**The Dissertation Committee for Erin Kennedy Darling Certifies that this is the approved version of the following dissertation:**


# Clay-Based Materials for Passive Control of Ozone and Reaction Byproducts in Buildings


**Committee:**

Richard L. Corsi, Supervisor

Atila Novoselac

Ying Xu

Maria G. Juenger

Barbara Brown Wilson

# Clay-Based Materials for Passive Control of Ozone and Reaction Byproducts in Buildings

by

**Erin Kennedy Darling, B.S.C.E., M.S.E.**

**Dissertation**

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

**Doctor of Philosophy**

The University of Texas at Austin

May 2016

# Dedication

To my grandpa, Jim Hartman, who would have wanted to be at the finish.

To those who supported me through hard times.

# Acknowledgements

My immense gratitude goes to Dr. Corsi for all of his encouragement over the years. Thank you for giving me the chance to work with you and your amazing graduate students when I was still an undergraduate. Thank you for the opportunity to perform experiments at the Danish Technical University - it was a life-changing experience.

I would also like to thank Dr. Neil Crain, whose guidance and presence in the lab was immeasurably helpful when I was in the dark. Thank you for volunteering your time. I am also forever thankful to Dori Eubank for so many reasons. Thank you for simplifying seemingly complicated (to me!) tasks, for all of the conversations, encouragement and friendship. I would also like to acknowledge Dr. Atila Novoselac for always being willing to lend out his equipment.

I couldn't have accomplished any of this research alone, and so I would like to acknowledge those who enriched my dissertation with their talents: Elliott Gall, Josh Aldred, Clément Cros, Glenn Morrison, Pawel Wargocki, Jakub Kolarik, Adam Targowski, and Dustin Poppendieck.

My first few years of graduate school were some of the best times I've had, thanks to some brilliant and adventurous colleagues and friends:  Priscilla Guerrero, Clément Cros, Matt Earnest, Matt Jordan, Jason Fialkoff, Éléna Nirlo, Jen Wang, Mark Jackson, Patrick Dunlap, David Rounce, James Seppi, Allison Osborne, Patrick Frasier, James Lo, Brent Stephens, Brandon Boor, Jordan Clark, and Yirui Liang.

I would also like to acknowledge my funding sources for making it possible to concentrate on my work: the NSF IGERT fellowship program, and the ASHRAE Grant-in-Aid Award.

Lastly I would like to thank my family, especially my Mama, who supports me in every way. And an extra special thank you to Conner LaRue, who is the yang to my yin. Thank you for talking to a sweaty stranger on Speedway one afternoon in June.

# Clay-Based Passive Removal Materials for Ozone and Reaction Byproduct Control in Buildings

by

Erin Kennedy Darling, Ph.D.

The University of Texas at Austin, 2016

SUPERVISOR: Richard L. Corsi

Tropospheric ozone that infiltrates buildings reacts readily with many indoor materials and compounds that are commonly detected in indoor air. These reactions lead to lower indoor ozone concentrations. However, the products of ozone reactions may be irritating or harmful to building occupants. While active technologies exist (i.e., activated carbon filtration in HVAC systems) to suppress indoor ozone concentrations, they can be costly and/or infeasible for dwellings that do not have these systems. Passive methods of ozone removal are an interest of building environment researchers. This dissertation involves (1) a review of the state of the knowledge on building materials and coatings that are intended to passively remove indoor ozone, especially clay-based materials; (2) a compilation of current data on ozone removal and reaction byproduct formation for these materials; (3) a model for ozone removal effectiveness for a selected clay-based material that is implemented in a hypothetical home; (4) a survey of the effects of a clay-based coating with and without ozone and a reactant source on human perceptions of air quality; (5) an investigation of the long-term potential for passive control of indoor ozone by two different clay-based surface coatings that were exposed to real indoor

environments; and (6) development of a location-specific model to estimate the monetary benefits versus costs of indoor ozone control using passive removal materials. The above tasks were completed through ongoing reviews of the literature, experimental studies conducted in small and large environmental chambers, and in the field.

Results of these studies suggest that clay or materials made from clay are a viable material for passive reduction of indoor pollution, due in part to clay's ability to catalyze ozone. Human sensory perceptions of indoor air quality were shown to significantly improve when a clay-based plaster was present in an ozonated environment. Based on modeling efforts, effective passive removal of indoor ozone is possible for realistic indoor scenarios when clay-based materials are implemented. There is a growing number of papers that are published on the subject of clay materials and indoor environmental quality, but few that investigate the longer term impacts and performance of clay materials, especially ones that have been exposed to real indoor environments.

# Contents

# Executive Summary

## 1. Introduction

### 1.1. Problem Statement

The indoor environment is a major determinant of human respiratory health, particularly given that Americans and those in many other developed countries spend on average almost 90% of their lives indoors (Klepeis et al., 2001; deCastro et al., 2007; Schweizer et al., 2007; Hussein et al., 2012). Populations that are more vulnerable to respiratory health complications, e.g., infants, elderly, and the chronically ill, spend an even greater portion of their time indoors (Allen et al., 2004; Wallace et al., 2006; Wheeler et al., 2011). Poor indoor environmental quality has been linked to transmission of respiratory infections (e.g., Kilpelainen et al., 2001; Wang et al., 2014a; Lappalainen et al., 2013), incidences of allergies and asthma (e.g., Bornehag et al., 2004; Rumchev et al., 2004; Araki et al., 2012), sick building syndrome (SBS), (Wargocki et al., 1999 and 2002; Apte et al., 2008; Buchanan et al., 2008; Elbayoumi et al., 2015) and decreased productivity (Fisk and Rosenfeld, 1997; Seppanen and Fisk, 2006)). Fisk and Rosenfeld (2000) estimated that the annual cost of respiratory infections, allergies and asthma, and SBS in the U.S. was roughly $103 billion, $22 billion, and $89 billion (all 2015 $), respectively.

Ozone can greatly affect the quality of the indoor environment. The primary source of indoor ozone is tropospheric ozone, which is a ubiquitous and reactive air pollutant that forms from reactions between nitrogen oxides (NOx) and VOCs in the presence of sunlight.

Ozone is entrained into buildings via outdoor air intakes, cracks in the building envelope, or through open doors and windows. Some indoor environments may have devices that produce ozone, such as laser printers and photocopiers, ion generators and electrostatic precipitators used for air cleaning (Destaillats et al., 2008 and references therein; Waring and Siegel, 2011; Singh et al., 2014).

The health effects of ozone are well-known and significant. When ozone enters the lungs it reacts with epithelial cells and polyunsaturated fatty acids in the tissue, leading to the formation of by-products and subsequent inflammation and increased permeability of the epithelial lining fluid (ELF) (Mudway and Kelly, 2000; Levy et al., 2001; USEPA, 2006). Increased permeability of the ELF allows for greater transport of pollutants from lung air into the blood stream (USEPA, 2006). Increases in ozone concentrations are associated with increases in respiratory-related morbidity and premature mortality (e.g., Bell et al., 2005; Gryparis et al., 2004; Ito et al., 2005; Jerrett et al., 2009; Parodi et al., 2005). Exposure to ozone has also been linked to increases in diagnoses of childhood asthma (McConnell et al., 2002), school absences (Hubbell et al., 2005), and increases in hospital emergency room visits among children and the elderly (Yang et al., 2003; Meng et al., 2010; Zheng et al., 2015).

Gas-phase, or homogeneous, reactions occur between ozone and some chemicals that are emitted into the air (e.g., alkenes) from building materials, furniture, and numerous cleaning and consumer products at time scales relevant to time scales of air exchange in buildings (Nazaroff and Weschler, 2004; Sarwar et al., 2004; Nazaroff et al., 2006; Singer et al., 2006; Coleman et al., 2008; Wisthaler and Weschler, 2010). Surface, or heterogeneous, reactions can occur on furniture, dust, building materials, and even human skin (e.g., Hyttinen et al., 2006; Tamas et al., 2006; Poppendieck et al., 2007b; Petrick and Dubowski, 2009; Wisthaler and Weschler, 2010; Gall et al., 2013). Products of these two types of reactions have been identified by several researchers. Heterogeneous reactions can produce $C_1$-$C_{10}$ carbonyls, dicarbonyls, and hydroxycarbonyls that may be irritating or harmful to building occupants (Cros et al., 2012; Lamble et al., 2011; Morrison and Nazaroff, 2002; Nicolas et al., 2007; Poppendieck et al., 2007a and 2007b; Wang and Morrison, 2006 & 2010; Wisthaler and Weschler, 2010; amongst others). Homogeneous reactions can produce secondary organic aerosols (Long et al., 2000; Wainman et al., 2000; Fan et al., 2003 and 2005; Destaillats et al., 2006; Rohr et al., 2003; Sarwar and Corsi, 2007; Sarwar et al., 2003 and 2004; Waring et al., 2011; Weschler and Shields, 1999), as well as a range of gaseous

oxidized products (Weschler et al., 1992a; Weschler and Shields, 1996 and 1997; Hodgson et al., 2000; Sarwar et al., 2002; Atkinson and Arey, 2003; Fan et al., 2003; Destaillats et al., 2006; Park and Ikeda, 2006; Singer et al., 2006). Under photocatalytic conditions, heterogeneous reactions may even form secondary organic aerosols (SOAs) (Ourrad et al., 2015). Products from ozone reactions with compounds in cleaning products and air fresheners include hydroxyl radicals and other radical species, formaldehyde, acetaldehyde, $C_3$ to $C_{10}$ saturated and unsaturated aldehydes, light monoketones, dicarbonyls, mono- and di-carboxylic acids, and secondary organic aerosols (Nazaroff and Weschler, 2004).

Although outdoor ozone concentrations are typically greater than concentrations indoors, Weschler (2006) estimated that 43-76% of human inhalation exposure to ozone of outdoor origin occurs indoors, and additionally that the average inhalation intake of ozone reaction products can be up to two times the indoor intake of inhaled ozone. Occupants of homes without centralized air conditioning systems may be at the greatest risk of exposure as the prevalence of these systems, and therefore lower air exchange rates and indoor ozone concentrations, have been shown to be inversely associated with ozone-related mortality (Smith et al., 2009). Further, Chen et al. (2012), in a modeling study encompassing 90 cities, predicted significant effects of indoor ozone on mortality. Aldred et al. (2015 and 2016) described the potentially high health benefit-cost ratios of ozone removal by activated carbon in HVAC systems.

Indoor ozone concentrations, and therefore total inhalation exposure to ozone can be reduced via active (i.e., energy-consuming) filtration methods such as treating building intake or indoor air using activated carbon filters (Shair, 1981; Shields et al., 1999; Lee and Davidson, 1999; Bekö et al., 2008 and 2009; Lin and Chen, 2014; Aldred et al., 2015 and 2016). However, many dwellers in the United States still live in homes that do not have any type of active filtration (U.S.E.I.A., 2011), much less access to affordable activated carbon filters.

Passive (i.e., no extra building energy consumption) filtration methods can be employed by strategically placing ozone-scavenging materials or material coatings

indoors. Passive removal materials (PRMs) are an alternative method for removing ozone from indoor environments without an energy demand, and with low reaction product formation. The concept of PRMs involves the application of select materials over large surface areas, generally walls and ceilings, onto or within which ozone reacts or decomposes. The four main characteristics of PRMs for indoor ozone removal are: (1) pollutant removal without consuming energy, other than the embodied energy in the production and manufacture of the material, (2) sustained pollutant removal over long time periods, (3) minimal reaction products, and (4) practical for use within buildings, meaning that the material can easily cover a large surface area while maintaining aesthetic appeal. Passive removal materials can be used as a supplement to active filtration systems, or as the sole filtration method.

For example, recent papers have focused on building materials or decorative material coatings (e.g., paint, plaster) in the context of passive reduction of ozone (e.g., Kunkel et al., 2010; Cros et al., 2012; Darling et al., 2012; Gall et al., 2013). The PRM concept is also being employed for other indoor pollutants, e.g., volatile organic compounds (VOCs) (Diamanti et al., 2013; Gallego et al., 2013; Nomura and Jones, 2013, 2014 and 2015; Popescu et al., 2013; Jo and Chun, 2014; Lin and Chen, 2014; Shen et al., 2014; Wang et al., 2014b).

### 1.2. Objectives of Dissertation

The overarching goal of this dissertation was to study whether specific inorganic building materials can be used to reduce human exposure to ozone, and to improve human perceptions of the indoor environment. Specific objectives included:

1. Review literature on building materials that have exhibited high ozone removal and low reaction byproduct emissions, and identify specific materials for experimental testing.
2. Survey human perceptions of air quality near a PRM under different ozone exposure scenarios.

4

3. Collect longitudinal data on ozone removal and byproduct emissions for two different clay-based coatings undergoing six months of aging in residential environments.
4. Develop a model to estimate benefit-cost ratios from using PRMs, such as clay-based coatings, in buildings.

## 1.3. Scope of Dissertation

The focus of the experimental work and research presented in this dissertation was on building materials composed of clay. Experimental work included human sensory surveys with clay plaster at the Danish Technical University, and laboratory and field experiments on two clay-based coatings at the University of Texas at Austin. Properties of these materials that were experimentally-determined include: ozone decay rates, deposition velocities, reaction probabilities, and byproduct molar yields. Results of these studies reflect a small subset of all commercially-available clay-based products. Target primary emissions and ozone-derived byproducts were limited to saturated n-aldehydes with more than five carbon atoms. Longitudinal laboratory and field experiments spanned six months. Field locations were based in five different rooms across two residences. A steady-state model was developed to estimate monetary health benefits vs. material cost ratios, and ozone removal effectiveness for implementation of clay-based materials in residences across 12 North American cities.

The major components (A-D) of this dissertation are shown in Figure 1. Component connections are represented by numbered links (1-5). The literature review (component A) was conducted alongside the other components. In component B, the effects of a PRM and ozone on human sensory perceptions of air quality were studied. Materials, methods, and interpretations of results from component B were informed (link 1) by some of the literature review. Component C was a longitudinal study of two different clay-based coatings, one coating being of the same kind studied in component B (link 2). This experiment lasted for six months while material specimens were exposed to real residential environments and periodically tested with ozone in laboratory chambers.

5

For Component D, a model was developed to estimate the monetary benefits and costs of implementing PRMs in buildings. Model parameters were culled from extensive web-based searches of published papers, reports, and databases (link 3). Inputs for PRM modeling were informed by experimental results from components B and C (links 4 and 5), as well as by several papers reviewed in Chapter 3. As a result of the extensive literature review conducted during component D, an unprecedented compilation of current data on PRM ozone removal and byproduct formation was created. This compilation is presented in Chapter 3 Section 3.3.2.
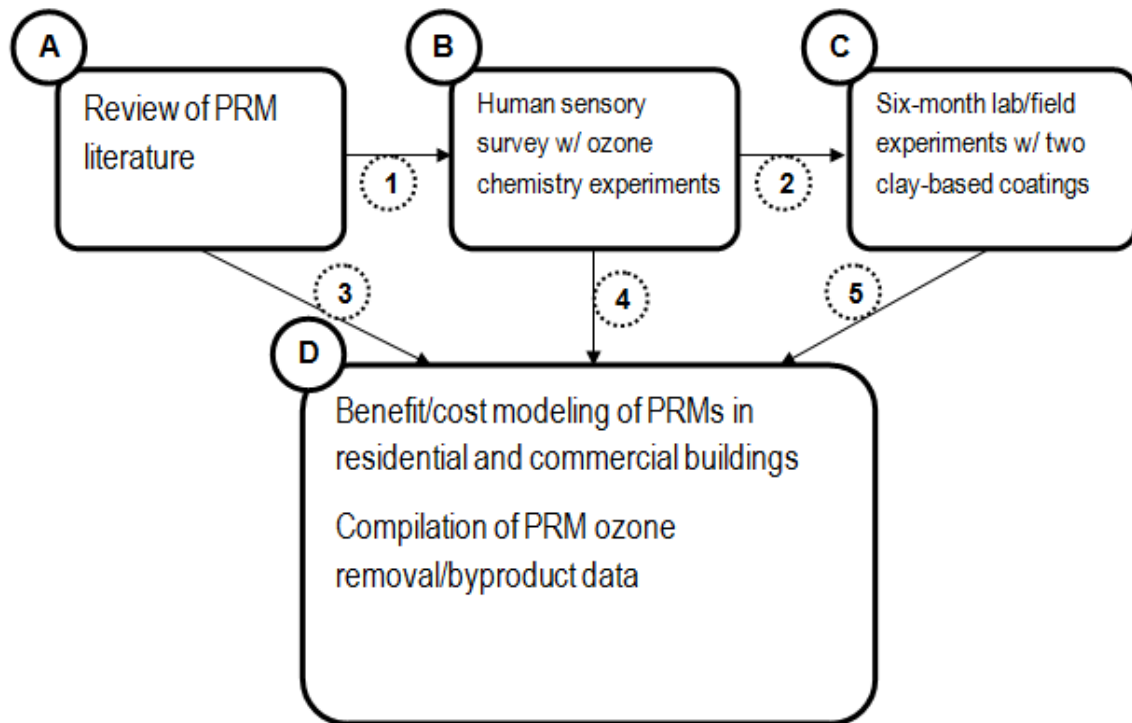
**Figure 1.** Research components (A-D) and their links (1-5) described in this dissertation.

## 1.4. Outline of Dissertation

A theoretical development with supporting background theory is provided in Chapter 2. Important terms are defined and equations relevant to various components of this dissertation are described.

A review of the literature (component A in Figure 1) is provided in Chapter 3. The review focuses on potential for ozone removal by PRMs and analyses of past research related to ozone removal and reaction product formation for potential PRMs.

The first experimental study (component B) is introduced in Chapter 4. Materials, equipment, and sampling and surveying methods are described, and major findings are presented. Further details of this study are placed in Appendices A and D.

The second experimental study (component C) is presented in Chapter 5. Materials, field locations, equipment, and analytical protocols are described, and major findings are presented. A detailed methodology and complete results are located in Appendix B, and supporting information is placed in Appendix E.

A third modeling study (component D) is described in Chapter 6. Model development, model inputs, and applied analyses are described, and results of the analyses are presented. Further details on the model are provided in Appendix F.

Each of the above studies is summarized with concluding remarks and limitations in Chapter 7. Recommendations for future research are also discussed.

The remainder of this dissertation is comprised of a list of references, papers that have been published or submitted to research journals (Appendices A through C), and supporting information for the research presented herein.

## 1.5. Papers

Listed below are the papers that stemmed from this dissertation:

∞ *Paper 1: Human perception studies*

Reference: Darling, E. K., Cros, C. J., Wargocki, P., Kolarik, J., Morrison, G. C., & Corsi, R. L. (2012). Impacts of a clay plaster on indoor air quality assessed using chemical and sensory measurements. *Build Environ, 57*, 370-376.

∞ *Paper 2: Longitudinal field/laboratory experiments*

Title: Darling, E. K. & Corsi, R. L. Field-to-lab analysis of clay wall coatings as passive removal materials for ozone in buildings, *Indoor Air* (submitted for publication)

∞ *Paper 3: Literature review*

Title: Darling, E. K., Morrison, G. C., & Corsi, R. L. Passive Removal Materials for Indoor Ozone Control, *Building and Environment* (submitted for publication)

∞ *Paper 4: Benefit/cost modeling of ozone removal by PRMs*

Title: Darling, E. K., Aldred, J. A., & Corsi, R. L. Literature and Product Review and Benefit/Cost Modeling of Ozone Removal by PRMs, (under preparation)

## 2. Theoretical Development

### 2.1. Definition of Terms

Several important equations are defined on the following pages. Variables are described after each equation. For ease of reference, these variables are also listed in alphabetical order in Table 1.

**Table 1.** Definitions and units of variables and constants used in calculations.

| Symbol | Units | Definition |
|---|---|---|
| $A_{prm}$ | m$^2$ | Surface area of a PRM |
| $A_s$ | m$^2$ | Horizontally-projected surface area of a specimen |
| $A_{tot}$ | m$^2$ | Total surface area of chamber or non-PRMs |
| *Benefit* | \$ | Monetary benefit associated with reduced DALYs |
| $C_{ch,i}$ | µg·m$^{-3}$, ppb | Steady-state concentration of compound $i$ inside chamber |
| $C_{in}$ | ppb | Chamber inlet ozone concentration |
| $C_{i,no\_control}$ | ppb, µg·m$^{-3}$ | Concentration of pollutant $i$ with ozone control device |
| $C_{i,control}$ | ppb, µg·m$^{-3}$ | concentration of pollutant $i$ with no ozone control device |
| $C_j$ | ppb | Indoor concentration of reactant $j$ |
| $C_o$ | ppb | Outdoor ozone concentration |
| $C_{out}$ | ppb | Chamber outlet ozone concentration |
| $C_{O3}$ | µg·m$^{-3}$, ppb | Concentration of ozone above a material surface, or steady-state concentration of indoor ozone |
| $C_{p,i}$ | µg·m$^{-3}$, ppb | Steady-state concentration of compound $i$ inside chamber or indoors |
| $C_{s,i}$ | µg·m$^{-3}$, ppb | Steady-state concentration of byproduct $i$ inside chamber with ozone |
| $DALYS_{disease}$ | yr | Total number of DALYs lost per disease incidence |
| *\$/DALY* | \$·yr$^{-1}$ | Value of one DALY |
| $\Sigma E$ | ppb·m$^3$·h$^{-1}$ | Total emission rate of ozone indoors |
| $E_{ch,i}$ | µg·h$^{-1}$ | Background emission rate of compound $i$ from chamber walls |
| $E_{p,i}$ | µg·h$^{-1}$ | Primary emission rate of compound $i$ from specimen |
| $E^*_{p,i}$ | µg·m$^{-2}$·h$^{-1}$ | Area-normalized primary emission rate of compound $i$ |
| $E_{s,i}$ | µg·h$^{-1}$ | Secondary emission rate of byproduct $i$ |
| $E^*_{s,i}$ | µg·m$^{-2}$·h$^{-1}$ | Area-normalized secondary emission rate of byproduct $i$ |
| $f$ | - | Fractional penetration through building envelope |
| $f_{f,O3}$ | - | Single-pass fractional removal of ozone by HVAC filter |
| $f_{f,p}$ | - | Single-pass fractional removal of reaction product by HVAC filter |
| $H_{on}$ | - | Average fraction of time that the HVAC system operates |

**Table 1.** Continued.

| | | |
|---|---|---|
| $k_{O3,ch}$ | s⁻¹, h⁻¹ | Ozone decay rate inside the empty chamber |
| $k_{O3,j}$ | ppb⁻¹·h⁻¹ | Bimolecular reaction rate constant for ozone and indoor reactant $j$ |
| $k_{O3,prm}$ | h⁻¹ | Decay rate of ozone to a PRM |
| $k_{O3,surf}$ | h⁻¹ | Decay rate of ozone in the absence of PRMs |
| $Occup$ | persons | Building occupancy |
| $Q$ | m³·h⁻¹ | Flow rate through chamber |
| $R$ | µg·h⁻¹ | Reaction rate of ozone with a material |
| $RF$ | yr⁻¹ | PRM replacement frequency |
| $V$ | m³ | Volume of air in control volume |
| $<v_b>$ | m·h⁻¹ | Boltzmann velocity of ozone in air (360 m·s⁻¹ at 20 °C) |
| $v_d$ | m·h⁻¹ | Ozone deposition velocity to a material |
| $v_t$ | m·h⁻¹ | Transport-limited deposition velocity |
| $y_i$ | mol·mol⁻¹ | Molar yield of byproduct $i$ |
| $YLD_{disease}$ | yr | Years of life lost due to disability from disease |
| $YLL_{disease}$ | yr | Years of life lost due to disease incidence |
| $y_{p,ij}$ | molᵢ·molⱼ⁻¹ | Molar yield of reaction product $i$ from bimolecular reactions between ozone and indoor reactant $j$ |
| $y_{prm,i}$ | mol·mol⁻¹ | Molar yield of reaction product $i$ from ozone reactions with PRM surface |
| $y_{surf,i}$ | mol·mol⁻¹ | molar yield of reaction product $i$ from ozone reactions with all non-PRM surfaces |
| $\alpha$ | m²·m⁻² | Non-PRM area reduction coefficient |
| $\gamma$ | - | Ozone reaction probability of a material |
| $\Delta DALYs$ | yr | Reduction in DALYs (relative to no PRM) when a PRM is used |
| $\Delta OPC$ | $ | overall cost of PRM above conventional material per 100,000 people |
| $\Delta PRM\$$ | $·m⁻² | Difference in cost between a PRM and conventional material |
| $\theta$ | µg·m⁻³·ppb⁻¹ | Conversion factor for SOA from ppb to µg·m⁻³ |
| $\lambda$ | s⁻¹, h⁻¹ | Air exchange rate |
| $\lambda_{rec}$ | s⁻¹, h⁻¹ | Recirculation air exchange rate |
| $\Omega_i$ | - | Fractional effectiveness of removal for pollutant $i$ |

## 2.2. Key Equations

### 2.2.1. Ozone Reactivity – Experimental Application

The reaction rate of ozone ($R$) with a material surface is defined by Equation 1:

$$R = v_d A_s C_{O3} \tag{1}$$

where $R$ is the reaction rate of ozone with the material ($\mu g \cdot h^{-1}$), $v_d$ is the ozone deposition velocity to the material ($m \cdot h^{-1}$), $A_s$ is the horizontally-projected surface area of the material ($m^2$), and $C_{O3}$ is the concentration of ozone above the surface ($\mu g \cdot m^{-3}$). The ozone deposition velocity is related to both fluid mechanics (i.e., turbulence, air speed, boundary layer development) and chemical reactivity of the material with ozone. The relationship of these two factors with $v_d$ is treated as a series of resistances. The overall resistance to ozone removal is the inverse of deposition velocity and is expressed by Equation 2 as:

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v_b \rangle} \tag{2}$$

where $v_t$ is the transport-limited deposition velocity at the material surface in the chamber ($m \cdot s^{-1}$), $\gamma$ is the ozone reaction probability of the material (-), and $\langle v_b \rangle$ is the Boltzmann velocity of ozone in air (~360 $m \cdot s^{-1}$ at 20 °C). The overall resistance to deposition is equal to the sum of the transport resistance, $1/v_t$, and the reaction resistance, $4/\gamma \langle v_b \rangle$ (Cano-Ruiz et al., 1993). Values of $v_t$ depend on mixing conditions in bulk air as well as boundary layer fluid mechanics near surfaces.

The ozone reaction probability ($\gamma$) indicates the potential of materials to remove ozone from air. For a specific material and pollutant, $\gamma$ expresses the fraction of collisions of pollutant molecules with the material surface that result in irreversible removal of the pollutant (Cano-Ruiz et al., 1993). Values of the ozone reaction probability ($\gamma$) vary over approximately four orders of magnitude for indoor materials, from values as low as $10^{-8}$, (e.g., for glass, [Grøntoft and Raychaudhuri, 2004]) and greater than $10^{-4}$ (e.g., for brick, [Simmons & Colbeck, 1990]). Solving Equation 2 for $\gamma$ yields Equation 3:

$$\gamma = \frac{4}{\langle v_b \rangle \left( \frac{1}{v_d} - \frac{1}{v_t} \right)} \tag{3}$$

To estimate the ozone deposition velocity, a mass balance on ozone (see Appendix G) is solved for the deposition velocity in the control volume, such as an experimental chamber, under well-mixed and steady-state conditions (Equation 4):

$$v_d = \frac{\lambda V}{A_s} \left( \frac{C_{in}}{C_{out}} - 1 - \frac{\alpha k_{O3,ch}}{\lambda} \right) \tag{4}$$

where $\lambda$ is the air exchange rate (s$^{-1}$), $V$ is the volume of air in the chamber (m$^3$), $A_s$ is the horizontally-projected surface area of the material (m$^2$), $C_{in}$ is the chamber inlet ozone concentration (ppb), $C_{out}$ is the ozone concentration at the chamber outlet (ppb), $k_{O3,ch}$ is the ozone decay rate inside the chamber without the material (s$^{-1}$), and the coefficient $\alpha$ accounts for the reduction of chamber or other non-PRM surface area when a PRM is used (Equation 5):

$$\alpha = \frac{(A_{tot} - A_s)}{A_{tot}} \tag{5}$$

Where $A_{tot}$ is the total surface area of the chamber or non-PRMs. The introduction of $\alpha$ is based on an assumption that a PRM covers or replaces non-PRM surfaces without adding to the total surface area. For non-chamber applications, it is possible to use a PRM that does not cover an existing surface, e.g., use of panels hung from a ceiling. In such a case, the value of $\alpha$ would be 1.

The $k_{O3,ch}$ is determined by performing a deposition velocity test in an empty chamber (Equation 6), under the same assumptions applied to Equation 4.

$$k_{O3,ch} = \lambda \left( \frac{C_{in}}{C_{out}} - 1 \right) \tag{6}$$

### 2.2.2. Emission Rates of Byproducts

Background emission rates of reaction byproducts from the chamber walls ($E_{ch,i}$) are calculated by solving a steady-state mass balance on a compound in a well-mixed empty chamber that has no sources outside of the chamber (Equation 7). The variable $C_{ch,i}$ represents the steady-state concentration of compound $i$ inside the chamber.

$$E_{ch,i} = QC_{ch,i} \tag{7}$$

To account for background emission rates from chamber surfaces, the area-normalized background emission rate from the chamber surfaces is subtracted from the total apparent primary emission rates (from material before ozone exposure) and from the total apparent secondary emission rates (from material after ozone exposure) using Equation 8 and Equation 9, respectively.

$$E_{p,i} = QC_{p,i} - E_{ch,i}\alpha \tag{8}$$

$$E_{s,i} = QC_{s,i} - E_{p,i} - E_{ch,i}\alpha \tag{9}$$

Where $E_{p,i}$ is the primary emission rate of compound $i$ ($\mu g \cdot h^{-1}$), $C_{p,i}$ is the steady-state concentration of compound $i$ inside the chamber without ozone ($\mu g \cdot m^{-3}$), $E_{s,i}$ is the secondary emission rate of compound $i$ ($\mu g \cdot h^{-1}$), $C_{s,i}$ is the steady-state concentration of compound $i$ inside the chamber with ozone ($\mu g \cdot m^{-3}$), and all other variables are as defined previously.

Area-normalized emission rates can be calculated by dividing the primary and secondary emission rates by the surface area of the material using Equations 10 and 11, respectively.

$$E_{p,i}^* = \frac{E_{p,i}}{A_s} \tag{10}$$

$$E_{s,i}^* = \frac{E_{s,i}}{A_s} \tag{11}$$

Where $E_{p,i}^*$ is the area-normalized primary emission rate of compound $i$ ($\mu g \cdot m^{-2} \cdot h^{-1}$), and $E_{s,i}^*$ is the area-normalized secondary emission rate of compound $i$ ($\mu g \cdot m^{-2} \cdot h^{-1}$).

### 2.2.3. Molar Yields of Byproducts

The molar yield of a reaction product ($y_i$, $mol \cdot mol^{-1}$) from a material is the ratio of moles of reaction product $i$ emitted from the material to moles of ozone removed by the

13

material. Molar yields for each secondary reaction byproduct are quantified experimentally by dividing the difference between the steady-state secondary byproduct concentration ($C_{s,i}$, all in parts per billion, ppb) and primary byproduct concentration ($C_{p,i}$) by the difference between the steady-state inlet (of the chamber) ozone concentration ($C_{in}$) and exhaust ozone concentration ($C_{out}$):

$$y_i = \frac{C_{s,i} - C_{p,i}}{C_{in} - C_{out}} \tag{12}$$

Molar yields can be used to compare ozone uptake and concomitant reaction byproduct emissions among different materials. Highly reactive materials with very low molar yields of reaction products are desirable for indoor air quality as they can scavenge substantial amounts of ozone without emitting large amounts of harmful or irritating reaction products.

### 2.2.4. Modeling Indoor Ozone and Reaction Products

The solution to a steady-state mass balance on ozone in a well-mixed interior space with inclusion of a PRM is represented by Equation 13:

$$C_{O3} = \frac{fC_o + \sum E / \lambda V}{1 + \lambda^{-1} H_{on} \lambda_{rec}(f_{f,O3}) + \lambda^{-1}(\alpha k_{O3,surf} + k_{O3,prm} + \sum k_{O3,j} C_j)} \tag{13}$$

where $C_{O3}$ is the steady-state concentration of indoor ozone (ppb), $f$ is the outdoor ozone penetration factor (0–1), $C_o$ is the outdoor ozone concentration (ppb), $E$ is the emission rate of ozone into the space (ppb·m$^3$·h$^{-1}$), $\lambda$ is the outdoor air exchange rate (h$^{-1}$), $V$ is the volume of air indoors (m$^3$), $k_{O3,surf}$ is the decay rate of ozone in the absence of PRM surfaces (h$^{-1}$), $\alpha$ is the chamber surface area reduction coefficient defined in Equation 5 (-), $k_{O3,prm}$ is the decay rate of ozone to the PRM (h$^{-1}$), $k_{O3,j}$ is the bimolecular reaction rate constant for ozone and indoor reactant $j$ (ppb$^{-1}$·h$^{-1}$), and $C_j$ is the indoor concentration of reactant $j$ (ppb).

14

The first term in the numerator of Equation 13 represents introduction of outdoor ozone to the indoor space. The second term in the numerator represents production of ozone from sources that may be present indoors. In the denominator, the second term represents removal of ozone by an HVAC particle filter in a recirculation duct. The first bracketed term in the denominator of Equation 13 represents the removal of ozone to non-PRM surfaces in the space. The second bracketed term represents the removal of ozone to the PRM, and the third bracketed term represents the total consumption of ozone via homogeneous reactions.

The additional decay rate to the PRM increases the denominator of Equation 13, and thereby reduces the steady-state ozone concentration, $C_{O3}$, provided that the decay rate to non-PRM surfaces ($k_{O3,surf}$) does not decrease more than $k_{O3,prm}$ as a result of being replaced by the PRM. If a PRM replaces a non-PRM surface that is highly reactive with ozone (e.g., carpet), then the benefit of reduced ozone would not be fully realized; however, a benefit would still be possible because of the potential reduction in total reaction byproduct emissions from reactive non-PRMs. Equation 14 represents the solution to a steady-state mass balance on a reaction byproduct when a PRM is included in the interior space:

$$C_{p,i} = \frac{y_{surf,i}\alpha k_{O3,surf}C_{O3} + y_{prm,i}k_{O3,prm}C_{O3} + \sum_j y_{p,ij}k_{O3,j}C_jC_{O3}\theta}{\lambda + H_{on}\lambda_{rec}(f_{f,p} - 1)}$$

(14)

where $C_{p,i}$ is the steady-state indoor concentration of reaction product $i$ (ppb), $y_{surf,i}$ is the molar yield of reaction product $i$ from ozone reactions with all non-PRM surfaces (mol·mol$^{-1}$), $y_{prm,i}$ is the molar yield of the reaction product from ozone reactions on the surface of the PRM (mol·mol$^{-1}$), $y_{p,ij}$ is the molar yield of reaction product $i$ from bimolecular reactions between ozone and indoor reactant $j$ (mol·mol$^{-1}$), and $\theta$ is a factor that converts SOA concentrations from µg·m$^{-3}$ to ppb. All other variables are as defined for Equation 13.

The first term in the numerator of Equation 14 represents formation of the reaction product when ozone reacts with non-PRM surfaces in the space. The second term in the numerator represents formation of the reaction product when ozone reacts with the surface of the PRM, and the third term in the numerator represents the total production rate of the reaction product when ozone reacts homogeneously with gaseous chemicals. In the denominator, the first term represents removal of the reaction product from the space via air exchange. The second term in the denominator represents removal of the reaction product by an HVAC particle filter in a recirculation duct. For simplicity, we do not consider adsorption and desorption processes to/from indoor surfaces for reaction products. However, these may be significant for higher molecular weight reaction products, or highly polar reaction products that are removed to polar materials such as gypsum wallboard.

Reducing the first term in the numerator of Equation 14 with addition of the second term, which should lead to less formation of the reaction product when ozone reacts with the surface of the PRM, should serve to decrease the numerator of Equation 1 relative to when a PRM is not in use. Effectively, this decreases the steady-state concentration, $C_p$, and thereby the molar yield of the reaction product throughout the interior space. Furthermore, the overall reduction in ozone concentration by introduction of a PRM should reduce byproduct production by reducing background heterogeneous and homogeneous reactions.

## 3. Review of Literature

### 3.1. Analyses of PRMs

Yu et al. (1993) were the first to express the utility of what were effectively PRMs for improving indoor air quality and conserving building energy. They focused on strategic placement of activated carbon sheets in buildings and modeled adsorption of select volatile organic compounds (VOCs) to those sheets in a hypothetical room. They emphasized the importance of placement of activated carbon sheets or other PRMs in locations where fluid mechanics are conducive to mass transfer. Sekine and Nishimura (2001) studied multiple air-permeable glass fiber sheets pressed together and embedded with activated carbon and manganese oxide. Laboratory and field tests (six and seven months) in new apartments showed the potential for significant reductions in formaldehyde in apartment air using this PRM. Moriske et al. (1998) also indicated that ozone removal was enhanced and the formation of formaldehyde reduced through the use of wallpaper coated on the back with activated carbon.

Ryhl-Svendsen (2011) studied clay in the form of unfired clay bricks for reduction of pollutant concentrations in museum archives. The introduction of stacked clay bricks led to a 71% reduction in organic acid (formic + acetic) concentrations relative to room conditions prior to addition of the bricks. Total VOC and formaldehyde concentrations in the room were also reduced by 27% and 9.4%, respectively.

Degradation of VOCs by titanium dioxide ($TiO_2$), a non-structural photocatalytic material that can be used to coat building materials, for example, by incorporation into mortars and mineral plasters, has been investigated recently by several researchers (e.g., Diamanti et al., 2013; Kibanova et al., 2009 & 2012; Gunschera et al., 2013). Nomura and Jones (2013, 2014 and 2015) studied formaldehyde adsorption capacities of aminosilicas, and suggest that aminosilicas could be useful as indoor formaldehyde adsorbents, especially because no UV-light is needed.

Since 2010, a number of studies have been completed to assess the potential for removal of indoor ozone using various PRMs (Kunkel et al., 2010; Lamble et al., 2011;

Cros et al., 2012; Darling et al., 2012; Gall et al., 2013). The goal has been to identify materials with high ozone removal potential without significant and harmful reaction product formation. In the following section, the focus is on the research that has been conducted on the removal of indoor ozone by PRMs.

### 3.2. The Potential for Ozone Removal

Several researchers have determined the deposition velocity ($v_d$) for ozone within various indoor environments for a range of environmental conditions (Nazaroff et al., 1993, and references therein); $v_d$ typically ranges from 1 to 3 m·h$^{-1}$. Others have determined ozone decay rates ($k_{O3,surf}$) ranging from 2.5 to 7.6 h$^{-1}$, respectively (Nazaroff et al., 1993, and references therein; Lee et al., 1999; Kunkel et al., 2010). Because values of $v_t$ and $\gamma$ have a wide range, $v_d$, and therefore the amount of ozone removed by materials, can vary greatly, even within a specific indoor environment. By applying a maximum transport-limited deposition velocity and a high ozone reaction probability to Equation 2, a near upper-bound ozone deposition velocity can be estimated.

Transport-limited deposition velocities have been inferred from Wilson (1968) to be 2.5 m·h$^{-1}$ for indoor natural convection, and 7.2 m·h$^{-1}$ for "when air is stirred sufficiently to move loose papers". Since that study, values of $v_t$ have been measured at specific locations within indoor environments, and they encompass the values gleaned from Wilson (1968). Under cabinets and desks, Morrison et al. (2006) measured values of $v_t$ between 2.2 and 3.2 m·h$^{-1}$, while in areas near hoods and computers where more air movement occurs, $v_t$ ranged from 4.3 to 5.2 m·h$^{-1}$. In one location near a window and a supply vent in an apartment, the $v_t$ was 18.7 m·h$^{-1}$ when the fan was switched on. Areas near doors and windows tend to have higher and more varying levels of $v_t$, that have been observed to range from 3.6 to 25.2 m·h$^{-1}$ (Morrison et al., 2003).

Brick, a material sometimes used in indoor environments, has a relatively high ozone reaction probability. Experiments by Simmons and Colbeck (1990) led to an ozone reaction probability of 2.2×10$^{-4}$ for both new and old brick. Substituting this value for $\gamma$, and a value of 7.2 m·h$^{-1}$ for $v_t$ (from Wilson, 1968) into Equation 2, results in an ozone

deposition velocity equal to 6.5 m·h$^{-1}$. Assuming that the majority of indoor surfaces are highly reactive and that the surface area-to-volume ratio is 3 m$^{-1}$ (Nazaroff et al., 1993, and references therein), leads to an ozone decay rate of 19.5 h$^{-1}$. Substituting this high-end decay rate into Equation 13, and assuming no homogeneous reactions ($\Sigma k_{O3,j}C_j = 0$), no indoor ozone sources ($\Sigma E = 0$), a penetration factor ($p = 0.79$) (Stephens et al., 2012), and an air exchange rate ($\lambda = 0.5$ h$^{-1}$), the concentration of ozone would be reduced by 98% relative to outdoors; this corresponds to an indoor/outdoor ozone concentration ratio (I/O) of 0.02. If the indoor ozone decay rate is 2.8 h$^{-1}$, a mean value experimentally-determined in homes by Lee et al. (1999), then the I/O ozone ratio would be 0.13. Typical I/O in buildings across various climates range from 0.2 to 0.7 (Weschler, 2000). The I/O for the highly reactive building scenario falls outside this range by an order of magnitude, and can mean a reduction of the indoor ozone concentration of 10 ppb or more, enough to reduce the risk of morbidity and mortality associated with ozone, even at low (~20 ppb) concentrations (Bell et al., 2006).

### 3.3. Analysis of Previous Research

Several researchers have studied ozone removal by PRMs. Key papers are listed in Table 2, and important findings of each are described in the following section.

**Table 2.** Studies conducted on materials that passively remove gaseous pollutants.

| Author | Material(s) | Pollutant(s) | Study Type |
|---|---|---|---|
| Moriske et al. (1998) | Wallpaper w/ AcC backing | $O_3$, formaldehyde | Lab & field |
| Kunkel et al. (2010) | Gypsum board, AcC cloth | $O_3$ | Lab & field |
| Lamble et al. (2011) | 19 green-certified materials, e.g., clay paint & plaster | $O_3$ & carbonyl byproducts | Lab |
| Gall et al. (2011a & 2011b) | Gypsum board, AcC cloth | $O_3$ | Modeling |
| Cros et al. (2012) | AcC cloth, zero-VOC paint on gypsum board, perlite ceiling tile, recycled carpet | $O_3$ & carbonyl byproducts | Lab & field, longitudinal |
| Darling et al. (2012) | Clay plaster on gypsum board | $O_3$ & carbonyl byproducts | Lab, sensory panel |

**Table 2.** Continued.

| Gall et al. (2013) | zero-VOC paint on gypsum board, perlite ceiling tile, recycled carpet | $O_3$ & carbonyl byproducts | Lab |
|---|---|---|---|
| Gall et al. (2014) | Cellulose filter papers, AcC cloth, pervious pavement, Portland cement concrete | $O_3$ | Lab |
| Rim et al. (2016) | Mineral fiber ceiling tile, mold-guard paint on drywall, and carpet tile | $O_3$ | Lab |

### 3.3.1. Ozone Removal

Removal of ozone by building materials has been quantified through several laboratory and field studies. Most of these studies have been short-term evaluations (i.e., up to 48 hours of ozone exposure). Furthermore, materials are usually tested as new, sometimes after a conditioning or airing out period, and far less often as aged materials.

Kunkel et al. (2010) completed experiments in a 14 $m^3$ laboratory chamber and 35 $m^3$ bedroom in a test house to evaluate the potential for ozone removal using activated carbon (AcC) cloth (a synthetic fiber media coated with finely ground activated carbon), and unpainted gypsum board (UGB). They used fans to simulate different air speeds adjacent to materials. For laboratory chamber experiments, the mean deposition velocity to activated carbon was over twice that of UGB, reflecting the increased reactivity of AcC relative to UGB. Increases in air speed adjacent to materials (from 10 to 19 cm·s$^{-1}$) significantly increased the removal of ozone to AcC, suggesting that transport-limitations are important for this highly reactive PRM. This was not the case for UGB; its performance as a PRM was not affected by changes in air speed over this range, suggesting significant reaction resistance. Increases in relative humidity from 20 to 60% consistently increased the ozone deposition velocity to AcC at the higher air speed condition, but not at the lower air speed. The use of 4.4 $m^2$ of AcC or UGB in a test house bedroom led to increases in the ozone decay rate, i.e., above background decay rates, by 2-7 h$^{-1}$ and 2-3 h$^{-1}$, respectively, depending on air speeds. Small amounts of AcC placed over ceiling fan blades increased the ozone decay rate by 1 h$^{-1}$ (33% above background decay) in the test house living room area when the fan was activated.

20

Lamble et al. (2011) studied the ozone reaction probability and molar yields for $C_1$-$C_{12}$ saturated n-aldehydes (+ acetone) for 19 indoor materials marketed as green-certified. Experiments were completed in small 10-L laboratory chambers. Reaction probabilities across all materials ranged over approximately two orders of magnitude, from 8.8 x $10^{-7}$ to 6.9 x $10^{-5}$. Total molar yields of reaction products ranged from non-detectable to 0.7 mol of total product per mole of ozone removed. A specific clay wall plaster with an accompanying tinting agent appeared to be the most promising as a PRM, with a relatively high reaction probability and a product molar yield that was below the detection limit for all species. Moriske et al. (1998) also noted the potential of two plaster materials for removal of ozone from indoor air.

Cros et al. (2012) studied the ozone removal performance of some of the materials tested by Lamble et al. (2011). Material specimens were placed in actual buildings over a six-month period, and periodically were brought back to the laboratory to be tested in small 48-L chambers to measure changes in ozone deposition velocity and reaction product emissions before placement back in the field. Activated carbon cloth was observed to maintain a relatively high reactivity with ozone across the six-month test period, independent of field location. Emission rates of reaction products were consistently low when AcC was exposed to ozone. A perlite-based ceiling tile also had a relatively high ozone deposition velocity in test chambers (25% lower than AcC cloth) that was sustained throughout the study. Reaction product emissions following exposure to ozone were greater than for AcC cloth but considerably lower than those for carpet. Emissions from ceiling tile placed in a kitchen environment increased with time, presumably due to surface soiling by unsaturated organic acids in cooking oils that react with ozone.

Gall et al. (2013) measured ozone deposition velocities and emissions of $C_1$ to $C_{10}$ carbonyls for large areas of three green building materials in a 68 $m^3$ environmental chamber. Each material was tested at 25%, 50%, and 75% relative humidity, and at low and high air mixing within the chamber, equivalent to 6 air changes per hour (ACH) and 12 ACH, respectively. While ozone deposition velocity to the carpet was the highest

(6.1 m·h$^{-1}$), molar yields of carbonyls after the carpet was exposed to ozone were also relatively high (0.28 at 50% RH). For perlite ceiling tile, however, ozone deposition velocity was moderate (2.3 m·h$^{-1}$), and molar yields of carbonyls were low (0.03). No consistent trends in ozone deposition and byproduct emissions were observed with changes in relative humidity across all materials. Results were generally in good agreement with those for the same materials tested by Lamble et al. (2011) and Cros et al. (2012).

Rim et al. (2016) measured ozone reaction probabilities for three different indoor materials (a synthetic fiber carpet, latex paint on mineral fiber ceiling tile, and mold-guard paint on drywall) while simulating diurnal ozone conditions (high concentrations during the day, zero concentration at night). Ozone reaction probabilities were determined for fresh materials and for the same materials after 1 and 2 months of placement in an occupied office building. Values decreased for all of the materials by the first month, and increased to varying degrees by the second month. Results of this study reinforce the fact that ozone reactivity of materials decreases with prolonged exposure to ozone. In addition, ozone reactivities of materials exposed to real indoor environments can fluctuate from month to month as the materials potentially come into contact with particles and organic molecules released during occupant activities.

Physical properties of porous materials and their effects on ozone reaction probability were investigated by Gall et al. (2014). Porosity, pore size distribution, and material thickness were determined for cellulose filter papers, activated carbon cloth, pervious pavement, and Portland cement concrete. Ozone reaction probabilities of each material were quantified under high and low transport deposition velocities ($v_t$) in an 11.4-L stainless steel chamber. Reaction probabilities of each material at the greatest thickness tested and under low $v_t$ were $7.2 \times 10^{-6}$ (mean) for the two filter papers, $1.2 \times 10^{-5}$ for pervious pavement, $2.2 \times 10^{-5}$ for Portland cement concrete, and $5.4 \times 10^{-5}$ for activated carbon cloth. Increasing material thickness increased reaction probabilities for the filter papers (at high and low $v_t$) and pervious pavement (at high $v_t$), but no dependence on thickness was observed for Portland cement concrete and activated carbon cloth.

22

Reaction probabilities for high porosity materials except for the filter papers (i.e., pervious pavement and activated carbon) increased by factors of 1.4 to 2.0 with increasing $v_t$.

Several other researchers have studied ozone deposition velocities, reaction probabilities and/or reaction product yields for a wide range of materials that are used indoors without specific attention to their selective use for ozone control. An evaluation of the literature suggests that, besides activated carbon, the most promising of such materials as PRMs for ozone control are inorganic materials, including clay bricks, calcareous stone, and ceiling tile made of mineral fibers or volcanic perlite. Ozone deposition velocities, reaction probabilities, and molar yields for many of these materials are listed in Table 3 in the next section.

