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Omed A. Abbass

*Portland State University*

David J. Sailor

*Arizona State University*

Elliott T. Gall

*Portland State University, gall@pdx.edu*

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## Effect of Fiber Material on Ozone Removal and Carbonyl Production from Carpets

Omed A. Abbass<sup>1,2</sup>, David J. Sailor<sup>3\*</sup>, and Elliott T. Gall<sup>1</sup>

1. Portland State University, Portland OR, USA; 2. University of Kirkuk, Kirkuk, Iraq; 3. Arizona State University, Tempe, AZ, USA

### ABSTRACT:

Indoor air quality is affected by indoor materials such as carpets that may act as sources and/or sinks of gas-phase air pollutants. Heterogeneous reactions of ozone with carpets may result in potentially harmful products. In this study, indoor residential carpets of varying fiber types were tested to evaluate their ability to remove ozone, and to assess their role in the production of carbonyls when exposed to elevated levels of ozone. Tests were conducted with six types of new unused carpets. Two sets of experiments were conducted, the first measured ozone removal and ozone deposition velocities, and the second measured primary carbonyl production and secondary production as a result of exposure to ozone. The tests were conducted using glass chambers with volume of 52 L each. Air exchange rates for all tests were  $3 \text{ h}^{-1}$ . The ozone removal tests show that, for the conditions tested, the polyester carpet sample had the lowest ozone removal (40%), while wool carpet had the greatest ozone removal (65%). Most carpet samples showed higher secondary than primary carbonyl emissions, with carpets containing polypropylene fibers being a notable exception. Carpets with polyester fibers had both the highest primary and secondary emissions of formaldehyde among all samples tested. While it is difficult to make blanket conclusions about the relative air quality merits of various carpet fiber options, it is clear that ozone removal percentages and emissions of volatile organic compounds can vary drastically as a function of fiber type.

Keywords: Indoor air quality, ozone deposition velocity, formaldehyde, aldehydes, measurements

\* Corresponding author: David.Sailor@asu.edu

## 29 1. INTRODUCTION

30 The existence of ozone indoors and its effect on indoor air quality has received significant  
31 attention in the research literature. In the absence of high-tension voltage equipment such as laser  
32 printers, copiers and UV light based air purifiers, infiltration of polluted ambient air through the  
33 building envelope and transmission through the ventilation system is the main source of ozone  
34 indoors. The ratio of indoor to outdoor ozone concentrations has been documented to be in the  
35 range of 0.2-0.7 for most buildings in the United States (Weschler, 2000). The reason for the  
36 lower indoor ozone concentrations is twofold. First, air passing through building envelope  
37 materials or ventilation system ductwork and filters undergoes surface oxidation reactions (Fick  
38 et al 2004; Stephens et al. 2012). Additionally, ozone that does penetrate into the indoor  
39 environment interacts with building materials such as carpets both through deposition associated  
40 with surface chemistry, and also through reaction with volatile organic compounds emitted by  
41 sources that include indoor building materials. This interaction can lead to harmful by-products  
42 that may be more harmful than the ozone itself (Lamble et al., 2011; Wisthaler and Weschler,  
43 2010). However, it should be noted that the average person in the US spends 89% of their time  
44 indoors (Klepeis et al., 2001); thus, despite lower indoor ozone concentrations, it can be argued  
45 that the chronic exposure to ozone is likely to be greater indoors than outdoors (Weschler 2006).

46 Materials high in organic content, such as carpets, wood, fabrics, and paint can off-gas  
47 carboxylic acids, volatile organic compounds (VOCs), and compounds that participate in  
48 chemistry that may lead secondary organic aerosol formation (Uhde and Salthammer, 2007;  
49 Waring and Siegel, 2013)—each of which may subsequently interact with ozone. Non-organic  
50 compounds such as glass and metals are known for their limited interaction with ozone, while

51 other materials such as gypsum, brick, and concrete interact with ozone exclusively through  
52 surface chemistry, without producing organic by-products.

53 Carpeting is a particularly common floor covering in the United States, although less common in  
54 Asia and Europe (Weschler, 2009). According to California Department of Resources Recycling  
55 and Recovery (CalRecycle, 2016), nylon fiber carpet is used in about 50% of the carpet sold in  
56 United States, while polypropylene fiber carpet is approximately 30% of market share. Because  
57 of the high surface area to volume ratio in an indoor space, carpets have the potential to  
58 significantly affect indoor air quality. This has led to a number of studies to explore the  
59 relationships among carpets, indoor ozone, and indoor air quality.

60         Researchers have suggested that when building materials are exposed to ozone,  
61 secondary emissions of carbonyls may increase considerably. For example, Weschler et al.  
62 (1992) used a 20-m<sup>3</sup> stainless steel room furnished with four types of new carpets. The carpets,  
63 with either nylon fibers or a combination of nylon and olefin fibers, were tested under ozone  
64 concentrations of 0, 30-50 and 400 ppb. Weschler found that the emissions of formaldehyde,  
65 acetaldehyde, and aldehydes with 5 to 10 carbon atoms increased significantly in the presence of  
66 ozone. Coleman et al., (2008) found that secondary emissions of VOCs are higher than primary  
67 emissions when aircraft cabin materials, including carpet specimens from aircraft cabins, are  
68 exposed to ozone. Morrison et al. (2002) conducted a study to investigate the production of  
69 aldehydes from two residential nylon fiber carpets, and two commercial carpets with olefin fibers  
70 when exposed to 100 ppb ozone. . The results showed that for C1-C13 carbonyls, especially  
71 nonanal, emissions increased significantly during exposure to ozone. One of the few studies  
72 conducted in situ was that of Wang and Morrison (2006), who investigated secondary aldehyde  
73 emissions from four indoor surfaces in four houses. Living room carpets were one of the surfaces

74 included in study. A Teflon chamber was used to take air samples after exposing the material on  
75 site to 100-150 ppb ozone. The results showed that newer carpets have higher secondary  
76 emissions than older carpets, but regardless of age, carpets are one of the major sources of  
77 aldehyde emissions indoors. Lamble et al (2011) explored the ozone removal and carbonyl  
78 emissions of nineteen sustainable “green” building materials including two recycled nylon  
79 carpets using a stainless steel test chamber.. They found that carpets were among the materials  
80 with the highest ozone deposition velocities (4.0 to 5.0 m h<sup>-1</sup>). Gall et al. (2013) performed full  
81 scale tests of three common indoor materials: recycled carpets, ceiling tiles, and recycled drywall  
82 painted with a low VOC paint. They found that ozone deposition velocity for carpets were the  
83 highest among the three building materials with values ranging from 5.5 – 8.0 m h<sup>-1</sup> for relative  
84 humidity in the range of 25%-75%. The aldehyde analysis results from that study showed that  
85 carpet was the indoor material with highest aldehyde emissions, especially for nonanal. Gall et  
86 al. conclude that care must be taken in choosing green materials because of potentially high  
87 primary and secondary emissions of aldehydes.

