10-2015

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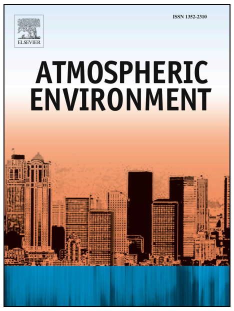
Citation Details

Rim, D., Gall, E.T., Maddalena, R.L., Nazaroff, W.W., Ozone reaction with interior building materials: influence of diurnal ozone variation, temperature and humidity, Atmospheric Environment (2015), doi: 10.1016/j.atmosenv.2015.10.093.



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PII: S1352-2310(15)30508-2
DOI: 10.1016/j.atmosenv.2015.10.093
Reference: AEA 14251

To appear in: *Atmospheric Environment*

Received Date: 6 July 2015
Revised Date: 29 October 2015
Accepted Date: 30 October 2015

Please cite this article as: Rim, D., Gall, E.T., Maddalena, R.L., Nazaroff, W.W., Ozone reaction with interior building materials: influence of diurnal ozone variation, temperature and humidity, *Atmospheric Environment* (2015), doi: 10.1016/j.atmosenv.2015.10.093.

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

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Abstract

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

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

1. Introduction

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

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

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

Ozone-surface reactions are prevalent indoors and compete with air-exchange rates as prominent removal mechanisms. Many studies have explored ozone reactions with building materials and indoor furnishings (Lamble et al., 2011; Gall et al., 2013; Morrison and Nazaroff, 2000; Wang and Morrison, 2006; Wang and Morrison, 2010; Hoang et al., 2009; Klenø et al., 2001; Grøntoft, 2002; Grøntoft and Raychaudhuri, 2004; Grøntoft et al., 2004; Nazaroff et al., 1993; Wechsler et al., 1992; Sabersky et al., 1973; Reiss et al., 1994; Nicolas et al., 2007; Lin and Hsu, 2015). These studies generally report ozone deposition velocities and reaction probabilities for different building materials under various chamber or building operation conditions. Several recent studies have also discussed the potential for exploiting ozone reactions on interior surfaces for low-energy indoor air cleaning (Kunkel et al., 2010; Cros et al., 2012; Gall et al., 2011).

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

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

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

2. Methods

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

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

2.1 Selection of test materials

Three types of common interior finishing materials — carpet tile, painted drywall, and ceiling tile — were selected to represent 1) materials commonly installed in commercial office spaces and 2) types of materials expected to comprise a large proportion of indoor surface area. The carpet tile (Figure 1a) consisted of 100% bulked continuous filament synthetic fiber with PVC backing (model Classic Modular Fasttrack; Weily Carpet). The thickness of carpet tile was 5.0 mm. The ceiling tiles (model Dune Max; Armstrong) were made of 74% recycled content and were composed of a wet-formed mineral fiber and a factory-applied surface coating of latex paint (Figure 1b). The ceiling tiles were marketed as qualifying for credits under the United States Green Building Council LEED program. The thickness of ceiling tile was 19 mm. The drywall (Figure 1c) was composed of a gypsum plaster core encased in durable, heavy-duty face and backing liner (model Standard Core; Boral) with a thickness of 12.5 mm. The drywall was painted with two coats of mold-guard paint (Mouldguard; Dulux) that was designed to prevent mold growth on the interior surface. The paint was a blend of water, acrylic emulsion binder, and non-lead pigments. The drywall was painted in two applications separated by 24 h to allow the first application to dry. Painted drywall samples were then allowed to dry for 48 h and placed in air-sealed plastic bags. Experiments were conducted with the painted drywall samples during the subsequent 8 months. The thickness of the drywall sample was 13 mm During experiments, all material samples were placed on a foil backing to restrict ozone exposure to one primary surface. The nominal material surface area exposed to bulk chamber air was 200 cm^2 for each tested sample.