### 3.3.2. Reaction Probabilities and Molar Yields

A few researchers have reported values of ozone reaction probabilities, or provided sufficient data to back-calculate $\gamma$, alongside corresponding values of byproduct molar yields. These data were compiled and are presented in Figure 2. Each data point contains a numbered label that corresponds to one type of material listed in Table 3, except for the materials tested by Wang and Morrison (2006 & 2010), who reported average molar yields among functionally similar materials that were tested in place in four different homes (see notes below Table 3 for more detail). The total molar yields include yields for $C_1$-$C_{10}$ carbonyls. Yields reported by Gall et al. (2013) also include yields for acetone, benzaldehyde, and o-tolualdehyde; yields from Morrison and Nazaroff (2000 & 2002) encompass $C_1$-$C_{13}$ n-aldehydes, and yields from Wang and Morrison (2006 & 2010) also include 2-nonenal. When reaction probabilities were not reported, ozone deposition velocities and – if provided – transport-limited deposition velocities were substituted into Equation 3 to estimate $\gamma$. Additional details about each of these experimental studies, including reaction probability and yield data are provided in Table 3.
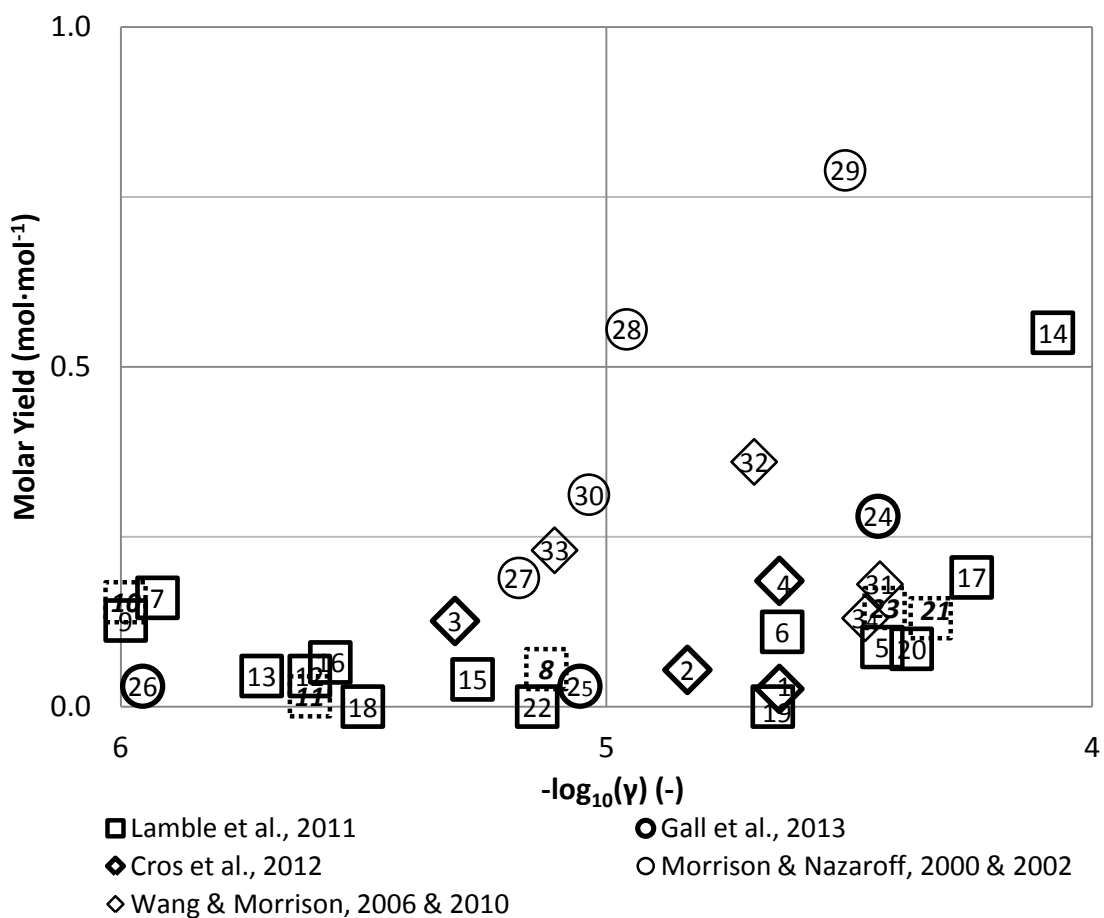
**Figure 2.** Ozone reaction probabilities (logarithmically transformed, note reverse values) and molar yields of $C_1$-$C_{10}$ carbonyls (unless noted otherwise in Table 3) for different materials tested by various researchers. Bolded, italicized data points surrounded by a dotted circle indicate yields with a higher prevalence of formaldehyde. Data in chart can be found in Table 3.

Materials located within the lower left-hand quadrant of Figure 2 are less reactive with ozone, but many have relatively low byproduct yields. For example, some of these materials include resilient floor tiles [(7) and (9)], cork wallboard (13), and low-VOC paint [(3) and (26)]. No materials have been reported to have relatively low ozone reaction probabilities and high byproduct yields, e.g., > 0.5. The upper right-hand quadrant of Figure 2 contains materials that are more reactive with ozone, but that also

have high byproduct yields, such as acoustic wall panel (14), olefin fiber carpet (28), and nylon fiber carpet (29). High molar yields from carpets are most likely due to products that are emitted when ozone reacts with low-volatility unsaturated oils present on the surface of carpet fibers (Weschler et al., 1992b; Morrison and Nazaroff, 2002). The large surface area of carpet fibers simultaneously contributes to high ozone reaction probabilities and byproduct emissions.

Materials with characteristics that indicate potential as PRMs are located in the lower right-hand quadrant, particularly those nearest to the horizontal axis, because they have high ozone reaction probabilities ($> 10^{-5}$) and low byproduct yields ($< 0.1$). Included within this quadrant, for example, are activated carbon cloth (1), perlite ceiling tile (2), recycled carpet (5), clay-based plaster (19), and unpainted gypsum board (20). Mineral fiber ceiling tile (*21*) and fiberglass ceiling tile (*23*) fall in this quadrant. However, formaldehyde was prevalent as a secondary byproduct from these materials. Other materials that have a high prevalence of formaldehyde as a secondary product are rubber floor tile (*8*), porcelain floor tile (*10*), and renewable wood flooring (*11*).

**Table 3.** Ozone reaction probabilities, $C_1$-$C_{10}$ molar yields, and experimental conditions for materials referenced in Figure 2.

| # | Material | γ (-) | y* (mol/mol) | HCHO Prevalent | T (°C), RH (%) |
|---|----------|-------|--------------|----------------|----------------|
| 1 | Activated carbon mat | 2.27E-05 | 0.026 | | na, 50 |
| 2 | Perlite ceiling tile | 1.47E-05 | 0.054 | | na, 50 |
| 3 | Low-voc paint on drywall | 4.88E-06 | 0.126 | | na, 50 |
| 4 | Recycled carpet | 2.27E-05 | 0.185 | | na, 50 |
| 5 | Recycled carpet | 3.70E-05 | 0.088 | | 25, 50 |
| 6 | Fabric-backed carpet | 2.30E-05 | 0.110 | | 25, 50 |
| 7 | Resilient floor tile | 1.19E-06 | 0.160 | | 25, 50 |
| 8 | Rubber floor tile | 7.52E-06 | 0.055 | * | 25, 50 |
| 9 | Bio-based resilient floor tile | 1.02E-06 | 0.127 | | 25, 50 |
| 10 | Porcelain floor tile | 1.02E-06 | 0.153 | * | 25, 50 |
| 11 | Renewable wood flooring | 2.45E-06 | 0.015 | * | 25, 50 |
| 12 | Finished bamboo flooring | 1.95E-06 | 0.045 | | 25, 50 |
| 13 | Cork wallboard | 2.45E-06 | 0.045 | | 25, 50 |
| 14 | Acoustic wall panel | 8.30E-05 | 0.550 | | 25, 50 |
| 15 | Rayon wall covering | 5.30E-06 | 0.040 | | 25, 50 |
| 16 | Latex paint | 2.70E-06 | 0.065 | | 25, 50 |
| 17 | Clay-based paint | 5.65E-05 | 0.190 | | 25, 50 |
| 18 | Collagen-based paint | 3.15E-06 | 0.000 | | 25, 50 |
| 19 | Clay-based plaster | 2.20E-05 | 0.000 | | 25, 50 |
| 20 | Drywall | 4.25E-05 | 0.085 | | 25, 50 |
| 21 | Mineral fiber ceiling tile | 4.65E-05 | 0.130 | * | 25, 50 |
| 22 | Perlite ceiling tile | 7.20E-06 | 0.000 | | 25, 50 |
| 23 | Fiberglass ceiling tile | 3.74E-05 | 0.145 | * | 25, 50 |
| 24 | Recycled carpet | 3.62E-05 | 0.280 | | 25.2, 50 |
| 25 | Perlite ceiling tile | 8.82E-06 | 0.030 | | 25.2, 50 |
| 26 | Low-voc paint on drywall | 1.11E-06 | 0.030 | | 25.2, 50 |
| 27 | Nylon fiber carpet 1 | 6.60E-06 | 0.189 | | 22.9, 50 |
| 28 | Olefin fiber carpet 1 | 1.10E-05 | 0.555 | | 22.9, 50 |
| 29 | Nylon fiber carpet 2 | 3.10E-05 | 0.789 | | 22.9, 50 |
| 30 | Olefin fiber carpet 2 | 9.20E-06 | 0.312 | | 22.9, 50 |
| 31 | Living room carpet | 3.66E-05 | 0.180 | | 14-28, 50 |
| 32 | Kitchen countertops | 2.01E-05 | 0.360 | | 14-28, 50 |
| 33 | Kitchen floors | 7.82E-06 | 0.230 | | 14-28, 50 |
| 34 | Bedroom carpets | 3.41E-05 | 0.130 | | 14-28, 50 |

*Molar yields include $C_1$-$C_{10}$ carbonyls (see notes below).

[a] Cros et al. (2012):  Values presented were measured prior to deployment of materials to field locations. Reaction probability was estimated from $v_d$ interpreted from a figure and an approximate $v_t$ based on measurements in the same chambers during another project.

[b] Lamble et al. (2011):  Reaction probabilities are averages from replicate experiments. Yields presented are from measurements after 2 hours of ozone exposure.

[c] Gall et al. (2013):  Yields presented include benzaldehyde, o-tolualdehyde, and acetone. Yields are from measurements after ~1 hour of ozone exposure when the concentration was 90 pbb $O_3$.

[d] Morrison and Nazaroff (2000 & 2002):  Materials were aired out for more than 12 months and then exposed to ozone for 48 hours. Yields of $C_1$-$C_{13}$ were estimated from the relation, emission rate ($\mu g\ m^{-3}$) $= yield \times v_d \times C_{O3}$, where $C_{O3} \approx 200\ \mu g\ m^{-3}$. Total byproduct emission rates were interpreted from a figure in the article.

[e] Wang and Morrison (2006 & 2010):  Materials were tested in situ in actual homes in 2005, 2006, and 2007 using a FLEC chamber. Yields presented include 2-nonenal. Materials varied among the homes; living room carpets included 3 nylon cut pile carpets and 1 wool rug; kitchen countertops included 2 resin and 2 laminate; kitchen floors included 2 ceramic tile, 1 hardwood, and 1 linoleum; all bedroom carpets were nylon cut pile.

## 4. Human Perception Studies

In this study (box B in Figure 1), a survey of human sensory perceptions of air quality was conducted under eight different conditions involving clay plaster, carpet, and ozone (Objective 2).

### 4.1. General Methodologies

#### 4.1.1. Materials

Carpet was purchased from a distributor in Denmark and aired out in a separate chamber for three weeks prior to experiments. Equally-sized carpet specimens were stapled back to back with the exposed edges covered with aluminum tape, and hung vertically on two metal racks – one for each chamber (Figure D1 in Appendix D). Clay plaster and mineral pigment were mixed according to manufacturer instructions and applied to both sides of gypsum wallboard (GWB). Samples were hung vertically on two metal racks (Figure D2 in Appendix D). The total areas of carpet and clay plaster on each rack were 14 $m^2$ and 10.6 $m^2$, respectively.

The plaster consisted of a proprietary blend of clay (50% kaolin, < 50% fire clay, ~ 1.7% montmorillonite) and crushed marble (aggregate size: 5-1000 μm). It was mixed with pigment that was made of naturally occurring mineral oxides, specifically iron oxide (< 70% by weight), magnesium silicate (< 12%), magnesite (< 0.2%), crystalline silica (< 2.8%), and other unspecified substances deemed non-hazardous by the manufacturer (< 20%). A primer made for the clay plaster was also used. The primer contained water, pumice, calcined kaolin, calcium carbonate, a proprietary acrylic copolymer, and sand. The sand helps the clay bond to smooth surfaces, such as the GWB that it was applied to in this study.

#### 4.1.2. Test Chambers

Experiments were performed in 30 $m^3$ stainless-steel chambers described by Albrechtsen (1988). Each chamber was ventilated at 1.5 air changes per hour of outdoor air filtered through HEPA and carbon filters. Air was introduced through perforations in

the floor and exhausted through four vents in the ceiling. The doors to the chambers were equipped with a pressurized seal. Temperature and relative humidity were maintained at 23°C and 33%, respectively, throughout all tests. Identical 2-m high, low-emitting laminated wood partitions were positioned in each chamber to block the materials from the view of panelists. Rotating fans were installed behind partitions to allow good mixing throughout each chamber and air contact with the material surfaces. The floor of each chamber was marked so that panelists stood at the same location in each chamber across all sensory events (Figure 3).

Ozone was injected into the chamber recirculation ducts. Ozone concentrations in the chambers were measured using a UV absorbance ozone monitor (Model 205, 2B Technologies). The ozone injection rate was set such that the steady-state ozone concentration was approximately 80 ppb in an empty chamber without materials. This ozone concentration was targeted to a level sufficient enough to react with VOCs on the carpet without overpowering the sensory assessments, and that would reflect typical residual indoor ozone concentrations during ozone events (Wainman, 2000; Weschler, 2000; Weschler, 2006). Chamber ozone decay rates and deposition velocities to chamber and clay surfaces were measured as described in Kunkel et al. (2010).
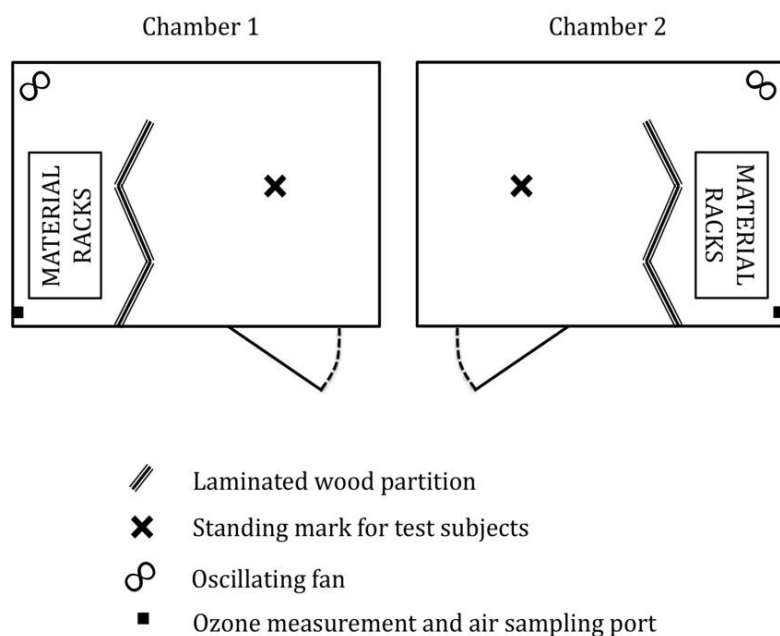
Chamber 1          Chamber 2

Laminated wood partition
✖ Standing mark for test subjects
Oscillating fan
■ Ozone measurement and air sampling port

**Figure 3.** Layout of test chambers[1].

### 4.1.3. Air Sampling

Immediately before panelists arrived on a given day, air samples were collected on Tenax-TA (Supelco Inc., 80/100 mesh) packed with glass wool into glass injection liners (SISS, open liners, tapered, frit, 3 mm I.D.) through ports in the chamber walls to be analyzed for $C_5$ to $C_{10}$ n-aldehydes, benzaldehyde and tolualdehyde. These aldehydes are commonly observed reaction products of ozone with carpet (Cros et al., 2012; Morrison and Nazaroff, 2002; Nicolas et al., 2007), and also act as an indicator for a broader set of irritating oxidized products generated at surfaces such as unsaturated aldehydes (Morrison and Nazaroff, 2002), carboxylic acids and dicarbonyl products (Weschler et al., 2007). A flow rate of $48 \pm 3$ ml min$^{-1}$ was drawn through the sorbent tubes by sampling pumps (model VSS-1, A.P. Buck Inc.) with low flow adapters. Prior to and after sampling, sorbent tubes were kept in individual, sealed stainless-steel holders and stored in a refrigerated glass jar containing activated carbon to scavenge VOCs. At the end of the experimental program, the jar was packed in ice and shipped to The

---

[1] Diagram credit: Clément Cros

30

University of Texas at Austin (UT) for GC analysis. Recoveries were greater than 75% on standards spiked with known masses of hexanal and decanal prior to shipping (Appendix D, Table D1). Tenax-TA tubes were analyzed by zero-path thermal desorption followed by gas chromatography with flame ionization detection (TD/GC/FID).

Ozone and by-product samples were collected on the side of the partition that contained materials, i.e., out of view of panelists. Because of the presence of mixing fans, it was assumed that the measured concentrations were representative of the spatial average concentrations throughout the chambers during sampling and during the perception surveys.

### 4.1.4. Perceived Air Quality Survey

A panel of 24 human subjects (12 males, 12 females), several of whom had previous experience participating in perception studies, was recruited among students at the Danish Technical University (DTU). Prior to the study, panelists were instructed to refrain from wearing scented products (e.g. perfume, deodorant, aftershave, etc.) and from drinking coffee in the facility during the surveys. On average, 20 panelists participated in each survey. Each panelist was instructed to enter a chamber, breathe the air and subsequently assess the air quality on a continuous scale (Figure 4), coded as follows: "clearly unacceptable" = -1, "just unacceptable/just acceptable" = 0, and "clearly acceptable" = 1 (Kolarik and Wargocki, 2010).

Panelists were exposed to all combinations of ozone, carpet, and clay using a cross-over design, i.e., each condition was completed in each of two chambers on consecutive days (Appendix D, Table D2). Materials were placed in the chambers the day before each experiment and the chambers were continuously ventilated overnight. In the morning, if necessary, ozone generator(s) were switched on at 8 a.m. and the chambers remained sealed until 12 p.m., when the first panelists arrived. This period allowed enough time to achieve a steady-state ozone concentration in the chambers. Air samples were collected from 11 a.m. to 12 p.m. The sensory assessments commenced at 12 p.m. and were completed by 2 p.m.
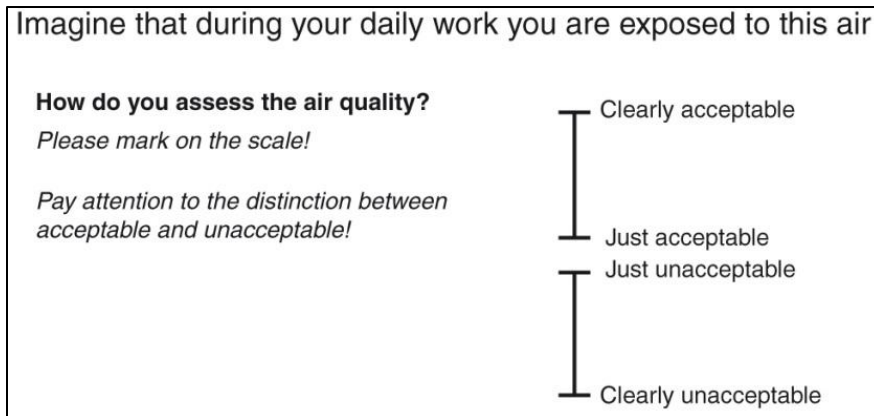
**Figure 4.** Perceived air quality assessment scale

### 4.1.5. Ozone Decay

Decay tests were performed on Day 8 after the final assessment session in order to determine an ozone decay rate and ozone deposition velocities to chamber walls and clay. Ozone was injected into Chamber 1, with clay samples remaining inside, until the concentration reached 30 ppb, after which injection ceased. The ozone concentration decay was then recorded, and then the clay was removed from the chamber for the next ozone decay test. For the second test, ozone was injected until the concentration in the chamber reached 80 ppb, and then the decay phase was initiated.

Additional details related to study design and methods can be found in the paper in Appendix A.

## 4.2. Major Findings

### 4.2.1. Perceived Air Quality and Air Sampling

The results of all perceived air quality (PAQ) experiments are presented as box plots in Figure 5. The ratings were not normally distributed. The box plots present the $25^{th}$ percentile (box bottom), $75^{th}$ percentile (box top), median (horizontal line inside the box), and minimum and maximum PAQ (lines extending outside the boxes). Outliers were omitted from data analyses and were identified as ratings either 1.5×IQR less than the lower quartile or 1.5×IQR greater than the upper quartile, where IQR is the

interquartile range. A non-parametric two-tailed Wilcoxon signed-rank test was used to examine whether the sensory assessments from the paired conditions on each day differed from one another using subjects as their own controls. The addition of clay on days 3 and 4 in the chambers containing ozone and carpet significantly improved PAQ (p = 0.017), while addition of ozone on days 7 and 8 to chambers containing clay significantly reduced PAQ (p = 0.0001). The assessments of PAQ were not significantly different when ozone was added to the empty chamber (day 1, p = 0.971) or when clay was added to the chamber containing carpet in the absence of ozone (days 5 and 6, p = 0.138).

Improved PAQ when clay panels were introduced to chambers that contained carpet and ozone (days 3 and 4) may be the result of one or more factors. First, on average the ozone concentration in chamber air was reduced by $37 \pm 20\%$ when clay was present. It is not clear that a reduction in ozone itself could affect PAQ over the short exposure period used in this study. Such an effect was not statistically significant for day 1 experiments that involved the presence or absence of ozone without carpet or clay in the chamber. Second, the ability of clay to react with ozone reduces the availability of ozone to react with carpet and to form reaction products that might lower PAQ. Third, the by-products that are formed and released as a result of ozone reactions with carpet might adsorb to clay, thereby reducing their concentrations and improving PAQ. The latter issue is similar to results described by Sakr et al. (2006), who used a panel-based study to determine the benefits of introducing painted gypsum board into offices containing either carpet or linoleum. In each case, PAQ was improved due to the presence of painted gypsum board, which presumably adsorbed pollutants that were emitted from the other sources. Sakr et al. did not introduce ozone into the test environment nor did they characterize chemicals that might have affected PAQ and that were removed by the painted gypsum board.

Aldehyde concentrations measured prior to sensory assessments are also shown in Figure 5. The dominant pollutant in chamber air was nonanal ($C_9$). Pentanal ($C_5$) and heptanal ($C_7$) were also frequently detected. The conditions with the lowest summed aldehyde concentrations on average were carpet with or without clay (no ozone) on days

5 and 6, and clay with or without ozone on days 7 and 8. The highest concentrations of aldehydes were observed in the chambers containing ozone and carpet on days 3 and 4; the total aldehyde concentration in the chamber on day 4 was half the concentration of the same condition on day 3, possibly because of decaying carpet emissions. A noticeable difference in odor between these two chambers was observed when researchers entered the chambers at the completion of assessments on days 3 and 4 to switch out the materials. When clay was added to chambers containing carpet and ozone, the total aldehyde concentrations decreased, most notably on day 3 (72% decrease), and to a lesser extent on day 4 (29% decrease). Although the clay plaster individually reduced ozone in the chambers just as effectively as the carpet, it emitted fewer aldehydes than did the carpet upon ozone exposure. The mean total aldehyde concentration in the chamber for clay and ozone was nine times lower than that in the chamber with carpet and ozone.
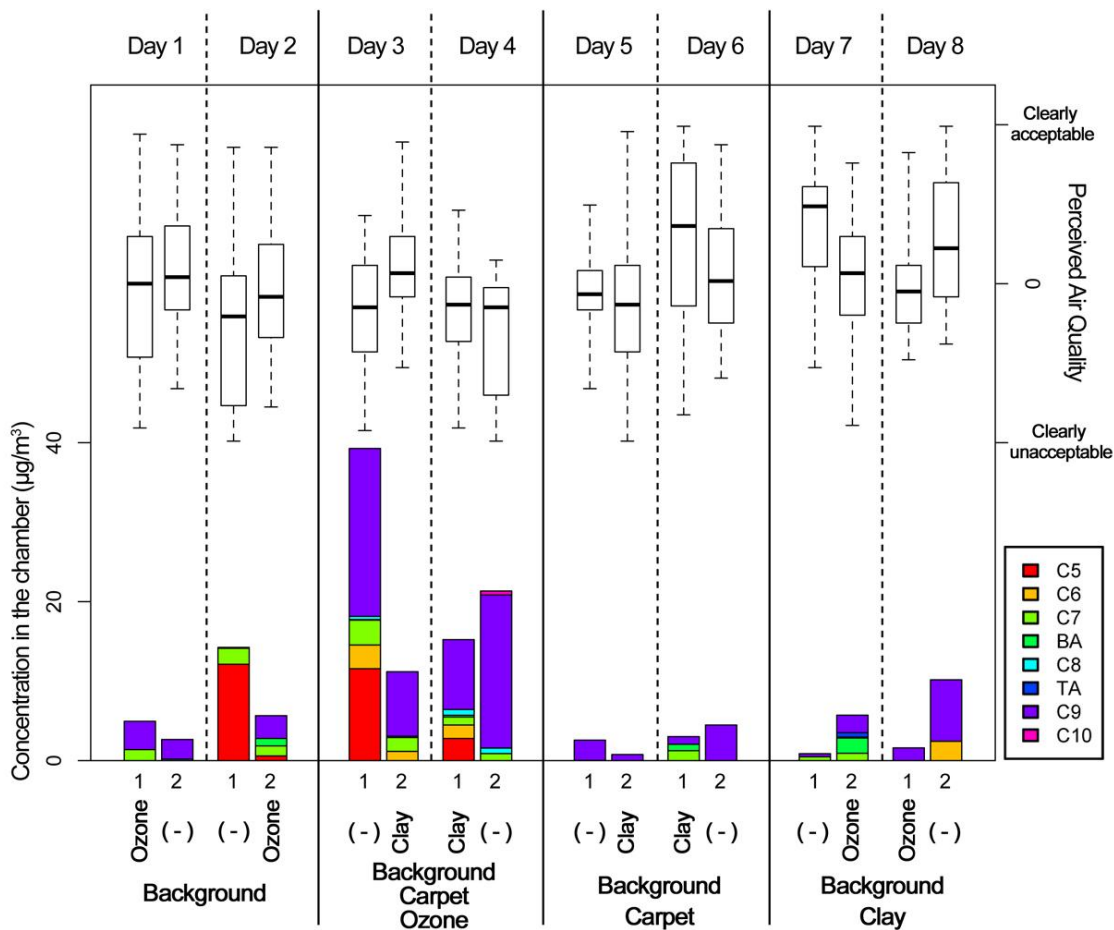
**Figure 5.** Perceived air quality and related n-aldehyde concentrations in test chambers.

In general, the median PAQ was inversely related to aldehyde concentrations measured in chamber air. For example, chamber 1 had a higher aldehyde concentration and lower median PAQ than that for chamber 2 on day 3. All experimental days exhibited this trend except for day 8, in which higher median PAQ and aldehyde concentrations were observed for the chamber containing only clay compared to the chamber containing clay and ozone. It is conceivable that clay sorbed carbonyls during previous experiments involving carpet and ozone and re-emitted them later when exposed to an environment without a carbonyl source, but this hypothesis was not tested.

In the chamber containing neither ozone nor materials (day 2) the total measured byproduct concentration was greater than the concentration in the adjacent chamber that contained approximately 80 ppb ozone, primarily due to a relatively high concentration

of pentanal in the chamber without ozone. However, the absolute difference in summed $C_5$ to $C_{10}$ aldehydes between the two chambers was only 8.6 µg m$^{-3}$, i.e., a few ppb.

On day 3, when carpet and ozone were compared with carpet, ozone, and clay, PAQ trends agreed well with the byproduct concentrations in both chambers; the air in the chamber with additional clay and fewer byproducts was rated more acceptable than the air in the chamber with only carpet and ozone, which also had the highest overall measured byproduct concentration. The two cases in which a chamber contained only carpet and ozone not only had the highest byproduct concentrations, but also the lowest median PAQs. Carpet has been associated with sick building syndrome (SBS) cases among office employees and school children (Fisk, 2000; Wargocki et al. 1999). Furthermore, relatively high emissions of secondary aldehydes and other carbonyls have been observed following the exposure of carpet to ozone (Cros et al., 2012; Morrison and Nazaroff, 2002; Weschler et al., 1992b).

Air samples were collected prior to the arrival of panelists in order to avoid adverse perceptions associated with noise of sampling pumps or the sample train. For this reason, samples did not capture products associated with ozone reactions with human skin oils and clothing (e.g., Pandrangi and Morrison, 2008; Wisthaler and Weschler, 2009; Weschler et al., 2007). This is potentially relevant for the eight scenarios in which ozone was injected into the chambers. However, the short amount of collective time that panelists spent in the chambers (10 to 15 seconds) should have minimized any effects of ozone reactions with panelists themselves. While the door to each chamber was opened briefly as each panelist entered and exited the chamber, the ozone concentration in chamber air did not vary appreciably during experiments. The coefficient of variation of the ozone concentration varied from 0.04 to 0.09 across all experiments involving ozone injection, and there was no consistent trend in terms of increasing or decreasing ozone concentration across experiments. This suggests that the conditions in the chambers were not substantially disturbed by the subjects entering or being present inside the chambers during assessments.

### 4.2.2. Perceived Air Quality by Gender

Differences between male and female PAQ results were also analyzed (Figure 6). Assessments by female panelists exhibited greater differences between the two conditions on a given day and greater negative PAQ scores. In general, males perceived less of a difference in air quality between conditions on a given day, whereas females clearly preferred some conditions to others. Overall, males were also more satisfied/less dissatisfied with the air quality, and collectively exhibited smaller ranges of PAQ on most days. In contrast, females were more often dissatisfied with the air quality, especially for the carpet-ozone combination. Females were most satisfied when clay was present with or without ozone (Days 7 & 8). These results are consistent with observations that females are more sensitive than men are to some odors (Doty et al., 2009). Several researchers have preferentially recruited female subjects for PAQ studies for this reason (e.g., Wargocki et al., 1999; Bakó-Biró et al., 2004). Wargocki et al. (1999) used a panel of 30 females in a real office setting to study PAQ, SBS symptoms, and productivity when a used carpet was present and absent from the room., Significant decreases in typing speed and increased dissatisfaction with the air quality were observed when the carpet was present; however, overall pollutant concentrations did not vary significantly between conditions.
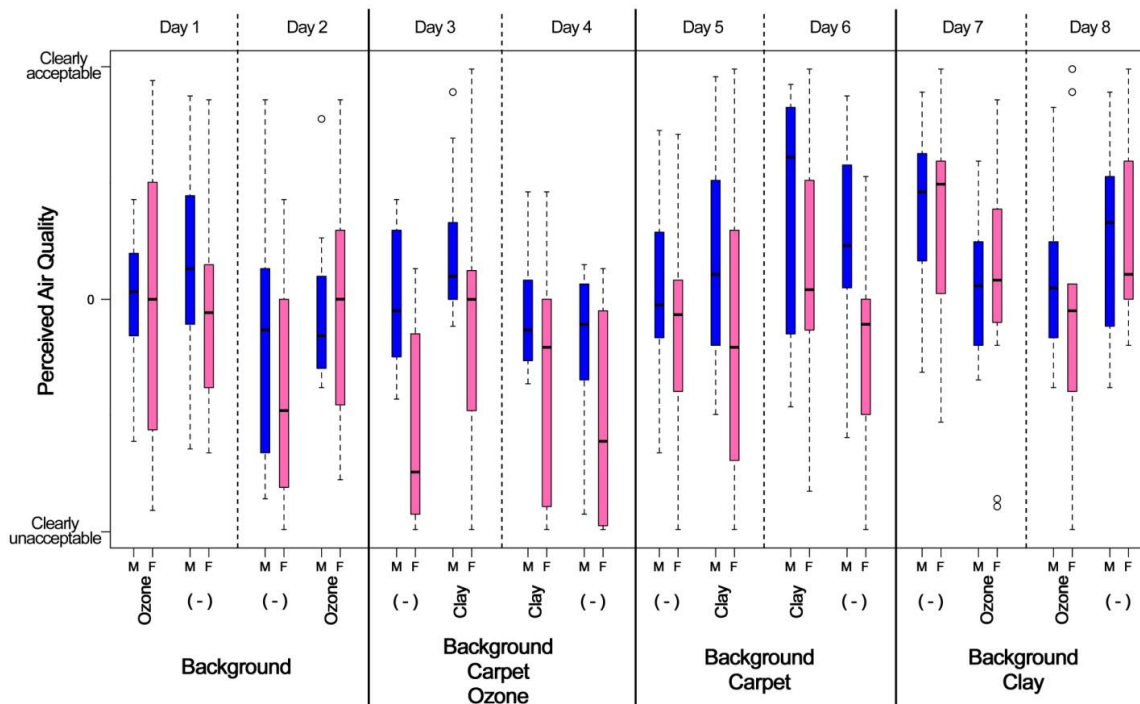
**Figure 6.** Male (M) and female (F) perceived air quality assessments. Circles indicate outliers.

### 4.2.3. Ozone Decay

The steady-state ozone concentrations for the pair of experiments involving an empty chamber with ozone injection were 73 and 77 ppb (Figure 7). For the same ozone injection rate of 9.6 mg·hr$^{-1}$, the steady-state ozone concentrations for two experiments during which clay panels were added to chambers were 29 and 24 ppb. The overall first-order ozone decay rates in the empty chamber and chamber containing clay panels were 0.65 hr$^{-1}$ and 4.4 hr$^{-1}$, respectively (Appendix D, Figure D3). The collective surfaces of the empty chamber were found to have an ozone deposition velocity of 0.34 m·hr$^{-1}$, and the clay plaster itself had a deposition velocity of 10.6 m·hr$^{-1}$.

It is clear that the clay panels led to significant removal of ozone. For these experiments the ratio of the area of clay panels to volume of chamber air was 0.35 m$^{-1}$. Larger areas are possible in buildings that have walls coated with clay plaster, but actual buildings are also characterized with additional competition for ozone removal by a wide

range of materials, particularly if carpet is present over much of the floor. The steady-state ozone concentrations for the pair of experiments involving carpet with ozone injection were 25 and 32 ppb. For the same conditions with clay added to the chambers the steady-state ozone concentrations were reduced to 19 and 16 ppb.
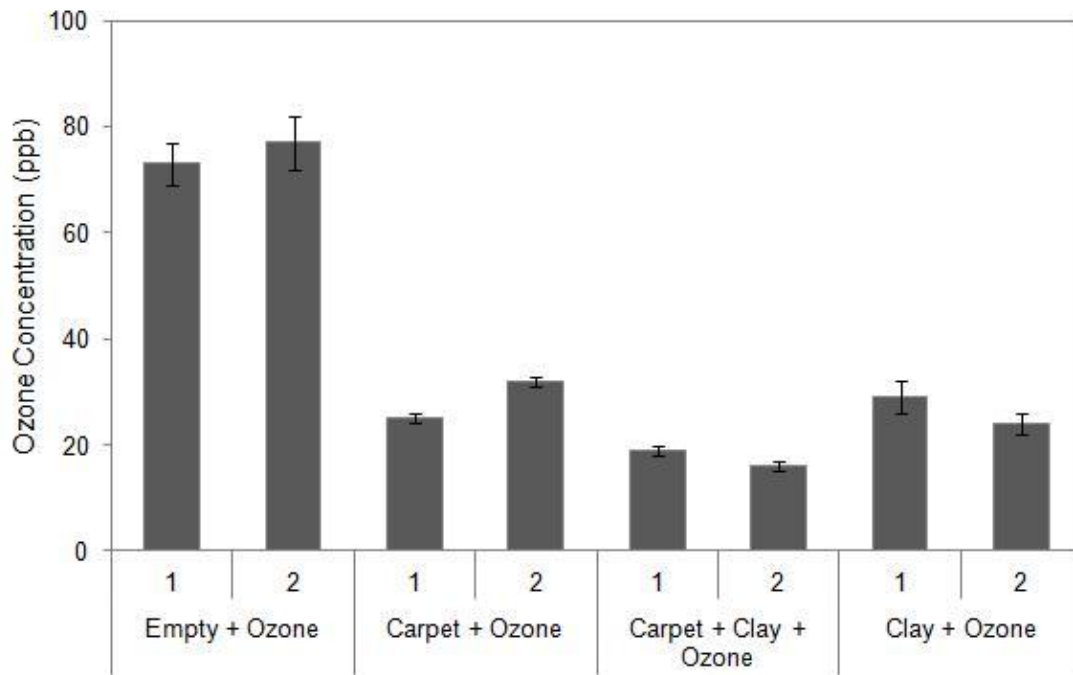


**Figure 7.** Steady-state ozone concentrations in chambers 1 and 2 during replicate experiments. Experiments during which no ozone was injected are omitted. Error bars denote standard deviations.

## 5. Longitudinal Field/Laboratory Study

This study involved the placement of small specimens of clay coatings applied to gypsum wallboard (GWB) in residential homes for six months with intermittent analysis in laboratory chambers to characterize ozone reaction metrics (Objective 3).

### 5.1. General Methodologies

#### 5.1.1. Materials

Two different types of commercially-available clay-based interior coatings were studied: paint and plaster. These two materials have been shown to reduce indoor ozone concentrations over short experimental time periods, and they have also been shown to emit fewer reaction products (e.g., saturated aldehydes), as well as possibly adsorbing emissions from other building materials (Lamble et al., 2011; Darling et al., 2012).

The clay plaster and sanded primer were of the same types that were used in the human perception study, but with a different color of mineral pigment. The ingredients in the clay paint are similar to those in the plaster, although the paint comes in liquid form, is self-priming, and requires no extra mixing. Ingredients in the paint include water, clay (type unspecified), chalk, porcelain clay, cellulose, "alcohol ester" (as a binder), and a preservative (compound(s) unspecified). The product is also labeled as not containing solvents and having zero VOCs.

Each type of coating was applied to squares of new GWB that were cut to an average top area of 206 cm$^2$. Seven plaster and eight paint specimens were prepared. To prepare the plaster for application, the sanded primer was first applied to the drywall and allowed to dry for six hours as per product instructions. The clay-pigment powder was mixed with water (237 mL into a 0.9-kg bag of powder), then applied with a trowel to the dry layer of sanded primer. The first layer of plaster was allowed to dry over night before application of a second layer. Once the second layer was applied, the specimen was allowed to air dry for 24 hours before handling for further preparation. The paint specimens were prepared similarly, but without priming. After the specimens dried, the

sides and backings were covered with aluminum foil to restrict exposure of these surfaces to ozone and indoor pollutants.

### 5.1.2. Field Locations

Approximately one week after paint or plaster application to the GWB, the 15 specimens were each placed in one of five dedicated field locations in Austin, Texas (Table 4). Images of the specimens at each location can be found in Figure E1 in Appendix E. During this study, the apartment was occupied by two adults, and the house was occupied by two adults as well as two dogs that lived both inside and outside. Prior to the deployment of the specimens to field locations, new carpet had recently been installed throughout the apartment, and solid wood flooring had just been installed throughout most of the house except for in the bedroom. Both residences had central air conditioning.

Each specimen was supported on a smooth chrome display stand while it was in the field to keep it nearly vertical (Appendix E, Figure E2). A portable temperature and relative humidity (RH) logger (Onset[®] HOBO[®]) was placed near each set of specimens to record data throughout the experimental program.

**Table 4.** Field locations, conditions, and specimen allocation.

| Building Type | Room Type | Building Age (years) | Bimonthly Average Range | | Number of Specimens | |
| | | | Temperature (°C) | RH (%) | Clay Paint | Clay Plaster |
| --- | --- | --- | --- | --- | --- | --- |
| Apartment | Living Room | 32 | 21-25 | 47-52 | 2 | 1 |
| Apartment | Kitchen | 32 | 23-24 | 46-52 | 1 | 2 |
| Apartment | Bedroom | 32 | 23-24 | 47-50 | 2 | 1 |
| House | Living Room | 19 | 20-25 | 45-51 | 1 | 2 |
| House | Bedroom | 19 | 19-24 | 49-55 | 2 | 1 |

### 5.1.3. Experimental Chambers

The specimens were tested in a system of three 10-liter stainless steel chambers (Figure 8) connected to a UV ozone generator (Perma Pure Zero-Air[TM], Model ZA-750-10). More details on the chamber system can be found in Appendix B. Chamber inlet air

was directed to the surface of the specimen through a stainless steel tube that extended from the center of the chamber lid down into the chamber two to three centimeters from the surface of the specimen. Chamber air exhausted through Teflon® PFA tubing fitted to the exterior of the chamber lid.

The volumetric flow rates through the mass flow controllers were measured using a bubble flow meter (Gillian® Gilibrator 2 with 20-6,000 mL/min sampling cell) at the beginning and end of each experiment. Inlet and chamber ozone concentrations were monitored with a single UV-cell ozone monitor (2B Technologies, Model 202). The collective inlet line and the outlet lines from the chambers could be manually opened or closed to the ozone monitor by adjustment of PFA plug valves. The relative humidity and temperature of the chamber air were also monitored (QTrak TSI$^{TM}$).

The mean (± standard deviation) experimental conditions in the test chambers throughout the 6-month test program were as follows: $1043 \pm 17$ ml min$^{-1}$ inlet flowrate through each chamber (average air exchange rate [AER] = $6.4 \pm 0.1$ h$^{-1}$), $24 \pm 0.5$ °C air temperature, $47 \pm 9\%$ RH, and $225 \pm 22$ ppb inlet ozone concentration when the ozone generator was switched on. The mean ozone concentrations in the chambers when paint and plaster specimens were inside were, respectively, $21 \pm 9$ ppb and $32 \pm 10$ ppb, realistic concentrations in many indoor environments.
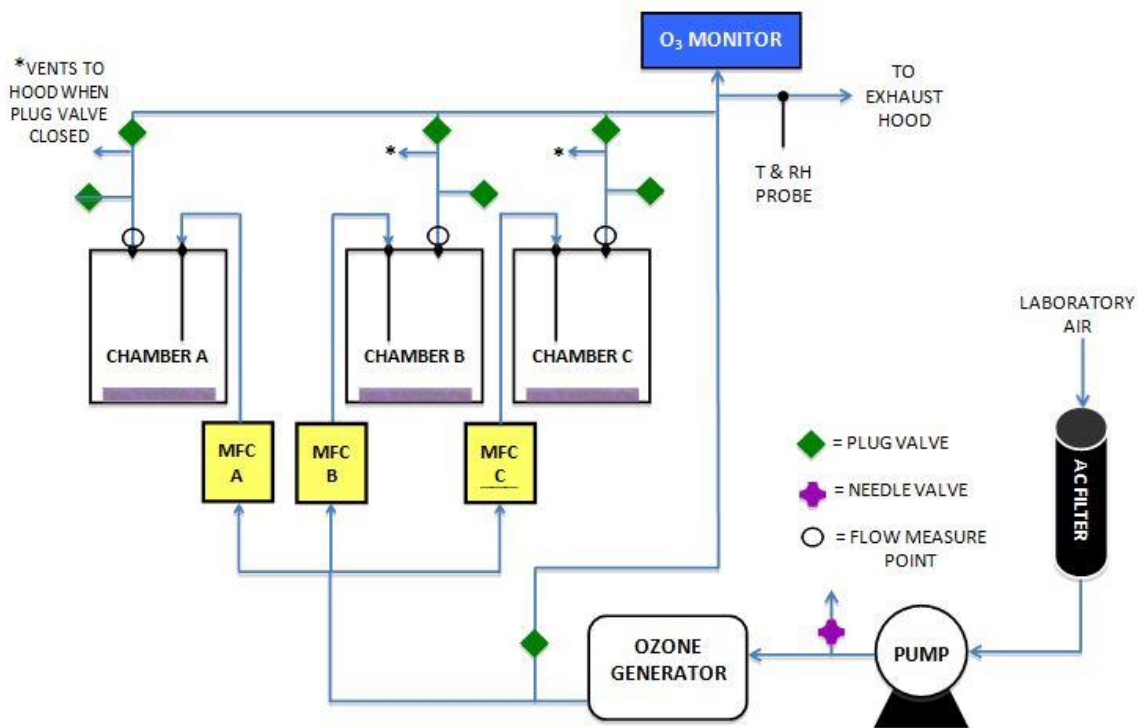
**Figure 8.** Environmental chamber system for testing specimens in the laboratory

### 5.1.4. Analytical Protocol

Paint and plaster specimens were tested in the laboratory chambers three days after preparation to measure ozone reaction probabilities and emission rates of $C_5$-$C_{10}$ saturated n-aldehydes before placement in the field. This test is referred to as Month 0. Specimens were then transferred to each of the five field locations (Table 1).

Every two months after Month 0, the specimens were taken back to the laboratory for analysis in the chambers. To transport the material specimens between the lab and the field locations, each was individually wrapped in aluminum foil and placed in a plastic box. Each material specimen was unwrapped from the foil (not the foil backing) and placed on the floor of the chamber with the coating surface exposed and projected horizontally. Pre-ozone emissions from the specimens were measured after 1 hour of exposure to ozone-free air in the chambers. Specimens were then exposed to elevated ozone concentrations for 2 hours; sampling of secondary emissions occurred during the last half hour of ozonation. Ozone concentrations were measured during the first 1.5

hours of the ozonation phase. During the 30-minute secondary sampling phase, the feed to the ozone monitor was cycled from the inlet ozone line to the exhaust line from chamber A, then chamber B, then chamber C. This cycle was repeated until the end of the secondary sampling period.

During the chamber experiments, the $C_5$-$C_{10}$ n-aldehydes were collected on large-volume glass injection liners pre-packed with Tenax-TA$^{®}$ sorbent and glass wool and subsequently analyzed by TD/GC/FID. A minimum five-point external calibration curve was generated for each compound with mid-point calibration before each experimental run. After completion of a test, specimens were returned to their respective locations within 24 hours. Specimens were brought to the lab two more times for testing at Month 4 and Month 6. The interior surfaces of each chamber were cleaned between tests using delicate task wipes (Kimwipe, Kimtech Science) and methanol, followed by passivation with high ozone concentrations, i.e., on the order of ppm.

## 5.2. Major Findings

### 5.2.1. Ozone Reaction Probability

Averages of ozone reaction probabilities from Month 0 to Month 6 for all clay paint specimens and for all clay plaster specimens independent of location are plotted in Figure 9. Ozone reaction probabilities have been log-transformed (base 10 to show trends more clearly). Reaction probabilities measured for the clay paint were greater than those measured for the clay plaster throughout the 6-month program. Both the paint and plaster had lower ozone reaction probabilities at Months 0 and 2 than at Months 4 and 6, with values being highest at Month 4.

At Month 0, before the paint specimens were placed in the field, the arithmetic mean ± standard deviation ozone reaction probability was $1.3 \pm 0.4 \times 10^{-4}$ among the seven specimens. By Month 2, the ozone reaction probability had decreased 40% to $7.9 \pm 0.7 \times 10^{-5}$, but then at Month 4 the average ozone reaction probability had risen by more than a factor of three to $2.6 \pm 3.0 \times 10^{-4}$. At Month 6, the average ozone reaction probability had decreased to $2.3 \pm 3.0 \times 10^{-4}$.

The average ozone reaction probability of the plaster specimens followed a similar trend, although with less variation over time. At Month 0, the mean ± standard deviation ozone reaction probability was $4.8 \pm 1.6 \times 10^{-5}$. At Month 2, the mean ozone reaction probability of the clay plaster was $4.8 \pm 1.9 \times 10^{-5}$, remaining unchanged on average from the previous assessment. By Month 4, the mean ozone reaction probability had increased by a factor of two to $1.0 \pm 0.4 \times 10^{-4}$, and finally at Month 6, the mean ozone reaction probability decreased by 41% to $5.9 \pm 1.3 \times 10^{-5}$.

The ozone reaction probabilities of clay plaster were in the range of those associated with its major component, kaolinite. The reaction probability of kaolinite, a hydrous aluminosilicate mineral that comprises 50% of the clay plaster, has been reported by Michel et al. (2003) to be $3 \pm 1 \times 10^{-5}$ for the mineral in powdered form. Michel et al. (2003) found the reaction probability to be particularly high for an iron oxide ($\alpha\text{-}Fe_2O_3$) powder, with an ozone reaction probability of $2.0 \pm 0.3 \times 10^{-4}$, while a silicon dioxide ($SiO_2$) powder had an ozone reaction probability of $5 \pm 1 \times 10^{-5}$ (Usher et al., 2003) to $6.3 \pm 0.9 \times 10^{-5}$ (Michel et al., 2003). Reactions of these mineral oxides with ozone are catalytic, resulting in net destruction of ozone without depletion of the reactivity of the metal oxide surface (Michel et al., 2003; Usher et al., 2003).

The average ozone reaction probability of the paint decreased from Month 0 to Month 2, but remained the same for the plaster during this period. The ozone reactivity of some materials, such as carpet and GWB, has been shown to decrease over time, the so-called ozone aging-effect (Wang and Morrison, 2006; Cros et al., 2012). However, reaction probabilities can fluctuate with relative humidity, as well as with modifications of the material surface that influence the amount of reactive substances (e.g., deposition of skin oils, cooking oils, sorbed reactive gases, airborne particles on the material) (Wang and Morrison, 2006; Cros et al., 2012).

Deposition of reactive substances on specimens in the field could have contributed to the increase in the average reaction probabilities at Month 4 and Month 6. Month 4 tests began in late November and lasted until late December, a time when activities around the major fall and winter holidays begin. In both the apartment and

house, activities such as cooking, cleaning, candle-burning, and entertaining of guests became more frequent during this period. These activities could have soiled the specimens with reactive gases, oils, and particles that consumed ozone during the chamber experiments. Average indoor temperatures and relative humidities did not change considerably (-0.67 °C; -1.1% RH) between Months 2 and 4, and therefore were unlikely to have influenced the ozone reaction probabilities. Alternatively, the specimens simply could have had more time to become soiled in the field regardless of the activities around the holidays, as the reaction probabilities remained relatively high on average beyond Month 4.

The same type of paint and plaster were tested by Lamble et al. (2011) inside 10-L chambers after 2 and 24 hours of exposure to 150 to 200 ppb ozone. The flow rate through the chambers (2 $L \cdot min^{-1}$) equated to nearly double the AER of this study. The average ozone reaction probabilities of the clay paint and clay plaster tested by Lamble et al. were $5.7 \pm 0.5 \times 10^{-5}$ and $2.2 \pm 0.5 \times 10^{-5}$, respectively, each lower than the values determined in this study.