88 The body of research describing the interaction of indoor ozone and carpets shows carpets are an  
89 important material contributing to indoor air pollution, particularly with respect to indoor ozone  
90 removal and carbonyl emissions. Most previous research, however, has focused on carpets with  
91 nylon and olefin fibers. However, carpets are commonly made from other fibers including wool,  
92 polyester, polypropylene and other synthetic fibers, and, there is scant data available regarding  
93 these different types of carpet fibers.

94 The present research aims to fill this research gap by studying the effect of six environmentally  
95 friendly carpet fiber materials on ozone removal by calculating the ozone deposition velocities,  
96 and determining emissions of carbonyls in the absence and presence of ozone (primary and

97 secondary emissions, respectively). This investigation also expands on prior studies through  
 98 measurement and reporting of a number of carbonyl species for carpet fibers not previously  
 99 investigated in studies of ozone-carpet interaction.

## 100 2. METHODOLOGY

### 101 2.1 MATERIALS TESTED

102 In this research, six types of commercial and residential carpets were tested. These carpets are  
 103 marketed as environmentally friendly because they contain recycled fibers, or they are made  
 104 from raw materials prepared from plant source polymers (e.g., Dupont<sup>TM</sup> Sorona<sup>®</sup> version of  
 105 triexta). Some of the tested carpet samples are made of synthetic materials such as nylon. All  
 106 carpet samples were unused prior to testing. The detailed description of carpet samples is given  
 107 in Table 1.

108  
 109 **Table 1.** Summary of characteristics of carpet samples investigated in this study.

Code <sup>#</sup>	Brand	Fiber material	Cut type	Green attribute
Triexta	Karastan	100% BCF* Triexta	Cut pile	Made of DuPont <sup>TM</sup> Sorona renewable polymer
Poly-triexta	Mohawk	75% BCF* Polyester, 25% BCF* Triexta	Cut pile	Contains 50% recycled content
PP	Royal	100% Polypropylene	Cut pile	-
Polyester	Mohawk	100% PET** BCF* polyester	Cut-loop pile	Partly made of recycled bottles
Nylon	Stainmaster	100% Nylon	Multi-level loop	-
Wool	Unbranded	100% Wool	Level loop	-

110 <sup>#</sup> An abbreviated code is given each carpet studies based on the fiber type

111 \* bulked continuous filament

112 \*\* polyethylene terephthalate

113

114

### 115 2.2 EXPERIMENTAL APPARATUS

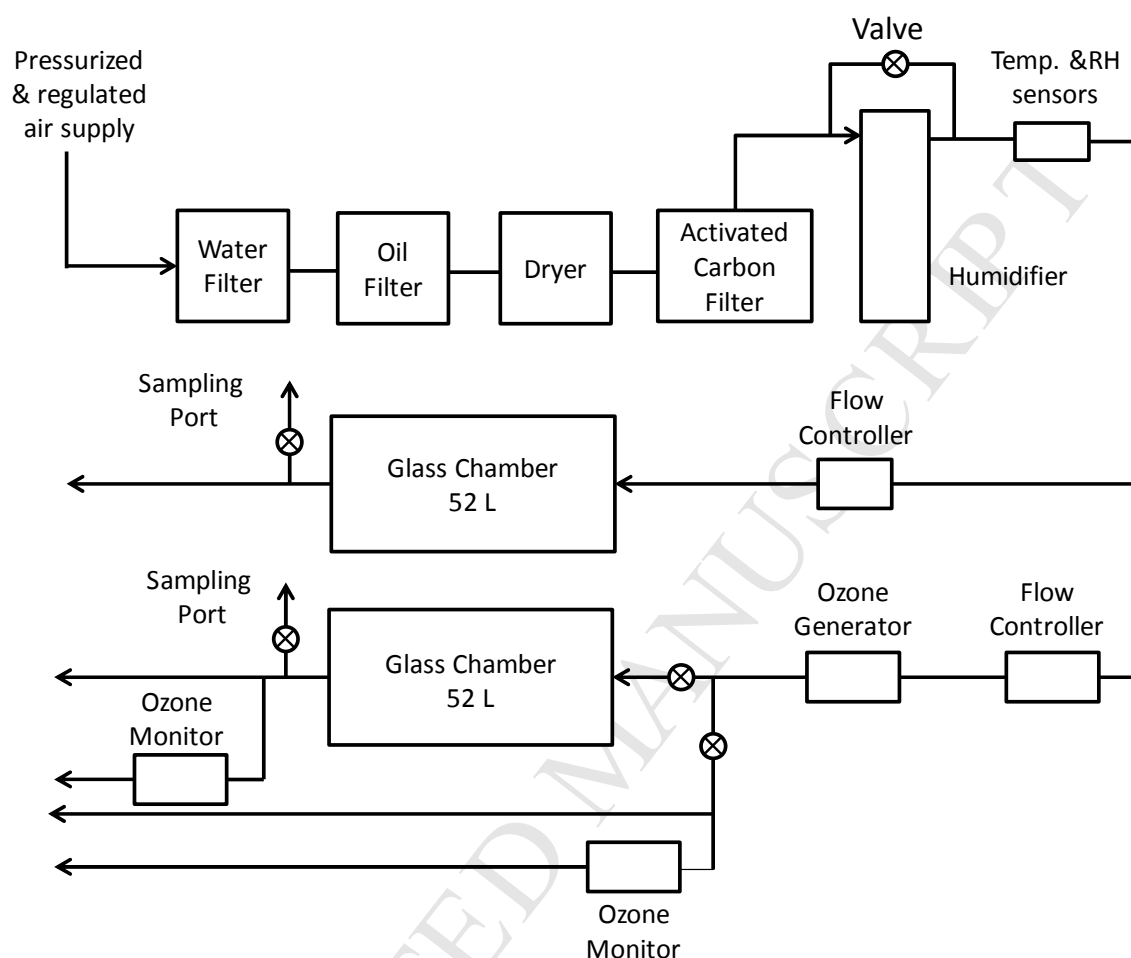
116 Figure 1 shows the experimental apparatus used in this study. It consists of an air supply system,  
 117 two glass chambers (constructed per ISO 16000-9), each with a volume of 52 L, ozone generator

