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

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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 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

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1. INTRODUCTION

The existence of ozone indoors and its effect on indoor air quality has received significant attention in the research literature. In the absence of high-tension voltage equipment such as laser printers, copiers and UV light based air purifiers, infiltration of polluted ambient air through the building envelope and transmission through the ventilation system is the main source of ozone indoors. The ratio of indoor to outdoor ozone concentrations has been documented to be in the range of 0.2-0.7 for most buildings in the United States (Weschler, 2000). The reason for the lower indoor ozone concentrations is twofold. First, air passing through building envelope materials or ventilation system ductwork and filters undergoes surface oxidation reactions (Fick et al 2004; Stephens et al. 2012). Additionally, ozone that does penetrate into the indoor environment interacts with building materials such as carpets both through deposition associated with surface chemistry, and also through reaction with volatile organic compounds emitted by sources that include indoor building materials. This interaction can lead to harmful by-products that may be more harmful than the ozone itself (Lamble et al., 2011; Wisthaler and Weschler, 2010). However, it should be noted that the average person in the US spends 89% of their time indoors (Klepeis et al., 2001); thus, despite lower indoor ozone concentrations, it can be argued that the chronic exposure to ozone is likely to be greater indoors than outdoors (Weschler 2006). Materials high in organic content, such as carpets, wood, fabrics, and paint can off-gas carboxylic acids, volatile organic compounds (VOCs), and compounds that participate in chemistry that may lead secondary organic aerosol formation (Uhde and Salthammer, 2007; Waring and Siegel, 2013)—each of which may subsequently interact with ozone. Non-organic compounds such as glass and metals are known for their limited interaction with ozone, while

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

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

Researchers have suggested that when building materials are exposed to ozone, secondary emissions of carbonyls may increase considerably. For example, Weschler et al. (1992) used a 20-m³ stainless steel room furnished with four types of new carpets. The carpets, with either nylon fibers or a combination of nylon and olefin fibers, were tested under ozone concentrations of 0, 30-50 and 400 ppb. Weschler found that the emissions of formaldehyde, acetaldehyde, and aldehydes with 5 to 10 carbon atoms increased significantly in the presence of ozone. Coleman et al., (2008) found that secondary emissions of VOCs are higher than primary emissions when aircraft cabin materials, including carpet specimens from aircraft cabins, are exposed to ozone. Morrison et al. (2002) conducted a study to investigate the production of aldehydes from two residential nylon fiber carpets, and two commercial carpets with olefin fibers when exposed to 100 ppb ozone. . The results showed that for C1-C13 carbonyls, especially nonanal, emissions increased significantly during exposure to ozone. One of the few studies conducted in situ was that of Wang and Morrison (2006), who investigated secondary aldehyde emissions from four indoor surfaces in four houses. Living room carpets were one of the surfaces

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

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

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

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

2. METHODOLOGY

2.1 MATERIALS TESTED

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

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

Code [#]	Brand	Fiber material	Cut type	Green attribute
Triexta	Karastan	100% BCF* Triexta	Cut pile	Made of DuPont™ 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	-

[#] An abbreviated code is given each carpet studies based on the fiber type

* bulked continuous filament

** polyethylene terephthalate

2.2 EXPERIMENTAL APPARATUS

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

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

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

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⁻¹ 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

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

2.3 CARBONYL SAMPLING

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

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

2.4 CARBONYL ANALYSIS

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

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

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

2.5 DATA ANALYSIS

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

2.5.1 Ozone deposition velocities

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

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

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

incorporating uncertainties of the ozone monitors of 2% of reading and flow controllers of 1.5%, resulting in an average uncertainty of ± 0.1 m/h

2.5.2 Carbonyl emissions and molar yield calculation

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

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

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

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

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

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

(mol/m³), and C_{ozone} represents the ozone concentration in the chamber exit (mol/m³). The other quantities are as mentioned before in equation 2. The uncertainty analysis using error propagation method was performed and found that the average uncertainty was ± 0.01 mole O₃/mole carbonyl formed.

3. RESULTS AND DISCUSSION

3.1 EXIT OZONE CONCENTRATION

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

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

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

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

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

3.2 OZONE DEPOSITION VELOCITY

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

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

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

3.3 CARBONYL EMISSIONS

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

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

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

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

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

Within the light carbonyls, carpet sample emissions of acetone (C3) were by far the highest and emissions of acetaldehyde (C2) were lowest. While primary emissions of acetone were quite variable, ranging from 19 to $59 \mu\text{g m}^{-2} \text{h}^{-1}$ for nylon and polypropylene samples, respectively, primary emissions of acetaldehyde were more uniform, ranging from 6 to $8 \mu\text{g m}^{-2} \text{h}^{-1}$. Furthermore, for nylon, polypropylene, and polyester carpets, the secondary emissions of acetone are less than the primary emissions. This behavior agrees with the findings of Cros et al. (2011) and Gall et al. (2013) who both reported decreases in acetone secondary emissions that were less than primary emissions for nylon fiber carpet.

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

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

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

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

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

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

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

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

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

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

4. CONCLUSIONS

The deposition velocities for carpet samples showed values ranging from about 2 to 6 m h^{-1} . This indicates that carpets are good sinks for ozone with potential to lower harmful ozone levels

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

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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