A previous field study on ozone removal by building materials was conducted by Cros et al. (2012). Ozone deposition velocities instead of ozone reaction probabilities were tracked monthly for 6 months for samples of activated carbon mat, new recycled-content carpet, perlite-based ceiling tile, and low-VOC paint on GWB. Over the six-month program, the ozone deposition velocity trended downward for the carpet and for the painted GWB, while no overall decay in the deposition velocity was observed for the activated carbon mat and the ceiling tile. Similar to the way the reactivity of the clay paint and clay plaster increased around the holiday months, the deposition velocities of the materials that Cros et al. tested also increased slightly during the month of December, five months after deployment to field locations.
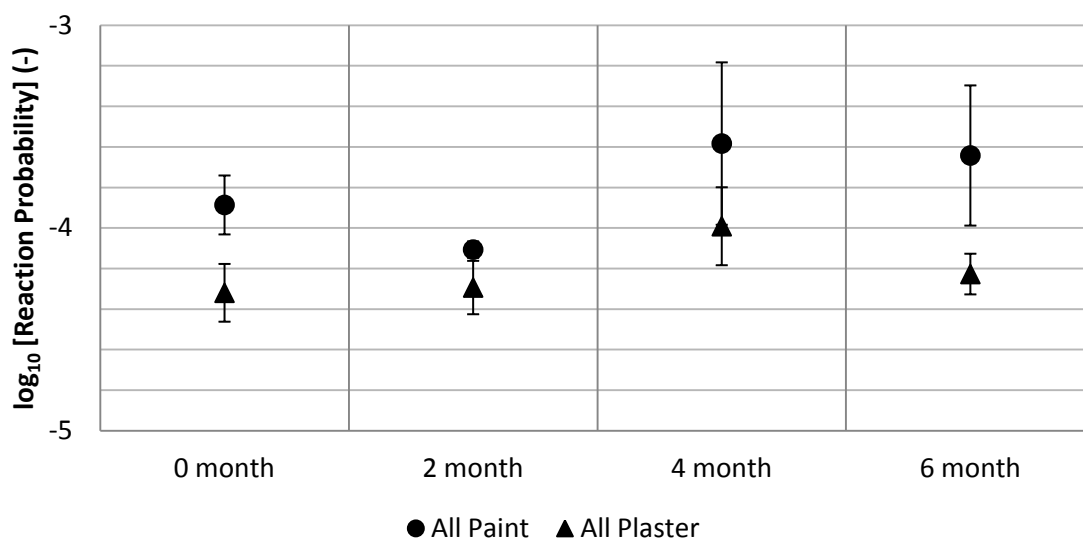
**Figure 9.** Ozone reaction probabilities (transformed to $\log_{10}$) averaged over all locations at Months 0, 2, 4, and 6. Error bars represent standard deviations.

### 5.2.2. Molar Yield

Molar yields of $C_5$-$C_{10}$ n-aldehydes averaged across all locations for both paint and plaster are shown in Figure 10. Importantly, these molar yields are only for the target chemicals and are limited to the period of sampling during ozonation. Had samples been collected for a longer post-ozonation period, the molar yields of the compounds would have increased. As such, the results shown here are generally more useful for cross-specimen comparisons and longitudinal changes in molar yields. See Appendix B (Figures B4 and B5) for discussion and results of primary and secondary emission rates.

The paint exhibited higher molar yields than did plaster, but yields for both materials decayed within the first two months. From Month 0 to Month 2, summed molar yields from the paint decreased by 91%, and the summed molar yields from the plaster decreased by 86%. After Month 2, molar yields from the paint increased slightly, but were still relatively low.

Molar yields from the clay paint at Month 0 were more than double the molar yields that Lamble et al., (2011) reported for clay paint. Lamble et al. measured an average total molar yield of $C_5$-$C_{10}$ n-aldehydes (2-hr and 24-hr) from the clay paint of

approximately 0.2. From Month 0 to Month 6, the majority of total molar yields from the paint consisted of nonanal and a smaller portion of hexanal, consistent with results from Lamble et al. (2011). For the clay plaster, the average total molar yield at Month 0 was 0.06. An analysis of data in Lamble et al. (2011) suggest an average total molar yield (2-hr and 24-hr) from the plaster of less than the detection limit ($< 0.05$). Unlike the paint at Month 0, more than half of the summed molar yields from the plaster consisted of pentanal and smaller portions of hexanal and heptanal. After Month 0, summed molar yields from the plaster were dominated by nonanal.

For a low-VOC paint, Cros et al. (2012) reported an initial total molar yield of $C_5$-$C_{10}$ n-aldehydes of 0.07, consisting mostly of nonanal. The six-month average molar yield from their low-VOC paint was 0.05, almost five times greater than the six-month average molar yield from the clay plaster in this study, and three times lower than that of the clay paint.  Gall et al. (2013) reported a higher molar yield (average of 0.11) for the same type of low-VOC paint; however these yields included light aldehydes (i.e., formaldehyde ($C_1$) through butanal ($C_4$)) in addition to the heavy aldehydes included in this study and in Cros et al. (2012) and Lamble et al. (2011).
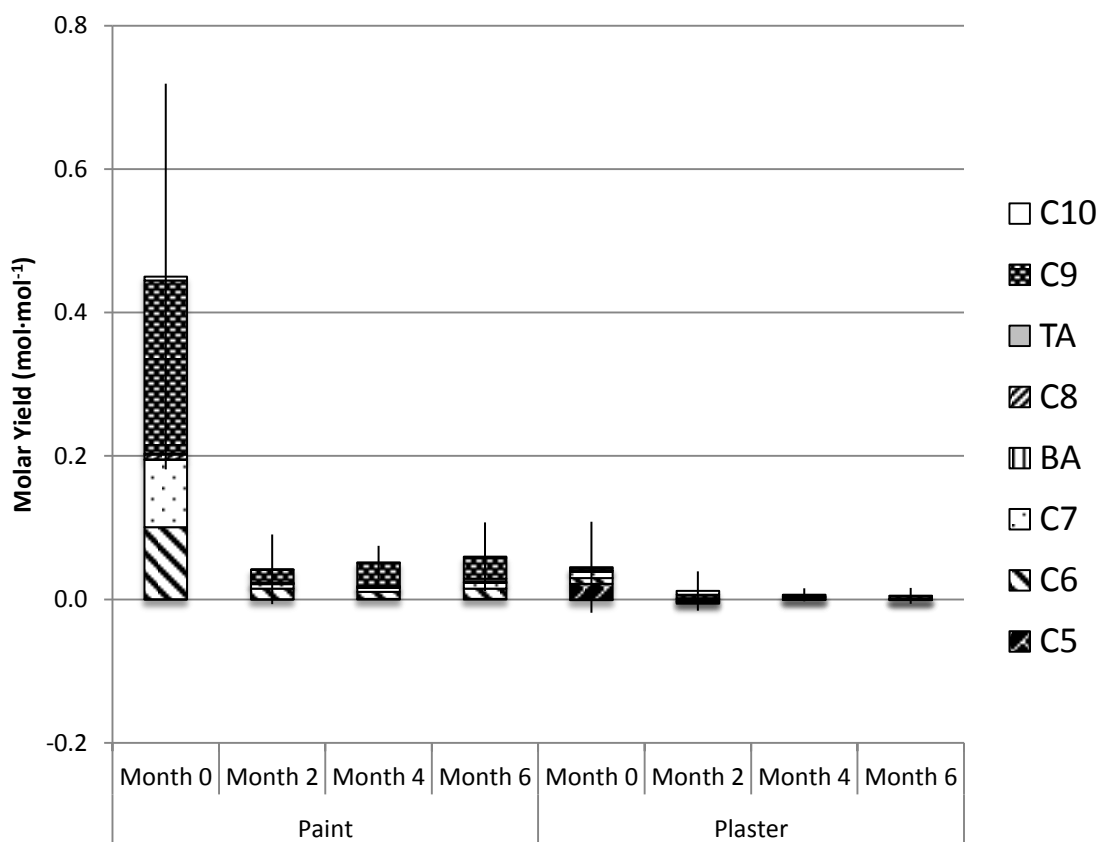
**Figure 10.** Molar yields of reaction products from clay paint and clay plaster averaged over all locations. Whiskers represent standard deviations across all samples.

The field studies completed for this dissertation provide an important contribution to the existing knowledge base. Results indicate that clay-based wall coverings may be viable PRMs for reducing ozone exposures in indoor environments. For further discussion on the viability of PRMs, see Appendix C, Figures C2 and C3. In these figures, ozone and formaldehyde removal effectiveness of clay paint inside a hypothetical home are plotted over a range of PRM surface areas and ozone deposition velocities, along with estimated costs of the clay paint.

## 6. Benefit-Cost Modeling of Ozone Removal by PRMs

This project was conducted to assess the potential economic and non-monetized benefits and costs associated with passive removal materials (PRMs) in occupied building spaces through development of a multi-functional model.

### 6.1. General Methodologies

#### 6.1.1. Conceptual Model

A conceptualized representation of major model components is shown in Figure 11. Component 1 encompasses an assessment of PRMs as an ozone control technology (see Chapter 3). Implementation of this control technology affects (link A) indoor ozone chemistry and fate (component 2) by reducing ozone concentrations. Ozone chemistry results in (link C) the formation of oxidized reaction products (component 3). The presence of indoor ozone and its reaction products then leads to (links B and D) impacts on occupant health (component 4). This project focused on the net benefit from reduction of these impacts as a result of implementation of an ozone control technology, relative to no implementation. Finally, in component 5, monetized benefits of reduced exposure to ozone and its reaction products (link E) are weighed against the direct costs of control technology implementation (link F) in a benefit-cost assessment.
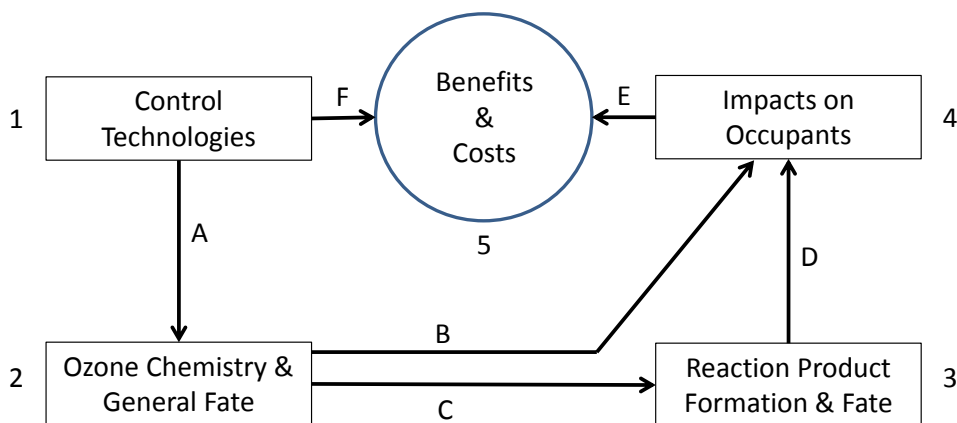


**Figure 11.** Conceptual model illustrating major model components and their interconnections.

The following series of objectives were met to complete this study:

**Objective A**. Complete an assessment of the state of knowledge related to the fate of ozone in buildings, including reaction products that stem from homogeneous and heterogeneous reactions involving ozone in buildings.

**Objective B**. Complete an assessment of the health effects of indoor ozone and its reaction products.

**Objective C**. Complete an assessment of the state of technology related to passive removal materials for ozone control in buildings.

**Objective D**. Develop a tool that integrates the components described in Figure 11 to assess the benefits and costs of passive removal materials in buildings.

**Objective E**. Complete city-specific population-wide analyses of the benefits and costs of PRM applications in residential buildings of 12 cities in the United States.

**Objective F**. Identify conditions for which benefit-cost ratios associated with application of PRMs are relatively high.

Outcomes of Objectives A through C are integrated into Chapters 1 through 3 of this dissertation.

### 6.1.2. Control of Ozone in Buildings Model

The model for calculating the benefits and costs of ozone control in buildings ($CO_3B$-Calc) is an integrated system of mathematical equations that address the major components and their interconnections illustrated in Figure 11. This system of equations accounts for ozone and reaction product fate (Equations 13 and 14, respectively), monetized health outcomes of reduced exposure to these pollutants (Equations in Section 6.1.3), and material costs (Equation 17). The model is designed to predict differences in ozone and reaction product concentrations for scenarios without any PRMs and scenarios

51

with PRMs in place. These results are used to quantify the health benefits of PRM implementation.

The $CO_3$B-Calc model is a spreadsheet application utilizing Microsoft Excel (MS Excel). There are four primary modules with each module assigned a separate sheet. The four modules include: user inputs, heterogeneous reactions, homogeneous reactions, and DALYs. The latter three sheets are hidden to reduce clutter and confusion during input. A fifth sheet labeled "Main" presents the results of the city-specific benefit-cost analysis for the scenario being modeled. The input sheet allows the user to test multiple scenarios by providing input cells for up to 45 parameters. The inputs are called by formulas to calculate variables throughout the hidden sheets. In addition to the scenario with a control, a baseline condition (no control) is also automatically modeled using the inputs provided by the user. All calculation processes are automated through the macro function; clicking a button on the Main spreadsheet after all values are input will run the macro, and the benefit-cost ratios are displayed on the Main sheet.

### 6.1.3. Modeling Health Benefits and Costs of Ozone Removal

Health benefits due to reduction in exposure to a pollutant such as ozone are estimated by calculating the reduction in disability-adjusted life-years (DALYs). Disability-adjusted life-years are used to quantify the burden of disease, incorporating years of life lost from premature mortality and from disability due to disease incidence (Equation 15):

$$DALYs_{disease} = YLL_{disease} + YLD_{disease} \tag{15}$$

Where $DALYs_{disease}$ is the total DALYs lost per disease incidence (yr), $YLL_{disease}$ is the years of life lost due to disease incidence (yr), and $YLD_{disease}$ is the years of life lost due to disability from the disease (yr).

The total monetary benefits of reduced exposure to indoor ozone are calculated using Equation 16:

$$Benefits = \frac{\$}{DALY} \times \Delta DALYs \qquad (16)$$

Where *Benefits* are the monetary benefits due to reduced DALYs per 100,000 people ($),
*$/DALY* is the monetary value of one DALY ($·yr$^{-1}$), and *ΔDALYs* is the reduction in
DALYs when a PRM is applied relative to when a PRM is not applied (yr). A more
detailed description of the procedure for calculating *ΔDALYs* for ozone and reaction
byproducts can be found in Corsi et al. (2013) and in Aldred et al (2015).

The costs of ozone removal with a PRM consider the cost of purchasing and
implementing the material in the building. For PRMs, cost estimates (each excluding the
cost of labor for installation) were obtained from the websites of companies that produce
and sell them. Estimates for costs of conventional materials (e.g., latex paint, mineral
fiber ceiling tile) were surveyed from national home improvement retailers. Unit costs of
some PRMs and their conventional analogs are provided in Table 5.

**Table 5.** Costs ($·m$^{-2}$) of PRMs, conventional materials, and their relative cost
differences.

| PRM | PRM Cost | Conventional Material | Conventional Material Cost | PRM Cost Above Conventional |
|---|---|---|---|---|
| Perlite Ceiling Tie | $10.46 | Mineral Fiber/Metal Ceiling Tile | $5.32 | $5.14 |
| Clay Paint | $3.39 | Latex Paint | $2.32 | $1.07 |
| Clay Plaster | $15.97 | Lime Plaster/Faux Venetian Plaster | $9.22 | $6.76 |

Values of material costs, surface areas, and replacement frequency may be
adjusted in the model. Additional PRMs may be included as more cost information
becomes available. Labor and installation costs are omitted under the assumption that
these costs are the same for a specific PRM and its conventional analog. The overall
PRM cost (*ΔOPC*) is calculated according to Equation 17:

$$\Delta OPC = [\Delta PRM\$] \cdot A_{prm} \cdot RF \cdot \left[\frac{100,000}{Occup}\right] \qquad (17)$$

Where *ΔPRM$* is the cost of the PRM above the conventional material ($), *RF* is the replacement frequency of the PRM (yr$^{-1}$), *Occup* is the household occupancy (persons per household), and all other variables are as defined above. The *ΔOPC* is normalized by building occupancy, and extrapolated for a population of 100,000 people. The resulting cost is the total cost of the PRM above the cost of a similar conventional material per 100,000 people.

The benefit-cost ratio (*B/C*) is calculated by dividing the summed benefits by the overall PRM cost, according to Equation 18:

$$B/C = \left( \left( \sum_{i=1}^{n} \Delta DALYs \right) \cdot \frac{\$}{DALY} \right) / \Delta OPC \qquad (18)$$

Where $\sum_{i=1}^{n} \Delta DALYs$ is the sum of DALYs over all health outcomes due to ozone exposure (yr), and the other variables are as defined above.

### 6.1.4. City-Specific Benefit-Cost Analysis in Residences

The cities analysis focused on the baseline conditions in 12 cities across the United States. At least two cities from each of the five climate zones defined by the Energy Information Administration were selected for the analysis. Climate zones were defined by number of heating degree-days and cooling degree-days. The cities selected for this analysis include: Atlanta, Austin, Buffalo, Chicago, Cincinnati, Houston, Miami, Minneapolis, New York City, Phoenix, Riverside, and Washington D.C. This sample of cities accounts for approximately 20% of the U.S. population and is a broad nationwide sample of population, climate, building stock, and ambient ozone concentrations. Housing data for each city were collected from multiple sources including the U.S. Census Bureau American Housing Survey (USCB, 2013), Chen et al. (2012a), and Persily et al. (2010).

City-specific parameters for PRM applications are presented in Table 6 and include annual ambient ozone concentration, building volume, annual HVAC operation fraction, and household occupancy, as well as outdoor air infiltration rate. The PRM

surface area was assumed to be 20% of the volume of the residential building (area/volume (A/V) = 0.2 m$^{-1}$). Surface areas specific to each city are shown in Table 6.

Clay paint was selected as the PRM due to its high ozone reaction probability, relatively low reaction product yields (Figure 2), and low cost differential compared to latex paint (Table 2). Other model inputs, including indoor terpene concentrations and bimolecular reaction rate constants are listed in further detail in Appendix F (Tables F1-F7).

Realistic ranges of gaseous reactant concentrations were selected for residential environments, with preference given to measurements made in North American buildings. Applications of PRMs did not include the use of activated carbon filters, and electricity costs did not factor into the PRM analysis.

**Table 6.** Model inputs for 12 U.S. cities for residential PRM applications.

| City | Outdoor Ozone (ppb) | Median Home Volume (m$^3$) | Outdoor air infiltration rate (h$^{-1}$) | HVAC Operation Fraction | Household Occupancy | PRM Surface Area (m$^2$) A/V=0.2 m$^{-1}$ |
|---|---|---|---|---|---|---|
| Atlanta | 25.18 | 543 | 0.43 | 0.21 | 2.18 | 109 |
| Austin | 27.29 | 498 | 0.50 | 0.30 | 2.37 | 100 |
| Buffalo | 24.72 | 448 | 0.70 | 0.03 | 2.24 | 90 |
| Chicago | 19.97 | 509 | 0.61 | 0.07 | 2.57 | 102 |
| Cincinnati | 26.23 | 467 | 0.52 | 0.11 | 2.17 | 93 |
| Houston | 23.06 | 498 | 0.50 | 0.30 | 2.67 | 100 |
| Miami | 27.80 | 487 | 0.35 | 0.38 | 2.58 | 97 |
| Minneapolis | 32.08 | 552 | 0.60 | 0.07 | 2.17 | 110 |
| New York | 19.59 | 509 | 0.62 | 0.10 | 2.61 | 102 |
| Phoenix | 25.43 | 445 | 0.42 | 0.37 | 2.64 | 89 |
| Riverside | 33.79 | 442 | 0.42 | 0.19 | 3.26 | 88 |
| Washington DC | 21.05 | 644 | 0.54 | 0.12 | 2.13 | 129 |

The model was set up to simulate three different scenarios with respect to background ozone decay rate and SOA as a reaction product: baseline decay without accounting for SOA, low decay without accounting for SOA, and baseline decay accounting for SOA. The background ozone decay rate ($k_{O3,surf}$) was weighted by the fraction of time that that the HVAC system was cycling to reflect higher decay rates

when the HVAC system cycles on, and lower decay rates when the HVAC system cycles off. The baseline ozone decay rate when the HVAC system was switched off was assumed to be 2.8 hr$^{-1}$ (Lee et al., 1999) and the decay rate when the HVAC system was switched on was assumed to be 5.4 hr$^{-1}$ (Sabersky et al., 1973). The low decay rate when the HVAC system was switched off (1.5 hr$^{-1}$) was assumed to be one standard deviation (1.3 hr$^{-1}$) below the mean reported by Lee et al. (1999). An adjustment to the ozone decay rate for reduction in background surface area assuming a PRM replaces background material was built into the model as according to Equations 5 and 13.

**Table 7.** Three modeling scenarios for city-specific analysis in residential buildings.

| | **Ozone** $k^*_{dep,O3}$ **HVAC Off** | **Ozone** $k^*_{dep,O3}$ **HVAC On** | **Ozone/SOA** |
|---|---|---|---|
| Baseline | 2.8 hr$^{-1}$ | 5.4 hr$^{-1}$ | ozone only |
| Low Decay | 1.5 hr$^{-1}$ | 5.4 hr$^{-1}$ | ozone only |
| Baseline + SOA | 2.8 hr$^{-1}$ | 5.4 hr$^{-1}$ | ozone + SOA |

For any modeling scenario, the ozone deposition velocity ($v_{d,prm}$) to clay paint was based on the average of transport-limited deposition velocities reported in Morrison et al. (2006), and on the ozone reaction probability for clay paint reported by Lamble et al. (2011). All three scenarios assumed an ozone deposition velocity to clay paint that depends on the fraction of time that that the HVAC system was cycling. For instance, clay paint may be applied around door or window frames, or around supply vents. Transport-limited deposition velocities have been shown to be higher in these areas, especially when an HVAC system cycles on (Morrison et al., 2006). Therefore, the transport-limited deposition velocity was weighted by the average fraction of time that HVAC systems operate in each city. For example, the HVAC operation fraction in Houston (0.30) was multiplied by the high ozone transport-limited deposition velocity (18 m·hr$^{-1}$) from Morrison et al. (2006), and then summed with the product of the fraction of time that the HVAC is not in operation (i.e., 1-0.30 = 0.70) and a lower transport-limited deposition velocity (1.2 m·hr$^{-1}$) from Morrison et al. (2006). The weighted transport-limited and ozone deposition velocities for each city are presented in Table 8.

**Table 8.** Transport-limited and ozone deposition velocities to clay paint.

| City | $v_t$ (m·h$^{-1}$) | $v_d$ (m·h$^{-1}$) |
|---|---|---|
| Atlanta | 4.73 | 3.22 |
| Austin | 6.24 | 3.85 |
| Buffalo | 1.70 | 1.46 |
| Chicago | 2.38 | 1.92 |
| Cincinnati | 3.05 | 2.34 |
| Houston | 6.24 | 3.85 |
| Miami | 7.58 | 4.33 |
| Minneapolis | 2.38 | 1.92 |
| New York | 2.88 | 2.24 |
| Phoenix | 7.42 | 4.27 |
| Riverside | 4.39 | 3.06 |
| Washington D.C. | 3.22 | 2.44 |

For all cities, the recirculation air exchange rate ($\lambda_{rec}$) was set equal to 7.6 hr$^{-1}$. This value was based on a previous analysis of residential and light commercial buildings by Stephens et al. (2011). The HVAC particle filter will react with recirculating ozone. Values reported in the literature are typically between 0.05 to 0.15 for realistic face velocities and particle loadings on filters (e.g., Bekö et al., 2006 and 2009; Hyttinen et al., 2006).  A single-pass fractional removal efficiency of 0.1 was assumed for all cities and scenarios.

The model calculates the removal effectiveness for ozone, SOA, and formaldehyde, using concentrations predicted from Equations 13 and 14. The removal effectiveness ($\Omega_i$) is the reduction in concentration of pollutant $i$ with ozone control (i.e., activated carbon or PRM) relative to the concentration of pollutant $i$ without ozone control.   For example, if $\Omega_i = 0.5$ the control device reduces the concentration of pollutant $i$ by 50%, or a factor of two reduction relative to the use of no control device. The removal effectiveness is determined by Equation 19.

$$\Omega_i = 1 - \frac{\overline{C}_{i,control}}{\overline{C}_{i,no\_control}} \tag{19}$$

$\Omega_i$ = fractional effectiveness of removal for pollutant $i$ (-)

$\overline{C}_{i,control}$ = concentration of pollutant $i$ with ozone control device (ppb or $\mu g \cdot m^{-3}$)

$\overline{C}_{i,no\_control}$ = concentration of pollutant $i$ with no ozone control device (ppb or $\mu g \cdot m^{-3}$)

All of three scenarios assume a situation that might resemble a new home under construction for which the designer selects a PRM instead of a conventional material. For instance, clay plaster could be applied to the walls instead of faux plaster. In this case, the cost is the difference between the PRM cost and the cost of the conventional material, assuming the labor cost is equal in each case. Compared to the other PRMs in Table 2, clay paint has the smallest cost difference ($1.07 m$^{-2}$) above its conventional analog, latex paint.

Key assumptions used in the city-specific analysis for PRM applications in residential buildings include:

- Weighted ozone decay rate [$k^*_{dep,O3}$ = 2.8 hr$^{-1}$ with HVAC off; $k^*_{dep,O3}$ = 5.4 hr$^{-1}$ with HVAC on]
- Recirculation air exchange rate of 7.6 hr$^{-1}$
- PRM replacement once every 10 years (= 0.10 yr$^{-1}$)
- City-specific annual mean ozone concentration (see Table 6)
- City-specific median house size, infiltration, and annual HVAC operational fraction (Table 6)
- 10% single-pass ozone removal efficiency for particle filters
- City-specific residential occupancy (USCB, 2012) (Table 6)
- Fraction of time spent in indoors (or exposure frequency) [0.87] (Klepeis et al., 2001)
- Average retail price of clay paint and average retail price of major brand interior latex paints (Table 2)

▪ Health outcomes for all ages – city-specific population age fraction (USCB, 2012) (Table E9)

## 6.2. Major Findings

### 6.2.1. Ozone Removal Effectiveness

City-specific ozone removal effectiveness and indoor ozone concentrations with and without the use of clay paint as a PRM in residential buildings for the baseline decay and low decay scenarios are shown in Figures 12 and 13. For the baseline decay scenario, most cities are characterized by ozone removal effectiveness values for the selected PRM and surface area of between 10% and 15%. Corresponding changes in indoor ozone concentrations are less than 1 pbb. For the case of a residence with a low background ozone decay rate, ozone removal effectiveness is slightly greater by a few percent (Figure 13). Having a lower background ozone decay rate increases the amount of indoor ozone that can be removed by the PRM because the PRM does not have to compete as much with other interior surfaces that react with ozone. Cities with relatively high removal effectiveness are those with a high HVAC operation fraction, which leads to more frequent deposition of ozone to the PRM due to enhanced mixing conditions in the indoor space.
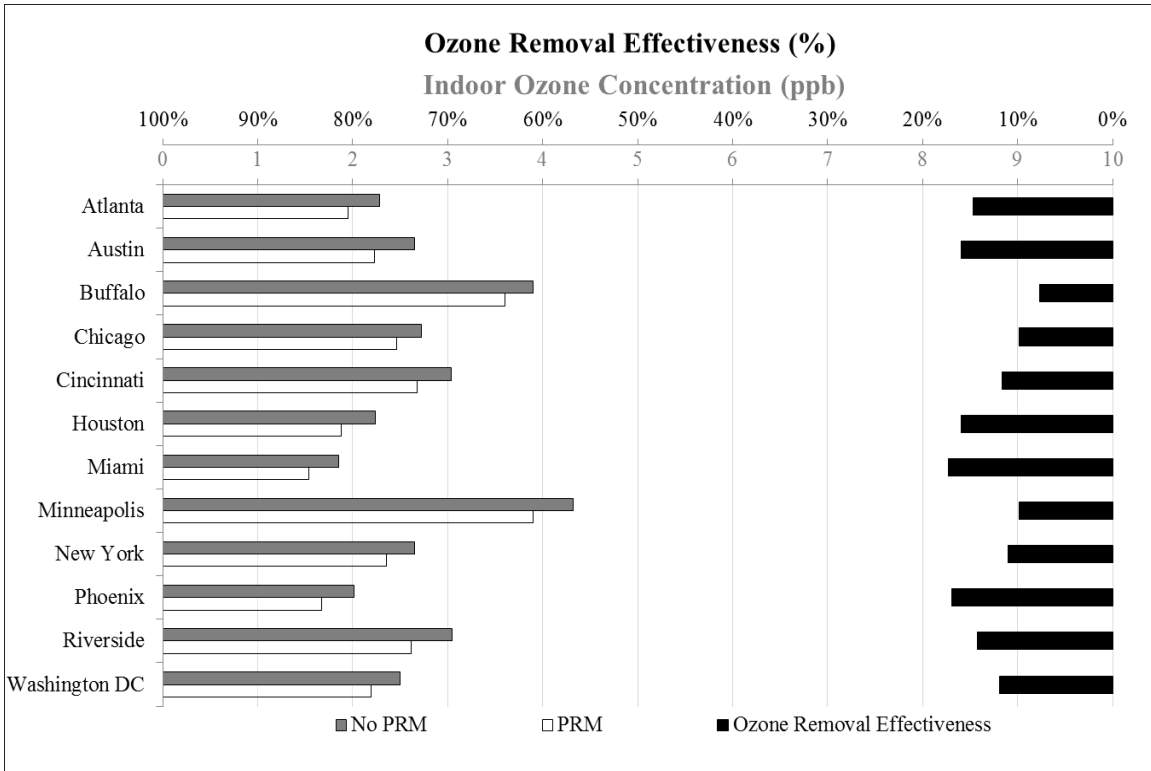
**Figure 12.** Ozone removal effectiveness of a clay paint (right) and indoor ozone concentrations in residences for the baseline scenario with and without the clay paint (left).
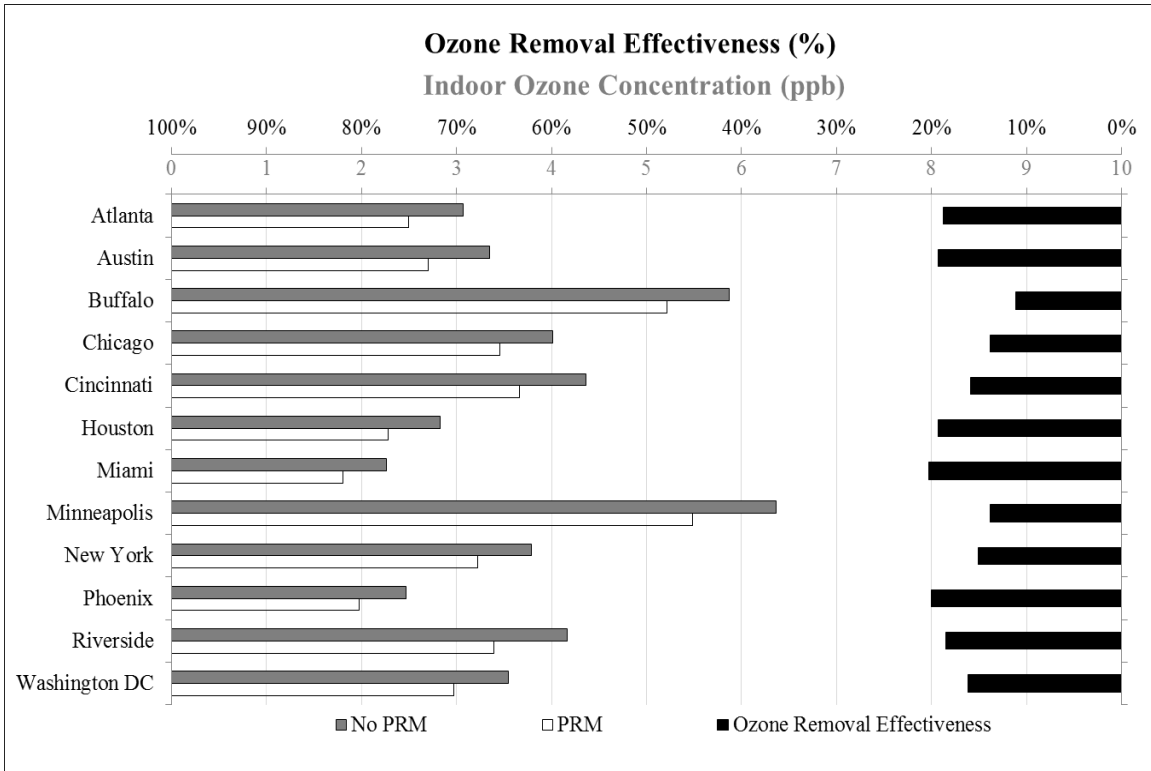
**Figure 13.** Ozone removal effectiveness of a clay paint (right) and indoor ozone concentrations with and without the clay paints (left) in residences with a low background ozone decay rate.

### 6.2.2. Benefit-Cost Analysis

Benefit-cost ratios for the baseline, low ozone decay, and the baseline with SOA scenarios are shown in Figure 14. The high and low bars on each plot point represent the values for the most and least sensitive populations, respectively, using 95% confidence intervals on health functions (Aldred et al. 2015). The decay rate of ozone to background surfaces heavily influences the B/C ratio. For sensitive populations (i.e., as children, people with asthma, and the elderly), the B/C ratio can be as high as 16 if the background ozone decay rate is low.

The predicted B/C ratio is greater than 2 for all target cities and scenarios, with the exception of Washington, D.C., where home volumes and therefore PRM surface areas are high. Additionally, the household occupancy in Washington, D.C. is lowest

among all target cities. The cities with the greatest predicted benefits from application of clay paint are Buffalo, Cincinnati, Miami, Minneapolis, and Riverside. Buffalo has a high outdoor air infiltration rate and a high population age fraction older than 65 years. Cincinnati is characterized a relatively high outdoor ozone concentration, and by a high population age fraction older than 75 years. Miami also has a large fraction of the population that is older than 65 years, along with a high HVAC operation fraction and therefore a high ozone deposition velocity. Minneapolis has a high annual average outdoor ozone concentration and a relatively high outdoor air infiltration rate. Over all three cases the highest B/C ratios are predicted for Riverside, with a B/C ratio approaching 10 for homes with low ozone decay rates. The B/C ratio is driven up by high outdoor ozone concentrations and high household occupancies in Riverside.

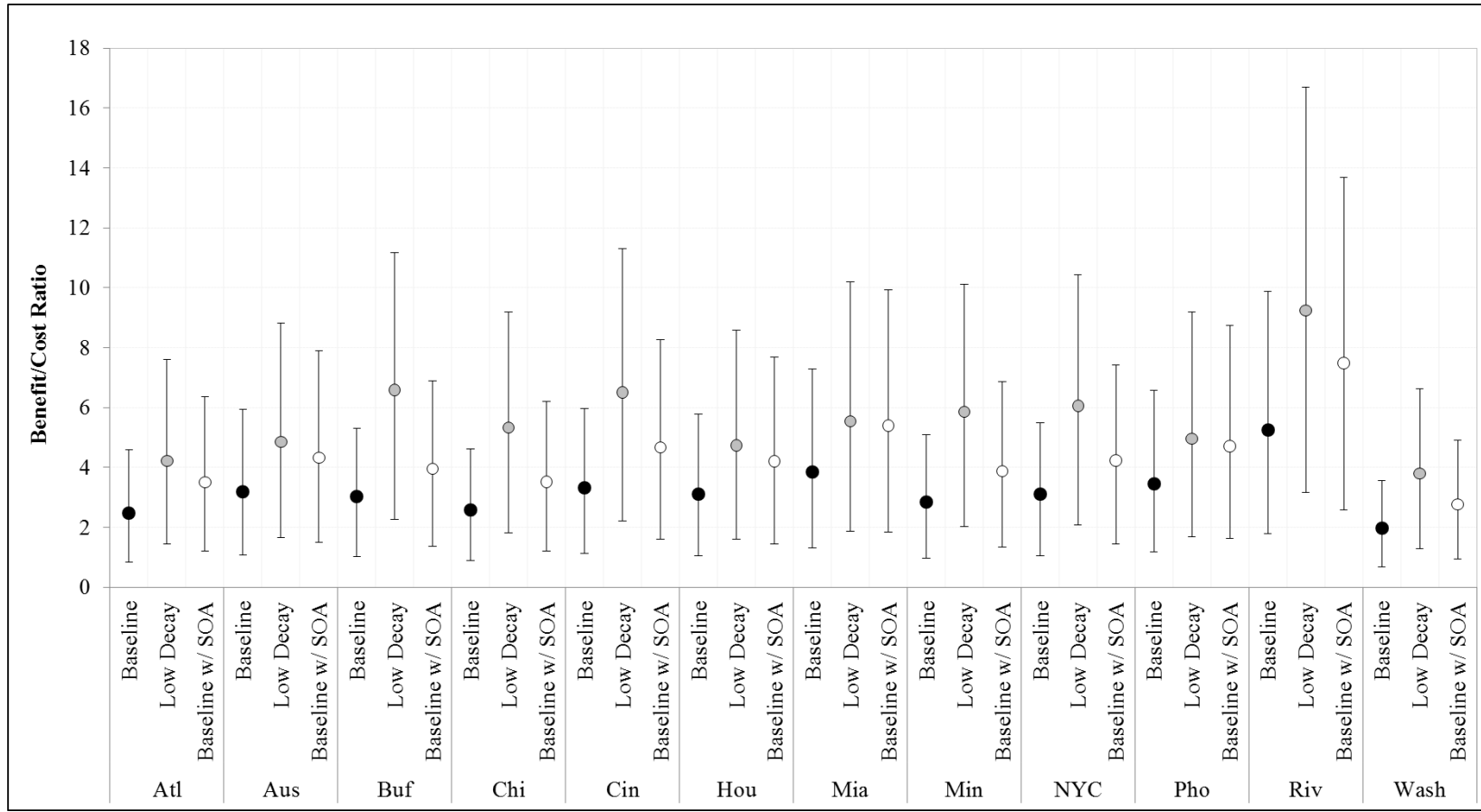**Figure 14.** Predicted benefit-cost ratio associated with use of a clay paint in residences under each of three cases (baseline, low background ozone decay rate, and baseline case with SOA formation), including reductions in disability-adjusted life-years (DALYs) and reductions in mortality. The range bars represent the 95% confidence intervals of the health functions used in the benefit analysis.

### 6.2.3. Maximizing PRM Value

There are conditions under which PRMs would be most beneficial, i.e., where benefit-cost ratios are maximized. These conditions are outlined below.

*Smaller buildings.* Passive removal materials can be more effective in smaller homes or other non-residential buildings that have small volumes. A smaller area of PRM can be applied for a given surface area-to-volume ratio. Therefore, less money is spent, reducing the overall cost, and increasing the B/C ratio. Riverside, California is an example where smaller home volumes lead to higher B/C ratios.

*Less reactive buildings.* As shown by the B/C ratio results for the "low decay" scenario (Figure 14), lower background surface ozone decay rates ($k_{O3,surf}$) contribute significantly to higher B/C ratios. Lower decay rates are characteristic of buildings with interiors that are less reactive with ozone, such as tile, glass, metal, and other non-fleecy materials that do not contain unsaturated organic compounds that react readily with ozone. As less ozone is removed to background surfaces, more ozone is likely to be removed by a PRM, thereby making the PRM more effective, increasing the B/C ratio. PRMs would be useful in more reactive homes if the PRM replaces a high byproduct-emitting surface.

*Higher-occupancy homes.* Homes that have higher occupancies would benefit from PRMs more than homes that have fewer occupants, such as those in Washington D.C. (figure 14). The PRM cost determined by Equation 17 is normalized by household occupancy. As such, for higher occupancy, the cost of the PRM invested per person is lower. Higher occupancy also increases the monetary benefits as determined by health functions (Corsi et al., 2013; Aldred et al., 2015).

*Older and younger populations.* Buildings where people aged 65 and older reside, such as long-term healthcare facilities, would benefit greatly from PRMs. Health benefits would also be realized in buildings where young children spend a lot of time, such as schools or nurseries. The health functions assume that these populations are at greater

risk for disease and death due to exposure to air pollution, including ozone (Aldred et al., 2015 and 2016). Additionally, people who suffer from asthma could benefit from PRMs.

*Higher outdoor air exchange rates and higher ambient ozone.* Buildings that are less tight, allowing more outdoor air exchange with the indoor environment, generally have higher indoor ozone concentrations, especially if the ambient ozone concentration is high, as in Riverside. Higher indoor ozone concentrations imply that there is more ozone available for the PRM to remove. This means that greater benefits would be realized for the occupants in "leaky" buildings located in places where the outdoor ozone concentration is high.

*More frequent HVAC operation.* People who reside in buildings that have high HVAC operation fractions ($H_{on}$) should benefit more from PRMs. The model weights the transport-limited ozone deposition velocity ($v_t$), and therefore the ozone decay rate to the PRM ($k_{O3,prm}$), to the amount of time that the HVAC is on. A higher ozone decay rate to the PRM would result in higher benefits, and therefore a higher B/C ratio. However, the relationship between this condition and the B/C is weaker compared to the first four conditions mentioned above.

## 7. Summary and Conclusions

### 7.1. Human Perception Studies

Human panelists were exposed to various combinations of ozone, carpet, and clay wall coverings inside test chambers, and were asked to assess perceived air quality (PAQ). Ozone, $C_5$ to $C_{10}$ saturated n-aldehydes, and two aromatic aldehydes were also measured to characterize chamber air. The following conclusions are made based on results of this study:

1. Reactions of ozone with carpet are associated with low PAQ. The least acceptable PAQ and the highest concentrations of aldehydes were observed when carpet and ozone were present together.

2. Clay wall coverings can improve PAQ, particularly in the presence of ozone or ozone and carpet. Perceived air quality was most acceptable and concentrations of aldehydes were lowest when only clay plaster or both clay plaster and carpet were present in the chambers without ozone. Addition of clay plaster to the least acceptable PAQ condition (carpet + ozone) considerably decreased both ozone and aldehyde concentrations and significantly improved PAQ.

3. There are gender differences in PAQ for air exposed to carpet and/or clay in the presence or absence of ozone. Males collectively exhibited smaller ranges of PAQ for most conditions. Females were more sensitive to differences in test conditions, and were most satisfied when clay panels were used either in the absence or presence of ozone.

Additional research is needed to confirm the results presented herein with a broader base of panelists and with longer exposure times that would allow for extended PAQ and productivity assessments. Field tests involving the performance of clay as an air purifier are needed over extended time periods. Additional passive removal materials should also be explored through systematic screening in small chambers, panel assessments and proof-of-concept field studies.

66

### 7.2. Longitudinal Field/Laboratory Study

Specimens of clay paint and clay plaster were placed in five different residential locations, and tested bi-monthly in laboratory chambers. Specimens were exposed to real indoor environments for a total of six months. Ozone reaction probabilities, primary and secondary emission rates of $C_5$ to $C_{10}$ saturated n-aldehydes and two aromatic aldehydes, and molar yields of these byproducts were characterized during each chamber test. Based on the experimental results, the following conclusions are made:

1. A clay paint and a clay plaster both sustained relatively high ozone reaction probabilities over six months, with the highest reaction probabilities recorded four months after placement in the field. The observed time variations in ozone reaction probabilities might reflect the influence that indoor environmental activities have on material surface interactions with ozone (e.g., from soiling by dust and oils or adsorption of reactive gases).

2. Although lower reaction probabilities were observed for specimens that were situated adjacent to a patio door where potentially more outdoor air infiltration occurred, reaction probabilities did not vary by location to a significant degree.

3. While the clay paint was statistically more reactive with ozone compared to the clay plaster, it also exhibited greater molar yields of $C_5$ to $C_{10}$ saturated n-aldehydes. Molar yields for both the clay paint and clay plaster were elevated during the initial tests at Month 0, and then decayed sharply afterward.

4. The emission rates determined during this study are similar to the results obtained by Lamble et al. (2011) for the same type of clay paint and plaster. Total molar yields of $C_5$ to $C_{10}$ saturated n-aldehydes from the clay paint were comparable to total molar yields determined by Cros et al. (2012) for a low-VOC conventional paint, while for the clay plaster the total molar yields were much lower in comparison.

5. The clay paint appears to be a good coating for ozone removal for at least six months, and appears similar to a low-VOC conventional paint, in terms of $C_5$-$C_{10}$ saturated n-

aldehyde emissions. Given its relatively high reactivity with ozone and reduced secondary emissions, the clay plaster might be a preferred PRM over the paint.

6. These two materials have been studied to a limited degree, and especially under realistic exposure conditions for extended periods of time. Therefore, broad conclusions about how they will affect indoor environments should be withheld until further testing helps to better understand the long-term effects of commercial clay coatings.

## 7.3. Benefit-Cost Modeling of Ozone Removal

Passive removal materials (PRMs) are an alternative or possibly supplemental approach to in-duct ozone removal (i.e., by using activated carbon filters). Based on a review of the published literature the following is concluded about the state of PRM technology for ozone removal in buildings:

1. Model evaluations suggest that some PRMs could significantly reduce indoor concentrations of ozone and some reaction products, and hence occupant exposures to these pollutants in residential buildings. Evaluations have not yet been completed for non-residential buildings.

2. From the standpoint of differential cost (with conventional analogs), aesthetics, and recent experimental data it appears that some clay-based paints and plasters might be viable as PRMs. A clay-based paint was used for $CO_3B$-Calc simulations in this study.

3. The benefit-cost ratio for clay paint as a control measure for ozone should be improved in buildings with low background reactivity with ozone, low differential cost between the clay paint and conventional interior paint, high building occupancy, high ozone deposition velocity to the PRM, high outdoor ozone concentration, higher PRM surface area-to-volume ratio, and long PRM replacement periods.

4. While the ozone removal effectiveness of PRMs can be considerable, absolute differences in the indoor concentrations can be small, i.e., less than 1 to 2 ppb, when

indoor levels are already less than 10 ppb. However, these differences should increase and become more important as indoor concentrations become higher.

5. Findings from the simulations completed in this study are predicated on an assumption that sustained ozone reactivity with clay paint can occur over time scales of at least 10 years (see Section 6.3 for discussion of limitations). While model results are encouraging, the high uncertainty associated with this assumption precludes any recommendations beyond the need for additional research to verify the long-term performance of clay paint and other PRMs.

**7.4. Limitations**

The modeling study described in Chapter 6 was the most rigorous to date regarding assessment of the benefits and costs of passive ozone control in buildings. Inherent limitations to this study are discussed in the following list.

1. Ambient ozone concentrations were averaged over an annual period. As a result, the health effects following high ozone events are not captured. Indoor ozone control during such events would increase the benefit-cost ratios described in this report, particularly for sensitive populations.

2. Indoor ozone concentrations are typically much lower than outdoor ozone concentrations, even without specific ozone control technologies. In this study, it was assumed that there is no threshold below which incremental reductions in indoor ozone concentration do not have a positive health effect. This is an important issue that has yet to be effectively resolved by the health science community. If a threshold is found to exist above typical indoor ozone concentrations the benefits described in this report might be substantially reduced. Importantly, if a threshold does exist it will be dependent on averaging time and lowest for long-term averages such as the annual averages used in this study.

3. The health effects of indoor secondary organic aerosols (SOA) are not well defined and related predictions were largely omitted from this study. The same is true of

many other ozone reaction products, including many carbonyls, di-carbonyls, carboxylic acids, peroxides, and more. Future incorporation of the health effects of these reaction products into CO$_3$B-Calc will increase predicted benefit-cost ratios to an extent that cannot be estimated at the time of this study.

4. In this study, lower-level productivity losses due to exposure to ozone or its quantifiable reaction products in the workplace were not estimated due to a lack of model parameters for estimating DALYs. Future incorporation of these effects will increase predicted benefit-cost ratios to an unknown extent.

5. Indoor sources of ozone were not included in this study. Such sources may be important in offices or schools with poorly maintained and highly operated photocopy machines and/or laser printers, or in residences or other buildings in which ion generators or electrostatic precipitators are used for particle control. For such scenarios the benefit-cost ratio of PRMs will increase. The CO$_3$B-Calc model developed for this study allows for predictions that include indoor sources of ozone.

6. The frequency and time of window opening can affect building occupant exposures to ozone. These factors were omitted from analysis in this study but may add some benefit to ozone control by PRMs.

7. In this study, the benefits and costs of ozone control are characterized entirely in economic terms that are supported by reference to published literature. This requires that reductions in physical suffering, e.g., from asthma, be quantified in a way that reflects average societal values, and not necessarily those of individuals who suffer the most from exposure to ozone. There are costs, both social and health, that are difficult to impossible to quantify with any degree of accuracy. Those who have the economic resources to spend more for health benefits may choose to do so. But there is also a bias against those for whom the required marginal costs are impractical to pay. These factors are difficult to capture and were not incorporated into the CO$_3$B-Calc model. As such, it is expected that the results presented herein underestimate

70

the overall benefit-cost ratio associated with ozone control, particularly for sensitive sectors of the population.

8. While there appear to be advantages of the two clay products studied with respect to indoor air quality, there are at least two potential disadvantages. First, even though benefit cost ratios in Chapter 6.2.2 were greater than 1, Commercially-available clay coatings may be unaffordable to many people, such as elderly people on fixed incomes, or parents earning minimum wage. Access to stores that sell these clay-based coatings may be another obstacle for some. In addition, the clay plaster is sold in powder form in 50-lb (22.7 kg) bags, and it must be mixed with water using a large paddle that can be attached to a drill. The labor and time-commitment involved in mixing and applying the clay plaster are likely to be deterrents to its use.

### 7.5. Recommendations for Future Research

Research on passive removal materials is in its early stages. The following areas for future research remain:

1. More field testing is needed to ascertain the long-term performance of passive removal materials. The key operational parameter is the PRM's reaction probability and how it changes over many years. Given *the* time frames needed it will likely not be feasible to follow a new PRM across its lifetime in real world applications. As such, one possible approach is to study a new PRM that is placed in the field and returned to a laboratory for analysis before returning to the field over a two or three year period. Such studies could be coupled with reaction probability measurements of similar materials that were used in buildings for much longer periods of time before being removed for purposes of renovation and acquired and analyzed by researchers.

2. Ensuring ease of use and affordability of PRMs that can be implemented in homes and other non-residential indoor environments is important. The more affordable and easily incorporated a commercially-available PRM is, the more likely it could be

selected by building contractors, business owners, and others. Nomura and Jones (2013, 2014, and 2015) have begun to include these considerations for removal of formaldehyde to aminosilicas.

3. Environmental sustainability of PRMs should be another focus of future research. Materials that are widely available, require little energy to be produced, are renewable or made from recycled materials, and non-toxic should be targeted for use as PRMs.