118 (UVP, model SOG-2), and ozone analyzers (2B Technologies, model 106-L). Compressed air  
119 from the laboratory air supply was purified by using oil and water filters to remove any droplets  
120 that may exist in the air stream. Then, a gas drying unit was used to dehumidify the air prior to  
121 passing it through an activated carbon filter to remove any VOCs present in inlet air (verified  
122 through subsequent inlet air sampling for carbonyls). The filtered air stream was then humidified  
123 to the required relative humidity by using a by-pass valve controlled impinger. The temperature  
124 and relative humidity of the supply air was measured and recorded at one minute intervals using  
125 a 12-bit temperature and relative humidity sensor from Onset (model S-THB-M002). The  
126 temperature of the laboratory was monitored and maintained within the range of  $21^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , and  
127 the relative humidity was  $50\% \pm 2\%$ . The purified air was divided into two streams, one to supply  
128 an un-ozonated control chamber, and the other to pass through an ozone generator. Two mass  
129 flow controllers (OMEGA FMA 5523) were used to supply a constant flow rate of air to each  
130 branch of the flow system. The UV-based ozone generator was used to generate ozone  
131 concentrations in the range of 40-400 ppb. All connectors and fittings were either stainless steel  
132 or Teflon to minimize reactivity with ozone.

133 The ozone deposition velocity tests were conducted using a single chamber, while the carbonyl  
134 emissions tests used one chamber as a control and one for testing. The air pressure inside the  
135 chambers was kept at a slight positive pressure relative to the laboratory to prevent air leakage  
136 into the chambers. For monitoring ozone, two portable photometric ozone analyzers were used to  
137 monitor and record ozone concentrations upstream and downstream the ozonated test chamber  
138 with one-minute interval.

139  
140  
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142



143

144 **Figure1.** Schematic diagram of the experimental apparatus.

145

146 Samples of carpets were prepared from unused carpet stock taken from local carpet stores. These  
 147 samples were prepared according to the California Department of Public Health specifications  
 148 for emission tests (CDPH, 2010). The carpets were cut into 20 cm squares such that each would  
 149 have a loading factor (test surface area divided by chamber volume) of 0.8 m<sup>-1</sup> under the given  
 150 flow conditions. The backsides of all samples were covered with aluminum foil to prevent  
 151 exposure to ozone ( Rim et al., 2016, CDPH 2010) and reduce the corresponding effects of  
 152 carpet backing. Chambers were cleaned thoroughly with distilled water and dried with a heat gun



153 prior to every test. Following the approach of Coleman et al. (2008) the test chambers were then  
154 quenched with a 350 ppb ozone air stream for 3 hours before testing samples. For each test, the  
155 ozonated chamber was supplied with a constant stream of ozone-laden air at  $3.0 \pm 0.045$  air  
156 exchanges per hour and  $120 \pm 2$  ppb ozone concentration. The ozone concentration was  
157 measured before and after the chamber using two separate ozone analyzers (with recent NIST-  
158 traceable calibrations).

### 159 2.3 CARBONYL SAMPLING

160 To investigate the primary and secondary VOC emissions from carpets, samples of air were  
161 taken from both ozonated and non-ozonated chambers to study the effect of ozone-material  
162 interactions on the release of specific carbonyls. The carbonyls covered by EPA standard TO-  
163 11a (EPA, 1999) were investigated. These compounds include: formaldehyde, acetaldehyde,  
164 acrolein, acetone, propionaldehyde, crotonaldehyde, methacrolein, n-butanaldehyde, 2-butanone,  
165 benzaldehyde, valeraldehyde, m-tolualdehyde, hexaldehyde. This set of carbonyls was  
166 supplemented by the analysis of five heavy aldehydes: cyclohexanone, heptanal, octanal,  
167 nonanal, and decanal. The air samples were collected using glass sampling tubes (SKC, model  
168 226-120) packed with silica gel coated with 2,4-dinitrophenylhydrazine (DNPH). These  
169 sampling tubes come with an integrated layer of ozone scrubbing material to avoid interaction of  
170 ozone with the active sampling media. A sampling pump from SKC (model 224-PCXR8) was  
171 used to collect a constant flow rate of 400mL/min for 60 min. through the sampling tube (similar  
172 to Gall et al., 2013). An orifice flowmeter with an OMEGA (PX653-03D5V) pressure transducer  
173 was used to measure and ensure constant flow rate through the sampling tube. For ozonated  
174 carpet tests, one 1-h air sample was taken from the exit of the chamber starting at 24 hours from  
175 the start of the experiment when the concentration of ozone was at steady state values. The 1- h

176 air sample from the non-ozonated chamber was taken starting at 25 hours after the start of the  
177 test. Solutions were extracted from sampling tubes according to guidelines from the TO-11A  
178 standards.

#### 179 **2.4 CARBONYL ANALYSIS**

180 Carbonyl analysis was performed using high performance liquid chromatography with mass  
181 spectrometry (HPLC/MS, Thermo Scientific LTQ XL) with auto sampler. Using mass  
182 spectrometry for detection instead of conventional UV detection has many benefits, including  
183 acquiring greater information about each compound in interest (e.g., retention time and  
184 molecular weight) and the ability to detect a wide range of compounds, from formaldehyde-  
185 DNPH to decanal-DNPH. The column used was a Poroshell 120 SB-C18 2.7 $\mu$ m  
186 (3mmx150mm). The solvent flow rate used was 0.4 mL/min with initial concentrations of 60%  
187 acetonitrile and 40% water. This ratio was kept constant for the first 4 minutes of each HPLC  
188 run, increased linearly to 100% acetonitrile over an 8-minute period, kept constant for 4 minutes,  
189 and then changed back to 60% acetonitrile and kept constant for an additional 4 minutes. The  
190 total time for every sample test was 20 minutes. The results from each run were analyzed to  
191 obtain specific carbonyl mass on the sorbent tube, which was then used to calculate to the gas-  
192 phase concentration of the compound during the experiment.

193 The response of the HPLC/MS to each of the 18 carbonyls was calibrated with a method that  
194 used a mix of 18 organic compounds at serial dilutions to obtain a five-point calibration for every  
195 compound, with all resulting  $R^2$  greater than 0.99, similar to the procedure used by Cros et al.,  
196 (2011) and Gall et al. (2013). This mixture was prepared using two types of standard solutions.  
197 The first was ERA-013K, a mix of 13 compounds from Sigma Aldrich. The other five  
198 compounds, cyclohexanone, heptanal, octanal, nonanal, and decanal were obtained as individual

199 solutions from AccuStandard. Inc. All standard solutions were mixed in specific ratios to form  
200 calibration standard solutions.

