-coated glass surface used in this study does not perfectly represent surface
225 boundary conditions for all tested building materials, since the surface morphology does not
226 match that of the more textured materials. However, this approach does allow for an estimation
227 of the nominal transport-limited deposition velocity that results in the determination of “effective”
228 reaction probabilities (Gall et al. 2015). We calculated reaction probabilities for each of the
229 temperature and humidity conditions in the chamber.

230 *2.4 Effects of surface conditioning in occupied indoor environments*

231 The rate of ozone-surface reactions may change with time as materials are exposed to conditions
232 in occupied built environments (Cros et al., 2012). The following phenomena could contribute:

233 (a) ozone-reactive chemicals on the material surface may be consumed or may volatilize leading
234 to a reduction in reactivity; and (b) sorption and desorption of ozone reactive semivolatile and
235 volatile organic compounds could change ozone-surface reactivity. To assess the gain or loss of
236 ozone reactivity on the material resulting from exposure in occupied built environments, the
237 ozone deposition velocity and surface reaction probability were measured for conditioned
238 materials. The material samples were conditioned by placing them for periods up to 2 months in
239 the central area of an air-conditioned office. During the conditioning period, the indoor set-point
240 temperature was 22.8 °C (73 °F) and there were 10-15 people present during normal working
241 hours (9 AM to 6 PM, weekdays). In the middle of the office, the carpet sample was placed on
242 the floor while the drywall and ceiling tile were placed at 1.5 m above the floor. Samples were
243 removed at one month and two months after initiating conditioning and the ozone deposition
244 velocities were measured in an environmental chamber at $T = 28$ °C and $RH = 50\%$. Ozone
245 uptake results were compared at three different stages of material conditioning: fresh, following
246 1 month of office exposure, and after 2 months of exposure.

247 *2.5 Quality assurance*

248 Before each experiment, the chamber was quenched with 120 ppb of ozone for a minimum of 20
249 hours to deplete any reactive sites on the chamber walls. At the beginning of the measurement
250 period, the UV absorbance ozone analyzer was calibrated against a UV photometric calibrator
251 across a concentration range from 0 to 200 ppb. The ozone measurement uncertainty was
252 estimated to be 7% based on the sum of the precision (greater of 1.0 ppb or 2%) and accuracy
253 (greater of 1.0 ppb or 2%), combined in quadrature. Repeating the experiments with a new set of
254 the same building material at 22 °C and 28 °C with 50% RH revealed concentration repeatability
255 errors to be less than 6%. Each test sample was preconditioned at least two days in an ozone-

256 free ventilated chamber with the temperature and humidity set to the desired experimental value.
257 This procedure led to stable moisture content of the material sample, which was confirmed by
258 observing variation by $< 0.5\%$ in the outlet temperature and RH condition over a 2-h monitoring
259 period. Uncertainty in determining deposition velocity was evaluated to be $\pm 9\%$ based on
260 combining in quadrature the instrument error ($\pm 7\%$) for the ozone analyzer, errors for airflow
261 measurements ($\pm 0.5\%$) and sample area measurements ($\pm 5\%$).