4. Additional research is needed to confirm the results presented in Chapter 4 with a broader base of human panelists performing repeated assessments and with longer exposure times that would allow for (1) extended PAQ and productivity assessments, and (2) determining relationships between PAQ and the presence of ozone reaction products. Field tests involving the performance of clay as an air purifier are needed over extended time periods. Additional passive removal materials should also be explored through systematic screening in small chambers, panel assessments, and proof-of-concept field studies.

5. Although temperature and relative humidity were tracked at each of the five locations, no effect on ozone removal or byproduct emissions could be ascertained. Temperature and relative humidity were monitored during the chamber experiments, but were neither controlled nor varied. Tests to determine whether the temperature and relative humidity inside the chambers affect ozone uptake to and byproduct emissions from clay specimens would be useful.

6. Ozone concentrations near the specimens in each of the field locations were not monitored or known, but it would be interesting to see whether higher ozone concentrations in the field result in lower ozone reaction probabilities and byproduct emissions due to consumption of reaction sites.

7. The water content of each clay product was not investigated. It is possible that the water content the clay products after application led to the higher initial emissions from the coatings compared to the emissions by Month 2. A future study could focus

on tracking ozone reaction probabilities and water contents of clays over time as specimens are dried under controlled conditions.

8.  Another property of clay that could influence the rate of ozone removal is texture, specifically surface roughness and pore size. It is unclear whether the roughness of the clay surface is important in terms of ozone removal. It is conceivable that the increased surface area of a clay with a rough finish would remove more ozone than the same type of clay with a smooth finish. The microstructure of clay could be even more important for ozone removal. Clays have the smallest grain size of all geological materials, and therefore more surface area within its pores. It would be helpful to ascertain how pore size or surface area, along with surface roughness, influence ozone removal by clays.

9.  The clay paint and plaster studied herein were applied to gypsum wallboard in a consistent manner, but coating thickness was not controlled or measured. Variations in coating thickness could have contributed to uncertainty in the results. It could be useful to study whether variation in coating thickness affects ozone reaction probability and emissions.

10. The radium content of clay products should be studied in future research. Radon emissions from clays with elevated radium content could pose a public health risk.

11. An important limitation of the modeling study in Chapter 6 is the lack of field data for evaluation with model results. Studies to test PRM performance in the field are highly recommended.

# Impacts of a Clay Plaster on Indoor Air Quality assessed using Chemical and Sensory Measurements[2]

Erin Darling[1], Clement Cros[1], Pawel Wargocki[2], Jakub Kolarik[2], Glenn C. Morrison[3] and Richard L. Corsi[1,*]

[1]University of Texas at Austin (UT)

[2]International Centre for Indoor Environment and Energy, Civil Engineering, Technical University of Denmark (DTU)

[3]Missouri University of Science and Technology (MS&T)

[*]*Corresponding email: corsi@mail.utexas.edu*

## ABSTRACT

Passive removal materials (PRMs) are building materials or furnishings that effectively control indoor pollution without substantial formation of chemical byproducts and without an energy penalty. Recent studies have suggested that clay might be an effective PRM for ozone. To assess clay wall plaster as a PRM for improving air quality by controlling ozone, perceived air quality (PAQ) was determined in the presence of eight combinations of an emitting and reactive pollutant source (new carpet), clay plaster applied to gypsum wallboard, and chamber air with and without ozone. A panel of 24 human subjects assessed air quality in twin 30 m$^3$ chambers using a continuous acceptability scale. Air samples were collected immediately prior to panel assessment to quantify concentrations of $C_5$ to $C_{10}$ saturated n-aldehydes and two aromatic aldehydes that are commonly produced by reaction of ozone with carpet. Perceived Air Quality was

---

[2] A version of this paper is published in Building and Environment with the following reference: Darling, E. K., Cros, C. J., Wargocki, P., Kolarik, J., Morrison, G. C., & Corsi, R. L. (2012). Impacts of a clay plaster on indoor air quality assessed using chemical and sensory measurements. *Build Environ, 57,* 370-376. The author of this dissertation was a co-leader of the research presented in this paper.

most acceptable and concentrations of aldehydes were lowest when only clay plaster or both clay plaster and carpet were present in the chambers without ozone. The least acceptable PAQ and the highest concentrations of aldehydes were observed when carpet and ozone were present together; addition of clay plaster for this condition improved PAQ and considerably decreased aldehyde concentrations.

**KEYWORDS**

*perceived air quality, clay, ozone removal, aldehyde, passive removal, green material*

**INTRODUCTION**

Increasing levels of tropospheric ozone have been related to numerous adverse effects on humans, including decreases in short-term lung function [1-2], increased rates of asthma symptoms in infants [3], and increases in morbidity and both non-traumatic mortality and cardiopulmonary death rates [4-6]. While much of the attention paid to ozone tracking, modeling, and reduction has focused on outdoor ozone, approximately 40-60% of population exposure to ozone of outdoor origin occurs indoors [7]. In addition, many sources of ozone exist indoors, including laser printers, photocopiers, and ion generators [8-11]. The indoor contribution to ozone exposure is probably greater for vulnerable populations, e.g., infants, elderly, and chronically ill, due to the greater average amount of time they spend indoors [7,12-13].

Ozone reacts with numerous chemicals in indoor environments. These reactions lead to the formation of oxidized reaction products, which can be toxic, irritating to mucosal membranes and other tissues, and harmful to indoor materials [14]. At low building air exchange rates the time for these reactions to occur and the residence times of reaction products increase [15]. Consequently, cumulative molar intake of ozone byproducts can be as high as twice the intake of unreacted ozone [7], and therefore decreases in indoor ozone concentrations are an important part of reducing total population exposure to both ozone and ozone reaction products. Interestingly, there have only been a few studies on sensory evaluations related to the effects of ozone reactions with interior building materials [16]; in particular, carpet exposed to ozone produced the

75

most negative effect on sensory perceptions compared to other building materials, including carpet not exposed to ozone.

Indoor ozone concentrations can be lowered by treating building intake air with activated carbon [17-18], using fibrous activated carbon filters in Heating, Ventilation, and Air Conditioning (HVAC) systems, or alternatively by strategically placing ozone-scavenging materials indoors [19]. The latter approach, i.e., application of passive removal materials (PRMs), should involve coverage of large surface areas, appear aesthetically acceptable, and not contribute appreciably to formation of ozone reaction products. The concept of passive removal of pollutants from indoor air was described two decades ago for removal of volatile organic compounds (VOCs) by Yu and Neretnieks [20].

Clay may be a promising PRM for ozone removal. It has the advantage of possible application over large interior surfaces, e.g., as a wall plaster. Lamble et al. [21] measured ozone reaction probabilities and reaction products for nineteen certified green building materials, and observed that a clay wall plaster had a relatively high reactivity with ozone and the lowest ozone-initiated reaction product emissions (secondary emissions). Furthermore, clay and other earthen materials have long-held acceptance as a building material for human habitation; 1/3 of the world's population now lives in earthen structures [22].

In this study we explored whether the clay wall plaster tested by Lamble et al. [21] can improve indoor air quality by lowering indoor ozone concentrations directly, as well as lowering the concentrations of oxidized reaction products due to lower ozone availability to react with a carpet. This was accomplished by surveying perceived air quality (PAQ) during single-blind experiments, and quantifying concentrations of ozone, six $C_5$-$C_{10}$ aliphatic aldehydes and two aromatic aldehydes inside walk-in chambers containing combinations of carpet and clay wall plaster in the presence and absence of ozone.

**MATERIALS AND METHODS**

**Experimental Chambers**

Experiments were performed in 30 m³ stainless-steel chambers illustrated in Figure A1 and described in detail by Albrechtsen [23]. Identical 2-m high, low-emitting laminated wood partitions were positioned in each chamber to block the materials from the view of panelists. The floor of each chamber was marked so that panelists stood at the same location in each chamber across all PAQ assessments. Each chamber was equipped with a piston flow type ventilation and recirculation system. Outdoor air filtered through HEPA and carbon filters provided an air exchange rate of 1.5 per hour as calibrated previously using tracer gas. Air was introduced through perforations in the floor and exhausted through four piston-type vents in the ceiling. To overcome the unmixed air distribution typical of displacement ventilation systems, an oscillating fan was installed behind the partitions to promote good mixing throughout each chamber, and to allow air contact with the material surfaces. The doors to the chambers were equipped with a pressurized seal. Temperature and relative humidity were maintained at $23 \pm 0.1°C$ and $33 \pm 5\%$, respectively.
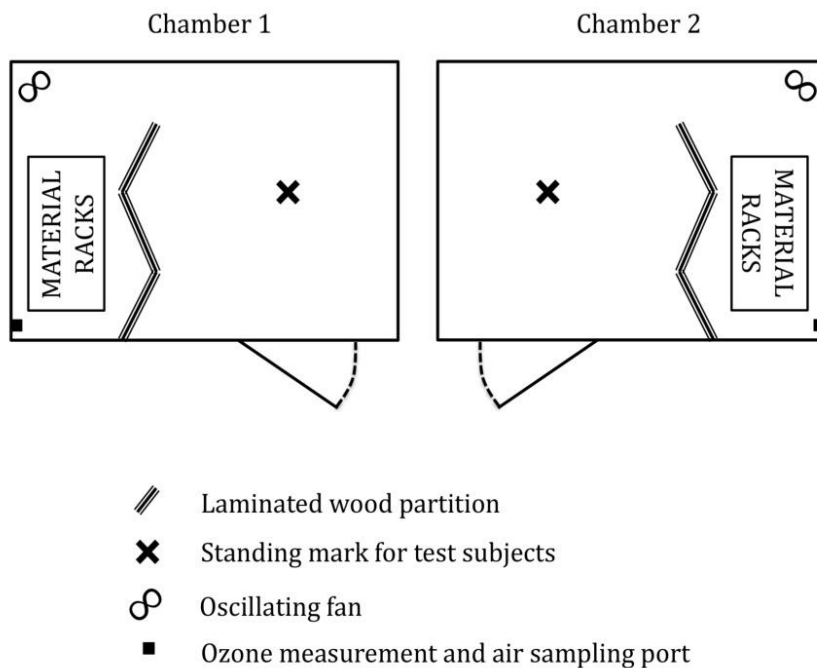


**Figure A1.** Layout of test chambers

**Materials**

Carpet (wall-to-wall nylon loop-fiber carpet with an attached 3 mm urethane foam backing) was purchased from a distributor in Denmark and aired out in a separate chamber for three weeks prior to experiments. Gloves were worn when handling the materials in order to prevent soiling with skin oils. Two equal-size pieces of carpet were stapled back to back with the exposed edges covered with aluminum tape, and hung vertically on two metal racks – one for each chamber.

A commercially available plaster consisting of a proprietary blend of clay (50% kaolin, < 50% fire clay, ~1.7% Montmorillonite) and crushed marble (aggregate size: 1000-5 μm) was used for this study; this was the same product used by Lamble et al. [21]. One-half of the clay plaster was prepared and applied to paper-backed gypsum wallboard at The University of Texas at Austin (UT) two months prior to experiments, and the other half was prepared at the Danish Technical University (DTU) one week prior to experiments. Both sides of the wallboard were covered with the clay plaster, and 30 cm x 30 cm samples were cut and hung vertically on two metal racks.

Preliminary calculations were completed to establish carpet and clay areas that would represent reasonable surface-to-volume ratios of each material in a room and that would increase secondary reaction products from carpet to measurable concentrations, based on ozone reaction probabilities and product yields provided in the published literature, e.g., [24-28]. The total areas of carpet and clay on each rack were 14 m$^2$ and 10.6 m$^2$, respectively, which approximate a room with a carpeted floor and only one wall plastered with clay.

**Ozone Generation and Measurement**

Ozone in each chamber was generated using UV-based ozone generators fed with pure oxygen (Airgas Inc.) and injected into the chamber recirculation ducts. Ozone generators were previously described by Weschler et al. [29]. Ozone concentrations in the chambers were measured using a UV absorbance ozone monitor (Model 205, 2B Technologies) with accuracy being the greater of +/- 1 ppb or 2% of the instrument

reading. The ozone injection rate was set such that the steady-state ozone concentration was approximately 80 ppb in an empty chamber without materials (see Figure A3).

**Air Sample Collection and Analysis**

Immediately before panelists arrived on a given day, air samples were collected through ports in the chamber walls to be analyzed for $C_5$ to $C_{10}$ n-aldehydes, benzaldehyde and tolualdehyde. These aldehydes are commonly observed reaction products of ozone with carpet [27-28,30], are themselves odorous, and also act as an indicator for a broader set of irritating oxidized products generated at surfaces, such as unsaturated aldehydes [27], dicarbonyls, and carboxylic acids [29]. The samples were collected on large-volume glass gas chromatography injection liners (SISS, open liners, tapered, frit, 3 mm I.D.) containing Tenax-TA (Supelco Inc., 80/100 mesh). A flow rate of $48 \pm 3$ ml min$^{-1}$ was drawn through the sorbent tubes by sampling pumps (model VSS-1, A.P. Buck Inc.) with low flow adapters that were calibrated using a bubble flow meter before each sample run. Ozone scrubbers (Supelco, LpDNPH, 505285) were used when sampling ozonated air to avoid sampling artifacts. Prior to and after sampling, sorbent tubes were kept in individual, sealed stainless-steel holders and stored in a refrigerated glass jar lined with strips of activated carbon mat. At the end of the experimental program the jar was packed in ice and shipped to UT for analysis. Recoveries on sorbent tubes were greater than 90% on standards spiked with known masses of hexanal and decanal prior to shipping.

Sorbent tubes were analyzed using zero-path thermal desorption with a programmable large-volume injector (ATAS Optic 2) followed by gas chromatography (Agilent 6890) with flame ionization detection (TD/GC/FID). The gas chromatograph was equipped with a RESTEK, Rxi-5Sil MS capillary column (30 m, 0.25 mm ID; 0.5 μm film thickness). A 15:1 split ratio in the injector was used for GC analyses. The injector temperature was ramped at 10˚C/sec from an initial temperature of 60˚C to 305˚C for a 20.67-minute desorption process. The oven temperature program was as follows: initial temperature of 50˚C for two minutes, ramp at 15˚C/min to 300˚C, and

79

hold at 300°C for two minutes. The GC/FID was calibrated using a five-point external calibration curve ($R2 > 0.99$) for each individual compound. The stock solutions for calibration contained pure chemicals purchased from Fisher Scientific, Inc. (pentanal, 97%, hexanal, 98%, heptanal, 95%, octanal, 99%, nonanal, 95%, decanal, 98%, benzaldehyde, 99%, tolualdehyde, 97%) dissolved in methanol (CHROMASOLV®, ≥ 99.9%). A calibration standard was prepared with high-purity methanol. A 2-μL volume of standard solution was drawn using a glass syringe and injected into a sorbent tube followed by a 20-minute $N_2$ (Airgas Inc.) purge prior to analysis. One standard and one blank sorbent tube were analyzed on each of the two days on which sample analysis occurred. None of the eight compounds were detected on the blank tubes. Lower detection limits (LDLs) were determined following EPA TO-17 protocol by which seven replicate samples near expected detection limits were analyzed [31]. LDL values for all compounds were below 0.5 ppb, in accordance with EPA TO-17.

Prior to experiments the packed glass liners were conditioned using a 200 mL min$^{-1}$ flow of $N_2$ at 330°C for 2 hours in a gas chromatograph oven (Hewlett-Packard 5890). Ozone scrubbers were conditioned in the gas chromatograph oven using a 200 mL min-1 flow of $N_2$ at 60°C for 24 hours. The flow rate of the sampling pumps and sample volume had been previously verified during breakthrough tests for all eight compounds by passing known volumes of fixed concentrations in air from a Tedlar bag (SKC Inc.) through two sorbent tubes in series.

**Perceived Air Quality Assessment**

A panel of 24 human subjects (12 males, 12 females), several of whom had previous experience participating in perception studies, was recruited among students at the Danish Technical University (DTU); the subjects were paid for participation. Prior to the study, panelists were instructed to refrain from wearing strongly scented products (e.g. perfume, deodorant, aftershave, etc.) in the facilities, and from drinking coffee or eating garlic or spicy foods on the days of the surveys in order to not disturb conditions in the chambers. On average, 20 panelists participated each day. The panelists made only

two assessments of air quality in the chambers each day. Each panelist was instructed to individually enter a chamber, immediately approach the mark on the floor, breathe the air, make the assessment, and leave the chamber, the entire stay in the chamber taking no more than 10-15 seconds and 4 to 5 minutes in total for each person during the 120-minute assessment session allotted to the entire group of subjects each day. The time for opening and closing the doors and the time each panelist spent inside the chambers was minimized in order to keep conditions as undisturbed as possible and to obtain first impression assessments. The subjects assessed whether the air quality was acceptable or not on a continuous scale (Figure A2), which after the measurements was coded as follows: "clearly unacceptable" = -1, "just unacceptable/just acceptable" = 0, and "clearly acceptable" = 1 [32]. The procedure of measurements was similar to that described in ASHRAE Standard 62 [33] except that the scale for assessment was continuous and not dichotomous as prescribed by the Standard. After completing the first assessment in a chamber, the panelist returned to the designated waiting area, which was a well-ventilated room at similar temperature and relative humidity as in the chambers, for five minutes in order to refresh the olfactory senses. Panelists were not allowed to discuss their assessments with each other. The panelist was then led individually into the other chamber where the assessment procedure was repeated exactly as in the former chamber. The sequence of entering chambers was random for all panelists; on some days a panelist would make the first assessment in chamber 1 and the second assessment in chamber 2, and on other days the panelist would make the first assessment in chamber 2 and the second assessment in chamber 1. Chamber doors were closed and sealed both during and between assessments. The minimum time between assessments in each chamber was 2-3 minutes.
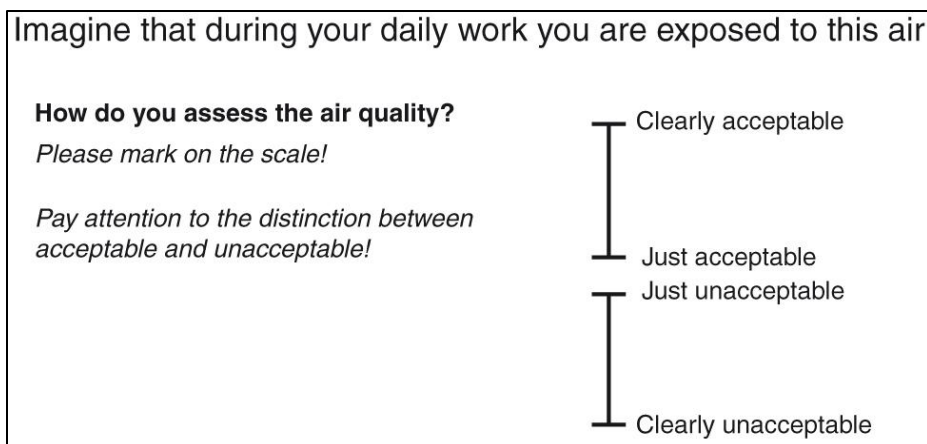
**Figure A2.** Perceived air quality assessment scale.

**Experimental plan**

Panelists were exposed to all combinations of ozone, carpet, and clay using a cross-over design, i.e., each condition was completed in each of two chambers on consecutive days (Table A1). The first two days considered the impact of ozone on background conditions in the chambers; the effect of adding clay to carpet and ozone was tested on days 3 and 4; the addition of clay to carpet without ozone present was tested on days 5 and 6; and the effect of ozone addition to a chamber containing only clay was studied on days 7 and 8. The cross-over design used in these experiments is a robust method that allowed for repetition of each condition on consecutive days in different chambers, and it enabled control for potential external factors disturbing the experiments, as well as possible differences in the performance of the twin chambers.

**Table A1.** Configurations of experimental chambers.

| Day | Chamber 1 | Chamber 2 | n[1] |
|-----|-----------|-----------|---|
| 1 | Background + Ozone | Background | 23 |
| 2 | Background | Background + Ozone | 19 |
| 3 | Carpet + Ozone | Carpet + Clay + Ozone | 21 |
| 4 | Carpet + Clay + Ozone | Carpet + Ozone | 20 |
| 5 | Carpet | Carpet + Clay | 18 |
| 6 | Carpet + Clay | Carpet | 19 |
| 7 | Clay | Clay + Ozone | 21 |
| 8 | Clay + Ozone | Clay | 20 |

[1] n = number of panelists

Materials were placed in the chambers the day before each experiment and the chambers were continuously ventilated overnight. In the morning, if necessary, ozone generator(s) were switched on at 8 a.m. and the chambers remained sealed until 12 p.m., when the first panelists arrived. This period allowed enough time to achieve a steady-state ozone concentration in the chambers given an air change rate of 1.5 hr$^{-1}$ (Figure A3). Air samples were collected from 11 a.m. to 12 p.m. The sensory assessments commenced at 12 p.m. and were completed by 2 p.m.
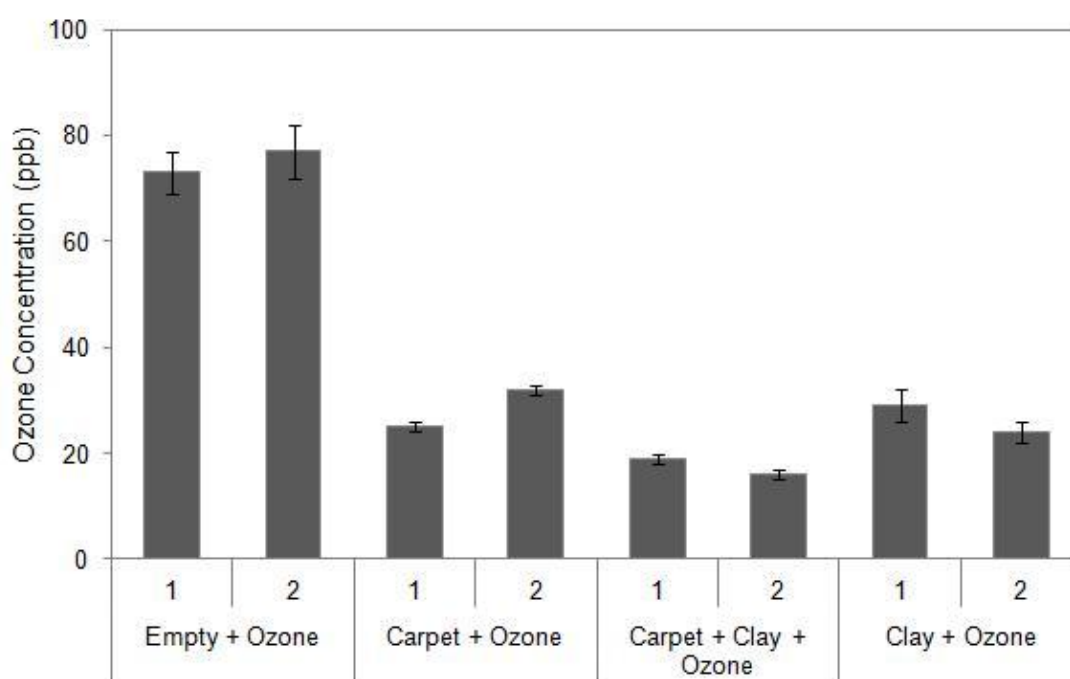


**Figure A3.** Steady-state ozone concentrations in chambers 1 and 2 during replicate experiments. Experiments during which no ozone was injected are omitted. Error bars denote standard deviations.

## RESULTS AND DISCUSSION

**Perceived Air Quality**

The results of all assessments of air quality made by the panelists are presented as box plots in Figure A4. As the ratings were not normally distributed, the box plots present the 25th percentile (box bottom), 75th percentile (box top), median (horizontal line inside the box), and minimum and maximum (lines extending outside the boxes) ratings of acceptability. Outliers were omitted from data analyses and were identified as ratings either 1.5×IQR less than the lower quartile or 1.5×IQR greater than the upper quartile, where IQR is the interquartile range. A non-parametric two-tailed Wilcoxon signed-rank test was used to examine whether the sensory assessments from the paired conditions on each day differed from one another using subjects as their own controls. Because we used a non-parametric test, we first compared the assessments taken on the same day and then combined p-values of replicate days (except for days 1 and 2, see following section) using Fisher's Method [33] to yield an overall estimate of the statistical significance for each of the four different pairs of conditions. The addition of clay on days 3 and 4 in chambers containing ozone and carpet significantly improved PAQ (p = 0.017), while addition of ozone on days 7 and 8 to chambers containing clay significantly reduced PAQ (p = 0.0001). The assessments of PAQ were not significantly different when ozone was added to the empty chamber (day 1, p = 0.971) or when clay was added to the chamber containing carpet in the absence of ozone (days 5 and 6, p = 0.138).

Figure A4 shows a great deal of variation in sensory assessments within each experimental condition and between the same conditions created in different chambers. There were also some differences in the repeated assessments of the same conditions over two days (days 1-2 and days 5-6). Reasons for these differences could not be ascertained.
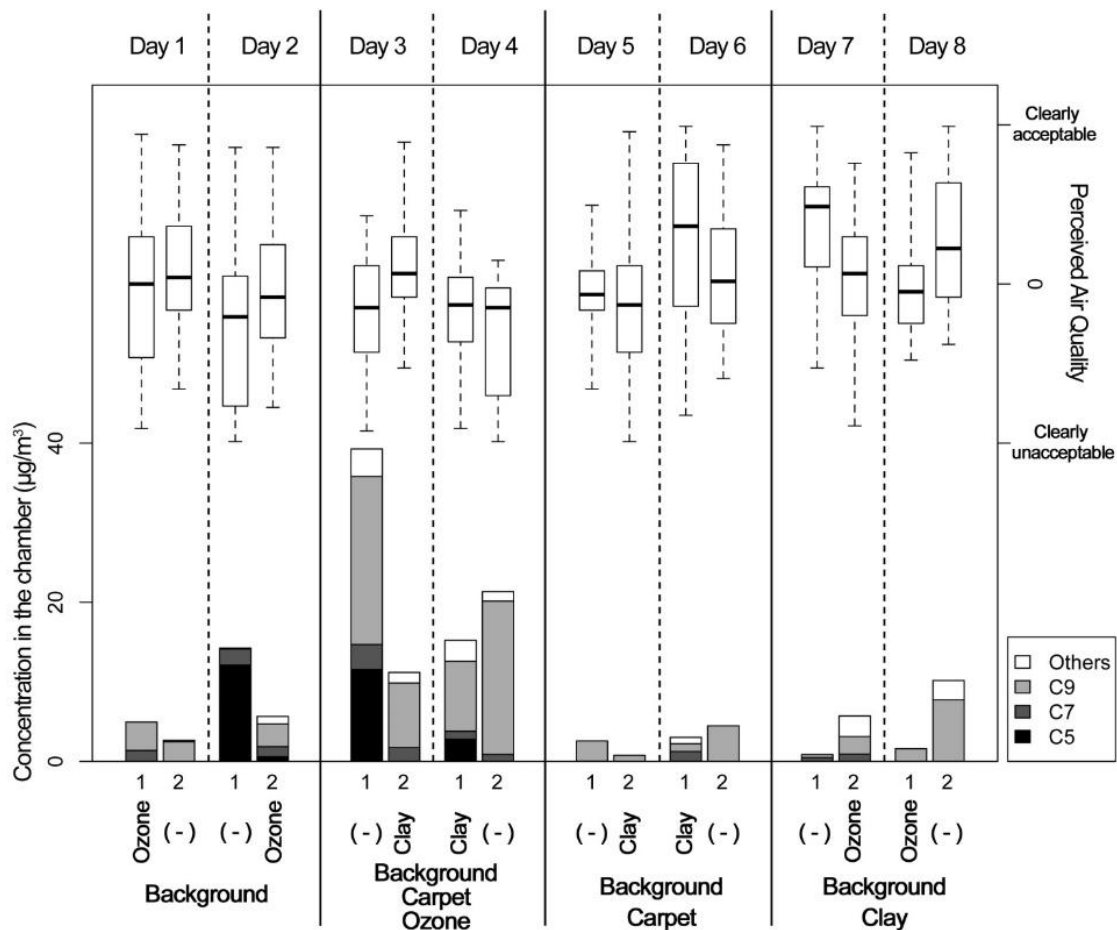
**Figure A4.** Perceived air quality and related aldehyde concentrations in test chambers (BA = benzaldehyde, TA = *o*-tolualdehyde).

### Byproduct Concentrations

Aldehyde concentrations measured prior to sensory assessments are also shown in Figure A4. The dominant pollutant in chamber air was nonanal ($C_9$). Pentanal ($C_5$) and heptanal ($C_7$) were also frequently detected. The conditions with the lowest summed aldehyde concentrations on average were carpet with or without clay (no ozone) on days 5 and 6, and clay with or without ozone on days 7 and 8. The highest concentrations of aldehydes were observed in the chambers containing ozone and carpet on days 3 and 4. When clay was added to chambers containing carpet and ozone, the total aldehyde concentrations decreased, most notably on day 3 (72% decrease) and on day 4 (29%

decrease). Although the clay plaster individually reduced ozone in the chambers just as effectively as the carpet (Figure A3), the clay plaster emitted fewer aldehydes than did the carpet upon ozone exposure. Further discussion of ozone removal by the clay plaster is provided as supplementary material. The mean total aldehyde concentration in the chamber for clay and ozone was nine times lower than that in the chamber with carpet and ozone.

Median PAQ assessments were, in general, lower when total heavy aldehyde concentrations increased, a trend similar to that observed by others, e.g., [35]. For example, on day 3 chamber 1 had a higher aldehyde concentration and lower median PAQ than those for chamber 2. All experimental days exhibited this trend except for day 8, in which both higher aldehyde concentrations and median PAQ were observed for the chamber containing only clay compared to the chamber containing clay and ozone. We were unable to ascertain a reason for this anomaly.

In the chamber containing neither ozone nor materials on day 2 the total measured byproduct concentration was greater than the concentration in the adjacent chamber that contained approximately 80 ppb ozone, primarily due to a relatively high concentration of pentanal in the chamber without ozone. However, the absolute difference in summed $C_5$ to $C_{10}$ aldehydes between the two chambers was only 8.6 µg m$^{-3}$, i.e., a few ppb. The median acceptability of PAQ for the ozonated chamber was also greater than that for the chamber without ozone on day 2. While only one experiment, it is interesting that the small increase in carbonyls in the non-ozonated chamber 1 may have led to a less acceptable PAQ than in the chamber with a far greater ozone concentration (chamber 2). However, it is possible that the contrasting PAQ results between days 1 and 2 were due to a malfunctioning door to chamber 1 on day 2; thus, PAQ data from day 2 were omitted from statistical analysis. Shortly after panelists began arriving to assess air quality the door to chamber 1 would not seal properly, which became obvious to panelists and thus might have affected individual PAQ. This incident did not affect the concentrations of byproducts measured in chamber 1, as sampling occurred before the malfunction. The

door was repaired after the experiment and sealed properly during all subsequent experiments.

On day 3, when carpet and ozone were compared with carpet, ozone, and clay, PAQ trends agreed well with the byproduct concentrations in both chambers; the air in the chamber with additional clay and fewer byproducts was rated more acceptable than that in the chamber with only carpet and ozone, which also had the highest overall measured byproduct concentration. The two cases in which a chamber contained only carpet and ozone not only had the highest byproduct concentrations, but also the lowest median PAQs. Carpet has been associated with sick building syndrome (SBS) cases in office environments [34-35]. Furthermore, relatively high emissions of secondary aldehydes and other carbonyls have been observed following the exposure of carpet to ozone [27-28,37].

Air samples were collected prior to the arrival of panelists in order to avoid adverse perceptions associated with the noise of sampling pumps and the sample train. For this reason, samples did not capture products associated with ozone reactions with human skin oils and clothing during the sensory assessments, e.g., [29,37-39]. This is potentially relevant for the eight scenarios in which ozone was injected into the chambers. However, the short amount of collective time that panelists spent in the chambers (10-15 seconds as indicated in the Methods section) should have minimized any effects of ozone reactions with panelists themselves. While the door to each chamber was opened briefly as each panelist entered and exited the chamber, the ozone concentration in chamber air did not vary appreciably during experiments. The coefficient of variation of the ozone concentration varied from 0.04 to 0.09 across all experiments involving ozone injection, and there was no consistent trend in terms of increasing or decreasing ozone concentration across experiments. This suggests that the conditions in the chambers were not substantially disturbed by the subjects entering or being present inside the chambers during assessments.

**Gender Effects**

Male and female PAQ results were also analyzed (Figure A5). Female assessments exhibited greater differences between the two conditions on a given day and greater negative PAQ scores. In general, males perceived less of a difference in air quality between conditions on a given day, whereas females clearly preferred some conditions to others. Overall, males were also more satisfied/less dissatisfied with the air quality, and collectively exhibited smaller ranges of PAQ on most days. In contrast, females were more often dissatisfied with the air quality, especially for the carpet-ozone combination. Females were most satisfied when clay was present with or without ozone (days 7 & 8). These results are consistent with observations that females are more sensitive than males to some odors [40]. Several researchers have preferentially recruited female subjects for PAQ studies for this reason [34,41].
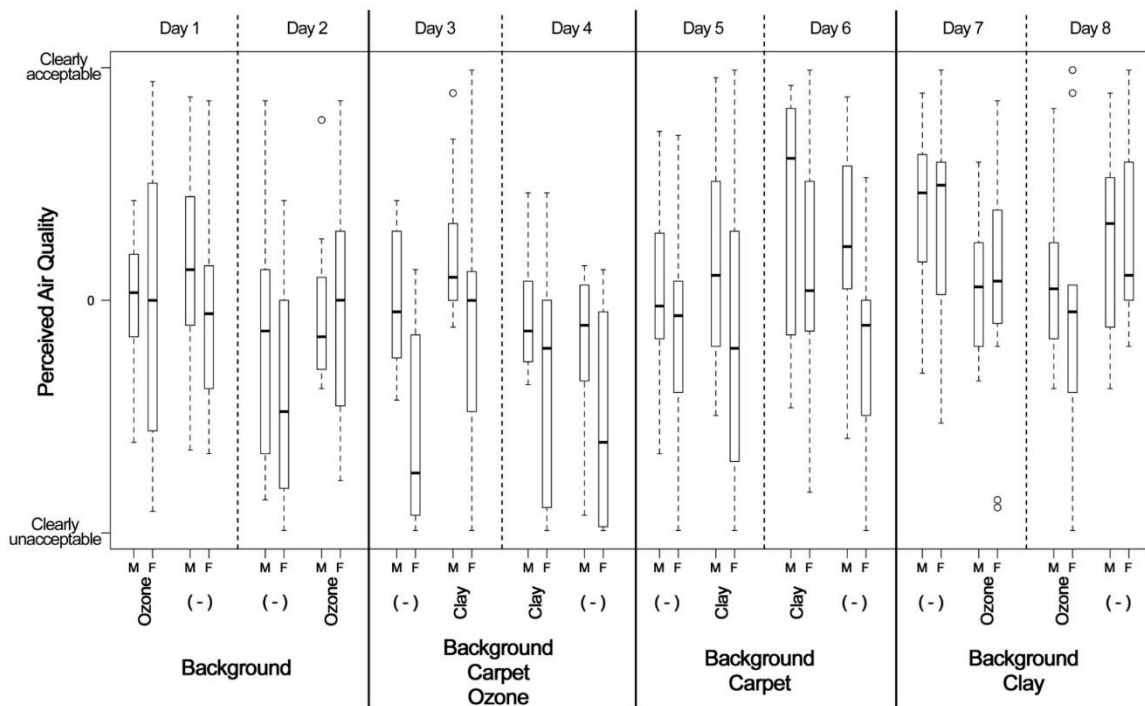


**Figure A5.** Comparison of male (M) and female (F) PAQ assessments. Circles indicate outliers.

## SUMMARY AND CONCLUSIONS

88

Human panelists were exposed to various combinations of ozone, carpet, and clay wall coverings inside test chambers, and were asked to assess perceived air quality (PAQ). Ozone, $C_5$ to $C_{10}$ saturated n-aldehydes, and two aromatic aldehydes were also measured to characterize chamber air. Based on the results of this study, we conclude:

1. Reactions of ozone with carpet are associated with low PAQ,
2. Clay wall coverings can improve PAQ, particularly in the presence of ozone or ozone and carpet,
3. There are gender differences in PAQ for air exposed to carpet and/or clay in the presence or absence of ozone; females were more sensitive to differences in test conditions and are more inclined toward unacceptable rankings.

Additional research is needed to confirm the results presented herein with a broader base of panelists performing repeated assessments and with longer exposure times that would allow for (1) extended PAQ and productivity assessments, and (2) relationships between PAQ and the presence of ozone reaction products. Field tests involving the performance of clay as an air purifier are needed over extended time periods. Additional passive removal materials should also be explored through systematic screening in small chambers, panel assessments and proof-of-concept field studies.

**ACKNOWLEDGEMENTS**

**REFERENCES**

[1] Mudway IS, Kelly, FJ. Ozone and the lung: a sensitive issue. Mol Aspects Med 2000;21:1-48.

[2] Levy JI, Corrothers TJ., Tuomisto JT, Hammitt JK, Evans JS. Assessing the public health benefits of reduced ozone concentrations. Environ. Health Persp 2001;109:1215-26.

[3] Triche EW, Gent JF, Holford TR, Belanger K, Beckett WS, Naeher L, et al. Low-level ozone exposure and respiratory symptoms in infants. Environ Health Persp 2006;114: 911-6.

[4] Bell ML, Dominici F, Samet JM. A meta-analysis of time-series studies of ozone and mortality with comparison to the national morbidity, mortality, and air pollution study. Epidemiology 2005;16:436-45.

[5] Bell ML, Peng RD, Dominici F. The exposure-response curve for ozone and risk or mortality and the adequacy of current ozone regulations. Environ Health Persp 2006;114: 532-6.

[6] Jackson JE, Yost MG, Karr C, Fitzpatrick C, Lamb BK, Chung SH, et al. Public health impacts of climate change in Washington State: projected mortality risks due to heat events and air pollution. Climatic Change 2010;102:159-86.

[7] Weschler CJ. Ozone's impact on public health: contributions from indoor exposures to ozone and products of ozone-initiated chemistry. Environ Health Persp 2006;114:1489-96.

[8] Britigan N, Alshawa A, Nizkorodov SA. Quantification of ozone levels in indoor environments generated by ionization and ozonolysis air purifiers. J Air Waste Manage Assoc 2006;56:601-10.

[9] Destaillats H, Maddalena RL, Singer BC, Hodgson AT, McKone TE. Indoor pollutants emitted by office equipment. A review of reported data and information needs. Atmos Environ 2008;42:1371-88

[10] Lee SC, Lam S, Fai HK. Characterization of VOCs, ozone, and PM10 emissions from office equipment in an environmental chamber. Build Environ 2001;36:837-42.

[11] Waring MS, Siegel JA, Corsi RL. Ultrafine particle removal and generation by portable air cleaners. Atmos Environ 2008;42:5003-14.

[12] Simoni M, Biavati P, Carrozzi L, Viegi G, Paoletti P, Matteucci G, et al. The Po River Delta (North Italy) indoor epidemiological study: home characteristics, indoor pollutants, and subjects' daily activity pattern. Indoor Air 1998;8:70-9.

[13] Williams R, Creason J, Zweidinger R, Watts R, Sheldon L, Shy C. Indoor, outdoor, and personal exposure monitoring of particulate air pollution: the Baltimore elderly epidemiology-exposure pilot study. Atmos Environ 2000;34:4193-4204.

[14] Weschler C. Ozone in indoor environments: concentration and chemistry. Indoor Air 2000;10:269-88.

[15] Sarwar G, Corsi R, Allen D, Weschler C. The significance of secondary organic aerosol formation ang growth in buildings: experimental and computational evidence. Atmos Environ 2003;37:1365-81.

[16] Knudsen HN, Nielsen PA, Clausen PA, Wilkins CK, Wolkoff P. Sensory evaluation of emissions from selected building products exposed to ozone. Indoor Air 2003;13:223-31.

[17] Shair FH. Relating indoor pollutant concentrations of ozone and sulfur dioxide to those outside: economic reduction of indoor ozone through selective filtration of the make-up air. ASHRAE Tran 1981;1:116-39.

[18] Shields HC, Weschler CJ, Naik D. Ozone removal by charcoal filters after continuous extensive use (5 to 8 years). Proceedings of the 8th International Conference on Indoor Air Quality and Climate, Indoor Air 1999, 4. Edinburgh.

[19] Kunkel DA, Gall ET, Siegel JA, Novoselac A, Morrison GC, Corsi RL. Passive reduction of human exposure to indoor ozone. Building and Environment 2010;45:445-52.

[20] Yu J-W, Neretnieks I. The effect of a passive adsorption sheet on reducing organic pollutants in indoor air. Indoor Air 1993;3:12-9.

[21] Lamble S, Morrison G, Corsi R. Passive air cleaning with green buildings materials: ozone deposition velocities. Proceedings of the 12th International Conference on Indoor Air Quality and Climate, Indoor Air 2011. Austin.

[22] Minke G. Building with earth: Design and technology of a sustainable architecture. Basel, Switzerland: Birkhauser; 2006.

[23] Albrechtsen, O. (1988). Twin climatic chambers to study sick and healthy buildings. Proceedings of Healthy Buildings, 3, pp. 25-30. Stockholm.

[24] Coleman BK, Destaillats H, Hodgson AT, Nazaroff W. Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. Atmospheric Environment 2008;42:642-54.

[25] Wang H, Morrison G. Ozone surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends. Indoor Air 2010;20:224-34.

[26] Morrison GC, Nazaroff WW. The rate of ozone uptake on carpets: experimental studies. Environ Sci Technol 2000;34:4963-68.

[27] Morrison GC, Nazaroff WW. Ozone interactions with carpet: secondary emissions of aldehydes. Environ Sci Technol 2002;36:2185-92.

[28] Cros CJ, Morrison GC, Siegel JA, Corsi RL. Long-term performance of passive materials for removal of ozone from indoor air. Indoor Air 2012;22:43-53.

[29] Weschler CJ, Wisthaler A, Cowlin S, Tamás G, Strøm-Tejsen P, Hodgson AT, et al. Ozone-initiated chemistry in an occupied simulated aircraft cabin. Environ Sci Technol 2007;41:6177-84.

[30] Nicolas M, Ramalho O, Maupetit F. Reactions between ozone and building products: impact on primary and secondary emissions. Atmos Environ 2007 41:3129-38.

[31] USEPA Method TO-17. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. U.S. Environmental Protection Agency 1999 Cincinnati, USA.

[32] Kolarik J, Wargocki P. Can a photocatalytic air purifier be used to improve the perceived air quality indoors? Indoor Air 2010;20:255-62.

[33] ASHRAE Standard 62-2010. Ventilation for acceptable indoor air quality. American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc 2010 Atlanta, USA.

[34] Winer BJ. Statistical principles in experimental design. 2nd edition. New York: McGraw-Hill; 1971.

[35] Wargocki P, Wyon DP, Baik YK, Clausen G, Fanger PO. Perceived air quality, sick buildings syndrome (SBS) symptoms and productivity in an office with two difference pollution loads. Indoor Air 1999;9:165-79.

[36] Fisk WJ. Health and productivity gains from better indoor environments and their relationship with building energy efficiency. Annu Rev Energy Env 2000;25:537-66.

[37] Weschler CJ, Hodgson AT, Wooley JD. Indoor chemistry: ozone, volatile organic compounds, and carpets. Environ Sci Technol 1992;26:2371-77.

[38] Pandrangi L, Morrison GC. Ozone interations with human hair: ozone uptake rates and product formation. Atmos Environ 2009;42:5079-89.

[39] Wisthaler A, Weschler CJ. Reactions of ozone with human skin lipids: sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. P Natl Acad Sci USA 2009;107:6568-75.

[40] Doty RL, Cameron EL. Sex differences and reproductive hormone influences on human odor perception. Physiol Behav 2009;97:213-28.

[41] Bakó-Biró Z, Wargocki P, Weschler CJ, Fanger PO. Effects of pollution from personal computers on perceived air quality, SBS symptoms and productivity in offices. Indoor Air 2004;14:178-87.

---

**Field-to-lab analysis of clay wall coatings as passive removal materials for ozone in buildings[3]**

Erin Darling[1], Richard L. Corsi[1,*]

[1]University of Texas at Austin (UT)

*Corresponding email: corsi@mail.utexas.edu; phone: 1-512-471-3611; fax: 1-512-471-5870*

## ABSTRACT

Ozone reacts readily with many indoor materials, as well as compounds in indoor air. These reactions lead to lower indoor than outdoor ozone concentrations when outdoor air is the major contributor to indoor ozone. However, the products of indoor ozone reactions may be irritating or harmful to building occupants. While active technologies exist to reduce indoor ozone concentrations (i.e., in-duct filtration using activated carbon), they can be cost-prohibitive for some and/or infeasible for dwellings that do not have heating, ventilating, and air conditioning systems. In this study, the potential for passive reduction of indoor ozone by two different clay-based interior surface coatings was explored. These coatings were exposed to occupied residential indoor environments and tested bimonthly in environmental chambers for quantification of ozone reaction probabilities and reaction product emission rates over a six-month period. Results indicate that clay-based coatings may be effective as passive removal materials, with relatively low byproduct emission rates that decay rapidly within two months.

## KEYWORDS

*Paint, Plaster, Reaction probability, Indoor chemistry, Emissions*

## PRACTICAL IMPLICATIONS

---

[3] Paper 2 was submitted for publication to Indoor Air in April 2016

Recent studies suggest that indoor ozone can be problematic for respiratory health. It may be possible to reduce indoor ozone exposures through the use of passive removal materials that require little energy penalty. Two commercially-available clay-based interior coatings sustained relatively high ozone reactivity while placed in real residential indoor environments for six months. Clay coatings might provide for improved indoor air quality without the energy penalty associated with active control systems.

## INDOOR OZONE AND ITS REMOVAL

Ground-level ozone is a ubiquitous air pollutant that has been linked to several negative health effects on humans. Ozone reactions with tissue cells promote inflammation and increased permeability of the epithelial lining fluid, which allows for greater penetration of pollutants from lung air into the blood stream (Mudway and Kelly, 2000; Levy et al., 2001; USEPA, 2006). Increases in ambient ozone concentrations are associated with increases in respiratory-related morbidity and premature mortality (e.g., Bell et al., 2005; Gryparis et al., 2004; Ito et al., 2005; Jerrett et al., 2009; Parodi et al., 2005). Diagnoses of childhood asthma, increased school absences, and increased hospital emergency room visits among children and the elderly have all been linked to increased exposure to ozone (McConnell et al., 2002; Yang et al., 2003; Hubbell et al., 2005; Meng et al., 2010; Zheng et al., 2015).

While most ozone is generated outdoors, significant human inhalation exposure to ozone occurs indoors. For example, Chen et al. (2012) estimated an association between short-term mortality and indoor ozone exposure based on mass balance modeling and data from 90 cities. And despite the fact that indoor ozone concentrations are generally much lower than outdoor concentrations, Weschler (2006) estimated that 43-76% of exposure to ozone of outdoor origin occurs indoors. This level of exposure occurs because people in many developed countries spend almost 90% of their lives indoors (Klepeis et al., 2001; deCastro et al., 2007; Schweizer et al., 2007; Hussein et al., 2012).

Gas-phase, or homogeneous, reactions occur between ozone and some chemicals that are emitted to indoor air, e.g., alkenes emitted from building materials, furniture, and

numerous cleaning and consumer products, at reaction rates relevant to time scales of air exchange in buildings (Nazaroff and Weschler, 2004; Sarwar et al., 2004; Nazaroff et al., 2006; Singer et al., 2006; Coleman et al., 2008; Wisthaler and Weschler, 2010). These homogeneous reactions can produce secondary organic aerosols (SOAs) (Long et al., 2000; Wainman et al., 2000; Fan et al., 2003 and 2005; Destaillats et al., 2006; Rohr et al., 2003; Sarwar and Corsi, 2007; Sarwar et al., 2003 and 2004; Waring et al., 2011; Weschler and Shields, 1999), as well as a range of gaseous oxidized products (Weschler et al., 1992a; Weschler and Shields, 1996 and 1997; Hodgson et al., 2000; Sarwar et al., 2002; Atkinson and Arey, 2003; Fan et al., 2003; Destaillats et al., 2006; Park and Ikeda, 2006; Singer et al., 2006). Products of ozone reactions with compounds found in cleaning agents and air fresheners include hydroxyl radicals and other radical species, formaldehyde, acetaldehyde, $C_3$ to $C_{10}$ saturated and unsaturated aldehydes, light monoketones, dicarbonyls, mono- and di-carboxylic acids, and secondary organic aerosols (Nazaroff and Weschler, 2004).

Surface, or heterogeneous, reactions can occur on furniture, dust, building materials, and even human skin (e.g., Hyttinen et al., 2006; Tamas et al., 2006; Poppendieck et al., 2007b; Petrick and Dubowski, 2009; Wisthaler and Weschler, 2010; Gall et al., 2013). These reactions can produce $C_1$-$C_{10}$ carbonyls, dicarbonyls, and hydroxycarbonyls that may be irritating or harmful to building occupants (Cros et al., 2012; Lamble et al., 2011; Morrison and Nazaroff, 2002; Nicolas et al., 2007; Poppendieck et al., 2007a and 2007b; Wang and Morrison, 2006 and 2010; Wisthaler and Weschler, 2010; amongst others). Heterogeneous reactions involving terpenes such as *d*-limonene can also form SOAs (Waring and Siegel, 2013; Ourrad et al., 2015).

To reduce exposure to indoor ozone, active filtration methods, such as treating building intake or recirculated indoor air with activated carbon filters, have been shown to be effective (Shair, 1981; Shields et al., 1999; Bekö et al., 2008 and 2009; Lin and Chen, 2014; Aldred et al., 2015 and 2016). However, many households, even in developed countries, do not have heating, ventilating, and/or air conditioning (HVAC) systems that allow for in-duct activated carbon filtration. Furthermore, the additional

pressure drop through hybrid filters that remove particles and contain activated carbon requires an energy penalty and additional cost to consumers.

Passive removal materials (PRMs) are an alternative method for removing ozone from indoor environments, even in buildings without HVAC systems. The main characteristics of PRMs for indoor ozone removal are: (1) ozone removal without consuming energy, other than the embodied energy in the production and manufacture of the material, (2) sustained ozone removal over long time periods, (3) minimal reaction product formation, and (4) large surface area coverage while maintaining aesthetic appeal.