## 201 2.5 DATA ANALYSIS

202 This section provides a brief summary of methods used to calculate specific air quality  
203 parameters for both the ozone and carbonyl aspects of this study.

### 204 2.5.1 Ozone deposition velocities

205 The ozone deposition velocity represents a mass transfer coefficient relating the bulk-air ozone  
206 concentration to the flux of ozone to the surface (Nazaroff et al., 1993). The steady-state ozone  
207 deposition velocity is calculated as described previously (Weschler, 2000; Nicolas et al., 2012)  
208 and shown in equation 1:

$$209 \quad k_s = AER \cdot \frac{V}{A_s} \left[ \frac{C_{inlet}}{C_{outlet}} - 1 \right] - k_g \frac{A_g}{A_s} \quad (1)$$

210 Here  $C_{inlet}$  and  $C_{outlet}$  represent the ozone concentrations in ppb in the inlet and outlet air flow of  
211 the chamber, respectively; AER is the air exchange rate ( $h^{-1}$ );  $A_s$  and  $A_g$  are the surface areas of  
212 the exposed sample and glass chamber, respectively;  $V$  is the volume of chamber; and  $k_g$  and  $k_s$   
213 are the ozone deposition velocities for glass chamber and specimen, respectively. Ozone  
214 deposition velocities are calculated for the chamber material first ( $k_g$ ) by running an empty  
215 chamber for a fixed AER until steady-state ozone concentrations are reached (defined here as the  
216 concentration changing by less than 2 ppb over a 20-minute period). Inlet and outlet  
217 concentrations of ozone averaged over the final 20 minutes of data collection are then used to  
218 solve (1) for  $k_g$ . The test is then repeated using different carpet samples, and solving (1) for the  
219 unknown values of  $k_s$ . An estimate of uncertainty was calculated using a propagation of errors,

220 incorporating uncertainties of the ozone monitors of 2% of reading and flow controllers of 1.5%,  
 221 resulting in an average uncertainty of  $\pm 0.1$  m/h

## 222 2.5.2 Carbonyl emissions and molar yield calculation

223 To quantify carbonyl emissions, the specific emission rate (SER), according to CEN (2001) and  
 224 Nicolas et al. (2007) is used:

$$225 \quad SER = C_{exit} \cdot \frac{AER}{A_s/V} \quad (2)$$

226 where  $C_{exit}$  is the concentration of the specific carbonyl of interest at the exit of the chamber in  
 227 ( $\mu\text{g m}^{-3}$ ); AER is the air exchange rate ( $\text{h}^{-1}$ );  $A_s$  is the surface area of carpet sample ( $\text{m}^2$ ); and V is  
 228 the volume of test chamber ( $\text{m}^3$ ). The uncertainty analysis based on error propagation for  
 229 equation 2 was performed. The uncertainty in SER for each compound was found using three  
 230 repeated measurements for every standard solution compound using HPLC/MS and incorporated  
 231 in the uncertainty analysis. The percentage RTD of the three readings was less than 20% for all  
 232 compounds. The uncertainty for primary emissions (averaged across all observed primary  
 233 carbonyl emissions) was  $\pm 2.3 \mu\text{g m}^{-2} \text{h}^{-1}$ , and  $\pm 1.8 \mu\text{g m}^{-2} \text{h}^{-1}$  for specific secondary emissions  
 234 (averaged across all secondary carbonyl emissions).

235 To quantify the amount of carbonyl release to ozone consumption, a molar yield, which  
 236 represents the moles of a compound formed divided by the moles of ozone consumed is  
 237 calculated from a steady-state mass balance on each carbonyl, as shown in equation 3:

$$238 \quad \gamma_{an} = AER \cdot \frac{V}{A \cdot k_s} \cdot \frac{C_{exit}}{C_{ozone}} \quad (3)$$

239 Where  $\gamma_{an}$  represents the molar yield for a specific compound (moles of compound released per  
 240 moles ozone consumed).  $C_{exit}$  represents the concentration of a compound in the chamber exit

241 ( $\text{mol/m}^3$ ), and  $C_{\text{ozone}}$  represents the ozone concentration in the chamber exit ( $\text{mol/m}^3$ ). The other  
242 quantities are as mentioned before in equation 2. The uncertainty analysis using error  
243 propagation method was performed and found that the average uncertainty was  $\pm 0.01$  mole  
244  $\text{O}_3/\text{mole}$  carbonyl formed.