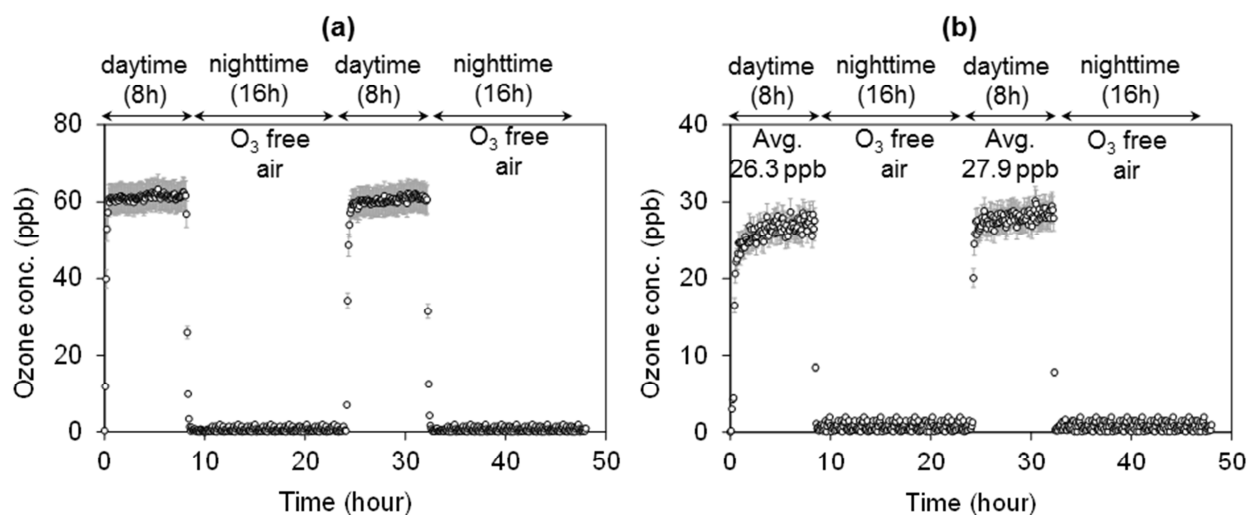
262 **3. Results and Discussion**

263 This section is organized into four subsections. We present 1) time-varying ozone deposition
264 velocity in response to the diurnally varying ozone exposure level and 2) the effects of indoor
265 temperature and humidity on ozone deposition velocities. The next subsection presents 3)
266 estimates of the ozone reaction probability for fresh materials tested with diurnal variation in
267 inlet ozone concentration. The last subsection assesses 4) the influence of material conditioning
268 in the occupied space on ozone reactivity.

269 *3.1 Time-varying ozone concentration and deposition velocity*

270 Figure 3 shows examples of time-varying ozone concentration observed with the empty chamber
271 (Figure 3a) and with painted drywall in the chamber (Figure 3b) while supplying a diurnally
272 varying ozone concentration for the two-day test period. During the 8-h ozone injection period,
273 average ozone concentration in the empty chamber is steady and reproducible, ranging from 60
274 to 62 ppb for the first and second days (Figure 3a). The ozone concentration measured in the
275 presence of painted drywall (Figure 3b) is lowest during the first hour of ozone supply and
276 gradually increases with time over the subsequent hours. Ozone reaction on the drywall surface
277 is largest when the material is initially exposed to ozone; as ozone-reactive sites are consumed,

278 the rate of reaction slowly decreases as evidenced by the higher average ozone mixing ratio
 279 across the second 8-h exposure (27.9 ppb) period as compared to the first (26.3 ppb).



280
 281 **Figure 3.** Two-day ozone concentration profiles for (a) empty chamber and (b) painted drywall
 282 placed in the chamber. Both experiments were conducted at $T = 28\text{ }^{\circ}\text{C}$ and $\text{RH} = 50\%$. The
 283 supply ozone concentration during the daytime was 61 ppb. Note that the y-axis scale differs
 284 between (a) and (b). Error bars denote measurement uncertainty, including precision (1 ppb or 2%
 285 of reading) and accuracy (1 ppb or 2% of reading).