The use of PRMs for ozone removal indoors has been an interest of building environment researchers for several years (Kunkel et al., 2010; Lamble et al., 2011; Cros et al., 2012; Darling et al., 2012; Gall et al., 2013).  For example, a specific wall plaster comprised of clay with an accompanying tinting agent appears to be a promising PRM, with a relatively high ozone reaction probability and a molar yield for reaction products that was below the detection limit for all species (Lamble et al., 2011).  Darling et al. (2012) completed studies of the clay wall plaster described by Lamble et al. (2011). Perceived air quality (PAQ) was determined using a panel of human subjects exposed to eight combinations of a reactive pollutant source (carpet), the clay wall plaster applied to gypsum wallboard (GWB), and chamber air with and without ozone.  The addition of clay plaster when carpet and ozone were present resulted in significantly improved PAQ and lower aldehyde concentrations. Cros et al. (2012) studied the ozone removal performance of some of the materials tested by Lamble et al. (2011). They placed material specimens in actual buildings over a six-month period, periodically brought the specimens back to the laboratory to be tested in 48-L chambers, and measured changes in ozone deposition velocity and reaction product emissions before placement back in the field.

Following the work of Cros et al. (2012), the objective of this study is to determine ozone reaction probabilities and reaction byproduct molar yields for two

different clay-based interior surface coatings exposed to real indoor environments for a period of six months.

## MATERIALS AND METHODS

This study involved the placement of small specimens of clay coatings applied to gypsum wallboard (GWB) at multiple locations in two residences for six months. Intermittent analyses were completed in laboratory chambers to characterize ozone reaction metrics.

### Materials

A commercially-available clay-based interior paint as well as a clay-based plaster were studied. These two materials have been shown to reduce indoor ozone concentrations over short experimental time periods (e.g., up to 24 hours), and have also been shown to emit fewer reaction products (e.g., saturated aldehydes), as well as possibly adsorbing emissions from other building materials (Lamble et al., 2011; Darling et al., 2012).

The plaster used in this study consists of a proprietary blend of clay (50% kaolin, < 50% fire clay, ~ 1.7% montmorillonite) and crushed marble (aggregate size: 5-1000 μm). It can be mixed with pigment that is made of naturally occurring mineral oxides, specifically iron oxide (< 70% by weight), magnesium silicate (< 12%), magnesite (< 0.2%), crystalline silica (< 2.8%), and other unspecified substances deemed non-hazardous by the manufacturer (< 20%). A primer made for the clay plaster was also used in this study. The primer contains water, pumice, calcined kaolin, calcium carbonate, a proprietary acrylic copolymer, and sand. The sand helps the clay bond to smooth surfaces, such as the GWB that it was applied to in this study. A package of pre-mixed clay plaster and pigment in powder form, and the sanded primer, were ordered from a company that sells eco-friendly building supplies.

The paint is produced by a different company than the plaster, comes in liquid form, is self-priming, and requires no extra mixing.  Ingredients in the paint include

water, clay (type unspecified), chalk, porcelain clay, cellulose, "alcohol ester" (as a binder), and a preservative (compound(s) unspecified). The product is also labeled as not containing solvents and having zero VOCs. The paint was ordered directly from the manufacturer.

Each type of coating was applied to square specimens of new GWB that were cut to an average top area of 206 cm$^2$. Seven plaster and eight paint specimens were prepared. To prepare the plaster for application, the sanded primer was first applied to the drywall and allowed to dry for six hours as per product instructions. The clay-pigment powder was mixed with water (237 mL into a 0.9-kg bag of powder), then applied with a trowel to the dry layer of sanded primer. The first layer of plaster was allowed to dry over night before application of a second layer. Once the second layer was applied, the specimen was allowed to air dry for 24 hours before handling for further preparation. The paint specimens were prepared similarly, but without priming. After the specimens dried, the sides and backings were covered with aluminum foil to restrict exposure of these surfaces to ozone and indoor pollutants.

### Field Locations

Approximately one week after paint or plaster application to the GWB, the 15 specimens were each placed in one of five dedicated field locations in Austin, Texas, as listed in Table 1. Three of the locations were in an apartment: a living room, a kitchen, and a bedroom. Two of the locations were in a single-family detached home: a living room and a bedroom. Images of the specimens at each location are presented in Appendix E (Figure E1). During this study, the apartment was occupied by two adults, and the house was occupied by two adults as well as two dogs that lived both inside and outside. Prior to the deployment of the specimens to field locations, new carpet had recently been installed throughout the apartment, and solid wood flooring had just been installed throughout most of the house except for in the bedroom. Both residences had central air conditioning.

Each specimen was supported on a smooth chrome display stand while it was in the field to keep it nearly vertical (Figure E2 in Appendix E). A portable temperature and relative humidity (RH) analyzer and data logger (Onset® HOBO®) was placed near each set of specimens to record data throughout the experimental program (see Table B1 for summary).

**Table B9.** Field locations, conditions, and specimen allocation.

| Building Type | Room Type | Building Age (years) | Bimonthly Average Range | | Number of Specimens | |
|---|---|---|---|---|---|---|
| | | | Temperature (°C) | RH (%) | Clay Paint | Clay Plaster |
| Apartment | Living Room | 32 | 21-25 | 47-52 | 2 | 1 |
| Apartment | Kitchen | 32 | 23-24 | 46-52 | 1 | 2 |
| Apartment | Bedroom | 32 | 23-24 | 47-50 | 2 | 1 |
| House | Living Room | 19 | 20-25 | 45-51 | 1 | 2 |
| House | Bedroom | 19 | 19-24 | 49-55 | 2 | 1 |

### Experimental Chambers

The specimens were tested in a system of three 10-L stainless steel chambers (Figure 8) connected to a UV ozone generator (Perma Pure Zero-Air™, Model ZA-750-10). Laboratory air was supplied to the system using a compression pump (Thomas, Model 607CA220) after passing through one Teflon® perfluoroalkoxy (PFA) filter tube packed with activated carbon (AC) cloth to prevent compounds in lab air from reacting with ozone in the system and to remove transients in ozone concentrations in lab air. A portion of the air passed through the ozone generator, while a bypass line connected to a ball valve allowed more or less of the air to flow through the ozone generator to adjust the concentration. The air then split two ways: to the inlet ozone sample line and to a three-way split that led to three mass flow controllers (MFCs) (Aalborg GCF17), and finally to the chamber inlet lines. Inlet air was directed to the surface of the specimen through a stainless steel tube that extended from the center of the chamber lid down into the chamber two to three centimeters from the surface of the specimen. Chamber air exhausted through Teflon® PFA tubing fitted to the exterior of the chamber lid. All

tubing in the system was flexible ¼-in OD PFA, and tube fittings and valves were either PFA or stainless steel (Swagelok). The entire system was placed in a walk-in fume hood.

The volumetric flow rates through the mass flow controllers were measured using a bubble flow meter (Gillian® Gilibrator 2 with 20-6,000 mL/min sampling cell) at the beginning and end of each experiment. Inlet and chamber ozone concentrations were monitored with a UV-absorbance ozone monitor (2B Technologies, Model 202). The collective inlet line and the outlet lines from the chambers could be manually opened or closed to the ozone monitor by adjustment of PFA plug valves. System air was exhausted through another Teflon filter packed with activated carbon and then fed toward the vent of the walk-in hood. The relative humidity and temperature of the chamber air were also monitored (TSI® QTrak).

The mean (± standard deviation) experimental conditions in the test chambers throughout the six-month test program were as follows: $1043 \pm 17$ ml min$^{-1}$ inlet flowrate through each chamber (average air exchange rate [AER] $= 6.4 \pm 0.1$ h$^{-1}$), $24 \pm 0.5$ °C air temperature, $47 \pm 9\%$ RH,  and $225 \pm 22$ ppb inlet ozone concentration when the ozone generator was switched on. The mean ozone concentrations in the chambers when paint or plaster specimens were inside were $21 \pm 9$ ppb and $32 \pm 10$ ppb, respectively, realistic concentrations in many indoor environments.
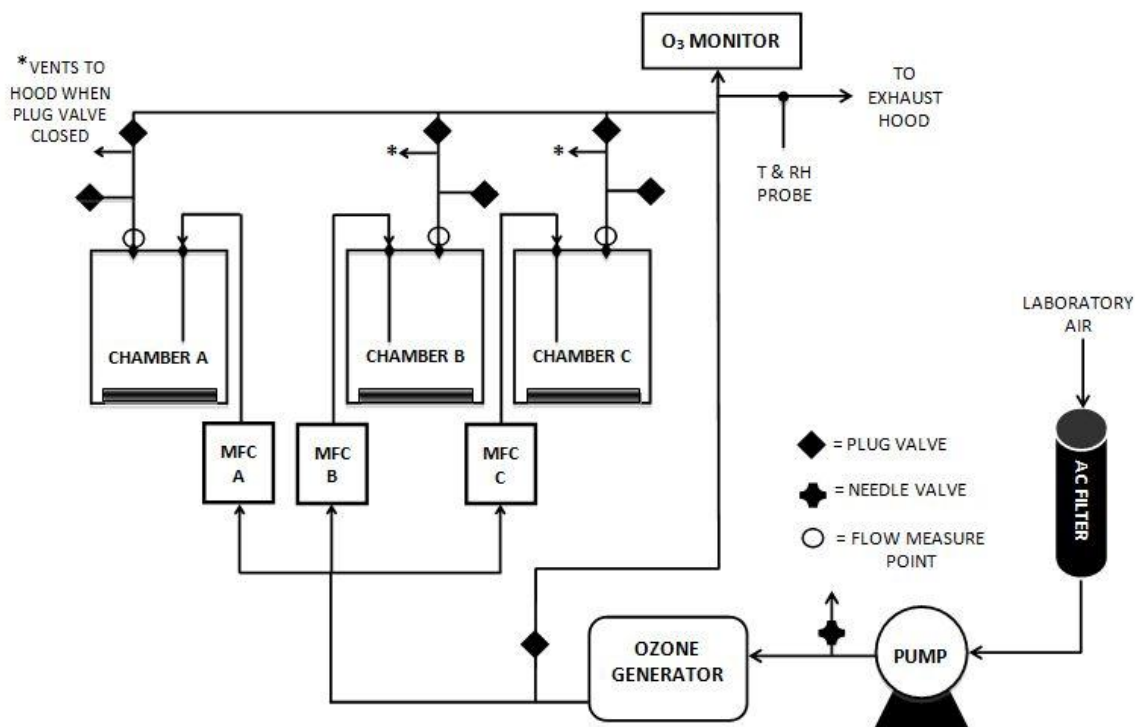
**Figure B15.** Environmental chamber system for testing specimens in the laboratory.

### Analytical Protocol

Paint and plaster specimens were tested in the laboratory chambers three days after preparation to measure ozone reaction probabilities and emission rates of $C_5$-$C_{10}$ saturated n-aldehydes before placement in the field. This test is referred to as Month 0. Specimens were then transferred to each of the five aforementioned field locations (Table B1).

Every two months after Month 0, the specimens were taken back to the laboratory for analysis in the chambers. To transport the material specimens between field locations and the lab, each specimen was individually wrapped in aluminum foil and placed in a plastic box. Each material specimen was unwrapped from the foil (not the foil backing) and placed on the floor of the chamber with the coating surface exposed and projected horizontally. The chambers were then closed, and the flow rate into each chamber was determined by connecting the bubble-flow meter to the outlet of the chamber (Figure B1).

103

Pre-ozone emissions from the specimens were measured after one hour of exposure to ozone-free air in the chambers. Specimens were then exposed to elevated ozone concentrations for two hours, and sampling of secondary emissions occurred during the last 30 minutes of ozone exposure. Ozone concentrations were measured during the first 1.5 hours of the ozonation phase. During the 30-minute secondary sampling phase, the feed to the ozone monitor was cycled from the inlet ozone line to the exhaust line from chamber A, then chamber B, then chamber C. This cycle was repeated until the end of the secondary sampling period.

During chamber experiments, $C_5$-$C_{10}$ n-aldehydes were collected on large-volume glass injection liners pre-packed with Tenax®-TA sorbent and glass wool and subsequently analyzed by TD/GC/FID. A minimum five-point external calibration curve was generated for each compound with mid-point calibration before each test of field samples. After completion of a test, specimens were returned to their respective locations within 24 hours. Specimens were brought to the lab two more times for testing at Month 4 and Month 6. The interior surfaces of each chamber were cleaned between tests using delicate task wipes (Kimwipe, Kimtech Science) and methanol, followed by passivation with high ozone concentrations, i.e., on the order of ppm.

## DATA ANALYSIS

### Ozone Reactivity

The reaction rate of ozone with a material surface is defined by Equation 1:

$$R = v_d A_s C_{O3} \tag{20}$$

where $R$ is the reaction rate of ozone with the material ($\mu g \cdot h^{-1}$), $v_d$ is the ozone deposition velocity to the material ($m \cdot h^{-1}$), $A_s$ is the horizontally-projected surface area of the material ($m^2$), and $C_{O3}$ is the concentration of ozone above the surface ($\mu g \cdot m^{-3}$). The ozone deposition velocity is related to both fluid mechanics (i.e., turbulence, air speed, boundary layer development) and chemical reactivity of the material with ozone. The

relationship of these two factors with $v_d$ is treated as a series of resistances. The overall resistance to ozone removal is the inverse of deposition velocity and is expressed by Equation 2 as:

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v_b \rangle} \tag{21}$$

where $v_t$ is the transport-limited deposition velocity at the material surface in the chamber (m·s$^{-1}$), $\gamma$ is the ozone reaction probability of the material (-), and $\langle v_b \rangle$ is the Boltzmann velocity of ozone in air (360 m·s$^{-1}$ at 20 °C). The overall resistance to deposition is equal to the sum of the transport resistance, $1/v_t$, and the reaction resistance, $4/\gamma \langle v_b \rangle$ (Cano-Ruiz et al., 1993). Values of $v_t$ depend on mixing conditions in bulk air as well as characteristics of the aerodynamic boundary layer adjacent to surfaces.

The ozone reaction probability ($\gamma$) indicates the potential of materials to remove ozone from air. For a specific material and pollutant, $\gamma$ expresses the fraction of collisions of pollutant molecules with the material surface that result in irreversible removal of the pollutant (Cano-Ruiz et al., 1993). Equation 2 was solved for $\gamma$ (Equation 3):

$$\gamma = \frac{4}{\langle v_b \rangle \left( \frac{1}{v_d} - \frac{1}{v_t} \right)} \tag{22}$$

To determine the ozone deposition velocity, a mass balance on ozone was solved for the deposition velocity in the chamber under well-mixed and steady-state conditions (Equation 4). During each experiment the ozone deposition velocity was determined for each specimen by introducing ozone into the chamber and recording the steady-state inlet and outlet ozone concentrations:

$$v_d = \frac{\lambda V}{A_s} \left( \frac{C_{in}}{C_{out}} - 1 - \frac{\alpha k_{O3,ch}}{\lambda} \right) \tag{23}$$

where $\lambda$ is the chamber air exchange rate (s$^{-1}$), $V$ is the volume of air in the chamber (m$^3$), $A_s$ is the horizontally-projected surface area of the specimen (m$^2$), $C_{in}$ is the chamber inlet ozone concentration (ppb), $C_{out}$ is the ozone concentration at the chamber outlet (ppb),

and $k_{O3,ch}$ is the ozone decay rate inside the chamber when it is empty (s$^{-1}$). The parameter $\alpha$ is a factor that corrects for the reduction of exposed chamber surface area when a specimen is in the chamber (Equation 5):

$$\alpha = \frac{(A_{ch} - A_s)}{A_{ch}} \tag{5}$$

where $A_{ch}$ is the total surface area of the inside of the chamber (m$^2$), and $A_s$ is as defined above. The value of $k_{O3,ch}$ is determined by performing a deposition velocity test in an empty chamber (Equation 6), under the same assumptions applied to Equation 4.

$$k_{O3,ch} = \lambda \left( \frac{C_{in}}{C_{out}} - 1 \right) \tag{6}$$

Transport-limited deposition velocities were quantified for each chamber by performing an ozone deposition velocity test on either a paint or plaster specimen that had been coated on the surface with potassium iodide, a compound that is highly reactive with ozone, as described by Lamble et al. (2011). An aqueous solution of 0.8 g·ml$^{-1}$ of potassium iodide was sprayed with a fine mist onto the specimens, and allowed to dry in a hood for at least 24 hours before testing. For these conditions, the reaction resistance is small and $v_t \simeq v_d$.

### Emission Rates

Concentrations collected from chamber air were used to quantify primary and secondary emission rates of $C_5$-$C_{10}$ n-aldehydes. The interior surface area of each chamber was 0.26 m$^2$. Background emission rates from chamber walls ($E_{ch,i}$) were calculated by solving a steady-state mass balance on a compound in a well-mixed empty chamber (Equation 7). The variable $C_{ch,i}$ represents the steady-state concentration of saturated n-aldehyde $i$ inside the chamber.

$$E_{ch,i} = Q C_{ch,i} \tag{7}$$

Area-normalized background emission rates from the chamber surfaces were subtracted from the total apparent primary emission rates (from material before ozone exposure) and from the total apparent secondary emission rates (from material after ozone exposure) using Equations 8 and 9, respectively.

$$E_{p,i} = QC_{p,i} - \alpha E_{ch,i} \tag{8}$$

$$E_{s,i} = QC_{s,i} - E_{p,i} - \alpha E_{ch,i} \tag{9}$$

Where $E_{p,i}$ is the primary emission rate of compound $i$ ($\mu g \cdot h^{-1}$), $C_{p,i}$ is the steady-state concentration of compound $i$ inside the chamber without ozone ($\mu g \cdot m^{-3}$), $E_{s,i}$ is the secondary emission rate of compound $i$ ($\mu g \cdot h^{-1}$), $C_{s,i}$ is the steady-state concentration of compound $i$ inside the chamber with ozone ($\mu g \cdot m^{-3}$), and all other variables are as defined previously. The average total $C_5$-$C_{10}$ n-aldehyde emission rate from the empty chambers ranged from 2% of average primary emissions from the clay paint at Month 0 to 13% at Month 4. Correspondingly, for clay plaster the average empty chamber emission rate of total $C_5$-$C_{10}$ n-aldehydes ranged from 4% to 23% of primary emissions.

### Molar Yields

The molar yield of a reaction product ($y_i$, $mol \cdot mol^{-1}$) is the ratio of moles of reaction product $i$ emitted from the material to moles of ozone removed by the material. Molar yields for each secondary reaction product were quantified by dividing the difference between the steady-state secondary concentration ($C_{s,i}$, all in ppb) and primary concentration ($C_{p,i}$) by the difference between the steady-state inlet ozone concentration ($C_{in}$) and exhaust ozone concentration ($C_{out}$):

$$y_i = \frac{C_{s,i} - C_{p,i}}{C_{in} - C_{out}} \tag{10}$$

Highly reactive materials with very low molar yields of reaction products are desirable for indoor air quality as they can scavenge substantial amounts of ozone without emitting large amounts of harmful or irritating reaction products.

107

## RESULTS AND DISCUSSION

### Ozone Reaction Probability

Averages of log-transformed ozone reaction probabilities from Month 0 to Month 6 for all clay paint and plaster specimens independent of location are plotted in Figure B2. Reaction probabilities measured for the clay paint were greater than those measured for the clay plaster throughout the 6-month program. Both the paint and plaster had lower ozone reaction probabilities at Months 0 and 2 than at Months 4 and 6, with values being highest at Month 4.
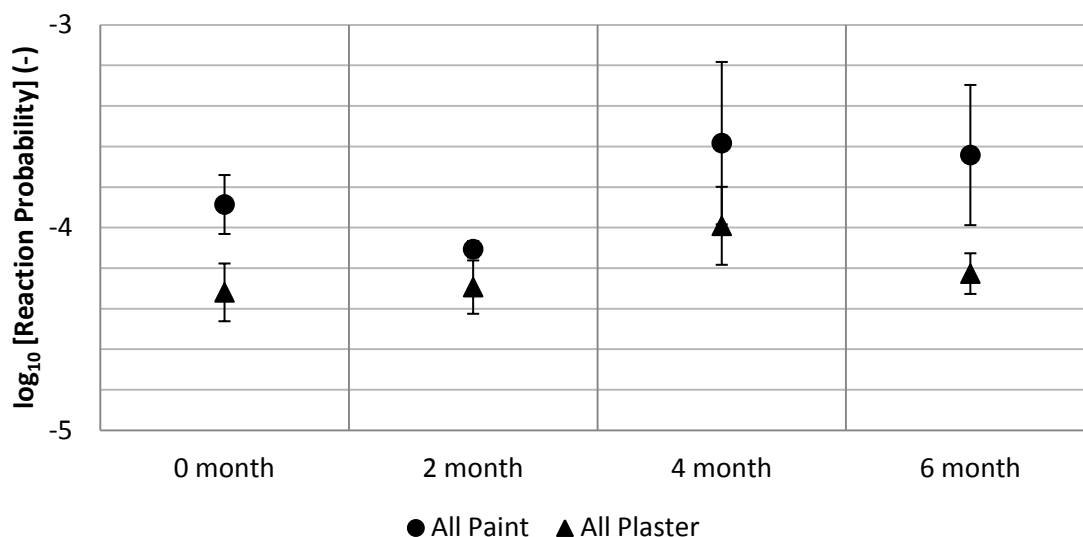


**Figure B16.** Ozone reaction probabilities (transformed to $\log_{10}$) averaged over all locations at Months 0, 2, 4, and 6. Error bars represent standard deviations.

At Month 0, before the clay paint specimens were placed in the field, the arithmetic mean ($\pm$ 1 standard deviation) ozone reaction probability was $1.3 \times 10^{-4}$ ($\pm 0.4 \times 10^{-4}$) among the seven specimens. By Month 2, the mean ozone reaction probability had decreased 40% to $7.9 \times 10^{-5}$ ($\pm 0.7 \times 10^{-5}$), but then at Month 4 the average ozone reaction probability had risen by more than a factor of three to $2.6 \times 10^{-4}$ ($\pm 3.0 \times 10^{-4}$). At

Month 6, the average ozone reaction probability had decreased slightly to $2.3 \times 10^{-4}$ ($\pm$ $3.0 \times 10^{-4}$).

The average ozone reaction probability of the plaster specimens followed a similar trend, although with less temporal variation. At Month 0, the mean ($\pm$ 1 standard deviation) ozone reaction probability was $4.8 \times 10^{-5}$ ($\pm 1.6 \times 10^{-5}$). At Month 2, the mean ozone reaction probability of the clay plaster was $4.8 \times 10^{-5}$ ($\pm 1.9 \times 10^{-5}$), remaining unchanged on average from the previous assessment. By Month 4, the mean ozone reaction probability had increased by a factor of two to $1.0 \times 10^{-4}$ ($\pm 0.4 \times 10^{-4}$). At Month 6, the mean ozone reaction probability decreased by 41% to $5.9 \times 10^{-5}$ ($\pm 1.3 \times 10^{-5}$).

The ozone reaction probabilities of clay plaster were in the range of those associated with its major component, kaolinite. The reaction probability of kaolinite, a hydrous aluminosilicate mineral that comprises 50% of the clay plaster, was reported by Michel et al. (2003) to be $3 \times 10^{-5}$ ($\pm 1 \times 10^{-5}$) for the mineral in powdered form. Michel et al. (2003) found the reaction probability to be particularly high for an iron oxide ($\alpha$-$Fe_2O_3$) powder, with an ozone reaction probability of $2.0 \times 10^{-4}$ ($\pm 0.3 \times 10^{-4}$), while a silicon dioxide ($SiO_2$) powder had an ozone reaction probability of $5 \times 10^{-5}$ ($\pm 1 \times 10^{-5}$) (Usher et al., 2003) to $6.3 \times 10^{-5}$ ($\pm 0.9 \times 10^{-5}$) (Michel et al., 2003). Reactions of these mineral oxides with ozone are catalytic, resulting in net destruction of ozone without depletion of the reactivity of the metal oxide surface (Michel et al., 2003; Usher et al., 2003).

The average ozone reaction probability of the paint decreased from Month 0 to Month 2, but remained the same for the plaster during this period. The ozone reactivity of some materials, such as carpet and GWB, has been shown to decrease over time, the so-called ozone aging-effect (Wang and Morrison, 2006; Cros et al., 2012). However, reaction probabilities can fluctuate with relative humidity, as well as with modifications of the material surface (e.g., deposition of skin oils, cooking oils, sorbed reactive gases, airborne particles on the material) (Wang and Morrison, 2006; Cros et al., 2012).

It is possible that deposition of reactive substances on specimens in the field contributed to the increase in the average reaction probabilities at Month 4 and Month 6.

Month 4 tests began in late November and lasted until late December, a time when activities around the major fall and winter holidays began in each residence. In both the apartment and house, activities such as cooking, cleaning, candle-burning, and entertaining of guests became more frequent during this period. These activities could have soiled the specimens with reactive gases, oils, and particles that enhanced ozone reactivity. Average indoor temperature and relative humidity did not change considerably (-0.67 °C; -1.1% RH) between Months 2 and 4, and therefore were unlikely to have influenced the ozone reaction probabilities. Alternatively, the specimens simply could have had more time to become soiled in the field regardless of the activities around the holidays, as the reaction probabilities remained relatively high on average beyond Month 4.

The same type of paint and plaster were tested by Lamble et al. (2011) inside 10-L chambers after 2 and 24 hours of exposure to 150 to 200 ppb ozone. The flow rate through the chambers (2 L·min$^{-1}$) equated to nearly double the AER of this study. The average ozone reaction probabilities of the clay paint and clay plaster tested by Lamble et al. were $5.7 \times 10^{-5}$ ($\pm 0.5 \times 10^{-5}$) and $2.2 \times 10^{-5}$ ($\pm 0.5 \times 10^{-5}$), respectively, each lower than the values determined in this study. The lower values reported by Lamble et al. (2011) may have been due to their specimens being exposed to more ozone than were specimens in this study, thus lowering the average number of ozone reaction sites during experiments.

A previous field study of ozone removal by building materials was conducted by Cros et al. (2012). Ozone deposition velocities, instead of ozone reaction probabilities, were tracked monthly for 6 months for samples of activated carbon mat, new recycled-content carpet, perlite-based ceiling tile, and low-VOC paint on GWB. Over the six-month program, the ozone deposition velocity trended downward for the carpet and for the painted GWB, while no overall decay in the deposition velocity was observed for the activated carbon mat and the ceiling tile. Similar to the way the reactivity of the clay paint and clay plaster increased around the holiday months, the deposition velocities of

the materials that Cros et al. tested also increased slightly during the month of December, five months after deployment to field locations.

Rim et al. (2016) measured ozone deposition velocities for three different indoor materials (a synthetic fiber carpet, latex paint on mineral fiber ceiling tile, and mold-guard paint on drywall), first when they were fresh and after one and two months of placement in an occupied office building. Deposition velocities decreased for all of the materials by the first month, and increased to varying degrees by the second month. These results further illustrate that a material's reactivity can fluctuate over time as the material is exposed to dynamic levels of particles, organic molecules, and ozone in real indoor environments.

Reaction probabilities at each location and for each sampling event are shown in Figure B17. At Month 4, the reaction probability of clay paint in the apartment living room ($6.2 \times 10^{-5}$) differed considerably from the reaction probability of clay paint in the house bedroom ($5.9 \times 10^{-4}$). This was not the case for the reaction probability of the clay plaster between these locations during this test period; the reaction probability was $4.9 \times 10^{-5}$ in the apartment living room and $5.6 \times 10^{-5}$ in the house bedroom. However, the reaction probability of clay plaster varied between other locations to a lesser extent. A combination of factors could account for these discrepancies. First, there could have been differences in how the paint and plaster were applied to the gypsum wallboard, affecting the coating thickness, porosity, surface area, and availability of ozone reaction sites. Second, unintentional soiling of the coating or foil surface with skin oil could have occurred, although this was minimized when handling specimens by using disposable Nitrile gloves. Third, variations in experimental scheduling could have affected the results as each set of co-located specimens was tested on different days. Lastly, some level of discrepancy could be attributed simply to uncertainty in experimental measurements. Across all testing events and locations, the average percent difference and standard deviation in reaction probability among co-located paint specimens was 55 ± 47%. For co-located plaster specimens, the percent difference in reaction probability was 23 ± 18% which, in comparison with the paint, suggests that the reactivity of the

plaster was more consistent in this study. For non-co-located specimens of the same coating type, there was roughly the same level of variation for the paint (52 ± 51%), but a higher level of variation for the plaster (39 ± 26%). Future analyses of the effects of location on ozone reaction probability and byproduct emissions, using a larger sample of co-located specimens across a variety of indoor environments, could provide a better understanding of the role of PRM placement location on its performance as an ozone sink.

Clay paint had a higher reaction probability than did clay plaster averaged over all locations and months, and this trend was consistent between co-located specimens at four of the five locations. For the three apartment locations (living room, kitchen, and bedroom) the ratio of the average six-month ozone reaction probability of paint to plaster was consistently 1.7. The corresponding ratio for the house living room was slightly higher, but similar at 1.9. However, the six-month average reaction probability of the paint was 5.4 times greater than that of the plaster in the house bedroom. The high reaction probability of paint in the house bedroom at Month 4, and the relatively low reaction probability of plaster in the house bedroom at Months 2 and 4, contributed greatly to this result. Specific reasons for this large discrepancy could not be resolved.
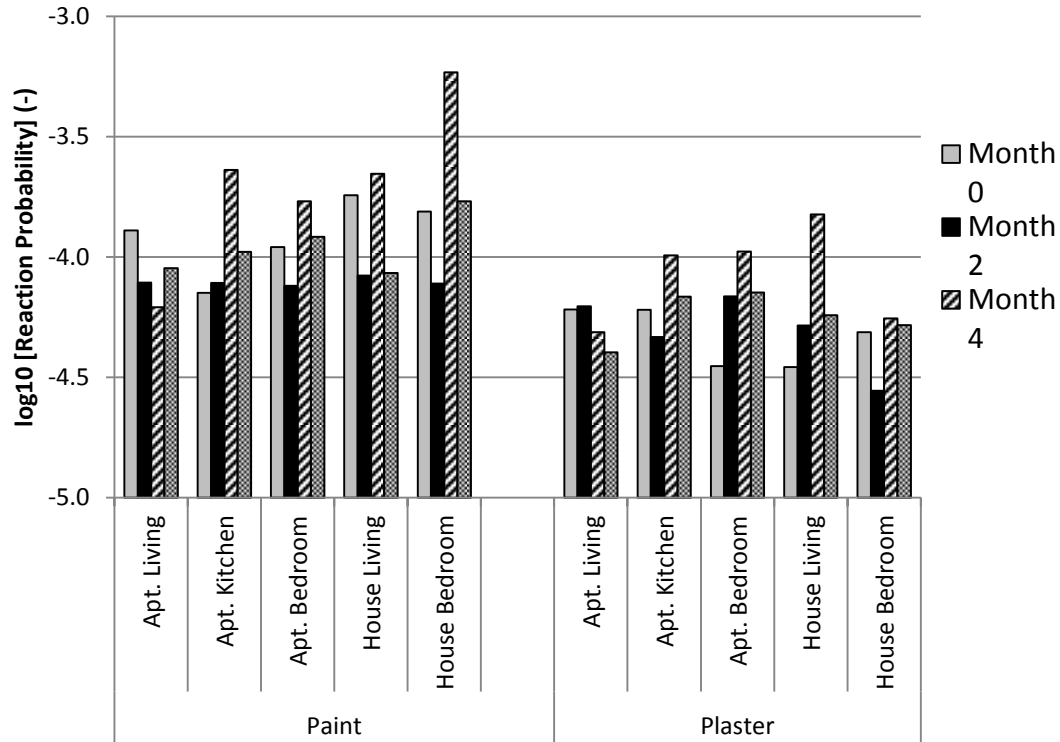
**Figure B17.** Ozone reaction probabilities (transformed to $\log_{10}$) of clay paint and clay plaster at each location.

Except for the increased reaction probabilities at Month 4 for both paint and plaster at all locations but the apartment living room, no discernible trends were observed for either the paint or the plaster. Two-tailed t-tests were used to determine significant patterns. Reaction probabilities were not statistically different between locations for either the paint or the plaster. The clay paint was statistically more reactive than the clay plaster over the six-month program in only the apartment bedroom ($p = 0.001$) and the house living room ($p = 0.048$). The reaction probability of the clay paint across all locations was statistically greater than that of the plaster initially at Month 0 ($p = 0.0006$) and at Month 2 ($p = 0.001$), but not during the latter half of the experimental program. This is possibly due to each type of specimen being modified by similar external factors as described above, although this was not confirmed. While the six-month average reaction probability of all specimens placed in the house ($1.3 \times 10^{-4}$) was greater than the

six-month average of all specimens placed in the apartment ($8.7{\times}10^{-5}$), there was no statistical difference in reaction probability between these two residences ($p > 0.05$).

At Month 4, the paint and plaster specimens that were placed in the apartment living room did not exhibit the increased ozone reaction probabilities that specimens at the other locations exhibited; rather, the ozone reaction probabilities for these specimens had decreased by Month 4. The specimens placed in the apartment living room were adjacent to a patio door that was opened and closed almost daily during the fall months. This could have led to an increase in local ventilation, and therefore somewhat higher local ozone concentrations compared to the other locations, e.g., as discussed by Howard-Reed et al. (2002). A higher ozone concentration in this area could have led to greater consumption of ozone reaction sites on the specimens, thus reducing the reaction probability of the material. Ozone concentrations were not monitored at the site locations. However, Cros et al. (2012) suggested that higher air exchange rate and ozone penetration for an office location may have been responsible for reaction site consumption and lower ozone deposition velocities relative to similar materials placed in residences.

Across all locations and test periods, the clay paint was statistically more reactive than the clay plaster ($p < 0.000001$). The clay paint contains a preservative of unknown composition, as well as cellulose and an unspecified alcohol ester. Cellulose and cellulose products will react and degrade upon exposure to ozone (Gall et al., 2014; Pouyet et al., 2014, Lemeune et al., 2004), and alcohol esters are also known to react with ozone (Grosjean et al, 1993).

**Emission Rates**

Primary and secondary emission rates calculated across all locations at each month are shown for paint in Figure B18, and for plaster in Figure B19. The clay-based paint had higher emission rates of $C_5$-$C_{10}$ n-aldehydes compared to the plaster. Both coatings exhibited a decaying trend in primary and secondary emission rates over the six month test period. From Month 0 to Month 2 the average primary and secondary

114

emission rates of $C_5$-$C_{10}$ n-aldehydes decreased by 79% and 84%, respectively, for the paint, and by 44% and 73%, respectively, for the plaster. After Month 2, emissions from the plaster continued to decay gradually, while the emissions from the paint remained fairly constant.
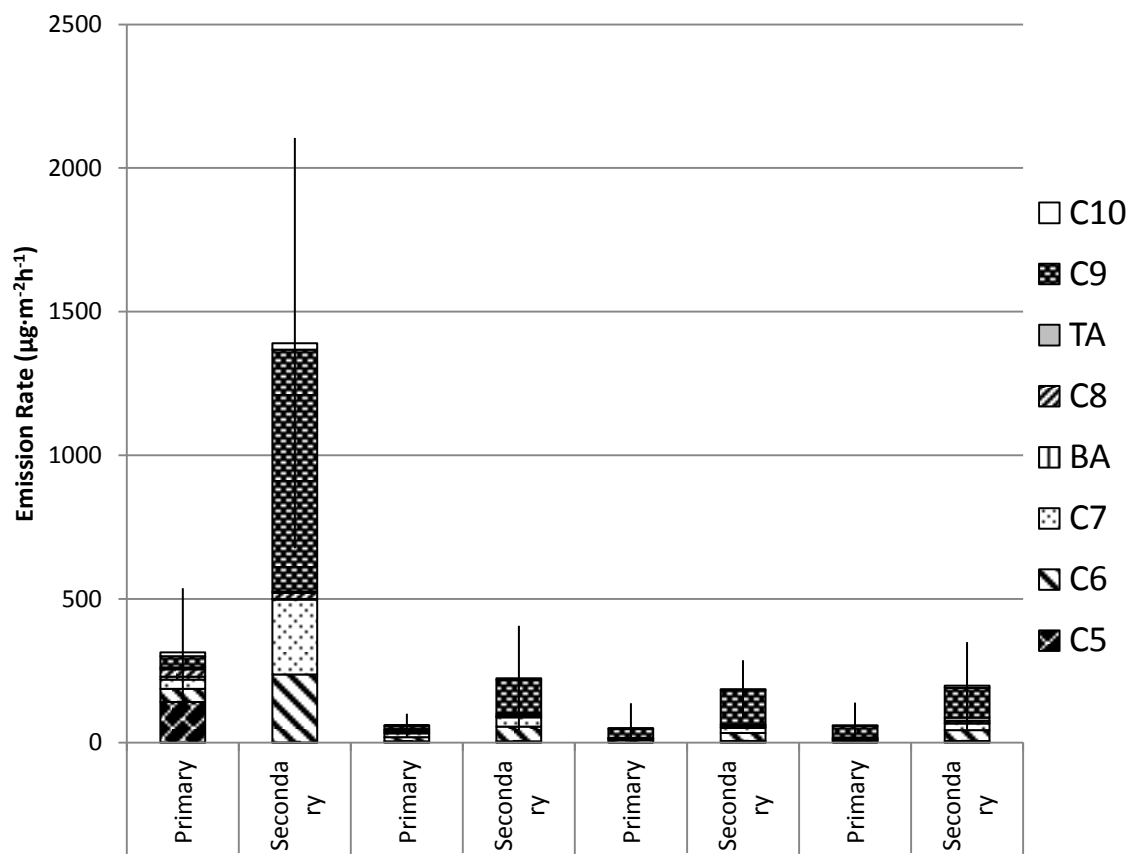


**Figure B18.** Primary and secondary emission rates of reaction products from clay paint averaged over all locations. Whiskers represent standard deviations across all samples.
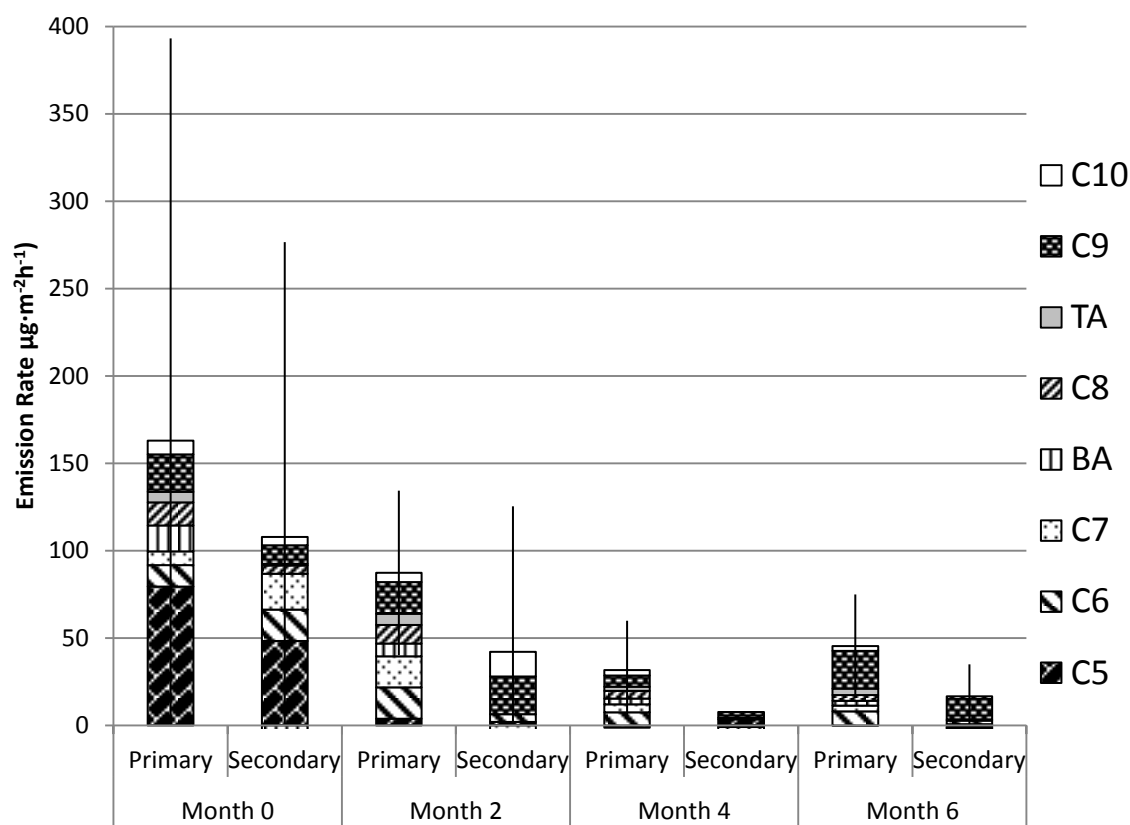
**Figure B19.** Primary and secondary emission rates of reaction products from clay plaster averaged over all locations. Whiskers represent standard deviations across all samples.

The secondary emissions (emissions *above* primary emissions) of $C_5$-$C_{10}$ n-aldehydes from the paint were greater than the primary emissions. This was not the case for the plaster; secondary emissions from the plaster were lower than the primary emissions during each test. These results are consistent with findings by Lamble et al. (2011). Other ingredients in the clay paint, such as the preservative, alcohol ester, and cellulose, may constitute the reactive sites that contributed to the higher secondary emissions.

Notable increases in average secondary emission rates of hexanal ($C_6$), heptanal ($C_7$), and nonanal ($C_9$) were observed for the clay paint at each test period; at Month 0, hexanal emissions were >400% higher than primary emissions, heptanal emissions were

nearly 700% higher, and nonanal emissions were >2000% higher than its primary emissions. Secondary emissions of hexanal, heptanal, and nonanal continued to be elevated above primary emissions during the remaining months, with increases ranging from >100% to >900%. The prominent increases in hexanal and nonanal emissions could have resulted from the ozone reacting with unsaturated fatty acids that are found indoors, e.g., as deposited cooking oils.

Large increases in secondary emission rates were not observed for the clay plaster. At Month 0, the average hexanal emission rate increased by 46%, and the heptanal emission rate increased by 162%, although the total secondary emissions were still lower than the total primary emissions. At Month 2, nonanal emissions increased by 19%, and decanal emissions increased by >160% above primary emissions, while the total secondary emission rate remained lower than total primary emission rate. Secondary emission rates of the heavy aldehydes from the plaster did not increase at Month 4 and Month 6.

Nonanal was the most prevalent aldehyde emitted from the paint throughout the program, except at Month 0 when pentanal ($C_5$) made up 45% of the total primary emissions.  Hexanal and heptanal were relatively significant secondary products after nonanal, with 19% of the total secondary emissions consisting of hexanal, and 14% consisting of heptanal. These aldehydes were also prevalent to varying degrees for emissions from clay plaster, with pentanal dominating both primary and secondary emissions at Month 0 (49% and 46%, respectively). On average, 53% of the total secondary emissions from plaster consisted of nonanal, and 16% consisted of hexanal. Secondary emission rates of heptanal from the plaster after Month 0 were negative, suggesting a loss of the compound that had reacted with ozone to form heptanal at Month 0.  Heptanal was, however, prevalent in the primary emissions throughout the program, with an average contribution to $C_5$-$C_{10}$ primary emissions of 11%.

**Molar Yields**

Molar yields of $C_5$-$C_{10}$ n-aldehydes averaged across all locations for both paint and plaster are shown in Figure B20. Only clay paint at Month 0 had a total molar yield (0.45 moles product/mole ozone consumed) that on average exceeded 0.1. Importantly, the molar yields reported here are only for the target chemicals and are limited to the period of sampling during ozonation. Had samples been collected for a longer post-ozonation period, the summed molar yields of the compounds would have increased. As such, the results shown here are generally more useful for cross-specimen comparisons and longitudinal changes in molar yields.

The paint exhibited higher molar yields than did plaster, but yields for both materials decayed within the first two months. From Month 0 to Month 2, summed molar yields from the paint decreased by 91%, and the summed molar yields from the plaster decreased by 86%. After Month 2, molar yields from the paint increased slightly, but were still relatively low.

Molar yields from the clay paint at Month 0 were more than double the molar yields that Lamble et al. (2011) reported for clay paint. Lamble et al. measured an average total molar yield of $C_5$-$C_{10}$ n-aldehydes (2-hr and 24-hr) from the clay paint of approximately 0.2. For this study, from Month 0 to Month 6 the majority of total molar yields from the paint consisted of nonanal and a smaller portion of hexanal, consistent with results reported by Lamble et al. (2011). For the clay plaster in this study, the average total molar yield at Month 0 was only 0.06 moles product/moles ozone consumed. An analysis of data in Lamble et al. (2011) suggests an average total molar yield (2-hr and 24-hr) from the clay plaster of less than 0.05. Unlike the clay paint at Month 0, more than half of the summed molar yields from the plaster consisted of pentanal and smaller portions of hexanal and heptanal. After Month 0, summed molar yields from the plaster were dominated by nonanal.

For a low-VOC paint, Cros et al. (2012) reported an initial total molar yield of $C_5$-$C_{10}$ n-aldehydes of 0.07, consisting mostly of nonanal. The six-month average molar yield from their low-VOC paint was 0.05, almost five times greater than the six-month average molar yield for the clay plaster in this study, and three times lower than that of

the clay paint. Gall et al. (2013) reported a higher molar yield (average of 0.11) for the same type of low-VOC paint used by Cros et al. (2012); however these yields included light aldehydes (i.e., formaldehyde ($C_1$) through butanal ($C_4$)) in addition to the heavy aldehydes included in this study and in Cros et al. (2012) and Lamble et al. (2011).
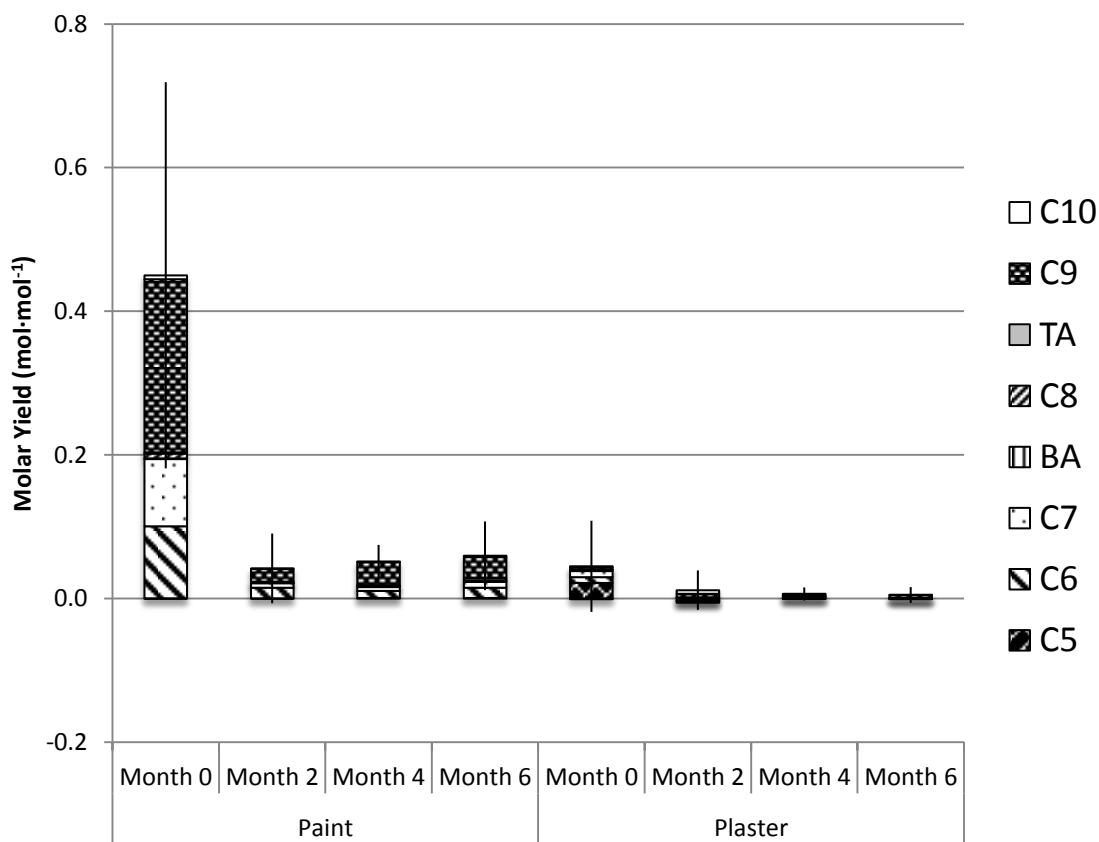


**Figure B20.** Molar yields of reaction products from clay paint and clay plaster averaged over all locations. Whiskers represent standard deviations across all samples.

## SUMMARY AND CONCLUSIONS

The commercially-available clay paint and clay plaster reported herein both sustained relatively high ozone reaction probabilities over six months, with the highest reaction probabilities recorded four months after placement in the field. The observed time variations in ozone reaction probabilities might reflect the influence that indoor environmental activities have on material surface interactions with ozone (e.g., from

119

soiling by dust and oils or adsorption of reactive gases). Although lower reaction probabilities were observed for specimens that were situated adjacent to a patio door where potentially more outdoor air infiltration occurred, on average reaction probabilities did not vary appreciably by location.

While the clay paint was statistically more reactive with ozone compared to the clay plaster, it also exhibited greater secondary emission rates and molar yields of $C_5$ to $C_{10}$ saturated n-aldehydes, thus reflecting a trade-off in use of these clay coatings as PRMs. Emission rates and yields for both the clay paint and clay plaster were elevated during the initial tests at Month 0, and then decayed sharply thereafter. The secondary emission rates from the clay paint were greater than the primary emission rates, however the secondary emission rates from the clay plaster were lower than the primary emission rates. The emission rates determined during this study are similar to the results obtained by Lamble et al. (2011) for the same type of clay paint and plaster. Total molar yields of $C_5$ to $C_{10}$ saturated n-aldehydes from the clay paint were comparable to total molar yields determined for a low-VOC conventional paint, while for the clay plaster the total molar yields were much lower.

The two clay coatings described in this paper appear promising as PRMs for ozone. However, broad conclusions about how they will affect indoor environments should be withheld until further testing helps to better understand the long-term performance and effects of such coatings in a wider range of indoor environments with varying environmental conditions, including fluid mechanics and potential surface modifiers.