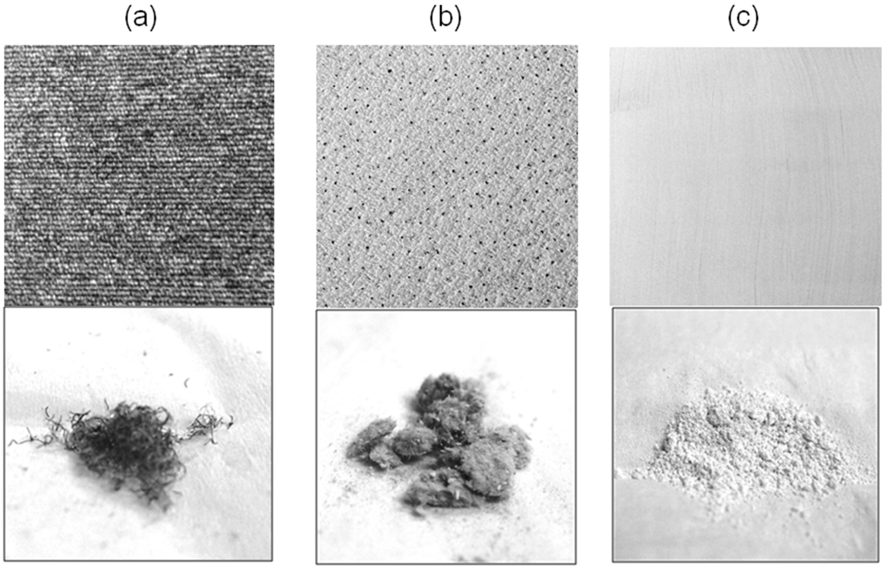

Figure 1. Three types of building materials selected as test materials for this investigation: a) carpet tile, b) ceiling tile, and c) painted drywall. Upper images show the product as purchased and tested. Lower images show the deconstructed material to illustrate the interior makeup of each building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

2.2 Environmental chamber and test conditions

Figure 2 shows the experimental apparatus employed to study the ozone-material surface reaction for the three test materials. The system comprised four 10.7-L (24 cm tall × 23.8 cm diameter) electropolished stainless-steel chambers housed in a constant temperature incubating enclosure. Ozone reaction rates were measured at two air temperatures — 22 °C and 28 °C — chosen to reflect upper and lower limits of indoor temperature during occupancy for typical air-conditioned office buildings in a tropical climate. The tests were performed for both temperatures at three levels of RH: 25%, 50%, and 75%. Relative humidity was measured at the inlet of the chambers using an RH probe (APT system, TEC, Minneapolis, MN, USA). Note that the three RH levels (25%, 50%, and 75%) correspond to absolute humidity values of 4.1, 8.3, and 12.5 g/kg at 22 °C and 5.9, 11.9, and 18.0 g/kg at 28 °C. The air exchange rate of the chamber was maintained at 10 ± 0.3 h^{-1} for all experiments. An exponential decay for a well-mixed chamber was fit to the transient decay of ozone in the empty quenched chamber. The range of decay rate estimates were from 9.18 to 11.0 h^{-1} , which are within 10% of the measured air exchange rate, determined from measurements of the flow rate entering the chamber.