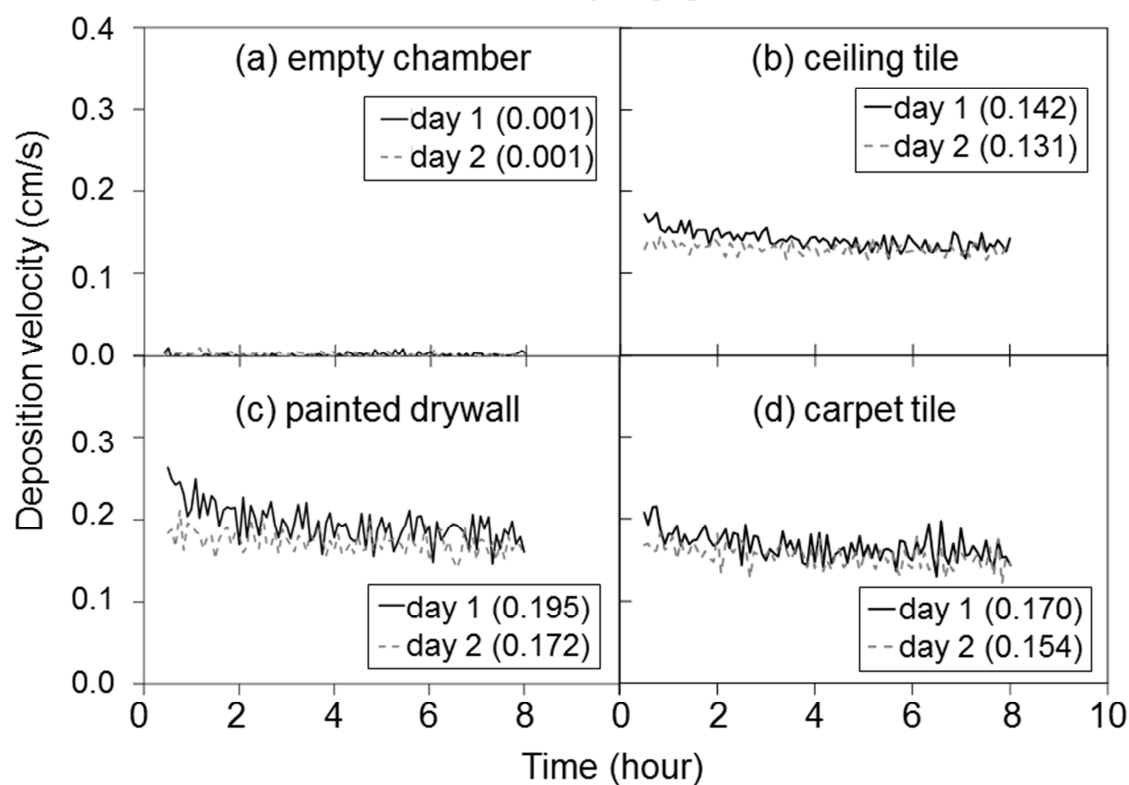
286 Figure 4 presents time-varying ozone deposition velocity during the 8-h ozone injection period
 287 for each day, as determined from eq 2 and utilizing the time-dependent ozone concentration
 288 measured at the chamber outlet. The empty quenched chamber contributes negligibly to the
 289 observed removal (Fig. 4a). As expected, the deposition velocity is the highest during initial
 290 ozone exposure, likely because of the abundance of reactive sites on the material surface. The
 291 deposition velocity gradually decreases with time as the reactive sites available for ozone
 292 reaction are consumed by ozone, a phenomenon known as “surface aging” (Morrison and
 293 Nazaroff, 2000). Comparing the two successive days, deposition velocities for all tested
 294 materials are higher for day 1 than for day 2. It is also observed that there is some recovery of
 295 ozone reactivity during the 16-h unexposed time between days. For painted drywall and for

296 carpet tile, in particular, the ozone deposition velocity at the beginning of day two is higher than
297 at the end of day one. Taken together, these materials exhibit both surface aging and recovery,
298 although the effects are not pronounced over the few-day measurement period. Recovery
299 observed in the present study appears smaller than that reported by Hoang et al. (2009). A
300 plausible explanation for the recovery phenomenon is that ozone-reactive chemicals diffuse from
301 the bulk material to the surface leading to a recovery of reactive sites during the non-exposed
302 periods. The differences between our findings and those of Hoang et al. regarding recovery
303 might be a consequence of a lesser abundance of transportable reactive chemicals beneath the
304 surface of the materials that we tested.

305 For the tested fresh material samples, the deposition velocity across all conditions was the
306 highest for the first hour of ozone exposure as compared to subsequent ozone exposure periods.
307 Table 1a provides a detailed summary of average deposition velocities for fresh samples across
308 all environmental conditions.

309 The deposition velocity values observed in this study are similar or slightly elevated relative to
310 values reported for the most comparable materials in the literature. For example, in the case of
311 painted drywall, Lamble et al. (2011) report an ozone deposition velocity of 0.18 cm/s for
312 unpainted samples and 0.03 cm/s for a drywall painted with a low-VOC paint. Some of the
313 difference may be a consequence of different values of the transport-limited deposition velocity
314 across studies. In the case of Lamble et al. (2011), v_t back-calculated from presented deposition
315 velocities and reaction probabilities for a carpet (FC-2) yield a transport-limited deposition
316 velocity for that study of ~ 0.3 cm/s, somewhat less than the value of 0.38 cm/s for our chamber.
317 Grøntoft and Raychaudhuri (2004) reported ozone deposition velocities for unpainted gypsum
318 drywall of 0.12-0.14 cm/s and 0.03-0.042 cm/s for a painted drywall. Reiss et al. (1994) reported