## ACKNOWLEDGEMENTS

## REFERENCES

Atkinson, R., and Arey, J. (2003) Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review, *Atmos Environ,* 37, 197-219.

Aldred, J.A., Darling, E., Morrison, G., Siegel, J., & Corsi, R.L. (2015). Benefit-cost analysis of commercially available activated carbon filters for indoor ozone removal in single-family homes, *Indoor Air,* DOI: 10.1111/ina.12220.

Bekö, G., Clausen, G., & Weschler, C. J. (2008). Sensory pollution from bag filters, carbon filters and combinations, *Indoor Air,* 18, 27-36.

Bekö, G., Fadeyi, M. O., Clausen, G., & Weschler, C. J. (2009). Sensory pollution from bag-type fiberglass ventilation filters: Conventional filter compared with filters containing various amounts of activated carbon, *Build Environ,* 44, 2114-2120.

Bell, M. L., Dominici, F., and Samet, J. M. (2005) A meta-analysis of time-series studies of ozone and mortality with comparison to the national morbidity, mortality, and air pollution study, *Epidemiology*, 16, 436-445.

Cano-Ruiz, J., Kong, D., Balas, R., and Nazaroff, W., W. (1993) Removal of reactive gases at indoor surfaces - Combining mass-transport and surface kinetics, *Atmos Environ A-Gen*, 27, 2039–2050.

Chen, C., Zhao, B., & Weschler, C. J. (2012). Assessing the influence of indoor exposure to "outdoor ozone" on the relationship between ozone and short-term mortality in U.S. communities, *Environ Health Persp,* 120, 235-240.

Coleman, B. K., Destaillats, H., Hodgson, A. T., and Nazaroff, W. W. (2008) Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics, *Atmos Environ,* 42, 642-654.

Cros, C. J., Morrison, G. C., Siegel, J. A., and Corsi, R. L. (2012) Long-term performance of passive materials for removal of ozone from indoor air, *Indoor Air,* 22, 43-53.

Darling, E. K., Cros, C. J., Wargocki, P., Kolarik, J., Morrison, G. C., and Corsi, R. L. (2012) Impacts of a clay plaster on indoor air quality assessed using chemical and sensory measurements, *Build Environ,* 57, 370-376.

deCastro, B.R., Sax, S.N., Chillrud, S.N., Kinney, P.L., and Spengler, J.D. (2007) Modeling time-location patterns of inner-city high school students in New York and Los Angeles using a longitudinal approach with generalized estimating equations, *J Expo Sci Env Epid,* 17, 233-247.

Destaillats, H, Lunden, M.M., Singer, B.C., Coleman, B.K., Hodgson, A.T., Weschler, C.J., and Nazaroff, W.W. (2006) Indoor secondary pollutants from household product emissions in the presence of ozone: A bench-scale chamber study, *Envion Sci Technol,* 40, 4421-4428.

Fan, Z., Lioy, P., Weschler, C., Fiedler, N., Kipen, H., and Zhang, J. (2003) Ozone-initiated reactions with mixtures of volatile organic compounds under simulated indoor conditions, *Environ Sci Technol,* 37, 1811-1821.

Fan, Z.H., Weschler, C.J., Han, I.K., and Zhang, J.F. (2005) Co-formation of hydroperoxides and ultra-fine particles during the reactions of ozone with a complex VOC mixture under simulated indoor conditions, *Atmos Environ,* 39, 5171-5182.

Gall, E., Darling, E., Siegel, J. A., Morrison, G. C., and Corsi, R. L. (2013) Evaluation of three common green building materials for ozone removal, and primary and secondary emissions of aldehydes, *Atmos Environ*, 77, 910-918.

Gall, E. T., Corsi, R. L., and Siegel, J. A. (2014) Impact of physical properties on ozone removal by several porous materials, *Environ Sci Technol*, 48, 3682-3690.

Grosjean., D., Grosjean, E., and Williams II, E.L. (1993) Rate constants for the gas-phase reactions of ozone with unsaturated alcohols, esters, and carbonyls, *Int J Chem Kinet*, 25, 783-794.

Gryparis, A., Forsberg, B., Katsouyanni, K., Analitis, A., Touloumi, G., Schwartz, J., and Dortbudak, Z. (2004) Acute effects of ozone on mortality from the "Air pollution

and health:  A European approach" project, *Am J Resp Crit Care*, 170, 1080-1087.

Hodgson, A.T., Rudd, A.F., Beal, D., and Chandra, S. (2000) Volatile organic compound concentrations and emission rates in new manufactured and site-built houses, *Indoor Air,* 10, 178-192.

Howard-Reed, C., Wallace, L.A., and Ott, W.R. (2002) The effect of opening windows on air change rates in two homes, *JAPCA J Air Waste Ma*, 52, 147-59.

Hubbell, B. J., Hallberg, A., McCubbin, D. R., and Post, E. (2005) Health-related benefits of attaining the 8-hr ozone standard, *Environ Health Persp*, 113, 73-82.

Hussein, T., Paasonen, P., and Kulmala, M. (2012) Activity pattern of a selected group of school occupants and their family members in Helsinki – Finland, *Sci Total Environ,* 425, 289-292.

Hyttinen, M., Pasanen, N., and Kalllokoski, P. (2006) Removal of ozone on clean, dusty and sooty supply air filters, *Atmos Environ,* 40, 315-325.

Ito, K., De Leon, S. F., and Lippmann, M. (2005) Associations between ozone and daily mortality - Analysis and meta-analysis, *Epidemiology*, 16, 446-457.

Jerrett, M., Burnett, R. T., Pope, C. A., Ito, K., Thurston, G., Krewski, D., and Thun, M. (2009) Long-term ozone exposure and mortality, *New Engl J Med*, 360, 1085-1095.

Klepeis, N. E., Nelson, W. C., Ott, W. R., Robinson, J. P., Tsang, A. M., Switzer, P., and Engelmann, W. H. (2001) The National Human Activity Pattern Survey (NHAPS): A resource for assessing exposure to environmental pollutants, *J Expo Anal Env Epid*, 11, 231-252.

Kunkel, D. A., Gall, E. T., Siegel, J. A., Novoselac, A., Morrison, G. C., and Corsi, R. L. (2010) Passive reduction of human exposure to indoor ozone, *Build Environ*, 45, 445-452.

Lamble, S. P., Corsi, R. L., and Morrison, G. C. (2011) Ozone deposition velocities, reaction probabilities and product yields for green building materials, *Atmos Environ,* 45, 6965-6972.

Lemeune, S., Jameel, H., Chang, H.-M., and Kadla, J.F. (2004) Effects of ozone and chlorine dioxide on the chemical properties of cellulose fibers, *J Appl Polym Sci,* 93, 1219-1223.

Levy, J. I., Carrothers, T. J., Tuomisto, J. T., Hammitt, J. K., and Evans, J. S. (2001) Assessing the public health benefits of reduced ozone concentrations, *Environ Health Persp,* 109, 1215-1226.

Lin, C.-C., & Chen, H.-Y. (2014). Impact of HVAC filter on indoor air quality in terms of ozone removal and carbonyls generation, *Atmos Environ*, 89, 29-34.

Long, C.M., Suh, H.H., and Koutrakis, P. (2000) Characterization of indoor particle sources using continuous mass and size monitors, *JAPCA J Air Waste Ma,* 50, 1236-1250.

McConnell, R., Berhane, K., Gilliland, F., London, S. J., Islam, T., Gauderman, W. J., and Peters, J. M. (2002) Asthma in exercising children exposed to ozone: A cohort study, *Lancet*, 359, 386-391.

Michel, A. E., Usher, C. R., and Grassian, V. H. (2003) Reactive uptake of ozone on mineral oxides and mineral dusts, *Atmos Environ,* 37, 3201-3211.

Meng, Y. Y., Rull, R. P., Wilhelm, M., Lombardi, C., Balmes, J., and Ritz, B. (2010) Outdoor air pollution and uncontrolled asthma in the San Joaquin Valley, California, *J Epidemiol Commun H,* 64, 142-147.

Morrison, G. C., and Nazaroff, W. W. (2002) Ozone interactions with carpet: Secondary emissions of aldehydes, *Environ Sci Technol,* 36, 2185-2192.

Mudway, I. S., and Kelly, F. J. (2000) Ozone and the lung: A sensitive issue, *Mol Aspects Med*, 21, 1-48.

Nazaroff, W. W., and Weschler, C. J. (2004) Cleaning products and air fresheners: exposure to primary and secondary air pollutants, *Atmos Environ,* 38, 2841-2865.

Nazaroff, W. W., Coleman, B. K., Destaillats, H., Hodgson, A. T., Liu, D.-L., Lunden, M. M., Singer, B. C., and Weschler, C. J. (2006). Indoor Air Chemistry: Cleaning Agents, Ozone and Toxic Air Contaminants (No. California Air Resources Boad Contract No. 01-336). Lawrence Berkeley National Laboratory.

Nicolas, M., Ramalho, O., and Maupetit, F. (2007) Reactions between ozone and building products: Impact on primary and secondary emissions, *Atmos Environ,* 41, 3129-3138.

Ourrad, H., Thevenet, F., Gaudion, V., and Riffault, V. (2015) Limonene photocatalytic oxidation at ppb levels: Assessment of gas phase reaction intermediates and secondary organic aerosol heterogeneous formation, *Appl Catal B-Environ,* 168-169, 183-194.

Park, J.S., and Ikeda, K. (2006) Variations of formaldehyde and VOC levels during 3 years in new and older homes, *Indoor Air,* 16, 129-135.

Parodi, S., Vercelli, M., Garrone, E., Fontana, V., and Izzotti, A. (2005) Ozone air pollution and daily mortality in Genoa, Italy between 1993 and 1996, *Public Health*, 119, 844-850.

Petrick, L. and Dubowski, Y. (2009) Heterogeneous oxidation of squalene film by ozone under various indoor conditions, *Indoor Air,* 19, 381-391.

Poppendieck, D., Hubbard, H., Ward, M., Weschler, C., and Corsi, R. L. (2007a) Ozone reactions with indoor materials during building disinfection, *Atmos Environ*, 41, 3166-3176.

Poppendieck, D., Hubbard, H., Weschler, C., and Corsi, R. L. (2007b) Formation and emissions of carbonyls during and following gas-phase ozonation of indoor materials, *Atmos Environ,* 41, 7614-7626.

Pouyet, F., Chirat, C., Potthast, A., and Lachenal, D. (2014). Formation of carbonyl groups on cellulose during ozone treatment of pulp: consequences for pulp bleaching, *Carbohyd Polym,* 109, 85-91.

Rim. D., Gall, E. T., Maddalena, R. L., and Nazaroff, W. W. (2016) Ozone reaction with interior building materials: Influence of diurnal ozone variation, temperature and humidity, *Atmos Environ,* 125, 15-23.

Rohr, A. C., Weschler, C J., Koutrakis, P., and Spengler, J. D. (2003) Generation and quantification of ultrafine particles through terpene/ozone reaction in a chamber setting, *Aerosol Sci Tech,* 37, 65-78.

Sarwar, G., Corsi, R., Kimura, Y., Allen, D., and Weschler, C.J. (2002) Hydroxyl radicals in indoor environments, *Atmos Environ,* 36, 3973-3988.

Sarwar, G., Corsi, R., Allen, D., and Weschler, C. (2003) The significance of secondary organic aerosol formation and growth in buildings: experimental and computational evidence, *Atmos Environ*, 37, 1365-1381.

Sarwar, G., Olson, D. A., Corsi, R. L., and Weschler, C. J. (2004) Indoor fine particles: The role of terpene emissions from consumer products*, JAPCA J Air Waste Ma,* 54, 367-377.

Sarwar, G., and Corsi, R. (2007) The effects of ozone/limonene reactions on indoor secondary organic aerosols, *Atmos Environ,* 41, 959-973.

Schweizer, C., Edwards, R.D., Bayer-Oglesby, L., Gauderman, W.J., Ilaqua, V., Juhani Jantunen, M., Lai, H. K., Nieuwenhuijsen, M, and Künzli, N. (2007) Indoor time-microenvironment-activity patterns in seven regions of Europe, *J Expo Sci Env Epid,* 17, 170-181.

Shair, F. H. (1981). Relating indoor pollutant concentrations of ozone and sulfur dioxide to those outside: economic reduction of indoor ozone through selective filtration of the make-up air, *ASHRAE Tran*, 87, 116-139.

Shields, H. C., Weschler, C. J., & Naik, D. (1999). Ozone removal by charcoal filters after continuous extensive use (5 to 8 years), In *Proceedings of the 8th International Conference on Indoor Air Quality and Climate* (Vol. 4, pp. 49-54).

Singer, B. C., Coleman, B. K., Destaillats, H., Hodgson, A. T., Lunden, M. M., Weschler, C. J., and Nazaroff, W. W. (2006) Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone, *Atmos Environ,* 40, 6696–6710.

Tamas, G., Weschler, C.J., Bako-Biro, Z., Wyon, D.P., and Strom-Tejsen, P. (2006) Factors affecting ozone removal rates in a simulated aircraft cabin environment, *Atmos Environ,* 40, 6122-6133.

USEPA (2006). *Air Quality Criteria for Ozone and Related Photochemical Oxidants*, Washington, DC: U.S. Environmental Protection Agency (No. EPA/600/R-05/004aF-cF).

Usher, C. R., Michel, A. E., Stec, D., and Grassian, V. H. (2003) Laboratory studies of ozone uptake on processed mineral dust, *Atmos Environ,* 37, 5337-5347.

Wainman, T., Zhang, J., Weschler, C.J., and Lioy, P.J. (2000) Ozone and limonene in indoor air: A source of submicron particle exposure, *Environ Health Persp, 108*, 1139-1145.

Wang, H., and Morrison, G. C. (2006) Ozone-initiated secondary emission rates of aldehydes from indoor surfaces in four homes, *Environ Sci Technol,* 40, 5263-5268.

Wang, H., & Morrison, G. (2010). Ozone-surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends, *Indoor Air,* 20, 224-234.

Waring, M. S., Wells, J. R., and Siegel, J. A. (2011) Secondary organic aerosol formation from ozone reactions with single terpenoids and terpenoid mixtures, *Atmos Environ,* 45, 4235-4242.

Waring, M. S., and Siegel, J. A. (2013) Indoor secondary organic aerosol formation initiated from reactions between ozone and surface-sorbed d-limonene, *Environ Sci Technol,* 47, 6341-6348.

Weschler, C. J., Brauer, M., and Koutrakis, P. (1992a) Indoor ozone and nitrogen-dioxide – a potential pathway to the generation of nitrate radicals, dinitrogen petaoxide, and nitric-acid indoors, *Environ Sci Technol,* 26, 179-184.

Weschler, C.J., and Shields, H.C. (1996) Production of the hydroxyl radical in indoor air, *Environ Sci Technol,* 30, 3250-3258.

Weschler, C. J., and Shields, H. C. (1997) Measurements of the hydroxyl radical in a manipulated but realistic indoor environment, *Environ Sci Technol,* 31, 3719-3722.

Weschler, C. J., and Shields, H. C. (1999) Indoor ozone/terpene reactions as a source of indoor particles, *Atmos Environ,* 33, 2301-2312.

Weschler, C. J. (2006) Ozone's impact on public health: Contributions from indoor exposures to ozone and products of ozone-initiated chemistry, *Environ Health Persp*, 114, 1489-1496.

Wisthaler, A., and Weschler, C. J. (2010) Reactions of ozone with human skin lipids: Sources of carbonyls,   dicarbonyls, and hydroxycarbonyls in indoor air. *P Natl Acad Sci USA,* 107, 6568-6575.

Yang, Q. Y., Chen, Y., Shi, Y. L., Burnett, R. T., McGrail, K. M., and Krewski, D. (2003) Association between ozone and respiratory admissions among children and the elderly in Vancouver, Canada, *Inhal Toxicol*, 15, 1297-1308.

Zheng, X. Y., Ding, H., Jiang, L. N., Chen, S. W., Zheng, J. P., Qiu, M., Zhou, Y. X., Chen, Q., and Guan, W. J. (2015) Association between air pollutants and asthma emergency room visits and hospital admissions in time series studies: A systematic review and meta-analysis, *PLoS ONE,* 10, e0138146.

**Passive Removal Materials for Indoor Ozone Control[4]**

Erin Darling[1], Glenn C. Morrison[2], Richard L. Corsi[1,*]

[1]University of Texas at Austin (UT)

[2]Missouri University of Science and Technology (MS&T)

*Corresponding email: corsi@mail.utexas.edu; phone: 1-512-471-3611; fax: 1-512-471-5870*

## ABSTRACT

The indoor environment can contribute significantly to population exposure to ozone. This paper reviews the state of knowledge on building materials and coatings that are intended to passively remove ozone from indoor air. These passive removal materials, or PRMs, have high ozone removal potential without significant and harmful reaction product formation. Ozone interactions with indoor environments, including surface and gas-phase reactions, known byproducts of these reactions, and health impacts of ozone and its byproducts are described. Research that has targeted PRMs for ozone removal is then summarized, and the materials in question are assessed in terms of their ability to reduce indoor ozone concentrations; ozone deposition velocities, reaction probabilities, as well as byproduct molar yields are presented and compared. This evaluation of the literature suggests that, besides activated carbon, the most promising PRMs for ozone control are inorganic materials, including clay-based bricks and plasters, calcareous stone, and ceiling tile made of mineral fibers or volcanic perlite. Simple model equations are presented and used to highlight the potential for PRMs as a means for reducing indoor ozone concentrations. The removal effectiveness for ozone and reaction-derived formaldehyde is predicted for a commercially-available wall coating (clay paint) applied

---

in a residential building. Removal effectiveness is also discussed in the context of required surface area and application costs for clay paint. A list of conclusions, limitations and research needs based on the existing knowledge base is also presented.

**KEYWORDS**

*Reaction probability, indoor air quality, clay, paint, plaster*

**INTRODUCTION**

The indoor environment is a major determinant of human respiratory health, particularly given that Americans and those in many other developed countries spend on average almost 90% of their lives indoors [1-4]. Populations that are more vulnerable to respiratory health complications, e.g., infants, elderly, and the chronically ill, spend an even greater portion of their time indoors [5-7]. Poor indoor environmental quality has been linked to transmission of respiratory infections [e.g.,8-10], incidences of allergies and asthma [e.g., 11-13], sick building syndrome (SBS), [14-18] and decreased productivity [19,20]. Fisk and Rosenfeld [19] estimated that the annual cost of respiratory infections, allergies and asthma, and SBS in the U.S. was roughly $103 billion, $22 billion, and $89 billion (all 2015 $), respectively.

Ozone can greatly affect the quality of the indoor environment. The primary source of indoor ozone is tropospheric ozone, which is a ubiquitous and reactive air pollutant that forms from reactions between oxides of nitrogen (NOx) and VOCs in the presence of sunlight. The health effects of ozone are well-known and significant. When ozone enters the lungs it reacts with epithelial cells and polyunsaturated fatty acids in fluids lining the lung, leading to the formation of by-products and subsequent inflammation and increased permeability of the epithelial lining fluid (ELF) [21-23]. Increases in ozone concentrations are associated with increases in respiratory-related morbidity and premature mortality [e.g., 24-28]. Exposure to ozone has also been linked to increases in diagnoses of childhood asthma [30], school absences [31], and increases in hospital emergency room visits among children and the elderly [32].

Although outdoor ozone concentrations are typically greater than concentrations indoors, Weschler [33] estimated that 43-76% of human inhalation exposure to ozone of outdoor origin occurs indoors, and additionally that the average inhalation intake of ozone reaction products can be up to two times the indoor intake of inhaled ozone. Occupants of homes without centralized air conditioning systems may be at the greatest risk of exposure as the prevalence of these systems, and therefore lower air exchange rates and indoor ozone concentrations, have been shown to be inversely associated with ozone-related mortality [34]. Further, Chen et al. [35], in a modeling study encompassing 90 cities, predict significant effects of indoor ozone on mortality. Logue et al. [36] estimated the burden of chronic exposure to average levels of indoor ozone (~9 ppb) to be equivalent to 6.7 (95% CI: 0.3, 160) disability-adjusted life-years (DALYs), or the years of life lost annually per 100,000 persons due to illness, disability, or early death. Aldred et al. [37] described the potentially high health benefit-cost ratios of ozone removal by activated carbon in HVAC systems.

Ozone is entrained into buildings via outdoor air intakes, cracks in the building envelope, or through open doors and windows. Some indoor environments may have devices that produce ozone, such as laser printers and photocopiers, ion generators and electrostatic precipitators used for air cleaning [38-40].

Indoor ozone concentrations, and therefore total inhalation exposure to ozone can be reduced via active (i.e., energy-consuming) filtration methods such as treating building intake or indoor air using activated carbon filters [37,41-46]. Passive (i.e., no extra building energy consumption) removal methods can be employed by strategically placing ozone-scavenging materials or material coatings indoors.

Recent studies have focused on building materials or decorative material coatings (e.g., paint, plaster) for passive reduction of ozone [e.g., 47-50]. These materials are referred to here as passive removal materials, or PRMs. The PRM concept is also being employed for other indoor pollutants, e.g., volatile organic compounds (VOCs) [51-59].

The concept of PRMs involves the application of select materials over large surface areas, generally walls and ceilings, onto or within which gaseous pollutants are

effectively removed via adsorption followed by slow desorption or chemical reaction. In addition to ozone, some other pollutants can be removed by reactions with material surfaces (e.g., chemisorption of formaldehyde to amino acids in wool [60, 61]). The four main characteristics of PRMs are: (1) pollutant removal without consuming energy, other than the embodied energy in the production and manufacture of the material, (2) sustained pollutant removal over long time periods, (3) minimal reaction products released, and (4) practical use within buildings, meaning that the material can easily cover a large surface area while maintaining aesthetic appeal. To date, there are no published articles that summarize the state of knowledge related to passive removal materials. This paper serves as a review of the published literature that covers the concept of passive removal of indoor pollutant concentrations. We focus on building materials and coatings that may be used for removal of indoor ozone, assessing their ability to reduce indoor ozone concentrations without contributing significantly to total indoor emissions of volatile reaction products.

## BACKGROUND

### Types and Applications of PRMs

Yu et al. [62] were the first to express the utility of what were effectively PRMs for improving indoor air quality and conserving building energy. They focused on strategic placement of activated carbon sheets in buildings and modeled adsorption of select volatile organic compounds (VOCs) to those sheets in a hypothetical room. They emphasized the importance of placement of activated carbon sheets or other PRMs in locations where fluid mechanics are conducive to mass transfer. Sekine and Nishimura [63] studied multiple air-permeable glass fiber sheets pressed together and embedded with activated carbon and manganese oxide. Laboratory and field tests (six and seven months) in new apartments showed the potential for significant reductions in formaldehyde in apartment air using this PRM. Moriske et al. [64] also indicated that

ozone removal was enhanced and the formation of formaldehyde reduced through the use of wallpaper coated on the back with activated carbon.

Ryhl-Svendsen [65] studied unfired clay bricks for reduction of pollutant concentrations in museum archives. The introduction of stacked clay bricks led to a 71% reduction in organic acid (formic + acetic) concentrations relative to room conditions prior to addition of the bricks. Total VOC and formaldehyde concentrations in the room were also reduced by 27% and 9.4%, respectively.

Degradation of VOCs by titanium dioxide ($TiO_2$), a non-structural photocatalytic material that can be used to coat or incorporate into building materials, such as mortars, mineral plasters, and wallpaper, has been investigated by several researchers [e.g., 51,66-70]. Nomura and Jones [53-55] studied formaldehyde adsorption capacities of aminosilicas, and suggested that aminosilicas could be useful as indoor formaldehyde adsorbents, especially because no UV-light is needed. The National Research Council of Canada published a review of indoor air quality solutions and technologies, which highlighted a few options for passive control of indoor pollutants, including ozone, using large surface areas (i.e., walls) [71]. Included among these passive technologies were activated carbon media, anti-microbial wall coatings, and photocatalytic coatings. Some examples of commercially-available products for PRM applications were provided.

During the past five years a number of studies have been completed to assess the potential for removal of indoor ozone using various PRMs [47-50, 72]. The goal has been to identify materials with high ozone removal potential without significant and harmful reaction product formation. In the remainder of this paper, we focus on the research that has been conducted on the removal of indoor ozone by materials intended as PRMs, or that might have characteristics consistent with PRMs even if not intended as such.

**Ozone Chemistry in Indoor Environments**

Indoor ozone reacts on surfaces and in the air with organic and inorganic chemicals. Surface, or heterogeneous, reactions can occur on furniture, dust, building materials, and even human skin [e.g., 50, 73-77]. Gas-phase, or homogeneous, reactions

133

occur with chemicals (e.g., alkenes) that are emitted to air from building materials, furniture, and numerous cleaning and consumer products [73, 78-82]. While such reactions reduce concentrations of ozone indoors, they also lead to the formation of oxidized reaction products that can contribute to decreases in respiratory function, allergic reactions, respiratory inflammation, and possible increases in cancer risk [83-88].

Products of heterogeneous and homogeneous reactions have been studied extensively. Heterogeneous reactions have been observed to produce $C_1$-$C_{10}$ carbonyls, dicarbonyls, and hydroxycarbonyls that may be irritating or harmful to building occupants [48, 72, 77, 89-92, amongst others]. Homogeneous reactions are known to produce secondary organic aerosols (SOAs) [79, 94-103], as well as a range of gaseous oxidized products [78, 81, 96, 98, 104-110]. Multi-functional carbonyl species such as limonaldehyde, 4-acetyl-1-methyl-1-cyclohexene and other dicarbonyl species have been identified as products of reactions between ozone and d-limonene, a common monoterpene used in many fragrances and cleaning products in buildings [111-115]. Nazaroff and Weschler [78] described a range of secondary products associated with ozone reactions with terpenes, terpene alcohols, and unsaturated fatty acids in cleaning products and air fresheners. Reaction products include hydroxyl radicals and other radical species, formaldehyde, acetaldehyde, $C_3$ to $C_{10}$ saturated and unsaturated aldehydes, light monoketones, dicarbonyls, mono- and di-carboxylic acids, and secondary organic aerosols (SOA).

One strategy for reducing exposure to ozone and its reaction products is to use PRMs to effectively remove ozone with low concomitant reaction product emissions. If designed properly, PRM applications can reduce indoor ozone concentrations, and thereby also the concentrations of its various reaction products. The effectiveness of materials for controlling ozone depends on many factors that relate to the material itself, as well as characteristics of the building and mass transport conditions associated with air in contact with the PRMs. The solution to a steady-state mass balance on ozone for a well-mixed interior space with inclusion of a PRM is represented by Equation 1:

$$C_{O3} = \frac{fC_o + \sum E / \lambda V}{1 + \lambda^{-1}\left(\alpha k_{O3,surf} + k_{O3,prm} + \sum k_{O3,j}C_j\right)}$$

(24)

where $C_{O3}$ is the steady-state concentration of indoor ozone (parts per billion, ppb), $f$ is the outdoor ozone penetration fraction (0–1), $C_o$ is the outdoor ozone concentration (ppb), $E$ is the emission rate of ozone into the space (ppb·m$^3$·h$^{-1}$), $\lambda$ is the outdoor air exchange rate (h$^{-1}$), $V$ is the volume of air indoors (m$^3$), $k_{O3,surf}$ is the decay rate of ozone in the absence of PRM surfaces (h$^{-1}$), $k_{O3,prm}$ is the decay rate of ozone to the PRM (h$^{-1}$), $k_{O3,j}$ is the bimolecular reaction rate constant for ozone and indoor reactant $j$ (ppb$^{-1}$ h$^{-1}$), and $C_j$ is the indoor concentration of reactant $j$ (ppb). The coefficient α accounts for the reduction of non-PRM surface area when a PRM is used (Equation 2):

$$\alpha = \frac{(A_{tot} - A_{prm})}{A_{tot}}$$

(25)

where $A_{tot}$ is the total surface area of non-PRMs, and $A_{prm}$ is the surface area of the PRM. The introduction of $\alpha$ is based on an assumption that a PRM covers or replaces non-PRM surfaces without adding to the total indoor surface area. However, it is possible to use a PRM that does not cover an existing surface, e.g., use of panels hung from a ceiling.

The first term in the numerator of Equation 1 represents introduction of outdoor ozone to the indoor space. The second term in the numerator represents production of ozone from indoor sources. The first bracketed term in the denominator represents the removal of ozone to non-PRM surfaces in the space. The second bracketed term represents the removal of ozone to the PRM, and the third bracketed term represents the total consumption of ozone via homogeneous reactions.

The additional decay rate to the PRM increases the denominator of Equation 1, and thereby reduces the steady-state ozone concentration, $C_{O3}$, provided that the decay rate to non-PRM surfaces ($k_{O3,surf}$) does not decrease more than $k_{O3,prm}$ as a result of being replaced by the PRM. If a PRM replaces a non-PRM surface that is highly reactive with

135

ozone (e.g., carpet), then the benefit of reduced ozone would not be fully realized; however, a benefit may still result if the total reaction product emissions are reduced.

Equation 3 represents the solution to a steady-state mass balance on reaction product $p$ when a PRM is included in the interior space:

$$C_{p,i} = \frac{y_{surf,i}\alpha k_{O3,surf}C_{O3} + y_{prm,i}k_{O3,prm}C_{O3} + \sum^{i} y_{p,ij}k_{O3,j}C_{j}C_{O3}}{\lambda}$$

(26)

where $C_{p,i}$ is the steady-state indoor concentration of reaction product $i$ (ppb), $y_{surf,i}$ is the molar yield of reaction product $i$ from ozone reactions with all non-PRM surfaces (mol·mol$^{-1}$), $y_{prm,i}$ is the molar yield of the reaction product from ozone reactions on the surface of the PRM (mol·mol$^{-1}$), and $y_{p,ij}$ is the molar yield of reaction product $i$ from bimolecular reactions between ozone and indoor reactant $j$ (mol·mol$^{-1}$). All other variables are as defined for Equation 1. The first term in the numerator of Equation 3 represents formation of the reaction product when ozone reacts with non-PRM surfaces in the space. The second term in the numerator represents formation of the reaction product when ozone reacts with the surface of the PRM, and the third term in the numerator represents the total production rate of the reaction product when ozone reacts homogeneously with gaseous chemicals. The denominator represents removal of the reaction product from the space via air exchange.

In theory, the sum of the first two terms in the numerator of Equation 3 should be less than the alternative situation without PRM application for two reasons. First, the PRM reduces the overall area of background surface with a new surface that has a lower reaction product yield. Second, it should be more effective at removing ozone than background surfaces, and thus reduces the ozone concentration available to react with those surfaces.

The molar yield of a reaction product ($y_i$), is the ratio of moles of reaction product $i$ emitted from a material to moles of ozone removed by the material:

$$y_i = \frac{moles\ of\ i\ emitted}{moles\ of\ ozone\ removed} \tag{27}$$

Highly reactive materials with negligible molar yields of reaction products are desirable for indoor air quality. Some materials that have exhibited low yields of common n-aldehydes, e.g., formaldehyde ($C_1$), acetaldehyde ($C_2$), and nonanal ($C_9$), are listed in Table C2. However, there are two major caveats when comparing molar yields between materials. First, molar yields become dependent on the ozone concentration when it is high enough. That is, molar yields have been observed to decrease for some materials as the ozone concentration is raised above 100 ppb (Poppendieck et al, 2007b; Coleman et al., 2008; Lamble et al, 2011). Second, molar yields do not include every possible reaction product due to the practical limitations on collecting, identifying, and quantifying the various compounds that could form (e.g., organic acids) when ozone reacts with a surface.

### Removal of Ozone to PRMs

The reaction rate of ozone with a material surface ($\mu g \cdot h^{-1}$) is defined by Equation 5.

$$R = k_{O3,prm}C_{O3}V = v_{d,prm}C_{O3}A_{prm} \tag{28}$$

where $v_{d,prm}$ is the ozone deposition velocity to a PRM ($m \cdot h^{-1}$), $A_{prm}$ is the horizontally-projected surface area of the PRM ($m^2$), and $C_{O3}$ is the concentration of ozone above the surface calculated in Equation 1 ($\mu g \cdot m^{-3}$). All other variables are as defined for Equation 1. For a specific material, the ozone deposition velocity is related to both fluid mechanics in air adjacent to the material and the chemical reactivity of the material with ozone. The relationship of these two factors with $v_d$ is treated as a series of resistances. The overall resistance to ozone removal is the inverse of deposition velocity and is expressed by Equation 6 as:

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v_b \rangle} \qquad\qquad (29)$$

where $v_t$ is the transport-limited deposition velocity (m·s$^{-1}$), $\gamma$ is the reaction probability (-), and $\langle v_b \rangle$ is the Boltzmann velocity of ozone in air (~360 m·s$^{-1}$ at 20 °C). The total resistance to deposition is equal to the sum of the transport resistance, $1/v_t$, and the reaction resistance, $4/\gamma \langle v_b \rangle$ [116].

Values of $v_t$ depend on mixing conditions in bulk air as well as boundary layer fluid mechanics near surfaces. The former is influenced by heat sources in a room, e.g., thermal plumes derived by building occupants, HVAC operation, ceiling fans, etc. Boundary layer transport phenomena can be affected by the roughness of a material and its spatial dimensions [117]. Values of $v_t$ can vary over an order of magnitude in the same room [118] and can be influenced by location within the room, fan operation, occupant movement, and even the level of furnishings that can serve to reduce air movement [117,119]. Maximizing transport of ozone to the PRM surface, rather than to other materials, is key to realizing the benefits of PRMs, particularly for highly reactive materials with low reaction resistance.

The magnitude of the ozone reaction probability ($\gamma$) is determined by the composition of the material surface. Reaction probability for a specific material is the fraction of collisions of ozone molecules with the material surface that result in a reaction [116]:

$$\gamma = \frac{ozone\ removal\ rate}{ozone-material\ collision\ rate} \qquad\qquad (30)$$

Values of $\gamma$ vary over four orders of magnitude for typical indoor materials, from low values of approximately $10^{-8}$ (e.g., for glass) to high values that can exceed $10^{-4}$, e.g., for bricks [116]. Ideally, PRMs should sustain high reactivity with ozone over time without appreciable structural or superficial degradation.

For a given material, the transport resistance and the reaction resistance are dynamic, fluctuating as the fluid mechanics and surface properties change. A highly

reactive material, or effectively a material with low reaction resistance, is known to be "transport-limited". Conversely, a less reactive material that, even under favorable transport conditions, exhibits a lower deposition velocity, and is described as "surface limited" or "reaction limited". For example, Kunkel et al. [47] showed that the ozone deposition velocity to activated carbon cloth increases considerably with air speed, due to its known high reactivity with ozone. In contrast, the ozone deposition velocity of unpainted gypsum board tested by Kunkel et al. did not increase with air speed, likely because surface reactions were not sufficient to compete with transport within the range of observed air speeds.

### The Potential for Ozone Removal

Several researchers have determined $v_d$ for ozone within various indoor environments for a range of environmental conditions [120, and references therein]; $v_d$ typically ranges from 1 to 3 m·h$^{-1}$. Others have determined ozone decay rates ($k_{O3,surf}$) ranging from 2.5 to 7.6 h$^{-1}$ [47, 120, 121]. Because values of $v_t$ and $\gamma$ each span a wide range, $v_d$ and therefore the amount of ozone removed by materials can vary greatly, even within a specific indoor environment. By applying a very high transport-limited deposition velocity and a high ozone reaction probability to Equation 6, a near upper-bound ozone deposition velocity can be estimated.

Transport-limited deposition velocities have been inferred from Wilson [122] to be 2.5 m·h$^{-1}$ for indoor natural convection, and 7.2 m·h$^{-1}$ for "when air is stirred sufficiently to move loose papers". Since that study, values of $v_t$ have been measured at specific locations within indoor environments, and they encompass the values reported by Wilson (1968). Under cabinets and desks, Morrison et al. [117] measured values of $v_t$ between 2.2 and 3.2 m·h$^{-1}$, while in areas near hoods and computers where more air movement occurs, $v_t$ ranged from 4.3 to 5.2 m·h$^{-1}$. In one location near a window and a supply vent in an apartment, the $v_t$ was 18.7 m·h$^{-1}$ when the fan was switched on. Areas near doors and windows tend to have higher and more varying levels of $v_t$, with an observed range from 3.6 to 25.2 m·h$^{-1}$ [123].

139

Brick, a material sometimes used in indoor environments, has a relatively high ozone reaction probability. Experiments by Simmons and Colbeck [124] led to an ozone reaction probability of $2.2 \times 10^{-4}$ for both new and old brick. Substituting this value for $\gamma$, and a value of 7.2 m·h$^{-1}$ for $v_t$ [from 122] into Equation 6, results in an ozone deposition velocity equal to 6.5 m·h$^{-1}$. Assuming that the majority of indoor surfaces are highly reactive and that the surface area-to-volume ratio is 3 m$^{-1}$ [120, and references therein], leads to an ozone decay rate of 19.5 h$^{-1}$. Substituting this high-end decay rate into Equation 1, and assuming no homogeneous reactions ($\Sigma k_{O3,j} C_j = 0$), no indoor ozone sources ($\Sigma E = 0$), a penetration factor of $f = 0.79$ [125], and an air exchange rate of $\lambda = 0.5$ h$^{-1}$, the concentration of ozone would be reduced by 98% relative to outdoors; this corresponds to an indoor/outdoor ozone concentration ratio (I/O) of 0.02. If the indoor ozone decay rate is 2.8 h$^{-1}$, a mean value experimentally-determined in homes by Lee et al. [121], then the I/O ozone ratio would be 0.13. Typical I/O in buildings across various climates range from <0.1 to ~0.7 [83, 121]. The I/O for the highly reactive building scenario falls below this range by an order of magnitude, and can mean a reduction of the indoor ozone concentration by 10 ppb or more, enough to reduce the risk of morbidity and mortality associated with ozone, even at low concentrations [126].

## ANALYSIS OF PREVIOUS RESEARCH

Several researchers have studied ozone removal by PRMs. Key papers are listed in Table 2, and important findings of each are described in the following section.

### Ozone Removal

Removal of ozone by building materials has been quantified through several laboratory and field studies. Most of these studies have been short-term evaluations (i.e., up to 48 hours of ozone exposure). Furthermore, materials are usually tested as new, sometimes after a conditioning or airing out period, and far less often as aged materials.

**Table C1.** Studies conducted on materials that passively remove gaseous pollutants.

| Author | Material(s) | Pollutant(s) | Study Type |
|--------|-------------|--------------|------------|
| Moriske et al. [64] | Wallpaper w/ AcC backing | $O_3$, formaldehyde | Lab & field |
| Kunkel et al. [47] | Gypsum board, AcC cloth | $O_3$ | Lab & field |
| Lamble et al. [72] | 19 green-certified materials, e.g., clay paint & plaster | $O_3$ & carbonyl byproducts | Lab |
| Gall et al. [127,128] | Gypsum board, AcC cloth | $O_3$ | Modeling |
| Cros et al. [48] | AcC cloth, zero-VOC paint on gypsum board, perlite ceiling tile, recycled carpet | $O_3$ & carbonyl byproducts | Lab & field, longitudinal |
| Darling et al. [49] | Clay plaster on gypsum board | $O_3$ & carbonyl byproducts | Lab, sensory panel |
| Gall et al. [50] | zero-VOC paint on gypsum board, perlite ceiling tile, recycled carpet | $O_3$ & carbonyl byproducts | Lab |
| Gall et al. [129] | Cellulose filter papers, AcC cloth, pervious pavement, Portland cement concrete | $O_3$ | Lab |
| Rim et al. [130] | Mineral fiber ceiling tile, mold-guard paint on drywall, and carpet tile | $O_3$ | Lab |

Kunkel et al. [47] completed experiments in a 14 $m^3$ laboratory chamber and 35 $m^3$ bedroom in a test house to evaluate the potential for ozone removal using activated carbon (AcC) cloth (a synthetic fiber media coated with finely ground activated carbon), and unpainted gypsum board (UGB). They used fans to simulate different air speeds adjacent to materials. For laboratory chamber experiments, the mean deposition velocity to AcC cloth was over twice that of UGB, reflecting the increased reactivity of AcC cloth relative to UGB. Increases in air speed adjacent to materials (from 10 to 19 cm·s$^{-1}$) significantly increased the removal of ozone to AcC cloth, suggesting that transport-limitations are important for this highly reactive PRM. This was not the case for UGB; its performance as a PRM was not affected by changes in air speed over this range, suggesting significant reaction resistance. Increases in relative humidity from 20 to 60% consistently increased the ozone deposition velocity to AcC cloth at the higher air speed condition, but not at the lower air speed. The use of 4.4 $m^2$ of AcC cloth or UGB in a test house bedroom led to increases in the ozone decay rate, i.e., above background decay

rates, by 2-7 h$^{-1}$ and 2-3 h$^{-1}$, respectively, depending on air speeds. Small amounts of AcC cloth placed over ceiling fan blades increased the ozone decay rate by 1 h$^{-1}$ (33% above background decay) in the test house living room area when the fan was activated.

Lamble et al. [72] studied the ozone reaction probability and molar yields for $C_1$-$C_{12}$ saturated n-aldehydes (+ acetone) for 19 indoor materials marketed as green-certified. Experiments were completed in small 10-L laboratory chambers. Reaction probabilities across all materials ranged over approximately two orders of magnitude, from 8.8 x 10$^{-7}$ to 6.9 x 10$^{-5}$. Total molar yields of reaction products ranged from non-detectable to 0.7 moles of total product per mole of ozone removed. A specific clay wall plaster with an accompanying tinting agent appeared to be the most promising as a PRM, with a relatively high reaction probability and a product molar yield that was below the detection limit for all species.

Darling et al. [49] completed additional studies of the clay wall plaster described by Lamble et al. [72]. Perceived air quality (PAQ) was determined using a panel of human subjects exposed to eight combinations of a reactive pollutant source (carpet), the clay wall plaster applied to gypsum wallboard, and chamber air with and without ozone. The conditions of highest (best) PAQ and lowest aldehyde concentrations in chamber air occurred when only clay plaster or clay plaster + carpet were present in the absence of ozone. The addition of clay plaster when carpet and ozone were present significantly improved PAQ and lowered aldehyde concentrations. Moriske et al. [64] also noted the potential of two plaster materials for removal of ozone from indoor air.

Cros et al. [48] studied the ozone removal performance of some of the materials tested by Lamble et al. [72]. Material specimens were placed in actual buildings over a six-month period, and periodically were brought back to the laboratory to be tested in 48-L chambers to measure changes in ozone deposition velocity and reaction product emissions before placement back in the field. Activated carbon cloth was observed to maintain a relatively high reactivity with ozone across the six-month test period, independent of field location. Emission rates of reaction products were consistently low when AcC was exposed to ozone. A perlite-based ceiling tile also had a relatively high

142

ozone deposition velocity in test chambers (25% lower than AcC cloth) that was sustained throughout the study. Reaction product emissions following exposure to ozone were greater than for AcC cloth but considerably lower than those for carpet. Emissions from ceiling tile placed in a kitchen environment increased with time, presumably due to surface soiling by unsaturated organic acids in cooking oils that react with ozone.

Gall et al. [50] measured ozone deposition velocities and emissions of $C_1$ to $C_{10}$ carbonyls for large areas of three green building materials in a 68 m$^3$ environmental chamber. Each material was tested at 25%, 50%, and 75% relative humidity, and at low and high air mixing within the chamber, equivalent to 6 air changes per hour (ACH) and 12 ACH, respectively. While ozone deposition velocity to the carpet was the highest (6.1 m·h$^{-1}$), molar yields of carbonyls after the carpet was exposed to ozone were also relatively high (0.28 at 50% RH). For perlite ceiling tile, however, ozone deposition velocity was moderate (2.3 m·h$^{-1}$), and molar yields of carbonyls were low (0.03). No consistent trends in ozone deposition and byproduct emissions were observed with changes in relative humidity across all materials. Results were generally in good agreement with those for the same materials tested by Lamble et al. [72] and Cros et al. [48].

Rim et al. [130] measured ozone deposition velocities for three different indoor materials (a synthetic fiber carpet, latex paint on mineral fiber ceiling tile, and mold-guard paint on drywall) while simulating diurnal ozone conditions (high concentrations during the day, zero concentration at night). Ozone reaction probabilities were determined for fresh materials and for the same materials after 1 and 2 months of placement in an occupied office building. Results of this study reinforce the fact that ozone reactivity of materials decreases with prolonged exposure to ozone. In addition, the ozone reactivity of materials exposed to real indoor environments can fluctuate from month to month as the materials potentially come into contact with particles and organic molecules released during occupant activities.

Physical properties of porous materials and their effects on ozone reaction probability were investigated by Gall et al. [129]. Porosity, pore size distribution, and

material thickness were determined for cellulose filter papers, activated carbon cloth, pervious pavement, and Portland cement concrete. Ozone reaction probabilities of each material were quantified under high and low transport deposition velocities ($v_t$) in an 11.4-L stainless steel chamber. Reaction probabilities of each material at the greatest thickness tested and under low $v_t$ were $7.2\times10^{-6}$ (mean) for the two filter papers, $1.2\times10^{-5}$ for pervious pavement, $2.2\times10^{-5}$ for Portland cement concrete, and $5.4\times10^{-5}$ for activated carbon cloth. Increasing material thickness increased reaction probabilities for the filter papers (at high and low $v_t$) and pervious pavement (at high $v_t$), but no dependence on thickness was observed for Portland cement concrete and activated carbon cloth. Reaction probabilities for high porosity materials except for the filter papers (i.e., pervious pavement and activated carbon) increased by factors of 1.4 to 2.0 with increasing $v_t$.

Several other researchers have studied ozone deposition velocities, reaction probabilities and/or reaction product yields for a wide range of materials that are used indoors without specific attention to their selective use for ozone control. An evaluation of the literature suggests that, besides activated carbon, the most promising of such materials as PRMs for ozone control are inorganic materials, including clay bricks, calcareous stone, and ceiling tile made of mineral fibers or volcanic perlite. Ozone deposition velocities, reaction probabilities, and molar yields for many of these materials are listed in Table C2.

### Reaction Probabilities and Molar Yields

A few researchers have reported values of ozone reaction probabilities, or provided sufficient data to back-calculate $\gamma$, alongside corresponding values of byproduct molar yields. These data were compiled and are presented in Figure C1. Each data point contains a numbered label that corresponds to one type of material listed in Table C2, except for the materials tested by Wang and Morrison [92, 93]. The latter reported average molar yields among functionally similar materials that were tested in place in four different homes (see notes below Table C2 for more detail). The total molar yields

include yields for $C_1$-$C_{10}$ carbonyls. Yields reported by Gall et al. [50] also include acetone, benzaldehyde, and o-tolualdehyde; yields from Morrison and Nazaroff [89, 131] encompass $C_1$-$C_{13}$ n-aldehydes, and yields from Wang and Morrison [92, 93] also include 2-nonenal. When reaction probabilities were not reported, ozone deposition velocities and, if provided, transport-limited deposition velocities were substituted into Equation 6 to estimate $\gamma$. Additional details about each of these experimental studies, including reaction probability and yield data, are provided in Table C2.
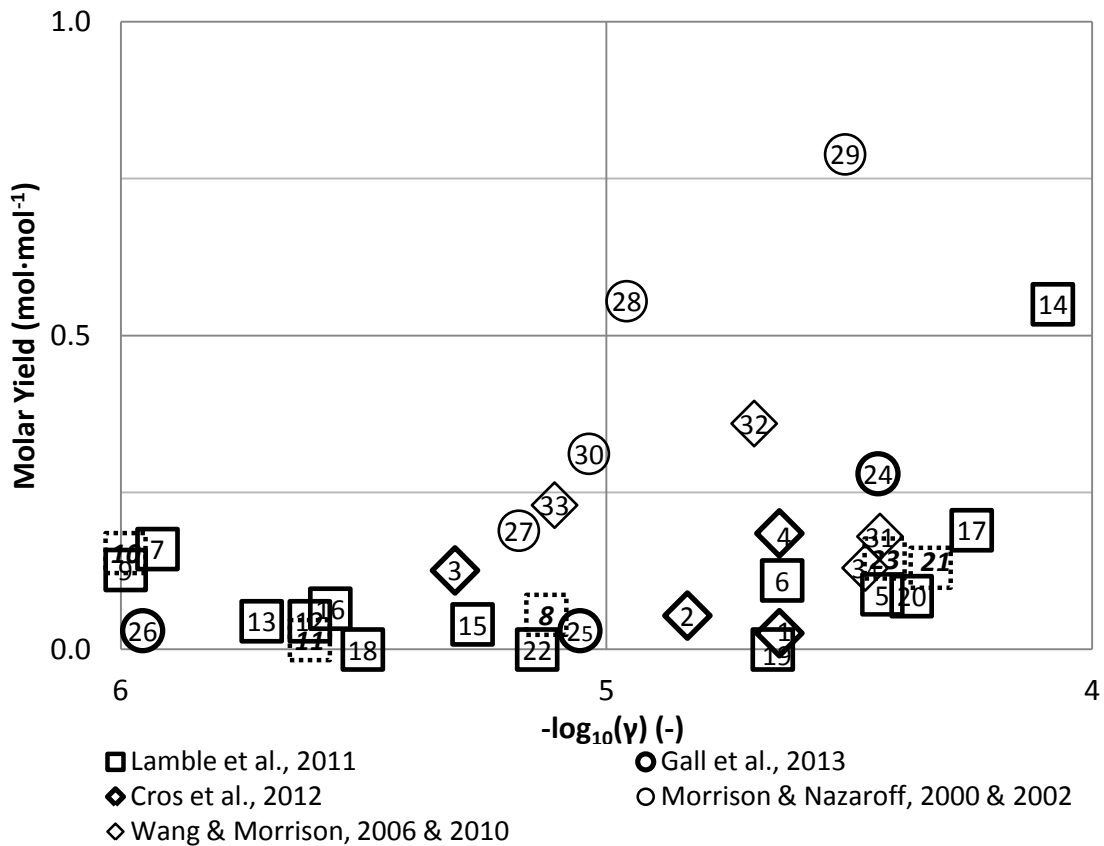


**Figure C1.** Ozone reaction probabilities (logarithmically transformed, note reverse values) and molar yields of $C_1$-$C_{10}$ carbonyls (unless noted otherwise in PREDICTING POTENTIAL **OZONE & REACTION PRODUCT REMOVAL & COSTS**

Much of the research on PRMs has been experimental in nature, with only one published study related to modeling of PRM effectiveness. Gall et al. [127, 128] completed Monte Carlo simulations to study the feasibility of PRM applications based on

data from 100 homes in Houston, Texas, and ozone deposition velocities reported by Kunkel et al. [47]. For reasonable ranges of test parameters they predicted a median ratio of indoor-to-outdoor ozone concentrations of 0.16 without the use of PRMs and 0.047 to 0.12 with PRMs installed. Median values of ozone removal effectiveness (% reduction in ozone concentration when a PRM is used relative to the case without a PRM) ranged from 22% (unpainted gypsum board with low air speeds) to 68% (activated carbon cloth with high air speeds). To achieve 50% removal of ozone in ½ of the homes would require 75 m2 of activated carbon cloth or 200 m2 of unpainted gypsum board.