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

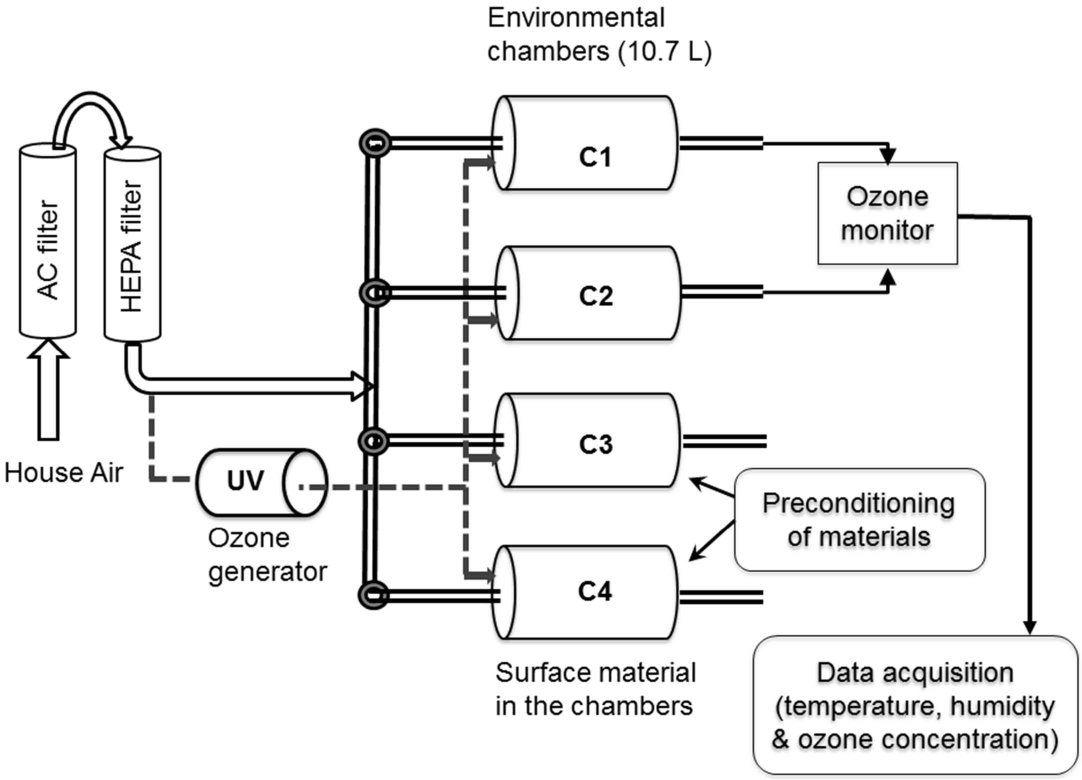

Figure 2. Schematic diagram of experimental apparatus.

2.3 Parameterizing ozone reaction rates on test materials

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

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

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

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

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

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

Eq 2 was solved using time-varying measured ozone concentrations with 5-min time steps (Δt = 300 s).

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

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v \rangle} \tag{3}$$

In eq 3, v_t is the transport-limited deposition velocity (cm/s), γ is the reaction probability (-), and $\langle v \rangle$ is the Boltzmann velocity for ozone (3.61×10^4 cm/s and 3.64 ×10^4 cm/s for 22 °C and 28 °C, respectively).

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

2.4 Effects of surface conditioning in occupied indoor environments

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

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

2.5 Quality assurance

Before each experiment, the chamber was quenched with 120 ppb of ozone for a minimum of 20 hours to deplete any reactive sites on the chamber walls. At the beginning of the measurement period, the UV absorbance ozone analyzer was calibrated against a UV photometric calibrator across a concentration range from 0 to 200 ppb. The ozone measurement uncertainty was estimated to be 7% based on the sum of the precision (greater of 1.0 ppb or 2%) and accuracy (greater of 1.0 ppb or 2%), combined in quadrature. Repeating the experiments with a new set of the same building material at 22 °C and 28 °C with 50% RH revealed concentration repeatibility errors to be less than 6%. Each test sample was preconditioned at least two days in an ozone-free ventilated chamber with the temperature and humidity set to the desired experimental value. This procedure led to stable moisture content of the material sample, which was confirmed by observing variation by < 0.5% in the outlet temperature and RH condition over a 2-h monitoring period. Uncertainty in determining deposition velocity was evaluated to be ±9% based on combining in quadrature the instrument error (±7%) for the ozone analyzer, errors for airflow measurements (±0.5%) and sample area measurements (±5%).

3. Results and Discussion

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

3.1 Time-varying ozone concentration and deposition velocity

Figure 3 shows examples of time-varying ozone concentration observed with the empty chamber (Figure 3a) and with painted drywall in the chamber (Figure 3b) while supplying a diurnally varying ozoneconcentration for the two-day test period. During the 8-h ozone injection period, average ozone concentration in the empty chamber is steady and reproducible, ranging from 60 to 62 ppb for the first and second days (Figure 3a). The ozone concentration measured in the presence of painted drywall (Figure 3b) is lowest during the first hour of ozone supply and gradually increases with time over the subsequent hours. Ozone reaction on the drywall surface is largest when the material is initially exposed to ozone; as ozone-reactive sites are consumed, the rate of reaction slowly decreases as evidenced by the higher average ozone mixing ratio across the second 8-h exposure (27.9 ppb) period as compared to the first (26.3 ppb).