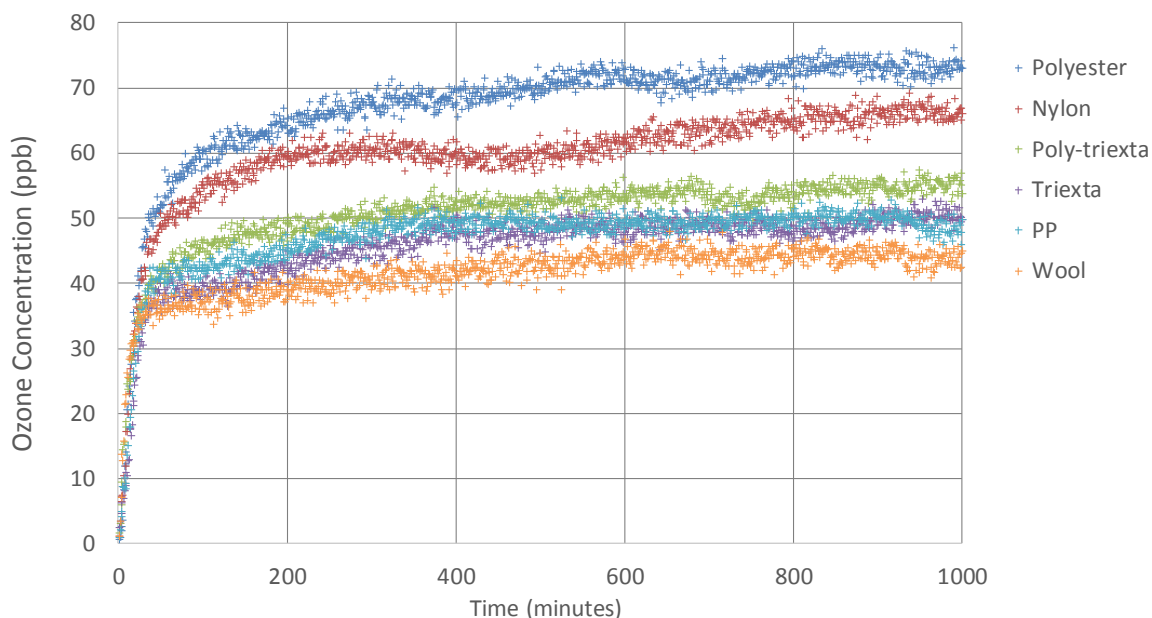
### 245 3. RESULTS AND DISCUSSION

#### 246 3.1 EXIT OZONE CONCENTRATION

247 Figure 2 shows the change of ozone concentration at the exit of the chamber with time for all six-  
248 carpet samples. It can be seen that the concentration increases rapidly during the first hour of  
249 each experiment. This exponential increase in ozone concentration is consistent with the  
250 displacement of the initial volume of “clean” air with ozonated air. Specifically, in the absence  
251 of chemical reactions or emissions, and assuming a well-mixed chamber, the concentration of  
252 ozone in the chamber at any given time will increase exponentially with a time constant of  
253  $1/\text{AER}$ , eventually approaching the concentration of the supply. The concentration in the  
254 chamber should reach 99% of the inlet concentration after about 4 time constants. Thus, the  
255 effects of initial test chamber concentrations are largely absent after several hours of testing.  
256 Nevertheless, each experiment was conducted for 16 hours to ensure steady-state conditions  
257 (concentration changing by less than 2 ppb over a 20-minute period). Figure 2 reveals that the  
258 highest chamber exit ozone concentration was for the polyester carpet sample ( $\sim 75$  ppb), and the  
259 lowest was for wool carpet ( $\sim 45$  ppb), indicating that polyester was least effective of the carpet  
260 samples tested at removing ozone from the air supplied to the chamber. Since ozone in the test  
261 chamber continually reacts with gas-phase VOCs emitted from the carpet samples, the  
262 concentration curves deviate from a simple exponential profile, with a prominent dip in the

263 ozone concentration from about 300 to 600 minutes into the experiment for the nylon test  
 264 specimen.

265



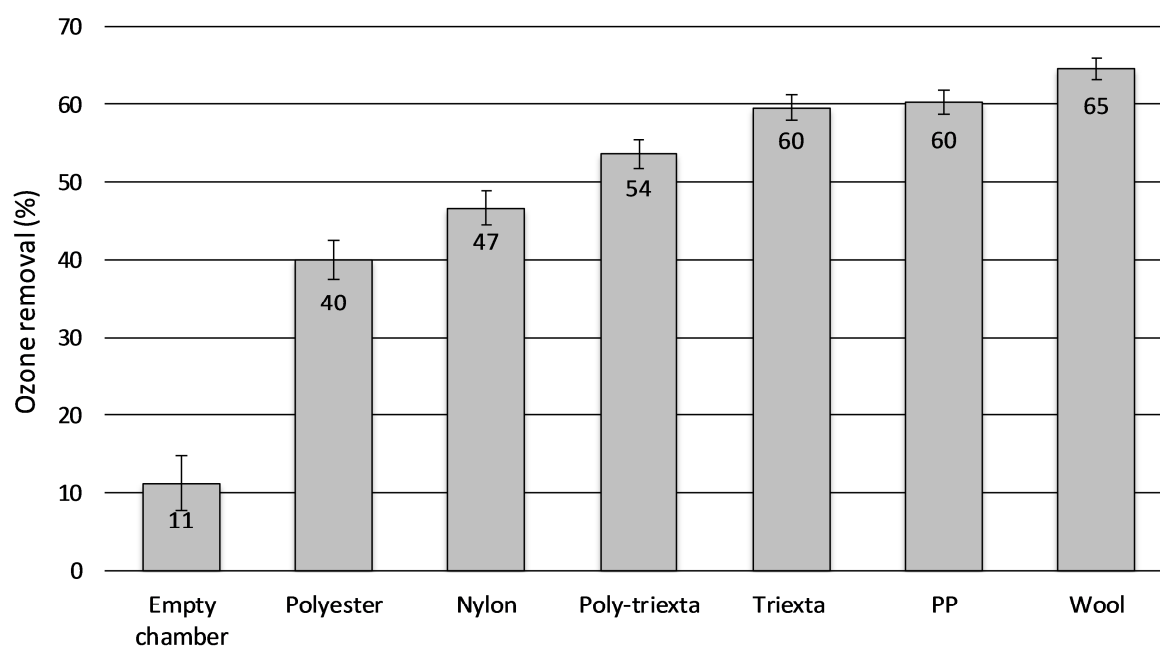
266  
 267  
 268 **Figure 2.** The change of exit ozone concentration with time for the six carpet types. The duration  
 269 of each experiment was 24 h. PP=polypropylene. Poly-triexta= mix of polyester and triexta  
 270 fibers.

271

272

273 The percentage of ozone removal from these tests is shown in figure 3. As expected, the ozone  
 274 removal for the empty chamber is the lowest at 11%. This suggests some interaction of ozone  
 275 with the glass chamber walls and the low-VOC sealant along each of the exterior edges of the  
 276 chamber. The wool carpet sample was most effective at removing ozone (65%) while the  
 277 polyester carpet was least effective (40%).

278



279 **Figure 3.** Ozone removal percentage at steady-state for carpet samples studied in this  
 280 investigation. Ozone removal percentages for materials include losses to the chamber surfaces.  
 281 Numeric value of the removal percentage is reported in the text label on each bar. The error bars  
 282 represent the instrumental propagation error. PP=polypropylene. Poly-triexta= mix of polyester  
 283 and triexta fibers.  
 284

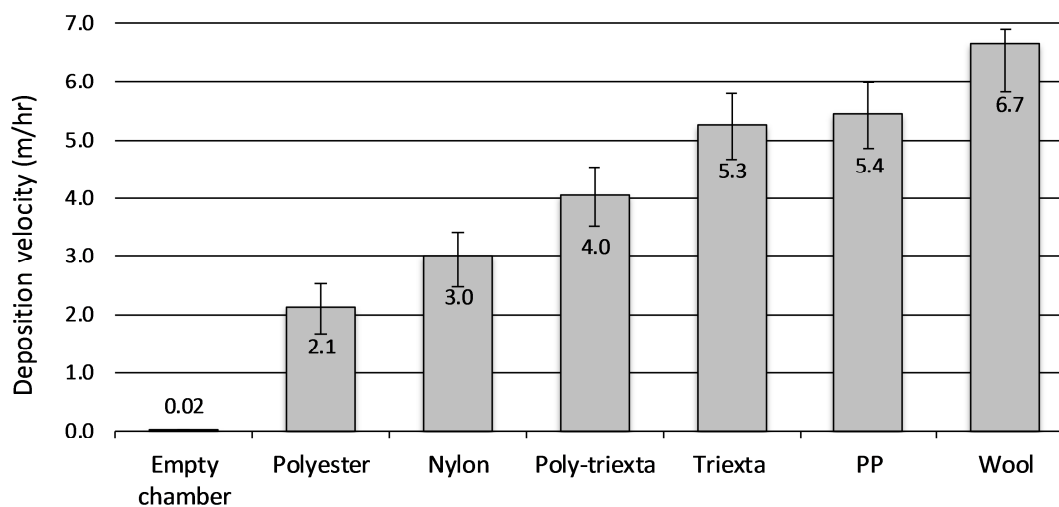
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### 287 3.2 OZONE DEPOSITION VELOCITY

