

# Long-term performance of passive materials for removal of ozone from indoor air

**Abstract** The health effects associated with exposure to ozone range from respiratory irritation to increased mortality. In this paper, we explore the use of three green building materials and an activated carbon (AC) mat that remove ozone from indoor air. We studied the effects of long-term exposure of these materials to real environments on ozone removal capability and pre- and post-ozonation emissions. A field study was completed over a 6-month period, and laboratory testing was intermittently conducted on material samples retrieved from the field. The results show sustained ozone removal for all materials except recycled carpet, with greatest ozone deposition velocity for AC mat (2.5–3.8 m/h) and perlite-based ceiling tile (2.2–3.2 m/h). Carbonyl emission rates were low for AC across all field sites. Painted gypsum wallboard and perlite-based ceiling tile had similar overall emission rates over the 6-month period, while carpet had large initial emission rates of undesirable by-products that decayed rapidly but remained high compared with other materials. This study confirms that AC mats and perlite-based ceiling tile are viable surfaces for inclusion in buildings to remove ozone without generating undesirable by-products.

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## Practical Implications

The use of passive removal materials for ozone control could decrease the need for, or even render unnecessary, active but energy consuming control solutions. In buildings where ozone should be controlled (high outdoor ozone concentrations, sensitive populations), materials specifically designed or selected for removing ozone could be implemented, as long as ozone removal is not associated with large emissions of harmful by-products. We find that activated carbon mats and perlite-based ceiling tiles can provide substantial, long-lasting, ozone control.

## Introduction

Ozone is harmful to human health. Numerous studies have shown a link between exposure to ozone and asthma, as well as decreased lung function (McDonnell et al., 1999; U.S. EPA, 2006). These effects are attributed to ozone-induced damage to lung lining (Levy et al., 2001). Others have shown up to a 4% increase in mortality from respiratory causes per 10-ppb increase in daily 1-h maximum ozone (Bell et al., 2005, 2006; Jerrett et al., 2009).

In the absence of indoor sources, ozone concentrations indoors are lower than outdoors, with the indoor/outdoor ozone concentration ratio depending on air exchange rate and the collective ozone reactivity of

indoor and building envelope surfaces (Walker et al., 2010; Weschler, 2000). However, Americans spend nearly 90% of their time indoors (Klepeis et al., 2001), leading to significant exposure to indoor ozone. On average, indoor ozone may account for 50% or more of total daily ozone exposure (Weschler, 2006).

Indoor exposure to ozone is also accompanied by exposure to the products of ozone-initiated chemistry that also have adverse health effects (Weschler, 2004, 2006). These products usually come from reactions between ozone and unsaturated organic compounds. Major sources of such compounds include occupants themselves (e.g., skin oils), soft wood, carpet, linoleum, paints, cleaning products, air fresheners, and soiled fabrics (Weschler, 2006).

The importance of indoor chemistry is increasing, as buildings are constructed and retrofitted to be more energy efficient. To reduce energy consumption associated with space conditioning, tighter envelopes that reduce the number of air exchanges between indoors and outdoors are increasingly used. As a result, reactions that were once too slow to compete with air exchange rates may affect indoor air quality.

Removing ozone from indoor environments could have beneficial effects on human health and comfort, as long as such removal does not create harmful by-products. Shair (1981) used an auxiliary filtration system containing nine activated charcoal filters to treat intake air on a university building, when outdoor ozone concentrations exceeded 80 ppb. The filter life to maintain at least 50% ozone removal was 3 years. Shields et al. (1999) used six panels of granular activated carbon (AC) to remove ozone prior to ventilation of clean rooms. They observed that charcoal filters can remove ozone for > 5 years. But the use of active systems leads to increased energy consumption. Others have tested AC filters loaded with volatile organic compounds (VOC) and showed reduced ozone removal capacity depending on the type of adsorbed VOC and the extent of the loading (Dusenbury and Cannon, 1996; Metts and Batterman, 2006). However, VOC-loaded carbon filters exposed to ozone did not show increased emissions of by-products, as most of the VOC mass remained adsorbed on the AC.

An alternative to conventional active (flow through) ozone removal systems is the passive use of materials that ozone contacts via normal airflows in the occupied space of buildings. We refer here to materials that enhance or maintain high indoor ozone removal, while forming negligible by-products and that do so with minimal to no energy usage, as passive removal materials (PRMs). Kunkel et al. (2010) demonstrated the potential of PRMs during short-term laboratory experiments, and Gall et al. (2011) investigated the possibilities and limitations associated with using such materials in homes. The study described herein focused on evaluating how three green building materials performed as PRMs after 6 months in real indoor environments. AC mat was also tested for comparison.

Ozone removal to conventional and green materials has been extensively studied (Grøntoft, 2002; Hoang et al., 2009; Klenø et al., 2001; Kunkel et al., 2010; Morrison and Nazaroff, 2000, Wang and Morrison, 2006), as have post-ozonation emissions produced from ozone reactions (Morrison and Nazaroff, 2002; Nicolas et al., 2007; Poppendieck et al., 2007b; Wang and Morrison, 2006, 2010). Researchers have shown that building materials can be important sinks for ozone indoors, but that post-ozonation emissions are often significant, especially for materials covering large surface areas.

Ozone removal rates (parameterized by deposition velocities) and pre- and post-ozonation emission rates of three green building materials were evaluated in this study. AC mats were also evaluated for comparison, as they have previously been shown to effectively remove ozone from indoor air. Wall, floor, and ceiling materials ('green' paint on gypsum wallboard, recycled carpet tile, and perlite-based ceiling tile) were chosen, as they represent a large fraction of indoor surfaces and can therefore significantly influence indoor air quality in a building.