319 mass accommodation coefficients that are comparable to reaction probabilities determined herein
320 (Table 1b). Estimates of reaction probabilities determined here for the first day of exposure at 25%
321 and 50% RH are an order of magnitude higher than 20-h reaction probabilities reported by Reiss
322 et al. (1994) at comparable RH values. At 75% RH, our results and theirs are in better agreement,
323 with the reaction probability determined here about 50% higher than the value reported by Reiss
324 et al. Removal of ozone on carpets has been reported in several previous studies.
325 Determinations for the carpet studied in this work agree well with the findings of the studies by
326 Lamble et al. (2011), Gall et al. (2013), and Morrison and Nazaroff (2000) who report values
327 ranging from 0.15 to 0.21 cm/s for various carpet surfaces. Lamble et al. (2011) also report a
328 deposition velocity of 0.19 cm/s for a mineral-fiber ceiling tile, moderately higher than the
329 ceiling tile result we obtained.

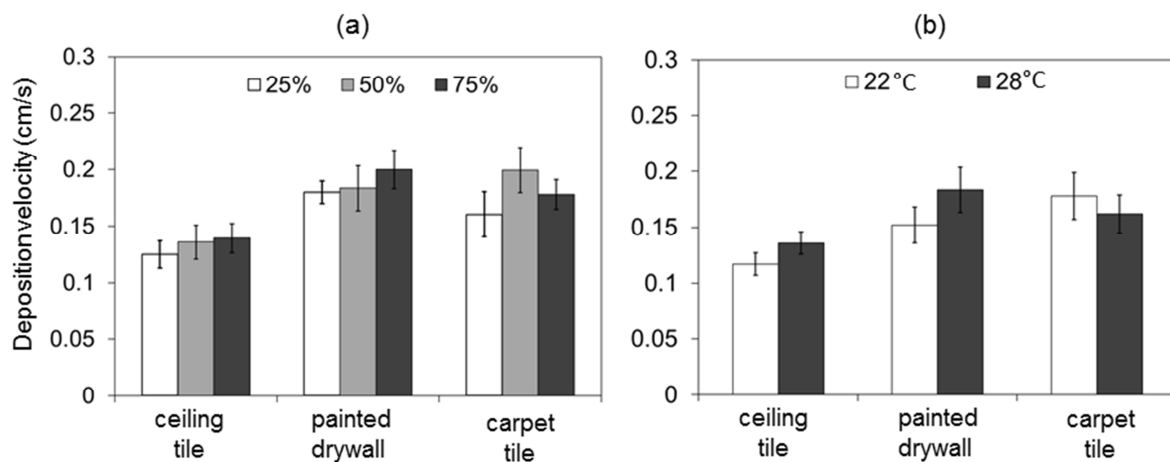


330

331 **Figure 4.** Ozone deposition velocity (cm/s) versus exposure time (h) for four cases and one set
 332 of environmental conditions ($T = 28\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$): a) empty chamber (background); b) ceiling
 333 tile; c) painted drywall; and d) carpet tile. The tested material samples were new. The estimated
 334 uncertainty is $\leq 9\%$ based on propagation of the measurement errors for ozone concentration,
 335 airflow, and surface area. The values in the parenthesis represent the average deposition velocity
 336 in units of cm/s across the 8-h ozone exposure period each day.

337 3.2 Effects of indoor temperature and humidity on deposition velocities

338 Figure 5 shows the effects of humidity and temperature on the measured average deposition
 339 velocities. Higher deposition velocities were observed for ceiling tile and painted drywall with
 340 increasing humidity and temperature, although the differences are moderate and within the range
 341 of measurement uncertainty. Regarding carpet tile, no impacts were observed with changes in
 342 humidity and temperature. Grøntoft et al. (2004) reported that humidity could have measurable
 343 influence on the ozone deposition velocity for some building materials. On the other hand, Gall
 344 et al. (2013) found minimal impacts of humidity and temperature in their estimates of ozone
 345 deposition velocities to selected green building materials. The present study results suggest a
 346 minimal impact of temperature and relative humidity on ozone deposition velocity in the
 347 parameter ranges common in air-conditioned buildings, at least for the tested samples of these
 348 three widely used indoor materials.