288 Figure 4 shows the ozone deposition velocity values for the empty chamber and the six carpet  
 289 samples. The figure reveals significant differences among materials. The empty glass chamber,  
 290 had a deposition velocity of  $0.02 \text{ m h}^{-1}$ , which is the same order of magnitude as that reported by  
 291 Grontoft (2004) for a similar chamber material study. For nylon carpet, which is the most studied  
 292 fiber material from previous research, reported values of ozone deposition velocities are  
 293 generally between  $2.0$  and  $7.0 \text{ m h}^{-1}$  (Lamble et al., 2011; Cross et al., 2011; and Gall, 2013). The  
 294 present study found a deposition velocity of  $3.0 \text{ m h}^{-1}$  for nylon. The wool carpet had the highest  
 295 deposition velocity at  $6.7 \text{ m h}^{-1}$ , while the polyester carpet had the lowest ozone deposition  
 296 velocity at only  $2.1 \text{ m h}^{-1}$ . For polyester, triexta, polyester-triexta fiber blend, and polypropylene,

297 no previous data were found to compare, although it is important to note the wide range of  
298 deposition velocities (by a factor of 3) for the samples tested. In general, all carpet samples are  
299 fabricated with a fiber pile with high surface area. The differences between carpets themselves  
300 may be attributed to physical factors, like pile geometry and resulting material porosity, as well  
301 as chemical factors like fiber composition, and additional materials used in fabrication, including  
302 dyes. For example, wool is mainly composed of an organic protein fiber where carbon forms  
303 about 50-52% of its composition (Crawshaw and Simpson 2002), but others such as polyesters  
304 are formed of long chain polymers that are likely less reactive in comparison with other fibers.  
305 Morrison and Nazzarof (2002) suggest that variability in uptake of ozone to different carpets is  
306 likely due to different surface treatments or backing materials.

307

308  
309

310 **Figure 4.** Ozone deposition velocities for different carpets used in the study. The error bars  
311 represent are the uncertainty as determined from an error propagation using instrument  
312 uncertainties. Ozone losses to background surfaces are included in calculated values of ozone  
313 deposition velocities to carpet samples. PP=polypropylene.

314  
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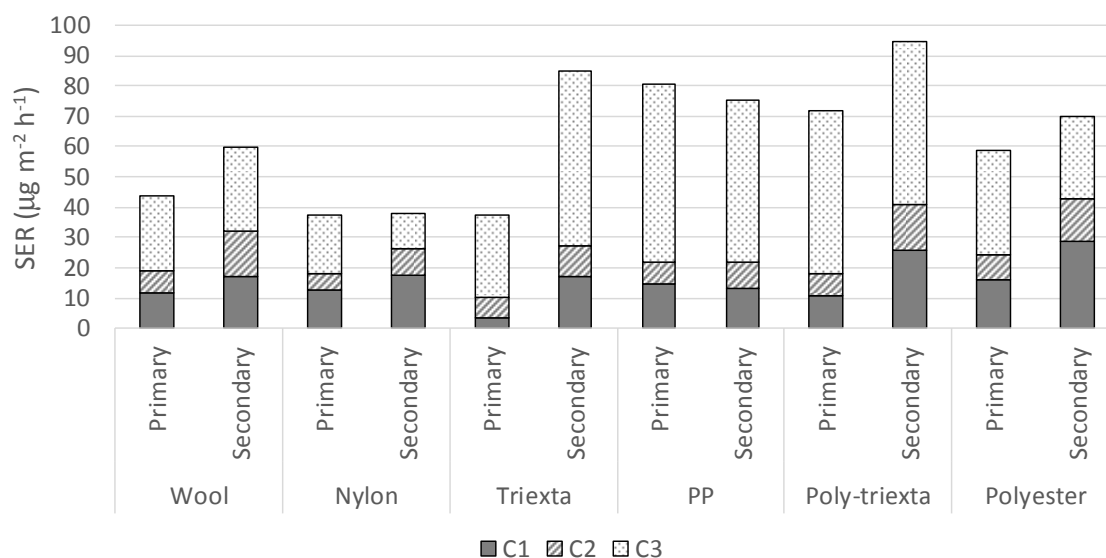
### 316 3.3 CARBONYL EMISSIONS

317 The discussion in this section divides the results into emissions for light carbonyls and heavy  
318 aldehydes. Of the 18 compounds targeted, some were either not detected or not distinguishable  
319 from other compounds with the same molecular weight (e.g., 2-butanone and n-butanaldehyde).  
320 Results for light carbonyls were obtained for formaldehyde (C1), acetaldehyde (C2), and acetone  
321 (C3). Heavy aldehyde results were obtained for heptanal (C7), octanal (C8), nonanal (C9), and  
322 decanal (C10). Primary emissions refer to emissions in the absence of ozone, and secondary  
323 emissions refer to emissions in the presence of ozone; reported values of secondary emission  
324 rates do not subtract primary emissions as a background value.

325 Figure 5 shows the primary and secondary emissions of light carbonyls. With one exception,  
326 total light carbonyl emissions from the carpet samples increased in the presence of ozone. The  
327 notable exception was the polypropylene carpet sample whose secondary emissions were 7%  
328 lower than its primary emissions. A large difference between primary and secondary emissions  
329 for any carpet sample is indicative of significant chemical interactions between either the carpet  
330 sample fibers and ozone or between the primary emissions and ozone or both.