## Materials and methods

### Materials

The AC mat (model C0150; GreMarco Inc., West Brookfield, MA, USA) used in this study was a non-woven polyester-based fabric (thickness = 0.5 cm) coated with AC (area normalized mass = 136 g/m<sup>2</sup>). The green ceiling tiles (model Eurostone Terric; Chicago Metallic Corporation, Chicago, IL, USA) were made of 100% recyclable materials and were marketed as having no VOCs or man-made mineral fibers. The carpet (model Worn Again; Interface FLOR, Lagrange, GA, USA) had a recycled content of 68–71%. It was made of a type 6 nylon loop pile of height 0.43 cm. The recycled gypsum wallboard (Sheetrock, synthetic from Galena: USG, Chicago, IL, USA) was obtained through a local distributor in Austin, TX. It was made of reclaimed gypsum and recycled paper. Three months before the beginning of experiments, a 100% acrylic, low-VOC primer (Eco Spec: Benjamin Moore, Montvale, NJ, USA) was applied on the gypsum wallboard, followed by two coats of 100% acrylic, low-VOC, flat finish paint (Benjamin Moore, Eco Spec).

All materials were new when obtained and were stored in their original packaging under ambient conditions until the beginning of experiments, except for the gypsum wallboard sheets that were painted and aired out for 3 months under ambient conditions in an unoccupied test house, described by Novoselac and Siegel (2009).

### Field study

Ozone deposition velocity and pre- and post-ozonation emission rates were quantified for each sample prior to placement in the field. Samples were then placed in real homes and commercial/institutional buildings located in Austin, Texas, for 6 months. Field locations covered a wide range of indoor environments as listed in Table 1. All residential field sites were equipped with heating, ventilation, and air conditioning (HVAC) systems, but no mechanical air intakes. The office building was continuously mechanically ventilated with

**Table 1** Field locations

Building type	Room type	Age (years)	Monthly average range		Number of samples			
			Temperature	Relative humidity (%)	Activated carbon	Carpet	Ceiling tile	Painted gypsum wallboard
Office building	Office	24	23–25°C	32–59	1	2	1	1
Occupied by up to three students during regular business hours								
House 1	Kitchen	5	19–25°C	51–57	1	1	2	1
Used by five residents daily								
House 2	Home Office	44	16–29°C	47–63	1	1	1	2
Occupied by one resident and a pet daily								
House 1	Bedroom	5	19–27°C	44–60	2	1	1	1
Occupied by one resident daily								
Unoccupied test house	Kitchen/Dining room	4	16–29°C	34–54	2	1	1	1
Occupancy and operation of the Test House varied greatly depending on experiments carried out								

10% outdoor air. Materials were removed from the field on a monthly basis and brought back to the laboratory for analysis. New ozone deposition velocities were determined every month. Pre- and post-ozonation emission rates were determined after 3 and 6 months. Following laboratory analysis, the materials were returned to their initial field locations.

Samples (20 cm × 25 cm) of AC, ceiling tile, and painted gypsum wallboard were mounted on metal wire stands and placed on shelves approximately 1.8 m from the floor, at each field site. Samples of carpet were placed on the floor in relatively protected areas, such as in room corners, to avoid having occupants repeatedly stepping on them during the field test. The backside and edges of samples were covered with aluminum foil to ensure that only one side of the material was directly exposed to air. This protection was also used during laboratory experiments to avoid measuring characteristics of surfaces that are not usually exposed indoors.

Indoor environmental conditions were monitored at each test location, so that their effect on material properties could be analyzed. Continuous temperature and relative humidity (RH) measurements were recorded using a HOBO U12-013 datalogger (Onset Corporation, Bourne, MA, USA). As an approximate measure of dustiness, dust samples were taken monthly from the shelves on which the samples were set using adhesive Scotch Magic tape (3M; St. Paul, MN, USA). The sampling area was wiped clean using a Swiffer dry cloth (Procter & Gamble, Cincinnati, OH, USA), after each sampling event. The tape strip was then applied to a microscope slide and analyzed using a microscope (BX40; Olympus, Center Valley, PA, USA) with image processing software (Image J; National Institutes of Health, Bethesda, MD, USA) to measure the percent area covered by dust. Finally, the total organic gaseous content of the air was measured using passive samplers made of large volume glass liners (Open liners, tapered, frit, 3 mm I.D.; SISS, Round Rock, TX, USA) for the injection port of a gas chromatograph (GC). The sampler was packed with Tenax-TA (80/100 mesh;

Supelco Inc., St. Louis, MO, USA), placed at each field location and replaced monthly.

#### Laboratory testing

*Experimental system.* A diagram of the experimental system used to test materials is provided in Figure 1. Three identical 48-L electro-polished stainless steel chambers (25 cm × 38 cm × 50 cm) were used in parallel. Chambers were cleaned with deionized water and a heat gun before the beginning of each experiment to remove particles and chemicals that could have deposited or adsorbed to chamber walls.