A screening assessment was completed for this review to predict ozone removal effectiveness of a PRM using Equation 1, which was used to model steady-state ozone concentrations in a well-mixed indoor environment over a range of ozone deposition velocities. Clay paint (17 in Figure C1) was selected as a PRM for this example. It has a relatively high ozone reaction probability, a moderate byproduct yield, but little ozone-derived formaldehyde formation potential. Removal effectiveness was also estimated for indoor formaldehyde (HCHO) using the model for ozone reaction products (Equation 3). The removal effectiveness is the percent reduction of the ozone or ozone-derived HCHO concentration due to the PRM ($\Omega$ in Equation 8).

$$\Omega = 1 - \frac{C_{prm}}{C_{noprm}} \tag{31}$$

where *Cprm* is the indoor ozone or HCHO concentration with the PRM present (ppb), and *Cnoprm* is the ozone or HCHO concentration with no PRM present (ppb). If the indoor ozone or reaction-generated HCHO concentration with the PRM is equal to the concentration without the PRM, then the last term in Equation 8 would equal 1 and the removal effectiveness would be 0, or 0%. Conversely, if the concentration with the PRM is 0 pbb, then the last term in the equation would equal 0 and the removal effectiveness would be 1, or 100%.

The assumptions applied to Equation 1 and Equation 3 were an outdoor ozone concentration (*Co*) of 80 ppb, air exchange rate ($\lambda$) of 0.5 h-1, a residence volume of 420

m3, and an ozone decay rate to background (i.e., non-PRM) surfaces of 2.8 h-1 [121]. The penetration factor ($f$) was assumed to be 0.79 (Stephens et al., 2012). The range of deposition velocities ($vd$) correspond to a range of transport-limited deposition velocities ($vt$) that were assumed to be spatially uniform throughout the residence, and a fixed ozone reaction probability of the clay paint ($5.65 \times 10$-5). Each $vd$ was estimated using Equation 6. Transport-limited deposition velocities were varied from 3.4 to 10 m·h-1, and surface area of the clay paint was varied from 0 to 150 m2, allowing the area-to-volume ratio to vary accordingly; by these assumptions the ozone decay rate to the clay paint ($kO3,prm = vd_{,O3,prm} \cdot (Aprm/V)$) ranged from 0 to 2.3 h-1.

**Table**) for different materials tested by various researchers. Bolded, italicized data points surrounded by a dotted circle indicate yields with a higher prevalence of formaldehyde. Data in chart can be found in Table C2.

Materials located within the lower left-hand quadrant of Figure C1 are less reactive with ozone, but many have relatively low byproduct yields. For example, some of these materials include resilient floor tiles [(7) and (9)], cork wallboard (13), and low-VOC paint [(3) and (26)]. No materials have been reported to have relatively low ozone reaction probabilities and high byproduct yields, e.g., > 0.5. The upper right-hand quadrant of Figure C1 contains materials that are more reactive with ozone, but that also have high byproduct yields, such as acoustic wall panel (14), olefin fiber carpet (28), and nylon fiber carpet (29). High molar yields from carpets are most likely due to products that are emitted when ozone reacts with low-volatility unsaturated oils present on the surface of carpet fibers [89,132]. The large surface area of carpet fibers simultaneously contributes to high ozone reaction probabilities and byproduct emissions.

Materials with characteristics that indicate potential as PRMs are located in the lower right-hand quadrant, particularly those nearest to the horizontal axis, because they have high ozone reaction probabilities ($> 10^{-5}$) and low byproduct yields ($< 0.1$). Included within this quadrant, for example, are activated carbon cloth (1), perlite ceiling tile (2), recycled carpet (5), clay-based plaster (19), and unpainted gypsum board (20). Mineral fiber ceiling tile (*21*) and fiberglass ceiling tile (*23*) fall in this quadrant. However, formaldehyde was prevalent as a secondary byproduct from these materials. Other materials that have a high prevalence of formaldehyde as a secondary product are rubber floor tile (*8*), porcelain floor tile (*10*), and renewable wood flooring (*11*).

## PREDICTING POTENTIAL OZONE & REACTION PRODUCT REMOVAL & COSTS

Much of the research on PRMs has been experimental in nature, with only one published study related to modeling of PRM effectiveness. Gall et al. [127, 128]

completed Monte Carlo simulations to study the feasibility of PRM applications based on data from 100 homes in Houston, Texas, and ozone deposition velocities reported by Kunkel et al. [47]. For reasonable ranges of test parameters they predicted a median ratio of indoor-to-outdoor ozone concentrations of 0.16 without the use of PRMs and 0.047 to 0.12 with PRMs installed. Median values of ozone removal effectiveness (% reduction in ozone concentration when a PRM is used relative to the case without a PRM) ranged from 22% (unpainted gypsum board with low air speeds) to 68% (activated carbon cloth with high air speeds). To achieve 50% removal of ozone in ½ of the homes would require 75 m$^2$ of activated carbon cloth or 200 m$^2$ of unpainted gypsum board.

A screening assessment was completed for this review to predict ozone removal effectiveness of a PRM using Equation 1, which was used to model steady-state ozone concentrations in a well-mixed indoor environment over a range of ozone deposition velocities. Clay paint (17 in Figure C1) was selected as a PRM for this example. It has a relatively high ozone reaction probability, a moderate byproduct yield, but little ozone-derived formaldehyde formation potential. Removal effectiveness was also estimated for indoor formaldehyde (HCHO) using the model for ozone reaction products (Equation 3). The removal effectiveness is the percent reduction of the ozone or ozone-derived HCHO concentration due to the PRM ($\Omega$ in Equation 8).

$$\Omega = 1 - \frac{C_{prm}}{C_{noprm}} \tag{31}$$

where $C_{prm}$ is the indoor ozone or HCHO concentration with the PRM present (ppb), and $C_{noprm}$ is the ozone or HCHO concentration with no PRM present (ppb). If the indoor ozone or reaction-generated HCHO concentration with the PRM is equal to the concentration without the PRM, then the last term in Equation 8 would equal 1 and the removal effectiveness would be 0, or 0%. Conversely, if the concentration with the PRM is 0 pbb, then the last term in the equation would equal 0 and the removal effectiveness would be 1, or 100%.

149

The assumptions applied to Equation 1 and Equation 3 were an outdoor ozone concentration ($C_o$) of 80 ppb, air exchange rate ($\lambda$) of 0.5 h$^{-1}$, a residence volume of 420 m$^3$, and an ozone decay rate to background (i.e., non-PRM) surfaces of 2.8 h$^{-1}$ [121]. The penetration factor ($f$) was assumed to be 0.79 (Stephens et al., 2012). The range of deposition velocities ($v_d$) correspond to a range of transport-limited deposition velocities ($v_t$) that were assumed to be spatially uniform throughout the residence, and a fixed ozone reaction probability of the clay paint ($5.65 \times 10^{-5}$). Each $v_d$ was estimated using Equation 6. Transport-limited deposition velocities were varied from 3.4 to 10 m·h$^{-1}$, and surface area of the clay paint was varied from 0 to 150 m$^2$, allowing the area-to-volume ratio to vary accordingly; by these assumptions the ozone decay rate to the clay paint ($k_{O3,prm} = v_{d,O3,prm} \cdot (A_{prm}/V)$) ranged from 0 to 2.3 h$^{-1}$.

**Table C2.** Ozone reaction probabilities, $C_1$-$C_{10}$ molar yields, and experimental conditions for materials referenced in Figure C1.

| # | Material | $\gamma$ (-) | y* (mol/mol) | HCHO Prevalent | T (°C), RH (%) |
|---|---|---|---|---|---|
| 1 | Activated carbon mat | 2.27E-05 | 0.026 | | na, 50 |
| 2 | Perlite ceiling tile | 1.47E-05 | 0.054 | | na, 50 |
| 3 | Low-voc paint on drywall | 4.88E-06 | 0.126 | | na, 50 |
| 4 | Recycled carpet | 2.27E-05 | 0.185 | | na, 50 |
| 5 | Recycled carpet | 3.70E-05 | 0.088 | | 25, 50 |
| 6 | Fabric-backed carpet | 2.30E-05 | 0.110 | | 25, 50 |
| 7 | Resilient floor tile | 1.19E-06 | 0.160 | | 25, 50 |
| 8 | Rubber floor tile | 7.52E-06 | 0.055 | * | 25, 50 |
| 9 | Bio-based resilient floor tile | 1.02E-06 | 0.127 | | 25, 50 |
| 10 | Porcelain floor tile | 1.02E-06 | 0.153 | * | 25, 50 |
| 11 | Renewable wood flooring | 2.45E-06 | 0.015 | * | 25, 50 |
| 12 | Finished bamboo flooring | 1.95E-06 | 0.045 | | 25, 50 |
| 13 | Cork wallboard | 2.45E-06 | 0.045 | | 25, 50 |
| 14 | Acoustic wall panel | 8.30E-05 | 0.550 | | 25, 50 |
| 15 | Rayon wall covering | 5.30E-06 | 0.040 | | 25, 50 |
| 16 | Latex paint | 2.70E-06 | 0.065 | | 25, 50 |
| 17 | Clay-based paint | 5.65E-05 | 0.190 | | 25, 50 |
| 18 | Collagen-based paint | 3.15E-06 | 0.000 | | 25, 50 |
| 19 | Clay-based plaster | 2.20E-05 | 0.000 | | 25, 50 |
| 20 | Drywall | 4.25E-05 | 0.085 | | 25, 50 |
| 21 | Mineral fiber ceiling tile | 4.65E-05 | 0.130 | * | 25, 50 |
| 22 | Perlite ceiling tile | 7.20E-06 | 0.000 | | 25, 50 |
| 23 | Fiberglass ceiling tile | 3.74E-05 | 0.145 | * | 25, 50 |
| 24 | Recycled carpet | 3.62E-05 | 0.280 | | 25.2, 50 |
| 25 | Perlite ceiling tile | 8.82E-06 | 0.030 | | 25.2, 50 |
| 26 | Low-voc paint on drywall | 1.11E-06 | 0.030 | | 25.2, 50 |
| 27 | Nylon fiber carpet 1 | 6.60E-06 | 0.189 | | 22.9, 50 |
| 28 | Olefin fiber carpet 1 | 1.10E-05 | 0.555 | | 22.9, 50 |
| 29 | Nylon fiber carpet 2 | 3.10E-05 | 0.789 | | 22.9, 50 |
| 30 | Olefin fiber carpet 2 | 9.20E-06 | 0.312 | | 22.9, 50 |
| 31 | Living room carpet | 3.66E-05 | 0.180 | | 14-28, 50 |
| 32 | Kitchen countertops | 2.01E-05 | 0.360 | | 14-28, 50 |
| 33 | Kitchen floors | 7.82E-06 | 0.230 | | 14-28, 50 |
| 34 | Bedroom carpets | 3.41E-05 | 0.130 | | 14-28, 50 |

*Molar yields include $C_1$-$C_{10}$ carbonyls (see notes below).

[a][48]:  Values presented were measured prior to deployment of materials to field locations. Reaction probability was estimated from $v_d$ interpreted from a figure and an approximate $v_t$ based on measurements in the same chambers during another project.

[b][72]:  Reaction probabilities are averages from replicate experiments. Yields presented are averages from replicate measurements after 2 hours of ozone exposure.

[c][50]:  Yields presented include benzaldehyde, o-tolualdehyde, and acetone. Yields are from measurements after ~1 hour of ozone exposure when the concentration was 90 pbb $O_3$.

[d][89,131]:  Materials were aired out for more than 12 months and then exposed to ozone for 48 hours. Yields of $C_1$-$C_{13}$ were estimated from the relation, emission rate (μg m$^{-3}$) = $yield \times v_d \times C_{O3}$, where $C_{O3} \approx$ 200 μg m$^{-3}$. Total byproduct emission rates were interpreted from Figure 2 in the 2002 article.

[e][92,93]:  Materials were tested in situ in actual homes in 2005, 2006, and 2007 using a 4.25-L flux chamber. Yields presented include 2-nonenal. Materials varied among the homes; living room carpets included 3 nylon cut pile carpets and 1 wool rug; kitchen countertops included 2 resin and 2 laminate; kitchen floors included 2 ceramic tile, 1 hardwood, and 1 linoleum; all bedroom carpets were nylon cut pile.

The molar yield of HCHO from ozone reactions with non-PRM surfaces ($y_{surf}$) was assumed to be 0.07 mol·mol$^{-1}$, based on work by Zhang et al. [133] and Waring and Siegel [102]. The HCHO molar yield from clay paint ($y_{prm}$) was assumed to be 0 mol·mol$^{-1}$, following an observation by Lamble et al. [72] of non-detectable formaldehyde yield. Figure S1 in Supporting Information illustrates removal effectiveness when the HCHO deposition velocity to the PRM is assumed to be 0.5 m·h$^{-1}$. Removal effectiveness for HCHO would be higher if HCHO is adsorbed to the clay in the PRM; clay has been shown to have a high capacity for adsorbing VOCs [134]. Additional details on model inputs are provided in Supporting Information.

Ozone removal effectiveness is plotted in Figure for four different ozone deposition velocities over a range of surface areas of clay-based paint applied in a single-family residence. Results for formaldehyde removal effectiveness are shown in Figure. Cost estimates for the clay paint are also shown for surface areas of 25, 75, and 125 m$^2$, assuming $3.70 per double-coated m$^2$. Labor costs are not included here, e.g., the homeowner paints the home.

By optimizing the deposition of ozone to the painted surface (i.e., by increasing $v_t$ and thereby $v_d$), even greater ozone removal could occur. If a total wall area of 25 m$^2$ is coated with the paint – enough to coat the walls of a small bedroom - then up to 10% of the ozone concentration could be reduced throughout the home. Alternatively, up to 57% of the ozone could be reduced within a 36 m$^3$ bedroom if all of the paint is applied to the bedroom walls. To cover this area would cost roughly $93. An area of 75 m$^2$ could cover the walls of a large bedroom and would cost around $227. At this level of coverage, up to 25% of the ozone concentration could be reduced throughout the home, or up to 70% could be reduced within a 60 m$^3$ bedroom. At the higher end, covering 125 m$^2$ of walls would cost roughly $462 and could reduce up to 36% of the indoor ozone throughout the home, or up to 66% of the ozone within a 120 m$^3$ living room.
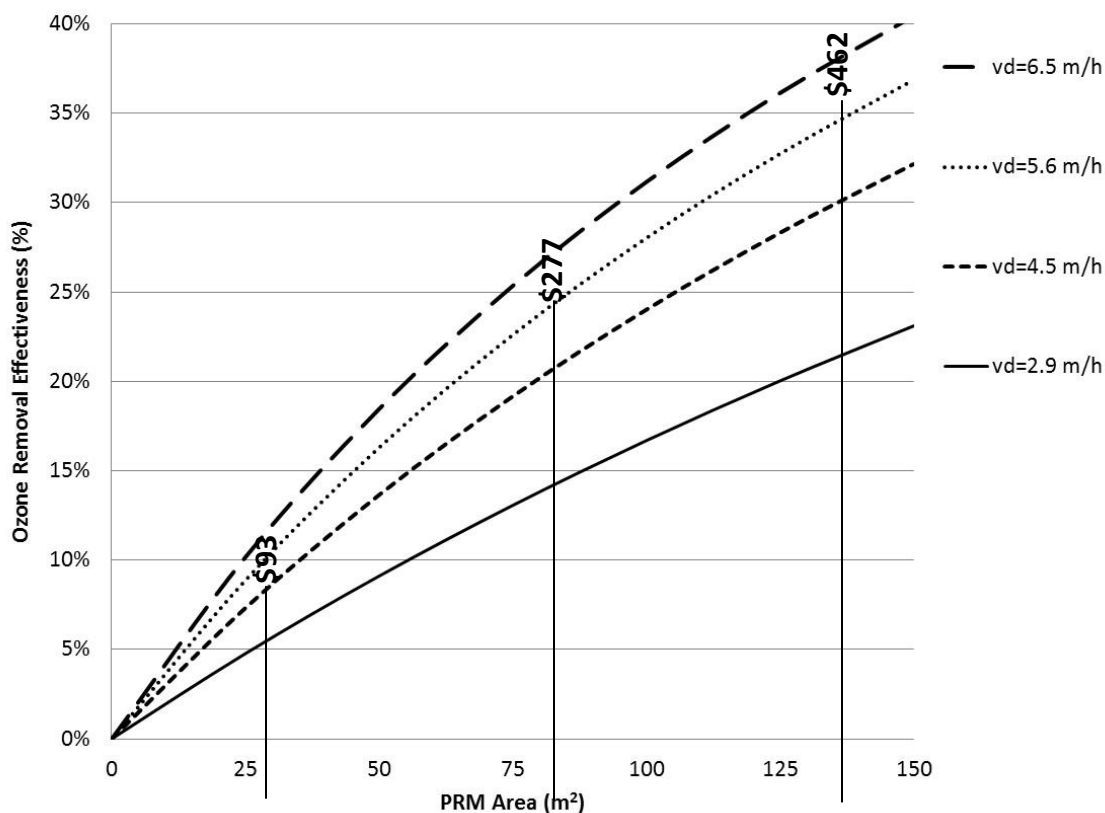
**Figure C2.** Ozone removal effectiveness for various ozone deposition velocities of clay paint. Vertical lines indicate estimated cost of clay paint for the corresponding surface area.

The indoor formaldehyde concentration could also be reduced by applying the clay paint to walls or other surfaces. A $93 investment could help reduce up to 10% (-0.4 ppb) of the HCHO concentration generated by surface chemistry throughout the home, or up to 57% (-2.2 ppb) of the chemistry-derived HCHO could be reduced within a 36 m$^3$ bedroom (i.e., assuming a volume of 36 m$^3$ instead of 420 m$^3$). For larger investments and surface areas of clay paint, the chemistry-derived HCHO concentration could be reduced in the home by up to 25% (-1.0 ppb) ($227) and 36% (-1.4 ppb) ($462). At $227, up to 70% (-2.7 ppb) of the chemistry-derived HCHO concentration in a large 60 m$^3$ bedroom could be reduced, and at $462, up to 66% (-2.6 ppb) of the chemistry-derived HCHO could be reduced in a 120 m$^3$ living room.

154
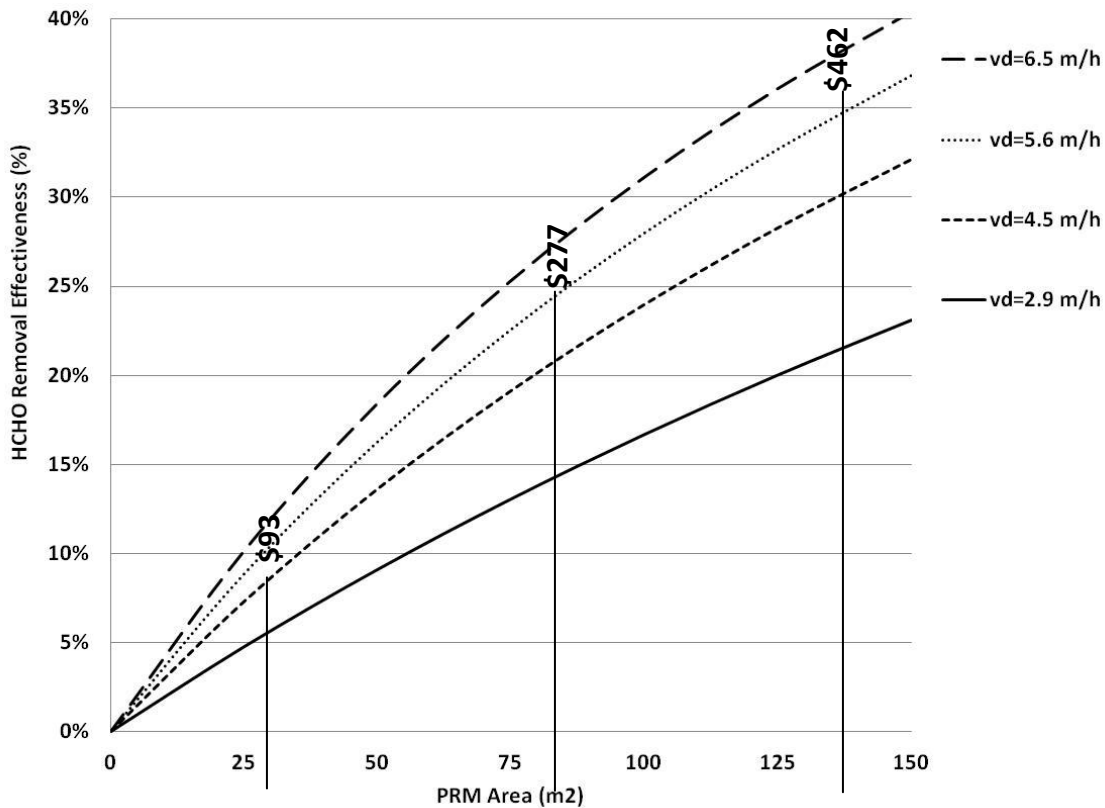
**Figure C3.** Percent removal of formaldehyde from indoor air for various ozone deposition velocities of clay paint under assumptions described above and in Supporting Information.

## LIMITATIONS & CONTINUING RESEARCH NEEDS & OPPORTUNITIES

Passive removal materials (PRMs) are an alternative or possibly supplemental approach to in-duct ozone removal (e.g., by using activated carbon filters). Based on a review of past and current published literature we conclude the following about the state of PRM technology for ozone removal in buildings:

1) Commercially-available materials that could be effective PRMs for ozone removal appear to exist today. However, long-term performance under field conditions is lacking

for most of these materials, and therefore effectiveness over realistic usage periods is currently speculative.

2) The materials described in (1) are generally inorganic in composition and include some clay-based paints/plasters, clay bricks, calcareous stone, perlite/mineral-based ceiling tiles, and unpainted gypsum wallboard.

3) Preliminary model evaluations suggest that some PRMs could significantly reduce indoor concentrations of ozone and some reaction products, and hence occupant exposures to these pollutants in residential buildings. Evaluations have not yet been completed for non-residential buildings.

4) While the ozone and HCHO removal effectiveness of PRMs can be considerable, absolute differences in the indoor concentrations can be small, i.e., less than 1 to 2 ppb, when indoor levels are already less than 10 ppb. However, these differences increase and become more important as indoor concentrations become higher.

Research on passive removal materials is in its early stages. The following areas for future research remain:

1) Field testing is needed to ascertain the long-term performance of passive removal materials. The key operational parameter is the PRM's reaction probability and how it changes over many years. Given the time frames needed it will likely not be feasible to follow a new PRM across its lifetime in real world applications. As such, one possible approach is to study a new PRM that is placed in the field and returned to a laboratory for analysis before returning to the field over a two or three year period. Such studies could be coupled with reaction probability measurements of similar materials that were used in buildings for much longer periods of time before being removed for purposes of renovation and acquired and analyzed by researchers.

2) Ensuring ease of use and affordability of PRMs that can be implemented in homes and other non-residential indoor environments is important. The more affordable and easily

incorporated a commercially-available PRM is, the more likely it could be selected by building contractors, business owners, and others. Nomura and Jones [53-55] have begun to include these considerations for removal of formaldehyde to aminosilicas.

3) Environmental sustainability of PRMs should be another focus of future research. Materials that are widely available, require little energy to be produced, are renewable or made from recycled materials, and non-toxic should be targeted for use as PRMs.

**ACKNOWLEDGEMENTS**

## References

[1] Klepeis, N. E., Nelson, W. C., Ott, W. R., Robinson, J. P., Tsang, A. M., Switzer, P., Engelmann, W. H. (2001). The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *J Expo Anal Env Epid*, *11*(3), 231-252, DOI: 10.1038/sj.jea.7500165.

[2] deCastro, B.R., Sax, S.N., Chillrud, S.N., Kinney, P.L., & Spengler, J.D. (2007). Modeling time-location patterns of inner-city high school students in New York and Los Angeles using a longitudinal approach with generalized estimating equations. *J Expo Sci Env Epid, 17*(3), 233-247, DOI: 10.1038/sj.jes.7500504.

[3] Schweizer, C., Edwards, R.D., Bayer-Oglesby, L., Gauderman, W.J., Ilaqua, V., Juhani Jantunen, M., … Künzli, N. (2007). Indoor time-microenvironment-activity patterns in seven regions of Europe. *J Expo Sci Env Epid, 17*(2), 170-181, DOI: 10.1038/sj.jes.7500490.

[4] Hussein, T., Paasonen, P., Kulmala, M. (2012). Activity pattern of a selected group of school occupants and their family members in Helsinki − Finland. *Sci Total Environ, 425*(15), 289-292, DOI: 10.1016/j.scitotenv.2012.03.002.

[5] Allen, R., Wallace, L., Larson, T., Sheppard, L., & Liu, L.J.S. (2004). Estimated hourly personal exposures to ambient and nonambient particulate matter among sensitive populations in Seattle, Washington. *J Air Waste Manage, 54*(9), 1197-1211.

[6] Wallace L, Williams R, Rea A, Croghan C. (2006). Continuous week-long measurements of personal exposures and indoor concentrations of fine particles for 37 health-impaired North Carolina residents for up to four seasons. *Atmos Environ, 40*(3), 399–414, DOI: 10.1016/j.atmosenv.2005.08.042.

[7] Wheeler, A.J., Xu, X.H., Kulka, R., You, H.Y., Wallace, L. et al. (2011). Windsor, Ontario exposure assessment study:  Design and methods validation of personal, indoor, and outdoor air pollution monitoring. *J Air Waste Manage, 61*(3), 324-338, DOI: 10.3155/1047-3289.61.3.324.

[8] Kilpelainen, M., Terho, E.O., Helenius, H., Koskenvuo, M. (2001). Home dampness, current allergic diseases, and respiratory infections among young adults. *Thorax 5*, 462-467, DOI: 10.1136/thorax.56.6.462.

[9] Wang, J., Engvall, K., Smedje, G., Norbäck, D. (2014a). Rhinitis, asthma and respiratory infections among adults in relation to the home environment in multi-family buildings in Sweden. *PLOS ONE, 9*(8), Article number e105125, DOI: 10.1371/journal.pone.0105125.

[10] Lappalainen, S., Salonen, H., Salmi, K., & Reijula, K. (2013). Indoor air particles in office buildings with suspected indoor air problems in the Helsinki area. *Int J Occcup Med Env, 26*(1), 155-164, DOI: 10.2478/s13382-013-0091-5.

[11] Bornehag, C.G., Sundell, J., Weschler, C.J., Sigsgaard, T., Lundgren, B., Hasselgren, M. & Hagerhed-Engman, L. (2004). The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. *Environ Health Perspect, 112*, 1393-1397, DOI: 10.1289/ehp.7187.

[12] Rumchev, K.*,* Spickett, J.*,* Bulsara, M.*,* Phillips, M. *&* Stick, S. *(*2004). Association of domestic exposure to volatile organic compounds with asthma in young children. *Thorax, 59, 746-751*, DOI: 10.1136/thx.2003.013680.

[13] Araki, A., Kanazawa, A., Kawai, T., Eitaki, Y., Morimoto, K., Nakayama, K. et al. (2012). The relationship between exposure to microbial volatile organic compound and allergy prevalence in single-family homes. *Sci Total Environ 423*, 18-26, DOI: 10.1016/j.scitotenv.2012.02.026.

[14] Wargocki, P., Wyon, D.P., Baik, Y.K., Clausen, G., & Fanger, P.O. (1999). Perceived air quality, sick building syndrome (SBS) symptoms and productivity in an office with two different pollution loads. *Indoor Air, 9*, 165–179, DOI: 10.1111/j.1600-0668.1999.t01-1-00003.x.

[15] Wargocki, P., Bakó-Biró, Z., Clausen, G., & Fanger, P.O. (2002). Air quality in a simulated office environment as a result of reducing pollution sources and increasing ventilation. *Energ Buildings, 34*(8), 775-783, DOI: 10.1016/S0378-7788(02)00096-8.

[16] Apte, M.G., Buchanan, I.S.H., & Mendell, M.J. (2008). Outdoor ozone and building-related symptoms in the BASE study. *Indoor Air, 18*(2), 156-170, DOI: 10.1111/j.1600-0668.2008.00521.x.

[17] Buchanan, I.S.H., Mendell, M.J., Mirer, A.G., & Apte, M.G. (2008). Air filter materials, outdoor ozone and building-related symptoms in the BASE study. *Indoor Air, 18*(2), 144-155, DOI: 10.1111/j.1600-0668.2008.00519.x.

[18] Elbayoumi, M., Ramli, N.A., Yusof, N.F.F.M., & Al Madhoun, W. (2015). Seasonal variation in schools' indoor air environments and health symptoms among students in an Eastern Mediterranean climate. *Hum Ecol Risk Assess, 21*(1), 184-204, DOI: 10.1080/10807039.2014.894444.

[19] Fisk, W. J., & Rosenfeld, A. H. (2000).Health and productivity gain from better indoor environments and their relationship with building energy efficiency. *Annu Rev Energy* Environ, 25, 537-566, DOI: 10.1146/annurev.energy.25.1.537.

[20] Seppanen, O.A., & Fisk, W. (2006). Quantitative relations between indoor environmental quality and work performance or health. *HVAC&R Res, 12*(4), 957-973.

[21] Mudway, I. S., & Kelly, F. J. (2000). Ozone and the lung: a sensitive issue. Molecular Aspects of Medicine, 21(1-2), 1-48, DOI: 10.1016/S0098-2997(00)00003-0.

[22] Levy, J. I., Carrothers, T. J., Tuomisto, J. T., Hammitt, J. K., & Evans, J. S. (2001). Assessing the public health benefits of reduced ozone concentrations. *Environ Health Persp, 109*(12), 1215-1226, DOI: 10.1289/ehp.011091215.

[23] USEPA (2006). *Air Quality Criteria for Ozone and Related Photochemical Oxidants* (No. EPA/600/R-05/004aF-cF). Washington, DC: U.S. Environmental Protection Agency.

[24] Bell, M. L., Dominici, F., & Samet, J. M. (2005). A meta-analysis of time-series studies of ozone and mortality with comparison to the national morbidity, mortality, and air pollution study. *Epidemiology*, *16*(4), 436-445, DOI: 10.1097/01.ede.0000165817.40152.85.

[25] Gryparis, A., Forsberg, B., Katsouyanni, K., Analitis, A., Touloumi, G., Schwartz, J., … & Dortbudak, Z. (2004). Acute effects of ozone on mortality from the "Air pollution and health:  A European approach" project. *Am J Resp Crit Care*, *170*(10), 1080-1087, DOI: 10.1164/rccm.200403-333OC.

[26] Ito, K., De Leon, S. F., & Lippmann, M. (2005). Associations between ozone and daily mortality - Analysis and meta-analysis. *Epidemiology*, *16*(4), 446-457, DOI: 10.1097/01.ede.0000165821.90114.7f.

[27] Jerrett, M., Burnett, R. T., Pope, C. A., Ito, K., Thurston, G., Krewski, D., … & Thun, M. (2009). Long-Term Ozone Exposure and Mortality. *New Engl J Med*, *360*(11), 1085-1095, DOI: 10.1056/NEJMoa0803894.

[28] Parodi, S., Vercelli, M., Garrone, E., Fontana, V., & Izzotti, A. (2005). Ozone air pollution and daily mortality in Genoa, Italy between 1993 and 1996. *Public Health*, *119*(9), 844-850, DOI: 10.1016/j.puhe.2004.10.007.

[30] McConnell, R., Berhane, K., Gilliland, F., London, S. J., Islam, T., Gauderman, W. J., … & Peters, J. M. (2002). Asthma in exercising children exposed to ozone: a cohort study. *Lancet*, *359*(9304), 386-391, DOI: 10.1016/S0140-6736(02)07597-9.

[31] Hubbell, B. J., Hallberg, A., McCubbin, D. R., & Post, E. (2005). Health-related benefits of attaining the 8-hr ozone standard. *Environ Health Persp*, *113*(1), 73-82, DOI: 10.1289/ehp.7186.

[32] Yang, Q. Y., Chen, Y., Shi, Y. L., Burnett, R. T., McGrail, K. M., & Krewski, D. (2003). Association between ozone and respiratory admissions among children and the elderly in Vancouver, Canada. *Inhal Toxicol*, *15*(13), 1297-1308, DOI: 10.1080/08958370390241768.

[33] Weschler, C. J. (2006). Ozone's impact on public health: Contributions from indoor exposures to ozone and products of ozone-initiated chemistry. *Environ Health Persp*, *114*(10), 1489-1496, DOI: 10.1289/ehp.9256.

[34] Smith, R. L., Xu, B., & Switzer, P. (2009). Reassessing the relationship between ozone and short-term mortality in U.S. urban communities. *Inhal Toxicol, 21*(Suppl 2), 37-61. DOI: 10.1080/08958370903161612.

[35] Chen, C., Zhao, B., & Weschler, C. J. (2012). Assessing the influence of indoor exposure to "outdoor ozone" on the relationship between ozone and short-term mortality in U.S. communities. *Environ Health Persp, 120*(2), 235-240, DOI: 10.1289/ehp.1103970.

[36] Logue, J. M., Price, P. N., Sherman, M. H., Singer, B. C. (2012). A method to estimate the chronic health impact of air pollutants in U.S. residences. *Environ Health Persp, 120*(2), 216-222, DOI: 10.1289/ehp.1104035.

[37] Aldred, J.A., Darling, E., Morrison, G., Siegel, J., & Corsi, R.L. (2015). Benefit-cost analysis of commercially available activated carbon filters for indoor ozone removal in single-family homes. *Indoor Air,* DOI: 10.1111/ina.12220.

[38] Destaillats, H., Maddalena, R. L., Singer, B. C., Hodgson, A. T., & McKone, T. E. (2008). Indoor pollutants emitted by office equipment: A review of reported data and information needs. *Atmos Environ, 42*(7), 1371-1388, DOI: 10.1016/j.atmosenv.2007.10.080.

[39] Waring, M. S., & Siegel, J. A. (2011). The effect of an ion generator on indoor air quality in a residential room. *Indoor Air, 21*(4), 267–276, DOI: 10.1111/j.1600-0668.2010.00696.x.

[40] Singh, B. P., Kumar, A., Singh, D., Punia, M., Kumar, K., & Jain, V. K. (2014). An assessment of ozone levels, UV radiation and their occupational health hazard estimation during photocopying operation. *J Hazard Mater, 275*, 55-62, DOI: 10.1016/j.jhazmat.2014.04.049.

[41] Shair, F. H. (1981). Relating indoor pollutant concentrations of ozone and sulfur dioxide to those outside: economic reduction of indoor ozone through selective filtration of the make-up air. *ASHRAE Tran*, *87*(1), 116-139.

[42] Shields, H. C., Weschler, C. J., & Naik, D. (1999). Ozone removal by charcoal filters after continuous extensive use (5 to 8 years). In *Proceedings of the 8th International Conference on Indoor Air Quality and Climate* (Vol. 4, pp. 49-54).

[43] Lee, P., & Davidson, J. (1999). Evaluation of activated carbon filters for removal of ozone at the ppb level. *Am Ind Hyg Assoc J, 60*(5), 589-600, DOI: 10.1080/00028899908984478.

[44] Bekö, G., Clausen, G., & Weschler, C. J. (2008). Sensory pollution from bag filters, carbon filters and combinations. *Indoor Air, 18*(1), 27-36, DOI: 10.1111/j.1600-0668.2007.00501.x.

[45] Bekö, G., Fadeyi, M. O., Clausen, G., & Weschler, C. J. (2009). Sensory pollution from bag-type fiberglass ventilation filters: Conventional filter compared with filters containing various amounts of activated carbon. *Build Environ, 44*(10), 2114-2120, DOI: 10.1016/j.buildenv.2009.03.002.

[46] Lin, C.-C., & Chen, H.-Y. (2014). Impact of HVAC filter on indoor air quality in terms of ozone removal and carbonyls generation. *Atmos Environ, 89*, 29-34, DOI: 10.1016/j.atmosenv.2014.02.020.

[47] Kunkel, D. A., Gall, E. T., Siegel, J. A., Novoselac, A., Morrison, G. C., & Corsi, R. L. (2010). Passive reduction of human exposure to indoor ozone. *Build Environ*, *45*(2), 445-452, DOI: 10.1016/j.buildenv.2009.06.024.

[48] Cros, C. J., Morrison, G. C., Siegel, J. A., & Corsi, R. L. (2012). Long-term performance of passive materials for removal of ozone from indoor air. *Indoor Air*, *22*(1), 43-53, DOI: 10.1111/j.1600-0668.2011.00734.x.

[49] Darling, E. K., Cros, C. J., Wargocki, P., Kolarik, J., Morrison, G. C., & Corsi, R. L. (2012). Impacts of a clay plaster on indoor air quality assessed using chemical and sensory measurements. *Build Environ*, *57*, 370-376, DOI: 10.1016/j.buildenv.2012.06.004.

[50] Gall, E., Darling, E., Siegel, J. A., Morrison, G. C., & Corsi, R. L. (2013). Evaluation of three common green building materials for ozone removal, and

primary and secondary emissions of aldehydes. *Atmos Environ*, 77, 910-918, DOI: 10.1016/j.atmosenv.2013.06.014.

[51] Diamanti, M. V., Del Curto, B., Ormellese, M., & Pedeferri, M. P. (2013). Photocatalytic and self-cleaning activity of colored mortars containing TiO2. *Constr Build Mater, 46*, 167-174, DOI: 10.1016/j.conbuildmat.2013.04.038.

[52] Gallego, E., Roca, F. J., Perales, J. F., & Guardino, X. (2013). Experimental evaluation of VOC removal efficiency of a coconut shell activated carbon filter for indoor air quality enhancement. *Build Environ, 67*, 14-25, DOI: 10.1016/j.buildenv.2013.05.003.

[53] Nomura, A., & Jones, C. W. (2013). Amine-functionalized porous silicas as adsorbents for aldehyde abatement. *ACS Applied Materials & Interfaces, 5*(12), 5569-5577, DOI: 10.1021/am400810s.

[54] Nomura, A., & Jones, C. W. (2014). Enhanced formaldehyde-vapor adsorption capacity of polymeric amine-incorporated aminosilicas. *Chem-Eur J, 20*(21), 6381-6390, DOI: 10.1002/chem.201304954.

[55] Nomura, A., & Jones, C. W. (2015). Airborne aldehyde abatement by latex coatings containing amine-functionalized porous silicas. *Ind Eng Chem Res, 54*(1), 263-271, DOI: 10.1021/ie504165d.

[56] Popescu, R. S., Blondeau, P., Jouandon, E., Costes, J. C., & Fanlo, J. L. (2013). Elemental modeling of adsorption filter efficiency for indoor air quality applications. *Build Environ, 66*, 11-22, DOI: 10.1016/j.buildenv.2013.01.025.

[57] Jo, W.-K., & Chun, H.-H. (2014). Application of fibrous activated carbon filter in continuous-flow unit for removal of volatile organic compounds under simulated indoor conditions. *Aerosol and Air Quality Research, 14*(1), 347-354, DOI: 10.4209/aaqr.2013.02.0057.

[58] Shen, J.-H., Wang, Y.-S., Lin, J.-P., Wu, S.-H., & Horng, J.-J. (2014). Improving the indoor air quality of respiratory type of medical facility by zeolite filtering. *JAPCA J Air Waste Ma, 64*(1), 13-18, DOI: 10.1080/10962247.2013.831798.

[59] Wang, M., Zhang, P., Li, J., & Jiang, C. (2014b). The effects of Mn loading on the structure and ozone decomposition activity of MnOx supported on activated carbon. *Chinese J Catal, 35*(3), 335–341, DOI: 10.1016/S1872-2067(12)60756-6.

[60] Huang, X., Wang, Y.-J., & Di, Y.-H. (2007). Experimental study of wool fiber on purification of indoor air. *Text Res J, 77*(12), 946-950, DOI: 10.1177/0040517507083519.

[61] Curling, S.F., Loxton, C., & Ormondroyd, G.A. (2012). A rapid method for investigating the absorption of formaldehyde from air by wool. *J Mater Sci, 47*(7), 3248-3251.

[62] Yu, J.-W., Christiansson, J., & Neretnieks, I. (1993). Modeling of a passive adsorption sheet to purify indoor air. *Indoor Air*, *3*(4), 310-314, DOI: 10.1111/j.1600-0668.1993.00013.x.

[63] Sekine, Y., & Nishimura, A. (2001). Removal of formaldehyde from indoor air by passive type air-cleaning materials. *Atmos Environ*, *35*, 2001-2007, DOI: 10.1016/S1352-2310(00)00465-9.

[64] Moriske, H. J., Ebert, G., Konieczny, L., Menk, G., & Schondube, M. (1998). Concentrations and decay rates of ozone in indoor air in dependence on building and surface materials. *Toxicol Lett*, *96-7*, 319-323, DOI: 10.1016/S0378-4274(98)00088-5.

[65] Ryhl-Svendsen, M. (2011). Passive sorption of organic compounds on clay bricks. *INDOOR AIR 2011, The 12 International Conference on Indoor Air Quality and Climate,* Austin, TX, 5-11 June 2011, 6pp. (paper 383).

[66] Ichiura, H., Kitaoka, T., & Tanaka, H. (2003). Removal of indoor pollutants under UV irradiation by a composite TiO2-zeolite sheet prepared using a papermaking technique. *Chemosphere, 50*(1), 79-83, DOI: 10.1016/S0045-6535(02)00604-5.

[67] Taoda, H., Fukaya, M., Watanabe, E., & Tanaka, K. (2006). VOC Decomposition by photocatalytic wall paper. *Mater Sci Forum, 510-511*, 22-25.

[68] Kibanova, D., Cervini-Silva, J. Destaillats, H. (2009). Efficiency of clay-TiO2 nanocomposites on the photocatalytic elimination of a model hydrophobic air pollutant. *Environ Sci Technol, 43*(5), 1500-1506, DOI: 10.1021/es803032t.

[69] Kibanova, D., Sleiman, M., Cervini-Silva, J., & Destaillats, H. (2012). Adsorption and photocatalytic oxidation of formaldehyde on a clay-TiO2 composite. *J Hazard Mater, 211*(SI), 233-239, DOI: 10.1016/j.jhazmat.2011.12.008.

[70] Gunschera, J., Markewitz, D., Koberski, U., & Salthammer, T. (2013). Catalyzed Reactions on Mineral Plaster Materials Used for Indoor Air Purification. *Clean-Soil Air Water, 41*(5), 437-446, DOI: 10.1002/clen.201100665.

[71] Sultan, Z. M., Magee, R. J., & Nilsson, G. (2011). *IAQ Solutions and Technologies: Review and Selection for Protocol Development* (No. NRCC-54495). National Institute for Research in Construction; National Research Council Canada.

[72] Lamble, S. P., Corsi, R. L., & Morrison, G. C. (2011). Ozone deposition velocities, reaction probabilities and product yields for green building materials. *Atmos Environ*, *45*(38), 6965-6972, DOI: 10.1016/j.atmosenv.2011.09.025.

[73] Hyttinen, M., Pasanen, N., & Kalllokoski, P. (2006). Removal of ozone on clean, dusty and sooty supply air filters. *Atmos Environ, 40*(2), 315-325, DOI: 10.1016/j.atmosenv.2005.09.040.

[74] Tamas, G., Weschler, C.J., Bako-Biro, Z., Wyon, D.P., & Strom-Tejsen, P. (2006). Factors affecting ozone removal rates in a simulated aircraft cabin environment. *Atmos Environ, 40*(32), 6122-6133, DOI: 10.1016/j.atmosenv.2006.05.034.

[75] Poppendieck, D., Hubbard, H., Ward, M., Weschler, C., & Corsi, R. L. (2007a). Ozone reactions with indoor materials during building disinfection. *Atmos Environ*, *41*(15), 3166-3176, DOI: 10.1016/j.atmosenv.2006.06.060.

[76] Petrick, L. & Dubowski, Y. (2009). Heterogeneous oxidation of squalene film by ozone under various indoor conditions. *Indoor Air, 19*(5), 381-391, DOI: 10.1111/j.1600-0668.2009.00599.x.

[77] Wisthaler, A., & Weschler, C. J. (2010). Reactions of ozone with human skin lipids: Sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air.

166

*Proceedings of the National Academy of Sciences of the United States of America, 107*(15), 6568-6575, DOI: 10.1073/pnas.0904498106.

[78] Nazaroff, W. W., & Weschler, C. J. (2004). Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmos Environ, 38*(18), 2841-2865, DOI: 10.1016/j.atmosenv.2004.02.040.

[79] Sarwar, G., Olson, D. A., Corsi, R. L., & Weschler, C. J. (2004). Indoor fine particles: The role of terpene emissions from consumer products. *JAPCA J Air Waste Ma, 54*(3), 367-377.

[80] Nazaroff, W. W., Coleman, B. K., Destaillats, H., Hodgson, A. T., Liu, D.-L., Lunden, M. M., … Weschler, C. J. (2006). Indoor Air Chemistry: Cleaning Agents, Ozone and Toxic Air Contaminants (No. California Air Resources Boad Contract No. 01-336). Lawrence Berkeley National Laboratory.

[81] Singer, B. C., Coleman, B. K., Destaillats, H., Hodgson, A. T., Lunden, M. M., Weschler, C. J., & Nazaroff, W. W. (2006). Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. *Atmos Environ, 40*(35), 6696–6710, DOI: 10.1016/j.atmosenv.2006.06.005.

[82] Coleman, B. K., Destaillats, H., Hodgson, A. T., & Nazaroff, W. W. (2008). Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. *Atmos Environ, 42*(4), 642-654, DOI: 10.1016/j.atmosenv.2007.10.001.

[83] Weschler, C. J. (2000). Ozone in indoor environments: concentration and chemistry. *Indoor Air*, *10*(4), 269-288, DOI: 10.1034/j.1600-0668.2000.010004269.x.

[84] Wolkoff, P., Clausen, P. A., Wilkins, C. K., Hougaard, K. S., & Nielsen, G. D. (1999). Formation of strong airway irritants in a model mixture of (+)-alpha-pinene/ozone. *Atmos Environ*, *33*(5), 693-698, DOI: 10.1016/S1352-2310(98)00292-1.

[85] Wolkoff, P., Clausen, P. A., Wilkins, C. K., & Nielsen, G. D. (2000). Formation of strong airway irritants in terpene/ozone mixtures. *Indoor Air*, *10*(2), 82-91, DOI: 10.1034/j.1600-0668.2000.010002082.x.

[86] Anderson, H. R., Spix, C., Medina, S., Schouten, J. P., Castellsague, J., Rossi, G., Katsouyanni, K. (1997). Air pollution and daily admissions for chronic obstructive pulmonary disease in 6 European cities: Results from the APHEA project. *Eur Respir J*, *10*(5), 1064-1071, DOI: 10.1183/09031936.97.10051064.

[87] Loh, M. M., Levy, J. I., Spengler, J. D., Houseman, E. A., & Bennett, D. H. (2007). Ranking cancer risks of organic hazardous air pollutants in the United States. *Environ Health Persp*, *115*(8), 1160-1168, DOI: 10.1289/ehp.9884.

[88] Oberdorster, G., Elder, A., Finkelstein, J., Frampton, M., Hopke, P., Peters, A., … Utell, M. (2010). *Assessment of Ambient UFP Health Effects:Linking Sources to Exposure and Responses in Extrapulmonary Organs* (No. EPA Grant R827354). University of Rochester.

[89] Morrison, G. C., & Nazaroff, W. W. (2002). Ozone interactions with carpet: Secondary emissions of aldehydes. *Environ Sci Technol, 36*(10), 2185-2192, DOI: 10.1021/es0113089.

[90] Nicolas, M., Ramalho, O., & Maupetit, F. (2007). Reactions between ozone and building products: Impact on primary and secondary emissions. *Atmos Environ, 41*(15), 3129-3138, DOI: 10.1016/j.atmosenv.2006.06.062.

[91] Poppendieck, D., Hubbard, H., Weschler, C., & Corsi, R. L. (2007b). Formation and emissions of carbonyls during and following gas-phase ozonation of indoor materials. *Atmos Environ, 41*(35), 7614-7626, DOI: 10.1016/j.atmosenv.2007.05.049.

[92] Wang, H., & Morrison, G. C. (2006). Ozone-initiated secondary emission rates of aldehydes from indoor surfaces in four homes. *Environ Sci Technol, 40*(17), 5263-5268, DOI: 10.1021/es060080s.

[93] Wang, H., & Morrison, G. (2010). Ozone-surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends. *Indoor Air, 20*(3), 224-234, DOI: 10.1111/j.1600-0668.2010.00648.x.

[94] Long, C.M., Suh, H.H., & Koutrakis, P. (2000). Characterization of indoor particle sources using continuous mass and size monitors. *JAPCA J Air Waste Ma, 50*(7), 1236-1250.

[95] Wainman, T., Zhang, J., Weschler, C.J., Lioy, P.J. (2000). Ozone and limonene in indoor air: a source of submicron particle exposure. *Environ Health Perspect, 108*, 1139-1145, DOI: 10.2307/3434825.

[96] Fan, Z., Lioy, P., Weschler, C., Fiedler, N., Kipen, H., & Zhang, J. (2003). Ozone-initiated reactions with mixtures of volatile organic compounds under simulated indoor conditions. *Environ Sci Technol, 37*(9), 1811-1821, DOI: 10.1021/es026231i.

[97] Fan, Z.H., Weschler, C.J., Han, I.K., Zhang, J.F. (2005). Co-formation of hydroperoxides and ultra-fine particles during the reactions of ozone with a complex VOC mixture under simulated indoor conditions. *Atmos Environ, 39*(28), 5171-5182, DOI: 10.1016/j.atmosenv.2005.05.018.

[98] Destaillats, H, Lunden, M.M., Singer, B.C., Coleman, B.K., Hodgson, A.T., Weschler, C.J., & Nazaroff, W.W. (2006). Indoor secondary pollutants from household product emissions in the presence of ozone: A bench-scale chamber study. *Envion Sci Technol, 40*(14), 4421-4428, DOI: 10.1021/es052198z.