331 The carpet samples with the lowest primary emissions of light carbonyls were nylon and triexta,  
332 both with  $37 \mu\text{g m}^{-2} \text{h}^{-1}$ . However, while nylon's secondary emissions were only slightly higher  
333 than its primary emissions, triexta's secondary emissions of light carbonyls were more than  
334 double its primary emissions ( $85 \text{ vs. } 37 \mu\text{g m}^{-2} \text{h}^{-1}$ ). In fact, among all carpet samples, triexta  
335 demonstrated the most significant difference between primary and secondary emissions of light  
336 carbonyls, with the poly-triexta blend having the second most prominent difference between  
337 primary and secondary emissions, and the highest overall secondary emissions of light carbonyls

338 at  $95 \mu\text{g m}^{-2} \text{h}^{-1}$ . One important finding evident from this figure is that both primary and  
 339 secondary emissions vary dramatically (by more than a factor of 2) across the fiber types tested.



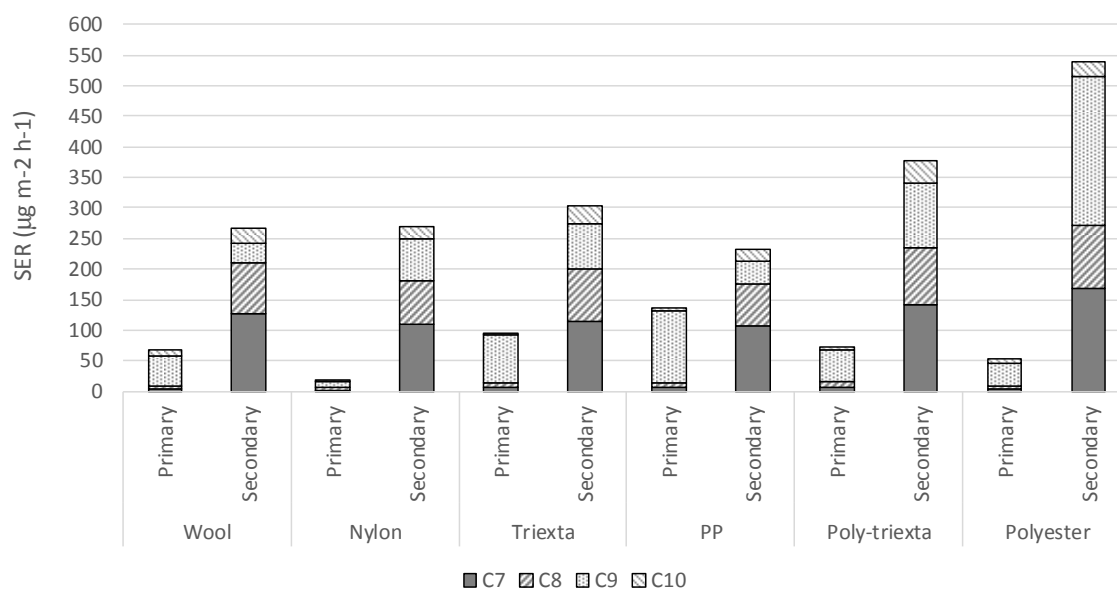
340  
 341  
 342 **Figure 5.** Primary and secondary light carbonyl emissions from carpet samples. Secondary  
 343 emissions are at ozone exposure of 120ppb for 24 hr. PP = polypropylene. C1 is formaldehyde,  
 344 C2 is acetaldehyde, C3 is acetone.

345  
 346  
 347 Within the light carbonyls, carpet sample emissions of acetone (C3) were by far the highest and  
 348 emissions of acetaldehyde (C2) were lowest. While primary emissions of acetone were quite  
 349 variable, ranging from 19 to  $59 \mu\text{g m}^{-2} \text{h}^{-1}$  for nylon and polypropylene samples, respectively,  
 350 primary emissions of acetaldehyde were more uniform, ranging from 6 to  $8 \mu\text{g m}^{-2} \text{h}^{-1}$ .

351 Furthermore, for nylon, polypropylene, and polyester carpets, the secondary emissions of  
 352 acetone are less than the primary emissions. This behavior agrees with the findings of Cros et al.  
 353 (2011) and Gall et al. (2013) who both reported decreases in acetone secondary emissions that  
 354 were less than primary emissions for nylon fiber carpet.

355 Formaldehyde (C1) is one of the carbonyls of most interest from a human health perspective due  
 356 to its classification as a known human carcinogen. Triexta and polyester carpet samples had the

357 lowest and highest primary emissions of formaldehyde at 3 and 16  $\mu\text{g m}^{-2} \text{h}^{-1}$ , respectively.  
 358 Secondary emissions of formaldehyde ranged from 13  $\mu\text{g m}^{-2} \text{h}^{-1}$  for polypropylene to 29  $\mu\text{g m}^{-2}$   
 359  $\text{h}^{-1}$  for polyester. Thus, with respect to secondary formaldehyde emissions, the polyester and  
 360 poly-triexta carpet samples were among the highest emitters. Nylon was the lowest emitter of  
 361 harmful light carbonyls, and the other carpet samples yielded mixed results.  
 362 For formaldehyde (C1) and acetaldehyde (C2), the secondary emissions are generally higher than  
 363 the primary emissions. This result agrees with the findings of Weschler et al. (1992), who  
 364 reported an increase in the concentrations of these two compounds for nylon carpets, and  
 365 Morrison and Nazaroff (2002) who reported an increase in all C1-C13 compounds. However, as  
 366 noted, the polypropylene carpet sample showed different behavior with the secondary emissions  
 367 of formaldehyde being slightly lower than the primary emissions. This is possibly due to the lack  
 368 of double bonds in polypropylene, making it more resistant to ozone attack.



369 **Figure 6.** Primary and secondary heavy aldehyde emissions from carpet samples. C7 is heptanal,  
 370 C8 is octanal, C9 is nonanal, and C10 is decanal.  
 371  
 372

373 Figure 6 shows the primary and secondary emissions of heavy aldehydes for all six carpet  
374 samples tested. The general trend for all heavy aldehyde compounds is that secondary emissions  
375 are higher than primary emissions, again, suggesting a high degree of interaction between carpet  
376 fibers and ozone, especially for C7-C10 aldehydes (Weschler 2002). Nylon carpet samples had  
377 the lowest primary emissions of heavy aldehydes at  $19 \mu\text{g m}^{-2} \text{h}^{-1}$  while polypropylene had the  
378 highest ( $137 \mu\text{g m}^{-2} \text{h}^{-1}$ ). In sharp contrast, however, polypropylene had the lowest total  
379 secondary emissions of heavy aldehydes. The poly-triexta and polyester carpet samples had the  
380 highest secondary emissions of heavy aldehydes at 377 and  $539 \mu\text{g m}^{-2} \text{h}^{-1}$ , respectively.