Room air was dehumidified and cleaned by passing through a column containing eight mesh indicating Drierite (Drierite Company, Xenia, OH, USA) and an AC filter. The airflow was then split into two streams, one delivered to a UV-based ozone generator (modified zero air generator; Perma Pure LLC, Toms River, NJ, USA) to introduce ozone to the air stream (except during pre-ozonation emission rate measurements). A split stream of air was then bubbled through an impinger to achieve the desired RH, measured at the inlet of the chambers using an RH probe (Q-Trak 8551; TSI, Inc., Shoreview, MN, USA). Mass flow controllers (GFC; Aalborg, Orangeburg, NY, USA) maintained a constant volumetric flow rate entering each chamber. The air entered and exhausted from the chamber through perforated stainless steel tubes extending across the interior length of each chamber. Sampling ports for ozone and VOC measurements were placed on the inlet and outlets of the chambers. Ozone concentrations in the inlet and exhaust streams were measured using a single UV absorbance cell ozone monitor (model 202; 2B Technologies, Boulder, CO, USA), recalibrated three times during the experimental period using an ozone calibration source (model 306; 2B Technologies).

Laboratory tests were completed under the following experimental conditions:  $50 \pm 2\%$  RH,  $147 \pm 10$  ppb inlet ozone concentration, two air exchanges per hour. The airflow rate through the chambers was measured

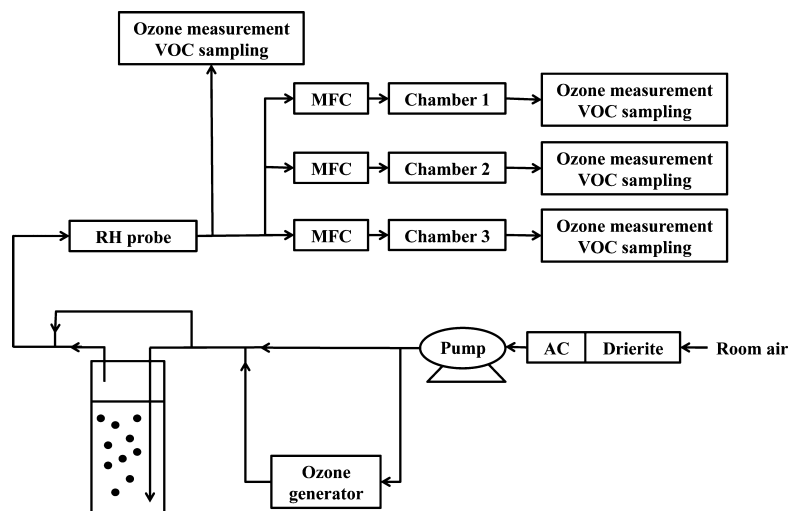


Fig. 1 Diagram of the experimental system. AC, activated carbon filter; MFC, mass flow controller; RH, relative humidity

using a bubble flow meter (Gilibrator 2; Sensidyne LP, Clearwater, FL, USA) to confirm the air exchange rate. The mean ( $\pm$  standard deviation) steady-state ozone concentration (across the entire experimental program) in chambers that contained materials ranged from  $51 \pm 7$  ppb for AC to  $89 \pm 11$  ppb for painted gypsum wallboard.

*Sampling of carbonyls.* Carbonyl emission rates from the materials were measured three times during the study. An initial measurement was made before samples were placed in the field. Carbonyl measurements were then made after 3 and 6 months. Target carbonyls included C<sub>1</sub> to C<sub>10</sub> saturated n-aldehydes, acetone, o-tolualdehyde, and benzaldehyde. Sampling methods followed those described by Morrison and Nazaroff (2002) and Poppendieck et al. (2007b). Light carbonyls (formaldehyde, acetaldehyde, acetone, propanal, butanal, and pentanal) were sampled on pre-packed DNPH tubes (SKC 226-119, Silica Gel, 150/300 mg sorbent). Heavy aldehydes (hexanal, heptanal, o-tolualdehyde, octanal, benzaldehyde, nonanal, and decanal) were sampled on large volume glass GC injection liners (SISS, open liners, tapered, frit, 3 mm I.D.) packed with Tenax-TA (80/100 mesh; Supelco Inc.). The  $400 \pm 3$  ml/min and  $50 \pm 2$  ml/min airflow through the DNPH and Tenax tubes, respectively, was provided by sampling pumps (model VSS-1; A.P. Buck Inc., Orlando, FL, USA).

Ozone scrubbers (LpDNPH, 505285; Supelco Inc.) were used when sampling ozonated air to avoid interferences that occur because of ozone reacting with sorbent materials and adsorbed organic compounds (Clausen and Wolkoff, 1996; Kleindienst et al., 1998; Pellizzari et al., 1984). Ozone scrubbers were cleaned according to a previously established protocol (Poppendieck et al., 2005).

Carbonyls were sampled in chamber air before and after ozone injection. Pre-ozonation emission rates were measured after the materials had been exposed to ozone-free air for 1.5 h. Materials were then exposed to ozone for 4 h, and samples were collected during the fourth hour of ozonation, to quantify emission rates during ozonation. For simplicity, we refer to these emissions as post-ozonation for comparison with pre-ozonation.

*Analysis of carbonyls.* DNPH tubes used to sample light carbonyls were wrapped in aluminum foil and placed in individual plastic bags after each experiment. The tubes were kept frozen until they were analyzed for C<sub>1</sub>–C<sub>5</sub> carbonyls using high-performance liquid chromatography with UV detection (HPLC/UV) (Waters 717plus autosampler; Waters 600 controllers, Waters 996 Photodiode Array Detector; Waters, Milford, MA, USA; column: Gemini 5u C18 110A, 250  $\times$  4.60 mm 5  $\mu$ m).

Tenax-TA tubes were analyzed by zero-path thermal desorption followed by gas chromatography with flame ionization detection (TD/GC/FID) (Optic 2; ATAS GL, Eidhenoven, The Netherlands; Agilent 6850; Agilent Technologies, Santa Clara, CA, USA, column: 30 m, Rxi-5Sil MS, 0.25 mm ID, film thickness: 0.5  $\mu$ m; Restek, Bellefonte, PA, USA).