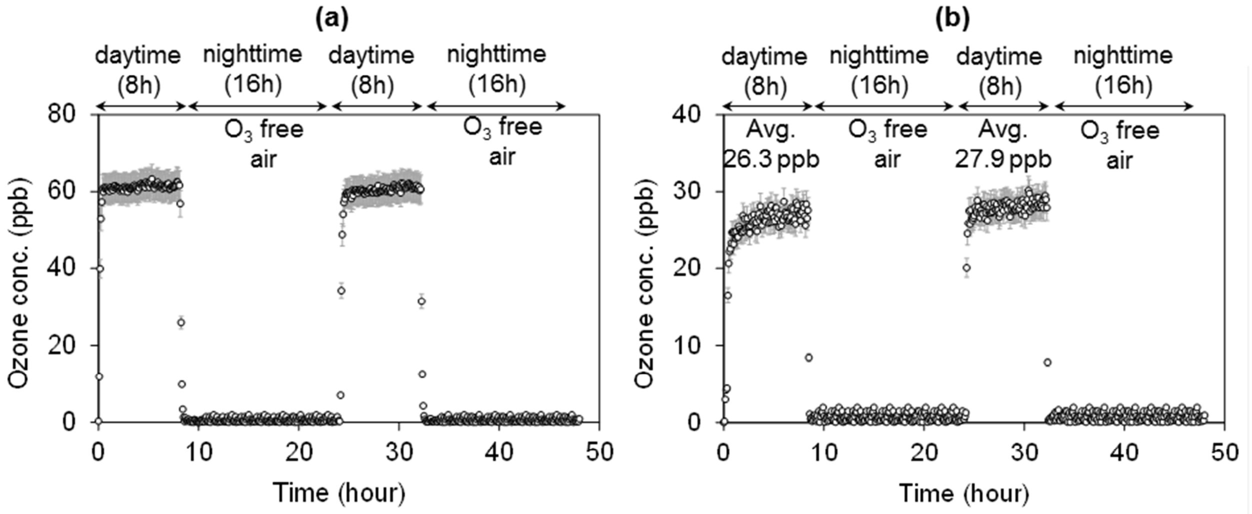

Figure 3. Two-day ozone concentration profiles for (a) empty chamber and (b) painted drywall placed in the chamber. Both experiments were conducted at *T* = 28 °C and RH = 50%. The supply ozone concentration during the daytime was 61 ppb. Note that the y-axis scale differs between (a) and (b). Error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

Figure 4 presents time-varying ozone deposition velocity during the 8-h ozone injection period for each day, as determined from eq 2 and utilizing the time-dependent ozone concentration measured at the chamber outlet. The empty quenched chamber contributes negligibly to the observed removal (Fig. 4a). As expected, the deposition velocity is the highest during initial ozone exposure, likely because of the abundance of reactive sites on the material surface. The deposition velocity gradually decreases with time as the reactive sites available for ozone reaction are consumed by ozone, a phenomenon known as "surface aging" (Morrison and Nazaroff, 2000). Comparing the two successive days, deposition velocities for all tested materials are higher for day 1 than for day 2. It is also observed that there is some recovery of ozone reactivity during the 16-h unexposed time between days. For painted drywall and for carpet tile, in particular, the ozone deposition velocity at the beginning of day two is higher than at the end of day one. Taken together, these materials exhibit both surface aging and recovery, although the effects are not pronounced over the few-day measurement period. Recovery observed in the present study appears smaller than that reported by Hoang el al. (2009). A plausible explanation for the recovery phenomenon is that ozone-reactive chemicals diffuse from the bulk material to the surface leading to a recovery of reactive sites during the non-exposed periods. The differences between our findings and those of Hoang et al. regarding recovery might be a consequence of a lesser abundance of transportable reactive chemicals beneath the surface of the materials that we tested.

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

The deposition velocity values observed in this study are similar or slightly elevated relative to values reported for the most comparable materials in the literature. For example, in the case of painted drywall, Lamble et al. (2011) report an ozone deposition velocity of 0.18 cm/s for unpainted samples and 0.03 cm/s for a drywall painted with a low-VOC paint. Some of the difference may be a consequence of different values of the transport-limited deposition velocity across studies. In the case of Lamble et al. (2011), v_t back-calculated from presented deposition velocities and reaction probabilities for a carpet (FC-2) yield a transport-limited deposition velocity for that study of ~ 0.3 cm/s, somewhat less than the value of 0.38 cm/s for our chamber. Grøntoft and Raychaudhuri (2004) reported ozone deposition velocities for unpainted gypsum drywall of 0.12-0.14 cm/s and 0.03-0.042 cm/s for a painted drywall. Reiss et al. (1994) reported mass accommodation coefficients that are comparable to reaction probabilities determined herein (Table 1b). Estimates of reaction probabilities determined here for the first day of exposure at 25% and 50% RH are an order of magnitude higher than 20-h reaction probabilities reported by Reiss et al. (1994) at comparable RH values. At 75% RH, our results and theirs are in better agreement, with the reaction probability determined here about 50% higher than the value reported by Reiss et al. Removal of ozone on carpets has been reported in several previous studies. Determinations for the carpet studied in this work agree well with the findings of the studies by Lamble et al. (2011), Gall et al. (2013), and Morrison and Nazaroff (2000) who report values ranging from 0.15 to 0.21 cm/s for various carpet surfaces. Lamble et al. (2011) also report a deposition velocity of 0.19 cm/s for a mineral-fiber ceiling tile, moderately higher than the ceiling tile result we obtained.

