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

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HIGHLIGHTS

- 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.

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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%–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.

1. Introduction

Elevated outdoor ozone concentrations have been associated with an increased incidence of adverse health effects, including premature mortality (Bell et al., 2006), asthma (Trasande and

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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-initiated 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, 2010; Hoang et al., 2009; Klenø et al., 2001; Grøntoft, 2002; Grøntoft and Raychaudhuri, 2004; Grøntoft et al., 2004; Nazaroff et al., 1993; Weschler 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, 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 (Fig. 1a) consisted of