The GC/FID was calibrated using a five-point external calibration curve ( $R^2 > 0.99$ ) for each individual compound. Calibration curves were created using stock solutions made from pure chemicals purchased from Fisher Scientific, Inc., Pittsburgh, PA, USA (pentanal, 97%; hexanal, 98%; heptanal, 95%; octanal, 99%; nonanal, 95%; decanal, 98%; benzaldehyde, 99%; and tolualdehyde, 97%). One blank Tenax-TA tube and one standard were analyzed each day that experiments were run.

Data analysis

**Ozone deposition velocity.** Ozone removal for different material samples was quantified in terms of ozone deposition velocity, a mass transfer coefficient defined in this research as the mass flux of ozone to the material surface divided by the ozone concentration in the chamber exhaust. The deposition velocity is a function of fluid mechanics (transport processes) and surface ozone decomposition kinetics. For constant fluid mechanical conditions, changes in ozone deposition velocity with time should only be due to changes in reactivity between ozone and material surfaces. Chamber tests were run for sufficient time that a steady-state condition with respect to ozone concentration was reached in the chamber. For every other set of experiments (three chambers operated in parallel), one of the chambers was left empty to allow calculation of the deposition velocity of ozone to the chamber walls. The empty chamber was switched between experiments.

The deposition velocity of ozone for the material tested,  $v_d$  (m/h), is based on a steady-state mass balance on a well-mixed chamber, including reaction at chamber walls:

$$v_d = \frac{\lambda V}{A_s} \left( \frac{c_{in}}{c} - 1 \right) - v_{d,w} \left( \frac{A_w}{A_s} - 1 \right) \quad (1)$$

where  $\lambda$  is the air exchange rate of the chamber (per h),  $V$  the volume of the chamber ( $m^3$ ),  $A_w$  is the total area of the chamber walls ( $m^2$ ),  $A_s$  is the horizontal projected area of the material sample ( $m^2$ ),  $c_{in}$  is the inlet ozone concentration (ppb),  $c$  is the ozone concentration in a chamber containing a material sample (ppb), and  $v_{d,w}$  is the ozone deposition velocity for the chamber walls (m/h).

Mean values are expressed with a corresponding standard deviation around the mean. For all other analyses, uncertainties in the measured deposition velocities were calculated with an error propagation analysis using the maximum of instrument error,  $\pm 2\%$  for the ozone analyzer,  $\pm 1\%$  for the bubble flow meter, and an error on horizontally projected area measurements that was estimated to be  $< 10\%$ .

**Carbonyl emission rates.** One chamber in the system was left empty in every other set of experiments to evaluate the carbonyl emission rates of chamber walls. The difference in carbonyl concentrations between empty chambers was on average  $< 2 \mu g/m^3$ . Emission rates of each compound from test specimens were calculated based on a mass balance on a well-mixed flow-through chamber at steady-state, accounting for emissions from chamber walls:

$$e_{k,s} = \frac{\lambda V(c_k - c_{k,in}) - \lambda V(c_{k,e} - c_{k,in}) \left( 1 - \frac{A_s}{A_w} \right)}{A_s} \quad (2)$$

where  $c_{k,in}$  is the inlet concentration of compound  $k$  ( $\mu g/m^3$ ),  $c_{k,e}$  is the concentration of compound  $k$  in an empty chamber ( $\mu g/m^3$ ),  $c_k$  is the concentration of compound  $k$  in a chamber containing a material sample ( $\mu g/m^3$ ),  $e_{k,s}$  is the emission rate of compound  $k$  for the material sample ( $\mu g/m^2$  per h), and all other variables are as previously described.

## Results and discussion

Ozone removal

Ozone deposition velocities averaged over the 6-month experimental period are shown in Figure 2. Vertical lines represent the standard deviation of deposition velocities determined across all 6 months. Figure 2