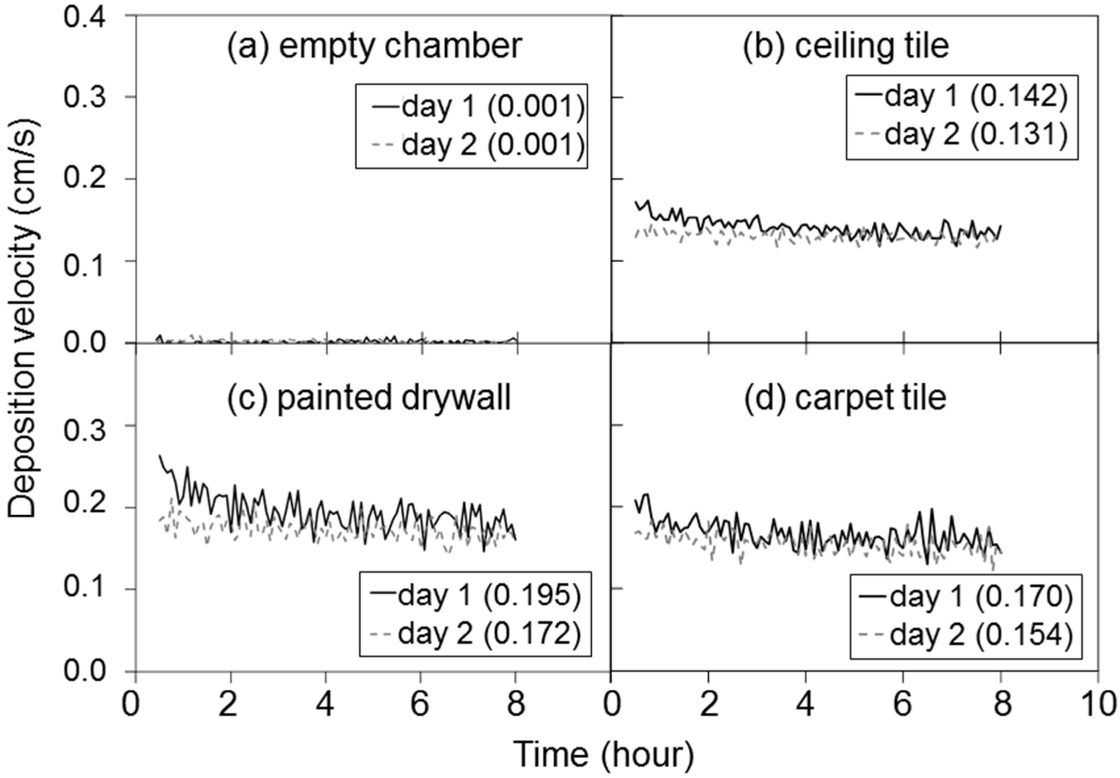

Figure 4. Ozone deposition velocity (cm/s) versus exposure time (h) for four cases and one set of environmental conditions (*T* = 28 °C, RH = 50%): a) empty chamber (background); b) ceiling tile; c) painted drywall; and d) carpet tile. The tested material samples were new. The estimated uncertainty is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