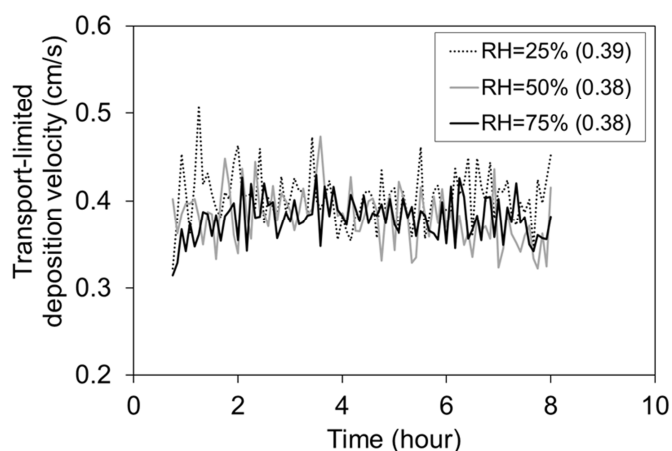


349

350 **Figure 5.** Effects of environmental condition on average ozone deposition velocity: a) effect of
 351 relative humidity at $T = 28\text{ }^{\circ}\text{C}$ and b) effect of temperature at $\text{RH} = 50\%$. Error bars represent the
 352 standard deviation of the average across the 8-h elevated ozone period. All tested samples were
 353 new.

354 3.3 Estimated ozone reaction probabilities

355 Deposition velocity varies with available reactive sites on the surface. However, transport-
 356 limited deposition velocity (v_t) is invariant if the airflow conditions in the surface boundary layer
 357 are constant. For the airflow condition of the chamber, v_t , determined with a polybutadiene-
 358 coated surface that was modeled as a perfect ozone sink in the chamber is 0.38 cm/s (Figure 6),
 359 with minimal influence of humidity. An early study measuring the uptake of SO_2 on room
 360 surfaces coated with sodium carbonate (Wilson, 1968) estimated a transport-limited deposition
 361 velocity of 0.07 cm/s for a laboratory room. More recently, Gall et al. (2013) estimated the
 362 transport-limited ozone deposition velocity of a 70 m^3 environmental chamber, configured to
 363 simulate a room-scale indoor environment with a mixing fan, to be 0.33-0.35 cm/s for a low
 364 mixing-rate condition and 0.56-0.70 cm/s for a high mixing-rate condition. Our experiments
 365 were conducted at a value of the transport-limited deposition velocity that is well within this
 366 broad range of prior observations for rooms.



367

368 **Figure 6.** Transport-limited deposition velocity observed for ozone reaction on a polybutadiene
 369 surface ($T = 28\text{ }^{\circ}\text{C}$).

370 Deposition velocity estimates were combined with the transport-limited deposition velocities to
 371 determine ozone-material reaction probabilities according to eq 3. Table 1b provides a summary
 372 of reaction probabilities for (a) the initial hour of exposure, (b) averaged over the first day, and (c)
 373 averaged over the second day of exposure. Results are reported for the three different materials
 374 for each of the temperature and humidity conditions tested. As shown in Table 1, the deposition
 375 velocity and corresponding reaction probability are consistently highest during the initial hour,
 376 and the values are lower for day 2 than for day 1. The calculated reaction probabilities for the
 377 first hour are in the range of $(2.6\text{-}3.3) \times 10^{-5}$ for ceiling tile, $(3.4\text{-}6.5) \times 10^{-5}$ for painted drywall,
 378 and $(3.9\text{-}6.2) \times 10^{-5}$ for carpet tile. Comparing the first hour with the day 2 average, one finds
 379 that the reaction probability decreases by a proportion ranging from 7% to 47% (median = 26%)
 380 across materials and test conditions.

381 **Table 1a.** Ozone deposition velocity (v_d , cm/s) for fresh materials.

Temp/ RH	Ceiling tile			Painted drywall			Carpet tile		
	1 h	day 1	day2	1 h	day 1	day 2	1 h	day 1	day 2
22 °C, 25%	0.16	0.15	0.14	0.21	0.20	0.18	0.21	0.20	0.18
22 °C, 50%	0.14	0.13	0.11	0.17	0.15	0.15	0.23	0.19	0.17
22 °C, 75%	0.17	0.15	0.14	0.18	0.16	0.17	0.19	0.17	0.16
28 °C, 25%	0.15	0.13	0.12	0.20	0.18	0.18	0.18	0.16	0.16
28 °C, 50%	0.16	0.14	0.13	0.23	0.20	0.17	0.19	0.17	0.15
28 °C, 75%	0.16	0.15	0.13	0.21	0.20	0.20	0.18	0.18	0.18

382

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386 **Table 1b.** Ozone reaction probability ($\gamma \times 10^{-5}$) for fresh materials.