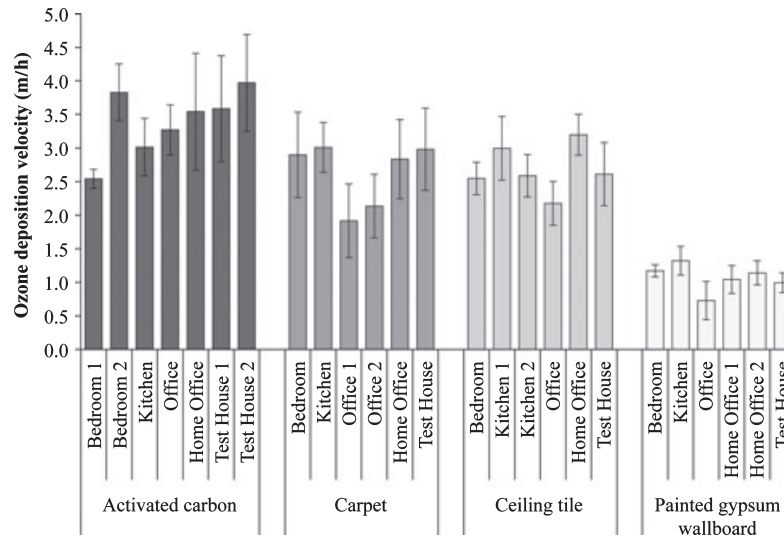


Fig. 2 Ozone deposition velocity on material samples averaged over time

allows a comparison among materials and specific locations of the ozone scavenging potential of each material. Note that, as airflow conditions in test chambers did not change during the experimental program, differences in deposition velocity should have been due solely to differences in material reactivity with ozone. Higher air speeds in the chamber would have probably led to greater differences in deposition velocity between materials, as transport limitations to ozone deposition would have been reduced and effects of reactivity magnified (Cano-Ruiz et al., 1993; Grøntoft and Raychaudhuri 2004). The deposition velocity for AC, which is highly reactive (Kunkel et al., 2010), is within the range of ozone transport-limited deposition velocities measured in an apartment (1.2–3.6 m/h) (Morrison et al., 2006). This suggests that mass transport conditions are consistent with residential settings. AC is the most effective material at removing ozone, with ozone deposition velocities in laboratory chambers ranging from 2.5 to 3.8 m/h. These values are slightly lower than those reported by Grøntoft (2002) and Kunkel et al. (2010), who observed deposition velocities ranging from 3.8 to 8.0 m/h. However, their testing methods involved the presence of mixing fans and higher air speeds adjacent to materials, which likely resulted in lower transport limitations to ozone removal leading to higher measured deposition velocities than those in this study. Ozone deposition velocities measured for carpet were slightly less than those for AC, ranging from 2.0 to 3.0 m/h. Wang and Morrison (2006) reported ozone deposition velocities for aged carpet in the range of 1.5–5 m/h, and Nicolas et al. (2007) reported deposition velocities on new carpet ranging from 1.4 to 2.7 m/h, i.e., in agreement with the results from this study. The ozone deposition velocities for the perlite-based ceiling tile ranged from 2.2 to 3.2 m/h. Deposition velocities previously re-

ported for ceiling tile range from 1.7 to 2.5 m/h (Hoang et al., 2009; Poppendieck et al., 2007a), similar to the range that we observed. Finally, ozone deposition velocities for painted gypsum wallboard were about two and a half to three times lower than for the other three materials, in the range of 0.7–1.3 m/h. Klenø et al. (2001) reported a deposition velocity of 1.5 m/h for gypsum wallboard freshly coated with acrylic paint. Wang and Morrison (2006) reported deposition velocities ranging from 1.2 m/h to 0.03 m/h in three houses between 1 and 10 years old (deposition velocities decreased with age).

All three green building materials exhibited reduced ozone deposition velocity for samples placed in the Office field location. Ozone removal by carpet and painted gypsum wallboard samples placed in this location decreased by 36% and 53%, respectively, between the first and the following months, while the decrease was only about 10% for the ceiling tile. Environmental conditions at other locations did not affect materials in such a consistent manner. This difference could not be explicitly resolved, but could be a result of consumption of reaction sites by somewhat higher ozone concentrations in the office location, relative to residential sites, due possibly to a higher air exchange rate, higher ozone penetration through the HVAC air intake, and surfaces with lower reactivities.

Ozone deposition velocities averaged over all locations are presented in Figure 3. Vertical lines represent one standard deviation. Ozone deposition velocities averaged over all field sites for AC and ceiling tile exhibited little variation over time. The deposition velocity for painted gypsum wallboard decayed by 30% for the first 2 months and then converged to a relatively low value. The deposition velocity for carpet started as high as the deposition velocity for AC, but

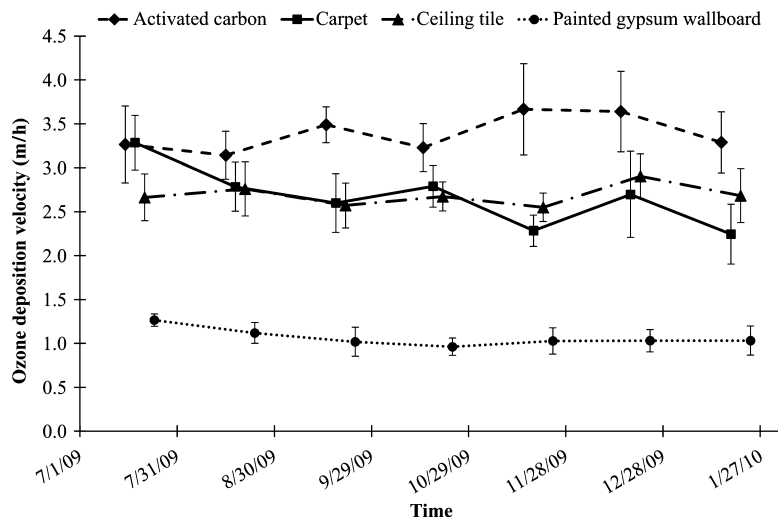


Fig. 3 Ozone deposition velocity on material samples averaged over all field sites

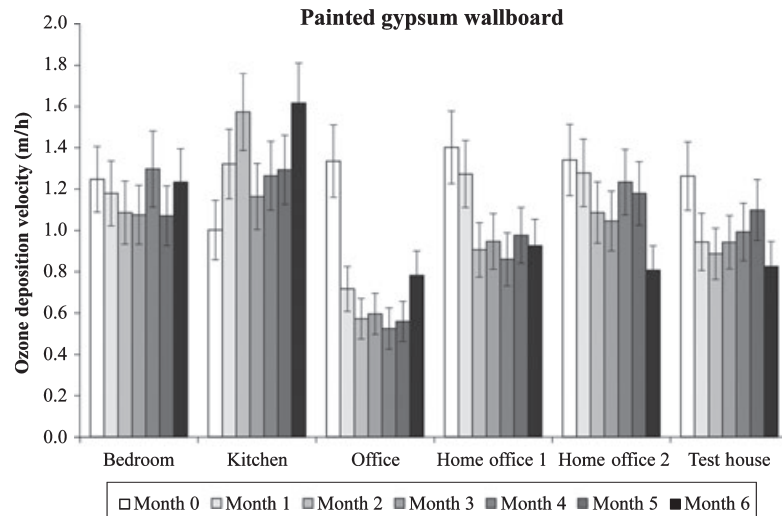


Fig. 4 Ozone deposition velocity results for painted gypsum wallboard

was lower than ceiling tiles by the end of the experimental period. After 6 months in the field, carpet removed about 30% less ozone than it did initially. This result is consistent with observations by Morrison and Nazaroff (2000), who tested four carpets and found that the reactivity of each material with ozone decreased with increasing cumulative exposure. Wang and Morrison (2006) also observed that ozone removal capacity of carpet decreases with age.