3.2 Effects of indoor temperature and humidity on deposition velocities

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

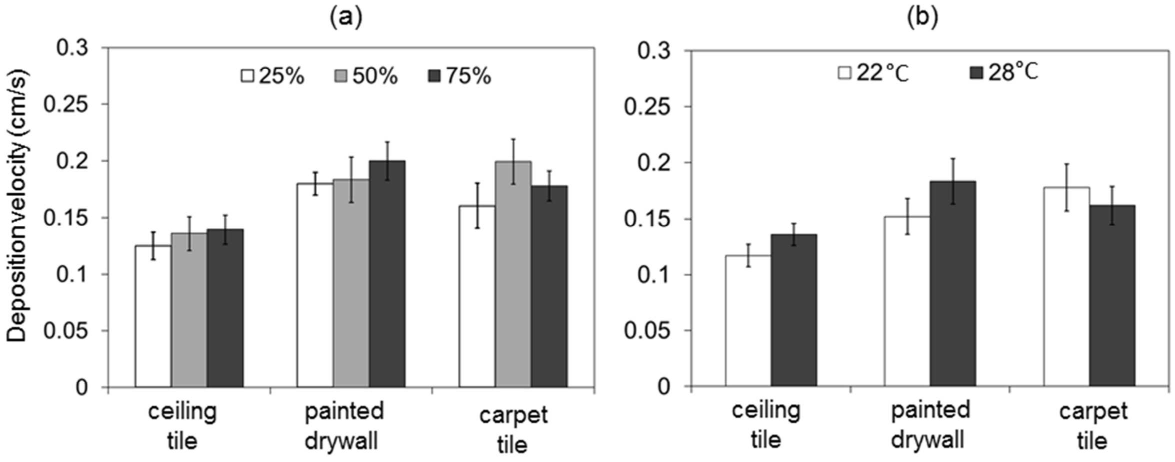

Figure 5. Effects of environmental condition on average ozone deposition velocity: a) effect of relative humidity at *T* = 28 °C and b) effect of temperature at RH = 50%. Error bars represent the standard deviation of the average across the 8-h elevated ozone period. All tested samples were new.

3.3 Estimated ozone reaction probabilities

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

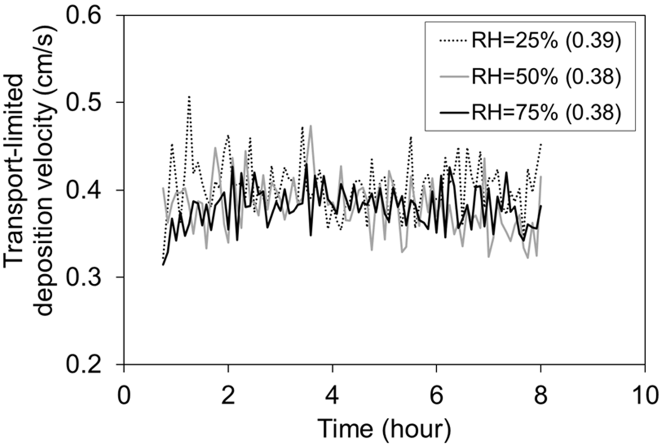

Figure 6. Transport-limited deposition velocity observed for ozone reaction on a polybutadiene surface (T = 28 °C).

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

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

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

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

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

3.4 Effects of surface conditioning in occupied indoor environments

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

Figure 7 shows variations of deposition velocity for the surfaces exposed in an occupied (10-15 people) office. Average deposition velocity decreased by 22%, 15%, and 16% for painted drywall, carpet, and ceiling tile, respectively, after 1-month of conditioning. After the second month of office exposure, deposition velocities increased relative to 1-month values for carpet and ceiling tile and were similar to 1-month values in the case of painted drywall. A plausible explanation for these observations is that, during the initial period, the ozone reactivity of the materials diminished as surface sites reacted with ozone and/or as volatile reactants were lost from the fresh materials. Subsequently, during the second month of exposure, carpet and ceiling tile regained some of their surface ozone reactivity, perhaps owing to soiling by particles and/or formation of films of organic molecules (such as squalene, an unsaturated constituent of human skin lipids) emitted from occupants and their activities (Weschler, 2015; Rim et al., 2009).

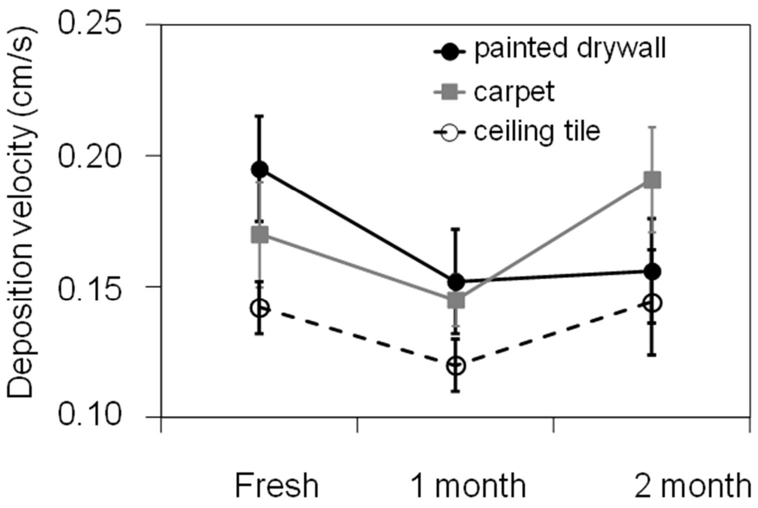

Figure 7. Deposition velocity for test materials conditioned in an occupied office environment (averages for 8-h ozone exposures during day 1 of testing at T = 28 °C, RH = 50%).Based on the measured transport-limited deposition velocity shown in Figure 6 and input to eq (3), Figure 8 presents initial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