381 Within the heavy aldehydes, primary emissions of heptanal (C7), octanal (C8), and decanal  
382 (C10), for all carpets were less than  $10.0 \mu\text{g m}^{-2} \text{h}^{-1}$ . However, secondary emission rates for these  
383 compounds ranged from  $19 \mu\text{g m}^{-2} \text{h}^{-1}$  of decanal for polypropylene carpet to  $169 \mu\text{g m}^{-2} \text{h}^{-1}$  of  
384 heptanal for the polyester carpet. For most carpet samples, secondary emissions of nonanal were  
385 substantially higher than primary emissions. This is particularly true for polypropylene,  
386 polyester, and nylon, for which the ratio of secondary to primary emissions of nonanal were 6, 8,  
387 and 11, respectively.

388 So, the nylon carpet sample was among the lowest emitting samples for both light and heavy  
389 aldehydes. However, while polypropylene was a high emitter of light carbonyls, it was among  
390 the lower emitting carpet samples for heavy aldehydes.

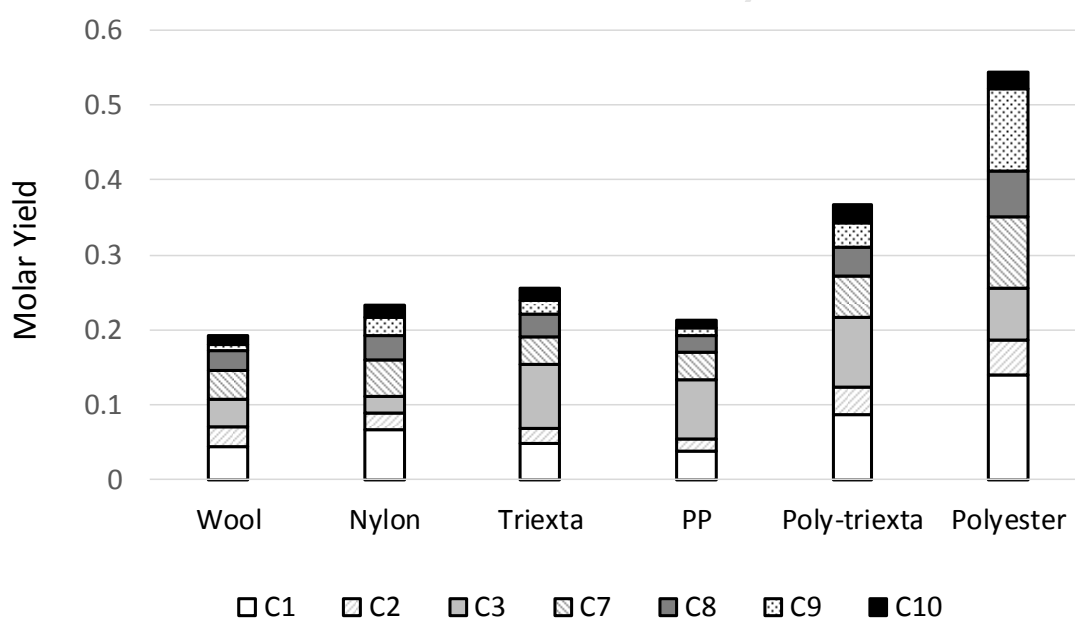
391 Figure 7 shows the molar yields, which is moles of carbonyl produced per moles of ozone  
392 consumed. The cumulative values of yields vary from 0.19 for wool fiber carpet to 0.54 for  
393 polyester fiber carpet. This suggests that wool carpet is the lowest emitter for the seven  
394 compounds relative to ozone removal, especially for acetaldehyde and nonanal. The polyester  
395 carpet is the highest emitter in the group, specifically for formaldehyde, heptanal, and nonanal.

396 By comparing this finding to the ozone removal, where the wool carpet showed the highest  
397 percentage ozone removal and highest ozone deposition velocity, it is concluded that the reaction  
398 pathway between ozone and wool fiber carpet does not result in formation of the carbonyls  
399 targeted here; further investigation is needed to determine the mechanism and nature of  
400 byproducts formed. For the yield of a specific compounds, formaldehyde has the maximum yield  
401 among all compounds with value of 0.14 for polyester carpet, and the minimum yields is 0.007  
402 for nonanal for the wool carpet.

403 Despite the variation in some carbonyl compounds of this research from others, the comparison  
404 of the total yield value for the nylon fiber carpet with value of 0.23, shows good agreement the  
405 cumulative yield for the carpet sample found by Gall et al. 2013 who report a total value of 0.28,  
406 for an analysis of a similar class of compounds. However, both values exceed the value of 0.12  
407 reported by Lamble et al. (2011). In general, the total yields give the same indication found in  
408 examining the specific emission rates that nylon, as the second least emitter, is a low emitting  
409 carpet in comparison to both polyester and poly-triexta carpet which showed higher secondary  
410 emissions.

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420 **Figure 7.** Molar yields (moles of product per mole of ozone) for secondary carbonyl emissions  
421 from carpet samples after ozone exposure of 120ppb for 24 hr. C1=Formaldehyde. C2  
422 Acetaldehyde. C3=Acetone C7=Heptanal C8=Octanal. C9=Nonanal. C10=Decanal.

423

#### 424 4. CONCLUSIONS

425 The deposition velocities for carpet samples showed values ranging from about 2 to 6 m h<sup>-1</sup>. This  
426 indicates that carpets are good sinks for ozone with potential to lower harmful ozone levels

427 indoors. On the other hand, carpets can emit significant levels of volatile organic compounds,  
428 and these emissions can be amplified in the presence of ozone. While nylon fiber carpets had  
429 among the lowest emissions of carbonyls they were also among the least effective at removing  
430 ozone from indoor air. Wool and polypropylene carpets were the least effective at removing  
431 ozone. Furthermore, while wool generated intermediate levels of carbonyl emissions,  
432 polypropylene carpets had the highest primary emissions of carbonyls. While it is difficult to  
433 make a strong case for any specific carpet being the best for indoor air quality, several  
434 conclusions can be drawn. First, nylon carpets are generally a good choice, particularly for  
435 locations that are not exposed to high levels of ambient ozone. Polypropylene fiber carpets, on  
436 the other hand, appear to be of limited benefit with respect to indoor air quality concerns, given  
437 that the data presented here show they result in only modest removal of ozone but are  
438 characterized by high aldehyde emissions.

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440

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442

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453

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## Highlights

- \* Indoor air quality impacts of six types of carpet were assessed in chamber tests
- \* Ozone deposition, primary and secondary emission of aldehydes were measured
- \* Wool and polypropylene carpets were the most effective at removing ozone
- \* Nylon carpets had low aldehyde emissions but were also poor at removing ozone
- \* Polypropylene carpets had the highest primary emissions of aldehydes

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