Activated carbon had the highest ozone removal capacity of all test materials and remained high even after several months at field locations. Perlite-based ceiling tile also appears to be a potentially viable PRM, as its reactivity is sustained over time. Painted gypsum wallboard was the least reactive material with ozone.

An entire set of results for painted gypsum wallboard is presented in Figure 4 and shows deposition velocities measured from month 0 to month 6. Some variation was observed for measurements at each location. The home office location exhibited a decreasing trend in ozone deposition velocity for the painted gypsum wallboard, but other materials did not show a similar trend. It is not possible to ascertain whether this is only because of experimental variations or whether the painted gypsum wallboard was actually affected by this particular environment. Isolated increases in reactivity could be due to changes in activity patterns at the field locations leading to a different level of soiling of the materials. For example, the UTest House (unoccupied test house facility) was heavily used for other experimental projects during month 5, which might explain the higher sample reactivity observed for that month.

#### Carbonyl emission rates

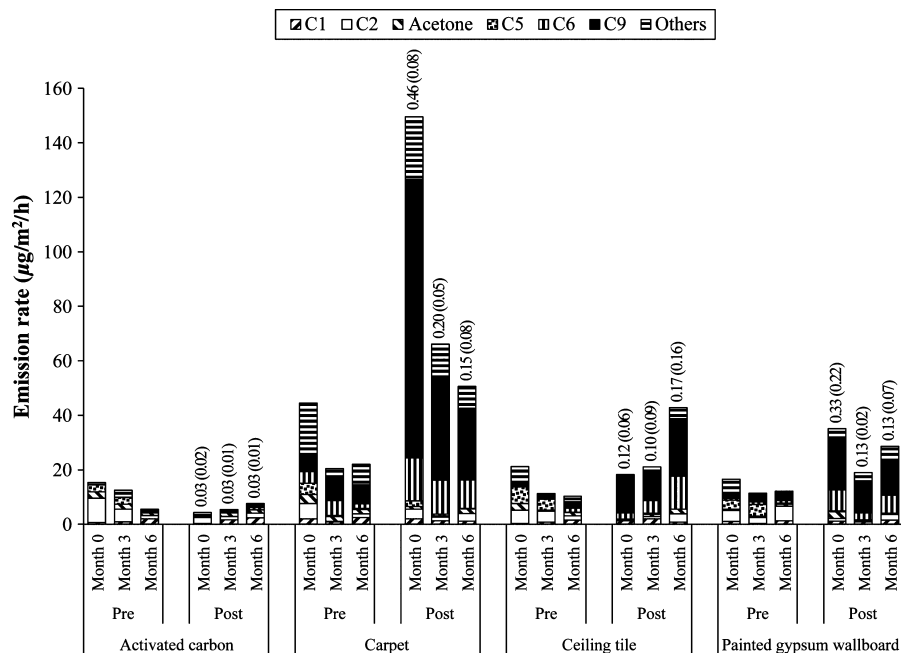
Pre-ozonation emissions refer to emissions that occurred before ozonated air was introduced into the test

chambers. Post-ozonation emission rates were measured after ozonated air was introduced into the chambers. Emission rates averaged over all locations are presented in Figure 5. Figure 5 allows a comparison of pre- and post-ozonation emission rates of the materials and their evolution over time.

Both pre- and post-ozonation emission rates from AC were lower than the other three materials. There is a trend of decreased emission rates over time for pre-ozonation emission rates, while post-ozonation emission rates increased slightly. The relatively low emission rates from AC were dominated by acetaldehyde (22% to 58% by mass) as well as formaldehyde, especially for post-ozonation emission rates (5% to 35%).

All three green materials had higher post-ozonation emission rates than pre-ozonation emission rates. In each case, post-ozonation emission rates were dominated by nonanal. This is consistent with results from Wang and Morrison (2006), who tested post-ozonation emission rates of various indoor surfaces in four homes between 1 and 14 years old. For similar test conditions, they also observed higher post-ozonation emission rates than pre-ozonation emission rates, also dominated by nonanal.

There were also differences in emission rates among test materials. Carpet exhibited the highest pre- and post-ozonation emission rates. Even though initial pre- and post-ozonation emission rates for carpet were relatively high, both were characterized by a dramatic reduction in emissions between the initial measurement and the one made after 3 months, and were observed for all field locations. After 3 months, pre- and post-ozonation emission rates from carpet decreased by approximately 55% from their initial level. After that period, pre-ozonation emission rates were relatively steady, while post-ozonation emission rates continued to decrease.