Temp/ RH	Ceiling tile			Painted drywall			Carpet tile		
	1 h	day 1	day2	1 h	day 1	day 2	1 h	day 1	day 2
22 °C, 25%	2.9	2.7	2.6	5.2	4.5	3.7	5.0	4.5	3.6
22 °C, 50%	2.6	2.1	1.7	3.4	2.9	2.8	6.2	3.3	3.3
22 °C, 75%	3.3	2.6	2.5	3.8	3.2	3.2	4.1	3.3	2.9
28 °C, 25%	2.8	2.1	2.0	4.9	3.9	3.6	3.9	3.2	3.0
28 °C, 50%	3.0	2.5	2.2	6.5	4.5	3.5	4.1	3.4	2.9
28 °C, 75%	2.9	2.7	2.2	5.1	4.7	4.6	4.0	3.7	3.7

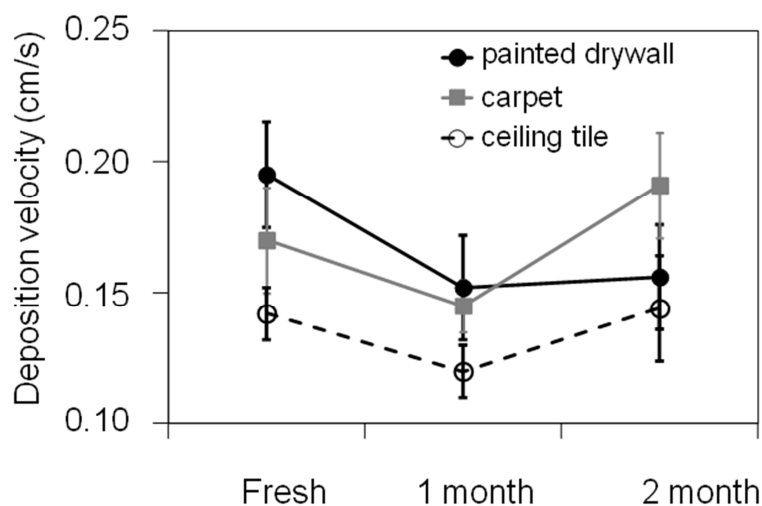
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388 *3.4 Effects of surface conditioning in occupied indoor environments*

389 Airborne particles and gases can deposit and sorb continuously on material surfaces in real
390 environments. During the primary experiments, test material samples were kept in a chamber
391 with exposure to clean (ozone-free and particle-free) air supply during the nighttime interval.
392 We conducted supplementary experiments to investigate how the reactivity with ozone might be
393 influenced by exposures to air in an ordinary occupied office environment.

394 Figure 7 shows variations of deposition velocity for the surfaces exposed in an occupied (10-15
395 people) office. Average deposition velocity decreased by 22%, 15%, and 16% for painted
396 drywall, carpet, and ceiling tile, respectively, after 1-month of conditioning. After the second
397 month of office exposure, deposition velocities increased relative to 1-month values for carpet
398 and ceiling tile and were similar to 1-month values in the case of painted drywall. A plausible
399 explanation for these observations is that, during the initial period, the ozone reactivity of the
400 materials diminished as surface sites reacted with ozone and/or as volatile reactants were lost
401 from the fresh materials. Subsequently, during the second month of exposure, carpet and ceiling

402 tile regained some of their surface ozone reactivity, perhaps owing to soiling by particles and/or
 403 formation of films of organic molecules (such as squalene, an unsaturated constituent of human
 404 skin lipids) emitted from occupants and their activities (Weschler, 2015; Rim et al., 2009).