Occupancy might have resulted in the preferential replenishment of the carpet surface with reactive compounds, because the carpet was placed on the floor where coarse particle shedding and resuspension might have contributed more to a change in the ozone-reactivity of the surface than for the other two materials, which were placed 1.5 m above the floor.

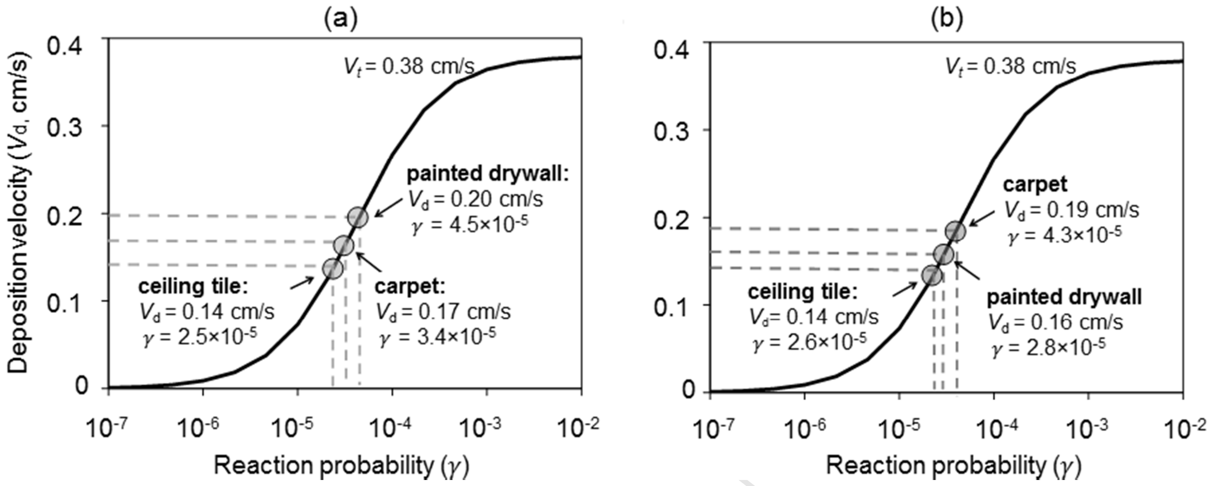

Figure 8. Reaction probabilities for test materials conditioned in an occupied office environment (determined for day 1 in the experimental apparatus at T = 28 °C, RH = 50%): (a) fresh sample vs. (b) 2-month old sample. The x-axis is on the logarithmic scale.

4. Conclusion

This study acquired new experimental information that adds insight into the important topic of how rapidly ozone reacts with common indoor materials. The deposition velocity is the highest during initial ozone exposure and gradually decreases with time as the reactive sites on the material surfaces are consumed by ozone. The present results suggest a moderate or minimal impact of temperature and relative humidity on ozone deposition velocity in the parameter ranges common in air-conditioned buildings. The surface reactivity with ozone can increase or decrease in an ordinary occupied office environment likely due to soiling by particles and/or the formation of films of organic molecules released from occupants and their activities. Some limitations should be noted. The present study used a high air exchange rate relative to typical indoor environments; therefore, the ozone concentration boundary layer might be thinner and transport-limited deposition velocity might be higher than in normal building operating conditions. The test materials were placed horizontally in the chamber. We note that the aerodynamics and mass transfer rate can vary with the surface orientation and indoor air flow conditions.

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

Acknowledgement

This research was funded by the Republic of Singapore's National Research Foundation through a grant to the Berkeley Education Alliance for Research in Singapore (BEARS) for the Singapore-Berkeley Building Efficiency and Sustainability in the Tropics (SinBerBEST) Program. BEARS has been established by the University of California, Berkeley as a center for intellectual excellence in research and education in Singapore.

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Highlight

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