**Fig. 5** Emission rates for selected carbonyl compounds averaged over all locations. Pre, pre-ozonation; Post, post-ozonation; mean carbonyl mass yields are presented at the top of each post-ozonation bar with standard deviation in parenthesis

Results for post-ozonation emissions from carpet were compared with findings from a study by Morrison and Nazaroff (2002), who tested four different types of carpet. Some of their samples were stored in original packaging before testing, similar to our initial tests. Morrison and Nazaroff (2002) also studied carpet that had been aired out for a year prior to testing. Similar to the results of this study, they observed post-ozonation emission rates that were higher than pre-ozonation emission rates and dominated by nonanal for all samples. Lower post-ozonation emissions also occurred from aired carpet, similar to what we observed for newly unpackaged carpet vs. carpet placed in the field for 6 months. However, pre-ozonation emissions differed between Morrison and Nazaroff (2002) and this study. They observed pre-ozonation emission rates from aired samples that were greater than pre-ozonation emission rates from stored samples. Waring and Siegel (2011) also measured carbonyl emissions in a room containing carpet with ozone and found increased levels of formaldehyde and nonanal.

Averaged results for perlite-based ceiling tile show a different temporal fingerprint of emissions relative to carpet. While pre-ozonation emission rates decreased by 50% during the 6-month study period, post-ozonation emission rates averaged across all field sites were more than doubled. Emission rates of samples in the kitchen location greatly influenced the average result. Emission rates in the kitchen location increased by about two orders of magnitude between the initial and final measurements. For other field locations, post-

ozonation emissions decreased over the course of the experimental period. The ceiling tiles used in this study were highly porous and might have adsorbed gases or retained particles deposited on their surface during cooking events, or retained secondary products. Adsorbed gases and deposited particles could later react with ozone during laboratory tests, explaining an increase in post-ozonation emission rates for the samples placed in the kitchen.

Finally, painted gypsum wallboard exhibited an emission pattern that was different from the other two green materials, but observable for most field locations. Pre- and post-ozonation emission rates were the highest initially, but declined by 36% and 50%, respectively, during the first 3 months. However, emission rates then increased during the next 3 months by 23% and 30%, respectively.

Results averaged over all field locations are relevant when considering emissions by PRMs inside an entire building. However, locations where emissions were greatest, such as the kitchen or the bedroom, tend to influence the average value. This is particularly true for the perlite-based ceiling tile for which averaged results were greatly influenced by kitchen results, where emissions were higher than for other locations. This result is discussed later.

Overall carbonyl mass yields were calculated by summing the mass emission rates of all carbonyls and normalizing by the mass uptake rate of ozone. Yields ( $\mu\text{g carbonyls}/\mu\text{g ozone removed}$ ) varied from 0.01 to 0.61, 0.01 to 0.27, and 0.01 to 0.43 for measurements made at months 0, 3, and 6, respectively. The highest

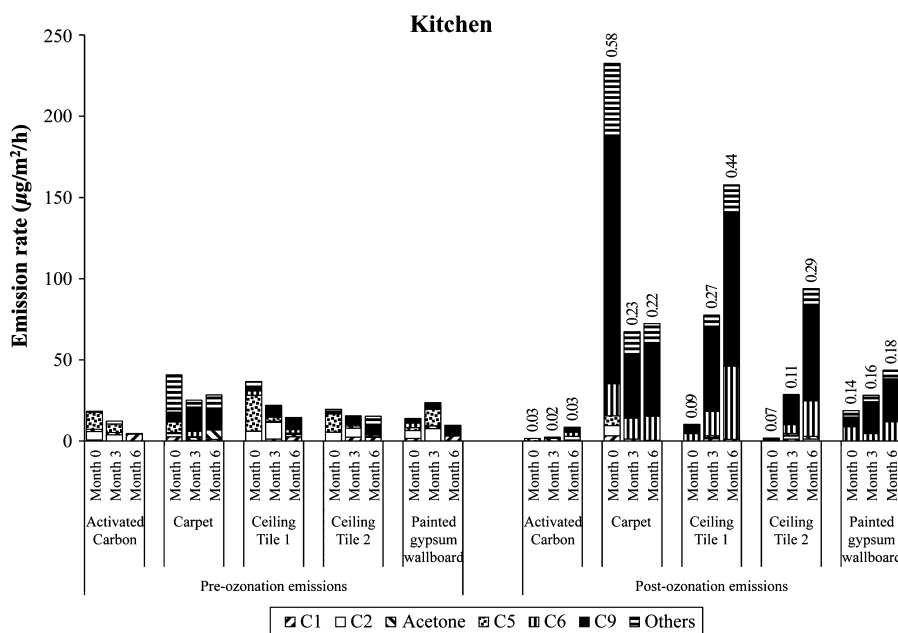
yields were observed for carpet, followed by painted gypsum wallboard, ceiling tile, and AC.

Pre-ozonation emissions were relatively consistent across locations. Greater variations were observed in post-ozonation emissions, possibly because of differences in environmental conditions, including soiling, at each field location. Over all locations, post-ozonation emission rates from carpet were the highest, followed by ceiling tile, painted gypsum wallboard, and finally AC. As such, it appears that, as the results are averaged over all locations, where all materials were placed, the nature of the material itself contributes significantly to the extent of post-ozonation emissions that will be produced. Nevertheless, samples placed in the bedroom and kitchen had noticeably higher post-ozonation emission rates than other locations. This result suggests that material soiling also affects post-ozonation emissions.

Results for pre- and post-ozonation emissions at the kitchen location for all four materials are shown in Figure 6. The pre-ozonation emissions for this location did not exhibit particular trends compared with other locations. However, the post-ozonation emissions were unique to this location (results for other locations are presented in online Supporting information). AC, ceiling tile, and painted gypsum wallboard each exhibited increased overall post-ozonation emission rates over time for test materials placed in the kitchen. The ceiling tile was especially affected, with overall post-ozonation emission rates after 6 months that increased 65 times compared with the initial test. Post-ozonation emission rates for painted gypsum wallboard doubled in 6 months, while post-ozonation emission rates for AC remained very low, but increased by a factor of five.