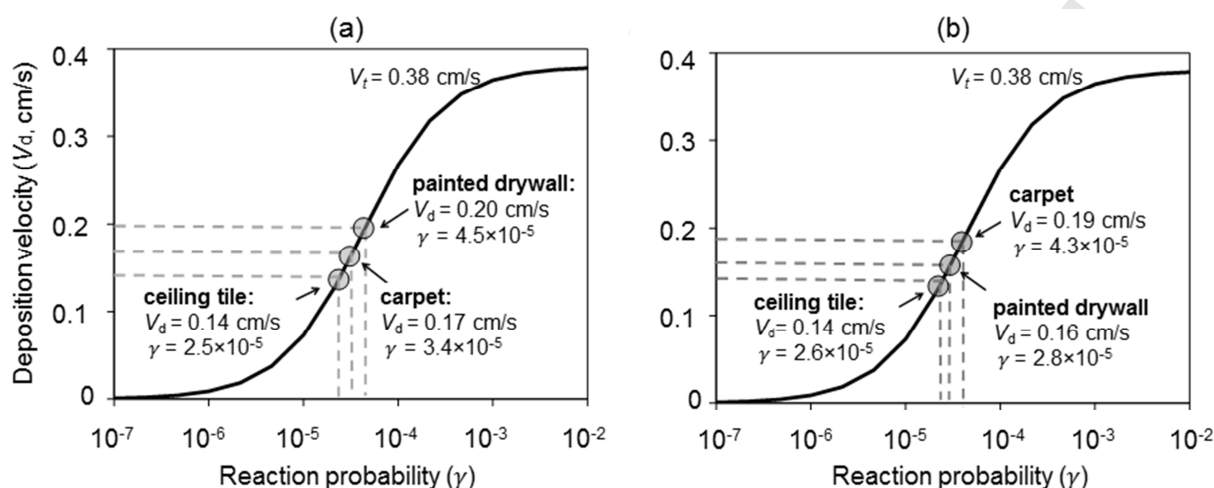
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406 **Figure 7.** Deposition velocity for test materials conditioned in an occupied office environment
 407 (averages for 8-h ozone exposures during day 1 of testing at $T = 28\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$). Based on the
 408 measured transport-limited deposition velocity shown in Figure 6 and input to eq (3), Figure 8
 409 presents initial reaction probabilities for the test materials when materials are fresh (panel a) and
 410 after two months of conditioning in the office environment (panel b). The reaction probabilities
 411 for the fresh materials are in the range $(2.5\text{-}4.5) \times 10^{-5}$ with the painted drywall exhibiting the
 412 highest value and ceiling tile the lowest. After two months in the occupied office, the reaction
 413 probability decreased 38% for the painted drywall, increased 26% for carpet, and is nearly
 414 unchanged for ceiling tile.

415 Occupancy might have resulted in the preferential replenishment of the carpet surface with
 416 reactive compounds, because the carpet was placed on the floor where coarse particle shedding

417 and resuspension might have contributed more to a change in the ozone-reactivity of the surface
 418 than for the other two materials, which were placed 1.5 m above the floor.

419



420

421 **Figure 8.** Reaction probabilities for test materials conditioned in an occupied office environment
 422 (determined for day 1 in the experimental apparatus at $T = 28\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$): (a) fresh sample
 423 vs. (b) 2-month old sample. The x-axis is on the logarithmic scale.

424 4. Conclusion

425 This study acquired new experimental information that adds insight into the important topic of
 426 how rapidly ozone reacts with common indoor materials. The deposition velocity is the highest
 427 during initial ozone exposure and gradually decreases with time as the reactive sites on the
 428 material surfaces are consumed by ozone. The present results suggest a moderate or minimal
 429 impact of temperature and relative humidity on ozone deposition velocity in the parameter
 430 ranges common in air-conditioned buildings. The surface reactivity with ozone can increase or
 431 decrease in an ordinary occupied office environment likely due to soiling by particles and/or the
 432 formation of films of organic molecules released from occupants and their activities. Some
 433 limitations should be noted. The present study used a high air exchange rate relative to typical

434 indoor environments; therefore, the ozone concentration boundary layer might be thinner and
435 transport-limited deposition velocity might be higher than in normal building operating
436 conditions. The test materials were placed horizontally in the chamber. We note that the
437 aerodynamics and mass transfer rate can vary with the surface orientation and indoor air flow
438 conditions.

439 Chamber experiments can provide material-specific surface reactivity information that should
440 reliably predict deposition velocities given suitable knowledge about near-surface airflow
441 conditions in real buildings. Future studies are warranted to examine the longer-term evolution
442 of ozone-material interactions in occupied settings on time scales more appropriate to the
443 renewal times of ozone surface reaction sites for common indoor environments.

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- 562

Highlight

- We examine ozone reaction with indoor surfaces considering diurnal ozone variation.
- Ozone deposition velocities are highest during the initial hour of ozone exposure.
- Surface-ozone reaction probability can decrease or increase in the occupied space.
- Influence of temperature and humidity on ozone-surface reactivity is moderate.