One possible explanation for these results is that ozone reacts with compounds emitted during cooking events that rise in hot cooking plumes and reach elevated materials, but that do not condense appreciably on floor materials. Vegetable cooking oils contain unsaturated fatty acids, such as oleic acid, that react with ozone to form several oxygenated compounds including aldehydes (Sadowska et al., 2008). Such interactions have been observed in simulated cooking events by Wang et al. (2005), who showed increased emission rates of heavy aldehydes, especially hexanal and nonanal, from kitchen surfaces. Similar interactions between ozone and compounds emitted during cooking events and adsorbed or condensed onto materials could explain the post-ozonation emissions observed during laboratory tests in this study. The results tend to validate this hypothesis, as materials that were set on shelves high above the floor show a similar trend of increased post-ozonation emission rates. Carpet does not exhibit a strong increase in post-ozonation by-product emissions after 3 months. It is possible that lower amounts of unsaturated fatty acids from cooking activities were deposited on carpet or that increases in reactivity from such deposition were offset by the otherwise lowering in reactivity of the carpet.

To a lesser extent, similar interactions between ozone and skin oils might have occurred in the bedroom location, where occupants spend approximately a third of their lives. Unsaturated fatty acids from human skin lipids have been shown to react with ozone to produce acetone, among other by-products (Wisthaler and Weschler, 2010). On average, acetone emission rates were highest for materials placed at the bedroom field site.



**Fig. 6** Carbonyl emission rates for samples from the kitchen location (mean carbonyl mass yields are presented at the top of each post-ozonation bar)

## Association with environmental parameters

Environmental parameters (temperature, RH, dustiness, and total volatile organic compounds) were measured each month at field locations, where material samples were installed. Single-variable associations were determined using linear correlations between an environmental parameter and either ozone deposition velocity, pre- or post-ozonation carbonyl emission rates.

For all parameters measured in the field, the associations between field conditions and ozone deposition velocities were weak, with  $R^2 < 0.2$  for most combinations of environmental parameter and material. Only one correlation was found to be statistically significant: a weak positive correlation ( $R^2 = 0.32$ ,  $P < 0.05$ ) was observed for ozone deposition on carpet vs. VOC abundance in air at field locations.

Pre-ozonation emission rates from AC had a weak but statistically significant positive association with field dustiness and temperature ( $R^2$  values of 0.33 and 0.32, respectively,  $P$ -values  $< 0.01$ ). Pre-ozonation emission rates from carpet were also positively associated with monthly VOC abundance and mean RH ( $R^2$  values of 0.43 and 0.26 respectively,  $P$ -values  $< 0.05$ ). Pre-ozonation emission rates for other materials did not exhibit a significant association ( $P$ -values  $> 0.05$ ) with any environmental parameter.

All three green building materials exhibited strong positive associations between post-ozonation emission rates and VOC abundance in air at field sites, with  $R^2$  of 0.50, 0.65, and 0.75 for ceiling tile, painted gypsum wallboard, and carpet, respectively ( $P$ -values  $< 0.01$ ). Carpet also exhibited a relatively strong positive association ( $R^2 = 0.55$ ,  $P < 0.001$ ) between post-ozonation emission rates and RH. Post-ozonation emission rates from AC did not exhibit any significant association ( $P$ -values were all above 0.05) with variations in environmental conditions. The association between increased post-ozonation emission rates and increased organic compounds in air at field sites may be due to reactive gases, e.g., unsaturated organic compounds, adsorbing to materials at field sites and reacting with ozone during ozonation of test chambers. Additional research is warranted to further explore and understand this association, as it might be an important consideration with respect to application of PRMs in environments with high VOC concentrations.

### Conclusions and future research

Activated carbon, perlite-based ceiling tile, recycled carpet, and painted gypsum wallboard can be used to passively remove ozone for 6 months and likely more, with sustained ozone reactivity, although the deposition velocity of carpet and painted gypsum wallboard

decreased by approximately 30% over 6 months. Painted gypsum board likely has little benefit with respect to reductions in ozone exposure. Further, post-ozonation emission rates from carpet are sufficiently high as to preclude its use as an effective PRM. Of the materials tested in this study, both AC and perlite-based ceiling tile are the most promising PRMs.

The choice and placement of PRMs should be considered in relation to the type of indoor environment that they would be used in, as certain indoor environments influence ozone deposition velocity or carbonyl emission patterns. PRMs could also be chosen according to the sensitivity to air pollution of the population occupying the building. Materials specifically designed for air purification, such as AC mat, could be used around sensitive populations, while more common materials such as ceiling tiles would be preferred in other settings.

This study is the first to explore the potential for long-term application of PRMs at actual field sites. Results of the study are encouraging and support the potential for sustained performance of PRMs in real buildings.

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### Supporting Information

Additional Supporting Information may be found in the online version of the article:

**Fig. S1** Carbonyl emission rates for samples from the Bedroom location (overall carbonyl yield is indicated atop of each post-ozonation bars).

**Fig. S2** Carbonyl emission rates for samples from the Office location (overall carbonyl yield is indicated atop of each post-ozonation bars).

**Fig. S3** Carbonyl emission rates for samples from the Home Office location (overall carbonyl yield is indicated atop of each post-ozonation bars).

**Fig. S4** Carbonyl emission rates for samples from the Test House location (overall carbonyl yield is indicated atop of each post-ozonation bars).

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