[99] Rohr, A. C., Weschler, C J., Koutrakis, P., & Spengler, J. D. (2003). Generation and quantification of ultrafine particles through terpene/ozone reaction in a chamber setting. *Aerosol Sci Tech, 37*(1), 65-78, DOI: 10.1080/02786820390112597.

[100] Sarwar, G., & Corsi, R. (2007). The effects of ozone/limonene reactions on indoor secondary organic aerosols. *Atmos Environ, 41*(5), 959-973, DOI: 10.1016/j.atmosenv.2006.09.032.

[101] Sarwar, G., Corsi, R., Allen, D., & Weschler, C. (2003). The significance of secondary organic aerosol formation and growth in buildings: experimental and computational evidence. *Atmos Environ*, 37(9-10), 1365-1381, DOI: 10.1016/S1352-2310(02)01013-0.

[102] Waring, M. S., Wells, J. R., & Siegel, J. A. Secondary organic aerosol formation from ozone reactions with single terpenoids and terpenoid mixtures. (2011). *Atmos Environ, 45*(25), 4235-4242, DOI: 10.1016/j.atmosenv.2011.05.001.

[103] Weschler, C. J., & Shields, H. C. (1999). Indoor ozone/terpene reactions as a source of indoor particles. *Atmos Environ, 33*(15), 2301-2312, DOI: 10.1016/S1352-2310(99)00083-7.

[104] Weschler, C. J., Brauer, M., & Koutrakis, P. (1992a). Indoor ozone and nitrogen-dioxide – a potential pathway to the generation of nitrate radicals, dinitrogen petaoxide, and nitric-acid indoors. *Environ Sci Technol, 26*(1), 179-184, DOI: 10.1021/es00025a022.

[105] Weschler, C.J., & Shields, H.C. (1996). Production of the hydroxyl radical in indoor air. *Environ Sci Technol, 30*(11), 3250-3258, DOI: 10.1021/es960032f.

[106] Weschler, C. J., & Shields, H. C. (1997). Measurements of the hydroxyl radical in a manipulated but realistic indoor environment. *Environ Sci Technol, 31*(12), 3719-3722, DOI: 10.1021/es960032f.

[107] Hodgson, A.T., Rudd, A.F., Beal, D., Chandra, S. (2000). Volatile organic compound concentrations and emission rates in new manufactured and site-built houses. *Indoor Air, 10*(3), 178-192, DOI: 10.1034/j.1600-0668.2000.010003178.x.

[108] Sarwar, G., Corsi, R., Kimura, Y., Allen, D., Weschler, C.J. (2002). Hydroxyl radicals in indoor environments. *Atmos Environ, 36*(24), 3973-3988, DOI: 10.1016/S1352-2310(02)00278-9.

[109] Atkinson, R., & Arey, J. (2003). Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmos Environ, 37*(S2), 197-219, DOI: 10.1016/S1352-2310(03)00391-1.

[110] Park, J.S., & Ikeda, K. (2006). Variations of formaldehyde and VOC levels during 3 years in new and older homes. *Indoor Air, 16*(2), 129-135, DOI: 10.1111/j.1600-0668.2005.00408.x.

[111] Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N.R., Hjorth, J. et al. (2000). Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone. *Environ Sci Technol, 34*(6), 1001-1010, DOI: 10.1021/es990445r.

[112] Jaoui, M., Corse, E., Kleindienst, T.E., Offenberg, J.H., Lewandowski, M., & Edney, E.O. (2006). Analysis of secondary organic aerosol compounds from the photooxidation of d-limonene in the presence of NOX and their detection in ambient PM2.5. *Environ Sci Technol, 40*(12), 3819-3828, DOI: 10.1021/es052566z.

[113] Walser, M.L., Desyaterik, Y., Laskin, J., Laskin, A., & Nizkorodov, S.A. (2008). High-resolution mass spectrometric analysis of secondary organic aerosol produced by ozonation of limonene. *Phys Chem Chem Phys, 10*(7), 1009-1022, DOI: 10.1039/b712620d.

[114] Bateman, A.P., Nizkorodov, S.A., Laskin, J., & Laskin, A. (2009). Time-resolved molecular characterization of limonene/ozone aerosol using high-resolution electrospray ionization mass spectrometry. *Phys Chem Chem Phys, 11*(36), 7931-7942, DOI: 10.1039/b905288g.

[115] Forester, C.D., Wells, J.R. (2009). Yields of carbonyl products from gas-phase reactions of fragrance compounds with OH radical and ozone. *Environ Sci Technol, 43*(10), 3561-3568, DOI: 10.1021/es803465v.

[116] Cano-Ruiz, J., Kong, D., Balas, R., & Nazaroff, W., W. (1993). Removal of reactive gases at indoor surfaces - combining mass-transport and surface kinetics. *Atmos Environ A-, 27*(13), 2039-2050, DOI: 10.1016/0960-1686(93)90276-5.

[117] Morrison, G. C., Zhao, P., & Kasthuri, L. (2006). The spatial distribution of pollutant transport to and from indoor surfaces. *Atmos Environ*, *40*(20), 3677–3685, DOI: 10.1016/j.atmosenv.2006.03.015.

[118] Nazaroff, W.W., Dung, K., & Gadgil, A.J. (1992). Numerical investigations of the deposition of unattached Po-218 and Pb-212 from natural-convection enclosure flow. *J Aerosol Sci, 23*(4), 339-352, DOI: 10.1016/0021-8502(92)90003-E.

171

[119] Thatcher, T. L., Lai, A. C. K., Moreno-Jackson, R., Sextro, R. G., Nazaroff, W. W. (2002). Effects of room furnishings and air speed on particle deposition rates indoors. *Atmos Environ, 36*(11), 1811-1819, DOI: 10.1016/S1352-2310(02)00157-7.

[120] Nazaroff, W.W., Gadgil, A.J., & Weschler, C.J. (1993). Critique of the use of deposition velocity in modeling indoor air quality. In *Modeling Indoor Air Quality and Exposure*, ASTM STP 1205, N.L. Nagda, 1993, American Society for Testing and Materials, Philadelphia, 81-104.

[121] Lee, K., Vallarino, J., Dumyahn, T., Ozkaynak, H., & Spengler, J. D. (1999). Ozone decay rates in residences. *JAPCA J Air Waste Ma*, *49*(10), 1238-1244.

[122] Wilson, M.J.G. (1968). Indoor air pollution, *Proc R Soc London, Ser A, 307*(1489), 215-221.

[123] Morrison, G. C., Ping, Z., Wiseman, D. J., Ongwandee, M., Chang, H., Portman, J., & Regmi, S. (2003). Rapid measurement of indoor mass-transfer coefficients. *Atmos Environ, 37*(39-40), 5611-5619, DOI: 10.1016/j.atmosenv.2003.09.034.

[124] Simmons, A. & Colbeck, I. (1990). Resistance of various building materials to ozone deposition. *Environ Sci Technol, 11*, 973-978.

[125] Stephens, B., Gall, E. T., & Siegel, J. A. (2012). Measuring the penetration of ambient ozone into residential buildings. *Environ Sci Technol*, *46*(2), 929–936, DOI: 10.1021/es2028795.

[126] Bell., M.L., Peng, R.D., & Dominici, F. (2006). The exposure-response curve for ozone and risk of mortality and the adequacy of current ozone regulations. *Environ Health Persp, 114*(4), 532-536, DOI: 10.1289/ehp.8816.

[127] Gall, E., Siegel, J. A., & Corsi, R. (2011a). Zero-Energy Removal of Ozone in Residences. *ASHRAE Tran 2011, 117*(Pt 1), 411-418.

[128] Gall, E. T., Corsi, R. L., & Siegel, J. A. (2011b). Barriers and opportunities for passive removal of indoor ozone. *Atmos Environ*, *45*(19), 3338-3341, DOI: 10.1016/j.atmosenv.2011.03.032.

[129] Gall, E. T., Corsi, R. L., & Siegel, J. A. (2014). Impact of physical properties on ozone removal by several porous materials. *Environ Sci Technol*, *48*(7), 3682-3690, DOI: 10.1021/es4051956.

[130] Rim. D., Gall, E. T., Maddalena, R. L., & Nazaroff, W. W. (2016). Ozone reaction with interior building materials: influence of diurnal ozone variation, temperature and humidity. *Atmos Environ, 125*(Part A), 15-23, DOI: 10.1016/j.atmosenv.2015.10.093.

[131] Morrison, G. C., & Nazaroff, W. W. (2000). The rate of ozone uptake on carpets: experimental studies. *Envion Sci Technol, 34*(23), 4963-4968, DOI: 10.1021/es001361h.

[132] Weschler, C. J., Hodgson, A. T., & Wooley, J. D. (1992b). Indoor chemistry: ozone, volatile organic compounds, and carpets. *Environ Sci Technol, 26*(12), 2371-2377, DOI: 10.1021/es00036a006.

[133] Zhang, J. F., He, Q. C., & Lioy, P. J. (1994). Characteristics of aldehydes – concentrations, sources, and exposures for indoor and outdoor residential microenvironments. *Environ Sci Technol, 28*(1), 146-152, DOI: 10.1021/es00050a020.

[134] Morrissey, F. A., & Grismer, M. E. (1999). Kinetics of volatile organic compound sorption/desorption on clay minerals. *J Contam Hydrol, 36*(3-4), 291-312, DOI: 10.1016/S0169-7722(98)00150-8.

**Figure D1.** Configuration of carpet and clay plaster specimens on metal racks for PAQ analyses.

**Figure D2.** Configuration of clay plaster specimens on metal racks for PAQ analyses.

**Table D1.** Change of mass on spiked sorbent tubes after transport from DTU to UT-Austin for perceived air quality study.

| Compound | Mass Injected (ng) | Sorbent Tube 1 | | Sorbent Tube 2 | | Sorbent Tube 3 | | Average Mass Loss (%) |
|---|---|---|---|---|---|---|---|---|
| | | Mass Remaining (ng) | Mass Loss (%) | Mass Remaining (ng) | Mass Loss (%) | Mass Remaining (ng) | Mass Loss (%) | |
| C6 | 122.8 | 135.3 | -10.2 | 128.6 | -4.8 | 127.3 | -3.7 | -6.2 |
| C10 | 149.2 | 101.9 | 31.7 | 107.4 | 28.0 | 125.0 | 16.2 | 25.3 |

**Table D2.** Material and ozone configurations in test chambers during perceived air quality analyses.

| Day | Chamber 1 | Chamber 2 |
|---|---|---|
| 1 | Background + Ozone | Background |
| 2 | Background | Background + Ozone |
| 3 | Carpet + Ozone | Carpet + Clay + Ozone |
| 4 | Carpet + Clay + Ozone | Carpet + Ozone |
| 5 | Carpet | Carpet + Clay |
| 6 | Carpet + Clay | Carpet |
| 7 | Clay | Clay + Ozone |
| 8 | Clay + Ozone | Clay |
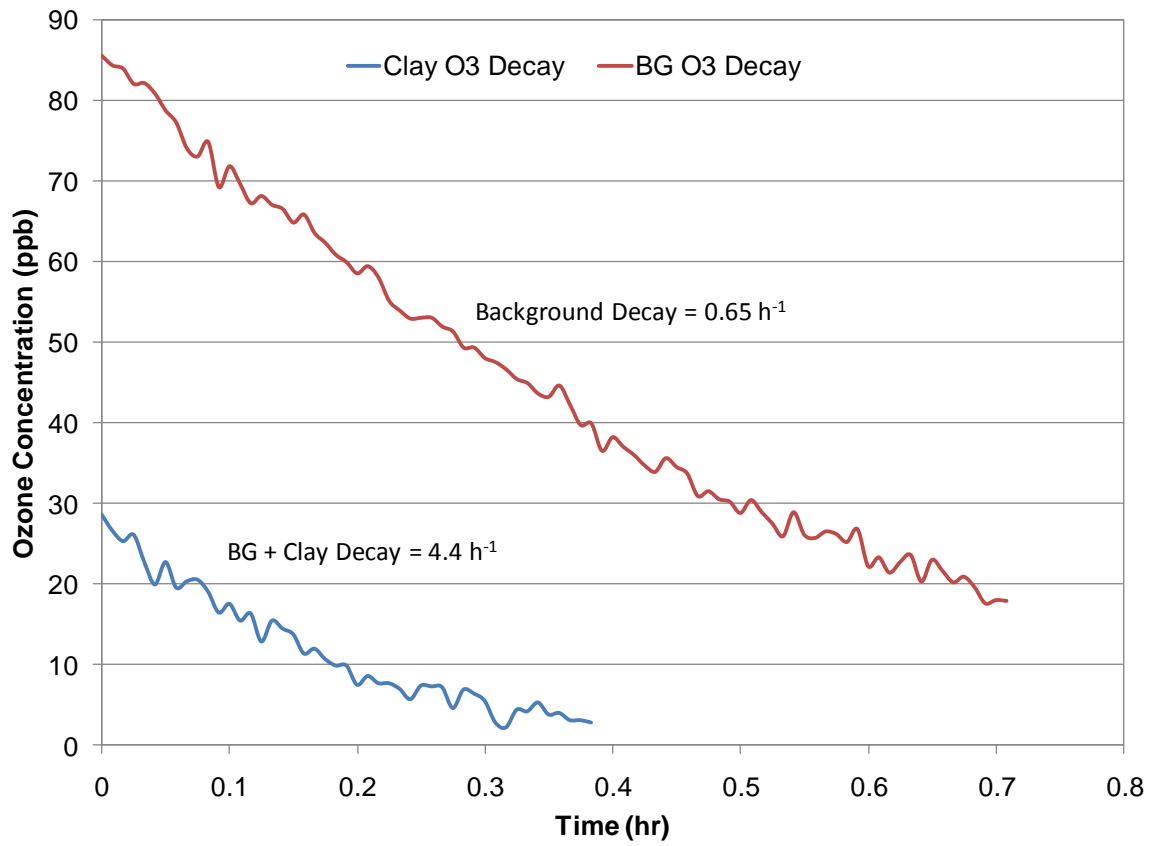
**Figure D3.** Ozone decay curves for clay plaster and chamber surfaces used in perceived air quality analyses.

**Figure E1.** Placement of specimens at each of the five field locations, including the apartment living room (1), the apartment kitchen (2), the apartment bedroom (3), the house living room (4), and the house bedroom (5).

**Figure E2.** Paint and plaster specimens supported on stands in the apartment living room.

**Table F1.** Bimolecular reaction rate constants and yields.

| Compound | $k_{O3,j}$ ppb$^{-1}$·hr$^{-1}$ | HCHO mol·mol$^{-1}$ | Yield CH$_3$CHO mol·mol$^{-1}$ | SOA µg·m$^3$ |
|---|---|---|---|---|
| d-Limonene | 0.019[a] 0.018[c,d] | 0.19[e] 0.10[e,f,g] | | 0.94[h,*] 0.63[h,*] 0.59[c,i,*] 0.22[f,*] 0.06[j] |
| α-Pinene | 0.0076[d,f,i] | 0.28[k] 0.15-0.22[e] 0.10[f] | 0.029[k] | 0.410[k,*] 0.190[f,*] 0.047[j] 0.043[j] |
| β-Pinene | 0.0014[k] 0.0013[a] | 0.65[k] 0.42[g] | 0.024[k] | 0.17[k,*] |
| Linalool | 0.04[a,l] | 0.34[k] | 0.14[k] | 0.01[k,*] |
| Styrene | 0.0015[a,d] | 0.34[o,p] | | |
| Isoprene | 0.001[d] | 0.90[e] | 0.03[e] | |
| α-Terpinene | 1.897[k] 1.872[a] | 0.04[k] | 0.01[k] | 0.47[k] |
| Δ-3-Carene | 0.003[a,k] | 0.25[k] 0.16[e] | 0.04[k] | 0.54[k] |
| α-Terpineol | 0.027[b] | | | |
| Geraniol | 0.084[m] | 0.15[n] | | |

* = seed particles present
a) Nazaroff and Weschler (2004)
b) Nazaroff et al. (2006)
c) Chen and Hopke (2010)
d) Weschler and Shields (1996)
e) Atkinson and Arey (2003)
f) Fan et al. (2003)
g) Grosjean and Grosjean (1993)
h) Leungsakul et al. (2005)
i) Ng et al. (2006)
j) Youssefi and Waring (2012)
k) Lee et al. (2006a)
l) Chen and Hopke (2009)
m) Forester et al. (2007)
n) Nunes et al. (2005)
o) Grosjean and Grosjean (1996)
p) Grosjean and Grosjean (1997)

**Table F2.** Styrene concentrations in residences.

| Mean ($\mu g \bullet m^{-3}$) | SD* ($\mu g \bullet m^{-3}$) | Median ($\mu g \bullet m^{-3}$) | Notes | Reference |
|---|---|---|---|---|
| 1.4[#] | 1.7[#] | 1.3[#] | Paris, cold season | Ranciere 2011 |
| 1.5[#] | 1.7[#] | 1.4[#] | Paris, warm season | |
| 0.04 | | | Europe, >200 homes | Geiss 2011a |
| 0.25 | | 0.16 | urban, industrial, semirural Argentina; 92 houses & schools; 3-year study | Massolo 2010 |
| 1.5 | 2.31 | | Germany | Schlink 2010 |
| | | 0.93 | France, 567 homes | Duboudin 2010 |
| 1.6 | | | Germany | Gokhale 2008 |
| 9.4 | | 6.5 | metropolitan Turkey, summer | Pekey 2008 |
| 11.7 | | 8.9 | metropolitan Turkey, winter | |
| 0.65[#] | 2.65[#] | 0.69[#] | Quebec City, 96 homes, 7 days during winter | Heroux 2008 |
| 0.51 | | 0.3 | urban, suburban, industrial Michigan; 159 residences | Jia 2008 |
| 1.1 | 1.9 | 0.46 | Boston, 55 locations (residential+office), winter | Dodson 2007 |
| 1.8 | 6 | 0.9 | California, 107 homes, 24-hour mean concentrations | Offermann 2009 |
| 0.9[#] | 2.8[#] | | | |
| 1.4 | 0.5 | 0.9 | urban & nonurban Minnesota, 284 residences | Adgate 2004 |
| 2.6 | 4.4 | 1.4 | Metropolitan Mexico City, homes & apartments (1998-1999) | Serrano-Trespalacios 2004 |
| 1.7[#] | 1.9[#] | | | |
| 1.4 | | 0.6 | Germany, 2103 residences (1994-2001, 2001-2002) | Schlink 2004 |
| 2.1 | 5 | 1 | Germany, 79 dwellings | Hippelein 2004 |
| 0.83[#] | | | | |
| 1.5 | | 0.61 | Leipzig, Germany (subset of Hippelein, 2004) | Rehwagen 2003 |

*SD : reported standard deviation

[#] : geometric mean, standard deviation, or median

**Table F3.** α-Pinene concentrations in residences.

| Mean (μg•m$^{-3}$) | SD* (μg•m$^{-3}$) | Median (μg•m$^{-3}$) | Notes | Reference |
|---|---|---|---|---|
| 14.5 | | 6.1 | | Geiss 2011a |
| 13.4 | 27.4 | 3.2 | | Geiss 2011b |
| 52 | | | new construction | |
| 2.4 | | | old construction | |
| 232 | | | new construction | in Marlet & Lognay 2011 |
| 26.4 | | | new construction | |
| 61 | | | new construction | |
| 20.8 | 16.4 | 16.3 | | Choi 2010a |
| 15.5 | | | winter | Missia 2010 |
| 5.5 | | | summer | |
| 35.2 | 51.1 | | | Schlink 2010 |
| 6.4 | | | | Gokhale 2008 |
| 9.7[#] | 2.7[#] | 8.0[#] | | Heroux 2008 |
| 9.0 | | 3.2 | | Jia 2008 |
| 11 | 32 | 2.6 | | Dodson 2007 |
| 15 | 13 | 11 | | Offermann 2009 |
| 9.3[#] | 3.3[#] | | | |
| 16.5 | | | | Lai 2004 |
| 8.7[#] | 2.9[#] | | | |
| 23.3 | | 9.8 | | Schlink 2004 |
| 29 | 46 | 13 | | Hippelein 2004 |
| 12[#] | | | | |
| 24.8 | | 11.8 | | Rehwagen 2003 |

*SD :  reported standard deviation

I/O :  mean indoor-to-outdoor concentration ratio

[#] :  geometric mean, standard deviation, or median

**Table F4.** d-Limonene concentrations in residences.

| Mean (μg•m⁻³) | SD* (μg•m⁻³) | Median (μg•m⁻³) | Notes | Reference |
|---|---|---|---|---|
| 10 | 9.1 | | concrete w/o air freshener | |
| 2.6 | 0.56 | | carpet w/o air freshener | Waring & Siegel 2011 |
| 53 | 10 | | concrete w/ air freshener | |
| 46 | 5.4 | | carpet w/ air freshener | |
| 29.2 | | 9.5 | | Geiss 2011a |
| 68.3 | 38 | 65.65 | | Geiss 2011b |
| 12 | | | new construction | |
| 4.8 | | | old construction | in Marlet & Lognay 2011 |
| 40.3 | | | new construction | |
| 18.2 | | | new construction | |
| 17.8 | 14.5 | 13.61 | | Choi 2010 |
| 29.0 | 36.4 | | | Schlink 2010 |
| 41.5 | | | winter | Missia 2010 |
| 17 | | | summer | |
| 14.6 | | | | Gokhale 2008 |
| 28.1[#] | 2.5[#] | 28.5[#] | | Heroux 2008 |
| 25.7 | | 16.6 | | Jia 2008 |
| 17 | 26 | 8.6 | | Dodson 2007 |
| 18 | 25 | 11 | | Offermann 2009 |
| 7.6[#] | 5[#] | | | |
| 19 | | | | Lai 2004 |
| 8[#] | 4[#] | | | |
| 32.9 | | 16 | | Schlink 2004 |
| 15 | 23 | 8.4 | | Hippelein 2004 |
| 7.6[#] | | | | |
| 36.7 | | 17.6 | | Rehwagen 2003 |

*SD : reported standard deviation

I/O : mean indoor-to-outdoor concentration ratio

[#] : geometric mean, standard deviation, or median

**Table F5.** β-pinene concentrations in residences.

| Mean (μg•m⁻³) | SD* (μg•m⁻³) | Median (μg•m⁻³) | Notes | Reference |
|---|---|---|---|---|
| 2.2 | | | old construction | |
| 73.9 | | | new construction | in Marlet & Lognay 2011 |
| 13 | | | new construction | |
| 11 | | | new construction | |
| 4.41 | 2.58 | 3.85 | | Choi 2010 |
| 3.44 | 3.38 | | | Schlink 2010 |
| 0.99 | | | | Gokhale 2008 |
| 2.7 | | 1.3 | | Schlink 2004 |
| 3.4 | 9.4 | 1.6 | | Hippelein 2004 |
| 1.4# | | | | |
| 3.01 | | 1.15 | | Rehwagen 2003 |

*SD : reported standard deviation

I/O : mean indoor-to-outdoor concentration ratio

# : geometric mean, standard deviation, or median

**Table F6.** Linalool concentrations in residences.

| Mean (μg•m⁻³) | SD* (μg•m⁻³) | Median (μg•m⁻³) | Notes | Reference |
|---|---|---|---|---|
| 0.63 | | | | |
| 0.19 | | | corridor | |
| 0.86 | | | | |
| 2.85 | | | kitchen | |
| 0.23 | | | bedroom | |
| 15.9 | | | corridor, after aerosol product application | |
| 31.6 | | | living room, after aerosol product application | Lamas 2010a |
| 30.8 | | | kitchen, after aerosol product application | |
| 26.2 | | | | |
| 20.9 | | | bedroom, after aerosol product application | |
| 7.54 | | | living room, after aerosol product application | |
| 6.84 | | | bedroom, after aerosol product application | |
| 14 | | | | |
| 104 | | | | |
| 136 | | | | |
| 43 | | | after product application | Lamas 2010b |
| 3.08 | | | | |
| 100 | | | | |
| 38 | | | | |

*SD : reported standard deviation

I/O : mean indoor-to-outdoor concentration ratio

**Table F7.** Population age fractions by metropolitan area.

| City | Population Age Fractions | | | | | | | | |
| | 1 to 4 | 5 to 14 | 15 to 24 | 25 to 34 | 35 to 44 | 45 to 54 | 55 to 64 | 65 to 74 | 75 to 84 | 85+ |
|---|---|---|---|---|---|---|---|---|---|---|
| Atlanta | 0.06 | 0.10 | 0.17 | 0.19 | 0.15 | 0.13 | 0.10 | 0.05 | 0.03 | 0.01 |
| Austin | 0.07 | 0.12 | 0.17 | 0.21 | 0.15 | 0.12 | 0.09 | 0.04 | 0.02 | 0.01 |
| Buffalo | 0.07 | 0.13 | 0.18 | 0.15 | 0.12 | 0.14 | 0.11 | 0.06 | 0.04 | 0.02 |
| Chicago | 0.07 | 0.12 | 0.15 | 0.19 | 0.14 | 0.13 | 0.10 | 0.06 | 0.03 | 0.02 |
| Cincinnati | 0.07 | 0.12 | 0.17 | 0.17 | 0.12 | 0.14 | 0.11 | 0.05 | 0.04 | 0.02 |
| Houston | 0.08 | 0.15 | 0.15 | 0.18 | 0.16 | 0.12 | 0.07 | 0.05 | 0.03 | 0.01 |
| Miami | 0.06 | 0.12 | 0.14 | 0.14 | 0.15 | 0.15 | 0.11 | 0.07 | 0.05 | 0.02 |
| Minn. | 0.06 | 0.12 | 0.18 | 0.21 | 0.16 | 0.12 | 0.06 | 0.04 | 0.03 | 0.02 |
| New York | 0.06 | 0.12 | 0.14 | 0.17 | 0.14 | 0.14 | 0.11 | 0.06 | 0.04 | 0.02 |
| Phoenix | 0.08 | 0.16 | 0.15 | 0.16 | 0.15 | 0.13 | 0.09 | 0.05 | 0.03 | 0.01 |
| Riverside | 0.08 | 0.18 | 0.17 | 0.15 | 0.16 | 0.12 | 0.06 | 0.05 | 0.03 | 0.01 |
| Wash DC | 0.06 | 0.09 | 0.17 | 0.20 | 0.14 | 0.13 | 0.11 | 0.06 | 0.04 | 0.02 |

**Source:** USCB (2012)

# Appendix G. Mass Balances

Mass balance on **<u>ozone</u>** in a well-mixed **<u>experimental chamber</u>**:

$$V\frac{dC_{O3}}{dt} = QC_{in} - QC_{out} - v_d A_s C_{out} - k_{O3,ch}C_{out}V$$

Divide through by V:

$$\frac{dC_{O3}}{dt} = \lambda C_{in} - \lambda C_{out} - \frac{v_d A_s}{V}C_{out} - k_{O3,ch}C_{out}$$

Assume steady-state, such that:

$$\frac{dC_{O3}}{dt} = \emptyset = \lambda C_{in} - \lambda C_{out} - \frac{v_d A_s}{V}C_{out} - k_{O3,ch}C_{out}$$

$$\therefore \emptyset = \lambda C_{in} - C_{out}\left(\lambda - \frac{v_d A_s}{V} - k_{O3,ch}\right)$$

$$\lambda\frac{C_{in}}{C_{out}} = \lambda - \frac{v_d A_s}{V} - k_{O3,ch}$$

Mass balance on **<u>ozone</u>** in a well-mixed **<u>indoor environment</u>**:

$$V\frac{dC_{O3}}{dt} = pQC_o + \sum E - QC_{O3} - \alpha k_{O3,surf}C_{O3}V - k_{O3,prm}C_{O3}V - \sum_j k_{O3,j}C_j C_{O3}V$$

Divide through by V:

$$\frac{dC_{O3}}{dt} = p\lambda C_o + \sum\frac{E}{V} - \lambda C_{O3} - \alpha k_{O3,surf}C_{O3} - k_{O3,prm}C_{O3} - \sum_j k_{O3,j}C_j C_{O3}$$

Assume steady-state, such that:

$$\frac{dC_{O3}}{dt} = \emptyset = p\lambda C_o + \sum\frac{E}{V} - \lambda C_{O3} - \alpha k_{O3,surf}C_{O3} - k_{O3,prm}C_{O3} - \sum_j k_{O3,j}C_j C_{O3}$$

187

$$\therefore \emptyset = p\lambda C_o + \Sigma\frac{E}{V} - \lambda C_{O3} - \alpha k_{O3,surf}C_{O3} - k_{O3,prm}C_{O3} - \Sigma_j k_{O3,j}C_jC_{O3}$$

Factor out $C_{O3}$ from terms:

$$\emptyset = p\lambda C_o + \sum\frac{E}{V} - C_{O3}\left(\lambda - \alpha k_{O3,surf} - k_{O3,prm} - \sum_j k_{O3,j}C_j\right)$$

Divide through by bracketed terms, and add $C_{O3}$ to both sides:

$$C_{O3} = \frac{p\lambda C_o + \Sigma\frac{E}{V}}{\lambda - \alpha k_{O3,surf} - k_{O3,prm} - \Sigma_j k_{O3,j}C_j}$$

Mass balance on **reaction byproduct _i_** in a well-mixed **indoor environment**:

$$V\frac{dC_{p,i}}{dt} = pQC_{p,i,o} + \sum E - QC_{p,i} + y_{surf,i}\alpha k_{O3,surf}C_{O3}V + y_{prm,i}k_{O3,prm}C_{O3}V$$
$$+ \sum_j y_{p,ij}k_{O3,j}C_jC_{O3}V$$

Assume negligible outdoor concentration of reaction byproduct, such that:

$$C_{p,i,o} = \emptyset$$

And assume negligible indoor source emitters of reaction byproduct, such that:

$$\sum E = \emptyset$$

$$\therefore V\frac{dC_{p,i}}{dt} = -QC_{p,i} + y_{surf,i}\alpha k_{O3,surf}C_{O3}V + y_{prm,i}k_{O3,prm}C_{O3}V + \Sigma_j y_{p,ij}k_{O3,j}C_jC_{O3}V$$

Divide through by V:

$$\frac{dC_{p,i}}{dt} = -\lambda C_{p,i} + y_{surf,i}\alpha k_{O3,surf}C_{O3} + y_{prm,i}k_{O3,prm}C_{O3} + \sum_j y_{p,ij}k_{O3,j}C_jC_{O3}$$

188

Assume steady-state, such that:

$$\frac{dC_{p,i}}{dt} = \emptyset = -\lambda C_{p,i} + y_{surf,i}\alpha k_{O3,surf}C_{O3} + y_{prm,i}k_{O3,prm}C_{O3} + \sum_{j} y_{p,ij}k_{O3,j}C_jC_{O3}$$

$$\therefore \ \emptyset = -\lambda C_{p,i} + y_{surf,i}\alpha k_{O3,surf}C_{O3} + y_{prm,i}k_{O3,prm}C_{O3} + \sum_{j} y_{p,ij}k_{O3,j}C_jC_{O3}$$

Divide through by $\lambda$, and add $C_{p,i}$ to both sides:

$$C_{p,i} = \frac{y_{surf,i}\alpha k_{O3,surf}C_{O3} + y_{prm,i}k_{O3,prm}C_{O3} + \sum_{j} y_{p,ij}k_{O3,j}C_jC_{O3}}{\lambda}$$

# References

Adgate, J. L., Eberly, L. E., Stroebel, C., Pellizzari, E. D., & Sexton, K. (2004). Personal, Indoor, and Outdoor VOC Exposures in a Probability Sample of Children. *J Expo Sci Env Epid*, *14*, S4–S13.

Albrechtsen, O. (1988). Twin climatic chambers to study sick and healthy buildings. *Proceedings of Healthy Buildings*, *3*, pp. 25-30. Stockholm.

Aldred, J.A., Darling, E., Morrison, G., Siegel, J., & Corsi, R.L. (2015). Benefit-cost analysis of commercially available activated carbon filters for indoor ozone removal in single-family homes. *Indoor Air,* DOI: 10.1111/ina.12220.

Aldred, J. A., Darling, E., Morrison, G., Siegel, J., & Corsi, R.L. (2016). Analysis of the cost effectiveness of combined particle and activated carbon filters for indoor ozone removal in buildings. *Sci Technol Built Environ, 22*(2), 227-236.

Allen, R., Wallace, L., Larson, T., Sheppard, L., & Liu, L.J.S. (2004). Estimated hourly personal exposures to ambient and nonambient particulate matter among sensitive populations in Seattle, Washington. *J Air Waste Manage, 54*(9), 1197-1211.

Apte, M.G., Buchanan, I.S.H., & Mendell, M.J. (2008). Outdoor ozone and building-related symptoms in the BASE study. *Indoor Air, 18*(2), 156-170.

Araki, A., Kanazawa, A., Kawai, T., Eitaki, Y., Morimoto, K., Nakayama, K. et al. (2012). The relationship between exposure to microbial volatile organic compound and allergy prevalence in single-family homes. *Sci Total Environ, 423*, 18-26.

Arts, J. H. E., Rennen, M. A. J., & De Heer, C. (2006). Inhaled formaldehyde: Evaluation of sensory irritation in relation to carcinogenicity. *Regul Toxicol Pharm*, *44*(2), 144–160.

Atkinson, R., & Arey, J. (2003). Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmos Environ, 37*(S2), 197-219

Bakó-Biró, Z., Wargocki, P., Weschler, C. J., & Fanger, P. O. (2004). Effects of pollution from personal computers on perceived air quality, SBS symptoms and productivity in offices. *Indoor Air, 14*, 178-187.

Bekö, G., Halas, O., Clausen, G., & Weschler, C. J. (2006). Initial studies of oxidation processes on filter surfaces and their impact on perceived air quality. *Indoor Air*, *16*(1), 56–64.

Bekö, G., Clausen, G., & Weschler, C. J. (2008). Sensory pollution from bag filters, carbon filters and combinations. *Indoor Air, 18*(1), 27-36.

Bekö, G., Fadeyi, M. O., Clausen, G., & Weschler, C. J. (2009). Sensory pollution from bag-type fiberglass ventilation filters: Conventional filter compared with filters containing various amounts of activated carbon. *Build Environ, 44*(10), 2114-2120.

Bell, M. L., Dominici, F., & Samet, J. M. (2005). A meta-analysis of time-series studies of ozone and mortality with comparison to the national morbidity, mortality, and air pollution study. *Epidemiology*, *16*(4), 436-445.

Bell, M.L., Peng, R.D., & Dominici, F. (2006). The exposure-response curve for ozone and risk of mortality and the adequacy of current ozone regulations. *Environ Health Persp, 114*(4), 532-536.

BLS (Bureau of Labor Statistics) (2014). Occupational Employment Statistics. Retrieved June 13, 2014, from http://www.bls.gov/oes/current/oes_stru.htm.

Bornehag, C.G., Sundell, J., Weschler, C.J., Sigsgaard, T., Lundgren, B., Hasselgren, M. & Hagerhed-Engman, L. (2004). The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. *Environ Health Perspect, 112*, 1393-1397.

191

Buchanan, I.S.H., Mendell, M.J., Mirer, A.G., & Apte, M.G. (2008). Air filter materials, outdoor ozone and building-related symptoms in the BASE study. *Indoor Air, 18*(2), 144-155.

Burnett, R. T., Smith-Doiron, M., Stieb, D., Cakmak, S., & Brook, J. R. (1999). Effects of particulate and gaseous air pollution on cardiorespiratory hospitalizations. *Arch Environ Health*, *54*(2), 130–139.

Cano-Ruiz, J., Kong, D., Balas, R., & Nazaroff, W., W. (1993). Removal of reactive gases at indoor surfaces - combining mass-transport and surface kinetics. *Atmos Environ A-, 27*(13), 2039-2050.

Checkoway, H., Boffetta, P., Mundt, D.J., & Mundt, K.A. (2012). Critical Review and Synthesis of the Epidemiologic Evidence on Formaldehyde Exposure and Risk of Leukemia and other Lymphohematopoietic Malignancie, *Cancer Cause Control*, *23*(11), 1747-1766.

Chen, L., Jennison, B. L., Yang, W., & Omaye, S. T. (2000). Elementary school absenteeism and air pollution. *Inhal Toxicol*, *12*(11), 997–1016.

Chen, Xi, & Hopke, P. K. (2009). A chamber study of secondary organic aerosol formation by linalool ozonolysis. *Atmos Environ*, *43*(25), 3935–3940.

Chen, X., & Hopke, P. K. (2010). A chamber study of secondary organic aerosol formation by limonene ozonolysis. *Indoor Air*, *20*(4), 320–328.

Chen, C., Zhao, B., & Weschler, C. J. (2012a). Assessing the influence of indoor exposure to "outdoor ozone" on the relationship between ozone and short-term mortality in U.S. communities. *Environ Health Persp, 120*(2), 235-240

Chen, C., Zhao, B., & Weschler, C. J. (2012b). Indoor exposure to "outdoor PM10" assessing Its Influence on the Relationship between PM10 and Short-term Mortality in US Cities. *Epidemiology*, *23*(6), 870–878.

Choi, H., Schmidbauer, N., Spengler, J., & Bornehag, C.-G. (2010). Sources of Propylene Glycol and Glycol Ethers in Air at Home. *International Journal of Environmental Research and Public Health*, *7*(12), 4213–4237.

Coleman, B. K., Destaillats, H., Hodgson, A. T., & Nazaroff, W. W. (2008). Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. *Atmos Environ, 42*(4), 642-654.

Corsi, R.L., Aldred, J.R., Darling, E., Siegel, J.A., & Morrison, G.C. (2013). Literature and Product Review and Cost Benefit Analysis of Commercially Available Ozone Air Cleaning for HVAC Systems. Task 1 (1491-RP) report to the American Society of Heating, Refrigerating, and Air Conditioning Engineers (project 1491-RP).

Cros, C. J., Morrison, G. C., Siegel, J. A., & Corsi, R. L. (2012). Long-term performance of passive materials for removal of ozone from indoor air. *Indoor Air,* 22, 43-53.

Darling, E. K., Cros, C. J., Wargocki, P., Kolarik, J., Morrison, G. C., & Corsi, R. L. (2012). Impacts of a clay plaster on indoor air quality assessed using chemical and sensory measurements. *Build Environ, 57*, 370-376.

deCastro, B.R., Sax, S.N., Chillrud, S.N., Kinney, P.L., & Spengler, J.D. (2007). Modeling time-location patterns of inner-city high school students in New York and Los Angeles using a longitudinal approach with generalized estimating equations. *J Expo Sci Env Epid, 17*(3), 233-247.

Destaillats, H, Lunden, M.M., Singer, B.C., Coleman, B.K., Hodgson, A.T., Weschler, C.J., & Nazaroff, W.W. (2006). Indoor secondary pollutants from household product emissions in the presence of ozone: A bench-scale chamber study. *Envion Sci Technol, 40*(14), 4421-4428.

Destaillats, H., Maddalena, R. L., Singer, B. C., Hodgson, A. T., & McKone, T. E. (2008). Indoor pollutants emitted by office equipment: A review of reported data and information needs. *Atmos Environ, 42*(7), 1371-1388.

Diamanti, M. V., Del Curto, B., Ormellese, M., & Pedeferri, M. P. (2013). Photocatalytic and self-cleaning activity of colored mortars containing TiO2. *Constr Build Mater, 46*, 167-174.

Dodson, R. E., Houseman, E. A., Levy, J. I., Spengler, J. D., Shine, J. P., & Bennett, D. H. (2007). Measured and Modeled Personal Exposures to and Risks from Volatile Organic Compounds. *Environ Sci Technol*, *41*(24), 8498–8505.

Doty, R. L., & Cameron, E. L. (2009). Sex differences and reproductive hormone influences on human odor perception. *Physiol Behav, 97*, 213-228.

Duboudin, C. (2010). Pollution inside the home: descriptive analyses Part II: Identification of groups of homogenous homes in terms of pollution. *Envir Risques Sante*, *9*(1), 27–38.

Elbayoumi, M., Ramli, N.A., Yusof, N.F.F.M., & Al Madhoun, W. (2015). Seasonal variation in schools' indoor air environments and health symptoms among students in an Eastern Mediterranean climate. *Hum Ecol Risk Assess, 21*(1), 184-204.

Fan, Z., Lioy, P., Weschler, C., Fiedler, N., Kipen, H., & Zhang, J. (2003). Ozone-initiated reactions with mixtures of volatile organic compounds under simulated indoor conditions. *Environ Sci Technol, 37*(9), 1811-1821.

Fan, Z.H., Weschler, C.J., Han, I.K., Zhang, J.F. (2005). Co-formation of hydroperoxides and ultra-fine particles during the reactions of ozone with a complex VOC mixture under simulated indoor conditions. *Atmos Environ, 39*(28), 5171-5182.

Fisk, W. J., & Rosenfeld, A. H. (2000).Health and productivity gain from better indoor environments and their relationship with building energy efficiency. *Annu Rev Energy Environ*, 25, 537-566.

Forester, C. D., Ham, J. E., & Wells, J. R. (2007). Geraniol (2,6-dimethyl-2,6-octadien-8-ol) reactions with ozone and OH radical: Rate constants and gas-phase products. *Atmos Environ*, *41*(6), 1188–1199.

194

Gall, E., Siegel, J. A., & Corsi, R. (2011a). Zero-Energy Removal of Ozone in Residences. *ASHRAE Tran 2011, 117*(Pt 1), 411-418.

Gall, E. T., Corsi, R. L., & Siegel, J. A. (2011b). Barriers and opportunities for passive removal of indoor ozone. *Atmos Environ*, *45*(19), 3338-3341.

Gall, E., Darling, E., Siegel, J. A., Morrison, G. C., & Corsi, R. L. (2013). Evaluation of three common green building materials for ozone removal, and primary and secondary emissions of aldehydes. *Atmos Environ*, *77*, 910-918.

Gall, E. T., Corsi, R. L., & Siegel, J. A. (2014). Impact of physical properties on ozone removal by several porous materials. *Environ Sci Technol*, *48*(7), 3682-3690.

Gallego, E., Roca, F. J., Perales, J. F., & Guardino, X. (2013). Experimental evaluation of VOC removal efficiency of a coconut shell activated carbon filter for indoor air quality enhancement. *Build Environ, 67*, 14-25.

Geiss, O., Barrero-Moreno, J., & Kotzias, D. (2011a). Measurements of volatile organic compounds in car showrooms in the province of Varese (Northern Italy). *Indoor Air*, *21*(1), 45–52.

Geiss, O., Giannopoulos, G., Tirendi, S., Barrero-Moreno, J., Larsen, B. R., & Kotzias, D. (2011b). The AIRMEX study - VOC measurements in public buildings and schools/kindergartens in eleven European cities: Statistical analysis of the data. *Atmos Environ*, *45*(22), 3676–3684.

Gokhale, S., Kohajda, T., & Schlink, U. (2008). Source apportionment of human personal exposure to volatile organic compounds in homes, offices and outdoors by chemical mass balance and genetic algorithm receptor models. *Sci Total Environ*, *407*(1), 122–138.

Gordon, S. M., Callahan, P. J., Nishioka, M. G., Brinkman, M. C., O'Rourke, M. K., Lebowitz, M. D., & Moschandreas, M. J. (1999). Residential environmental measurements in the National Human Exposure Assessment Survey (NHEXAS)

pilot study in Arizona: preliminary results for pesticides and VOCs. *J Expo Sci Env Epid*, *9*(5), 456–470.

Grosjean, D., Williams, E., Grosjean, E., Andino, J., & Seinfeld, J. (1993). Atmospheric Oxidation of Biogenic Hydrocarbons -- Reaction of Ozone with Beta-Pinene, D-Limonene and Trans-Caryophyllene. *Environ Sci Technol*, *27*(13), 2754–2758.

Grosjean, E., & Grosjean, D. (1996). Carbonyl products of the gas-phase reaction of ozone with 1-alkenes. *Atmos Environ*, *30*(24), 4107–4113.

Grosjean, E., & Grosjean, D. (1997). Gas phase reaction of alkenes with ozone: Formation yields of primary carbonyls and biradicals. *Environ Sci Technol*, *31*(8), 2421–2427.

Grøntoft, T., & Raychaudhuri, M. R. (2004). Compilation of tables of surface deposition velocities for O-3 NO2 and SO2 to a range of indoor surfaces. *Atmos Environ, 38*(4), 533-544.

Gryparis, A., Forsberg, B., Katsouyanni, K., Analitis, A., Touloumi, G., Schwartz, J., Samoli, E., Medina, S., Anderson, H. R., Niciu, E. M., Wichmann, H. E., Kriz, B., Kosnik, M., Skorkovsky, J., Vonk, J. M., & Dortbudak, Z. (2004). Acute effects of ozone on mortality from the "Air pollution and health: A European approach" project. *Am J Resp Crit Care*, *170*(10), 1080-1087.

Gunschera, J., Markewitz, D., Koberski, U., & Salthammer, T. (2013). Catalyzed Reactions on Mineral Plaster Materials Used for Indoor Air Purification. *Clean-Soil Air Water, 41*(5), 437-446.

Heroux, M.-E., Gauvin, D., Gilbert, N. L., Guay, M., Dupuis, G., Legris, M., & Levesque, B. (2008). Housing characteristics and indoor concentrations of selected volatile organic compounds (VOCs) in Quebec City, Canada. *Indoor Built Environ*, *17*(2), 128–137.

Hippelein, M. (2004). Background concentrations of individual and total volatile organic compounds in residential indoor air of Schleswig-Holstein, Germany. *J Environ Monitor*, *6*(9), 745–752.

Hodgson, A.T., Rudd, A.F., Beal, D., Chandra, S. (2000). Volatile organic compound concentrations and emission rates in new manufactured and site-built houses. *Indoor Air, 10*(3), 178-192.

Hong, K.-S., Saver, J. L., Kang, D.-W., Bae, H.-J., Yu, K.-H., Koo, J., Lee, B.-C. (2010). Years of optimum health lost due to complications after acute ischemic stroke disability-adjusted life-years analysis. *Stroke*, *41*(8), 1758–1765.

Hubbell, B. J., Hallberg, A., McCubbin, D. R., & Post, E. (2005). Health-related benefits of attaining the 8-hr ozone standard. *Environ Health Persp*, *113*(1), 73-82.

Huijbregts, M. A. J., Rombouts, L. J. A., Ragas, A. M. J., & Meent, D. van de. (2005). Human-Toxicological Effect and Damage Factors of Carcinogenic and Noncarcinogenic Chemicals for Life Cycle Impact Assessment. *Integrated Environ Assess Manage*, *1*(3), 181–244.

Hussein, T., Paasonen, P., Kulmala, M. (2012). Activity pattern of a selected group of school occupants and their family members in Helsinki − Finland. *Sci Total Environ, 425*(15), 289-292.

Hun, D. E., Corsi, R. L., Morandi, M. T., & Siegel, J. A. (2010). Formaldehyde in residences: long-term indoor concentrations and influencing factors. *Indoor Air*, *20*(3), 196–203.

Hyttinen, M., Pasanen, N., & Kalliokoski, P. (2006). Removal of ozone on clean, dusty and sooty supply air filters. *Atmos Environ, 40*(2), 315-325.

Ichiura, H., Kitaoka, T., & Tanaka, H. (2003). Removal of indoor pollutants under UV irradiation by a composite TiO2-zeolite sheet prepared using a papermaking technique. *Chemosphere, 50*(1), 79-83.

Ito, K., De Leon, S. F., & Lippmann, M. (2005). Associations between ozone and daily mortality - Analysis and meta-analysis. *Epidemiology*, *16*(4), 446-457.

Jerrett, M., Burnett, R. T., Pope, C. A., Ito, K., Thurston, G., Krewski, D., Shi, Y. L., Calle, E., & Thun, M. (2009). Long-Term Ozone Exposure and Mortality. *New Engl J Med*, *360*(11), 1085-1095.

Jia, C., Batterman, S., & Godwin, C. (2008). VOCs in industrial, urban and suburban neighborhoods, Part 1: Indoor and outdoor concentrations, variation, and risk drivers. *Atmos Environ*, *42*(9), 2083–2100.

Jo, W.-K., & Chun, H.-H. (2014). Application of fibrous activated carbon filter in continuous-flow unit for removal of volatile organic compounds under simulated indoor conditions. *Aerosol and Air Quality Research, 14*(1), 347-354.

Kibanova, D., Cervini-Silva, J. Destaillats, H. (2009). Efficiency of clay-TiO2 nanocomposites on the photocatalytic elimination of a model hydrophobic air pollutant. *Environ Sci Technol, 43*(5), 1500-1506.

Kibanova, D., Sleiman, M., Cervini-Silva, J., & Destaillats, H. (2012). Adsorption and photocatalytic oxidation of formaldehyde on a clay-TiO2 composite. *J Hazard Mater, 211*(SI), 233-239.

Kilpelainen, M., Terho, E.O., Helenius, H., Koskenvuo, M. (2001). Home dampness, current allergic diseases, and respiratory infections among young adults. *Thorax 5*, 462-467.

Klepeis, N. E., Nelson, W. C., Ott, W. R., Robinson, J. P., Tsang, A. M., Switzer, P., Engelmann, W. H. (2001). The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *J Expo Anal Env Epid*, *11*(3), 231-252.

Kolarik, J., & Wargocki, P. (2010). Can a photocatalytic air purifier be used to improve the perceived air quality indoors? *Indoor Air, 20*, 255-262.

Kunkel, D. A., Gall, E. T., Siegel, J. A., Novoselac, A., Morrison, G. C., & Corsi, R. L. (2010). Passive reduction of human exposure to indoor ozone. *Build Environ, 45*(2), 445-452.

Lai, H. K., Kendall, M., Ferrier, H., Lindup, I., Alm, S., Hänninen, O., Nieuwenhuijsen, M. J. (2004). Personal exposures and microenvironment concentrations of PM2.5, VOC, NO2 and CO in Oxford, UK. *Atmos Environ*, *38*(37), 6399–6410.

Lamas, J. P., Sanchez-Prado, L., Garcia-Jares, C., & Llompart, M. (2010a). Determination of fragrance allergens in indoor air by active sampling followed by ultrasound-assisted solvent extraction and gas chromatography–mass spectrometry. *J Chromatogr A*, *1217*(12), 1882–1890.

Lamas, J. P., Sanchez-Prado, L., Lores, M., Garcia-Jares, C., & Llompart, M. (2010b). Sorbent trapping solid-phase microextraction of fragrance allergens in indoor air. *J Chromatogr A*, *1217*(33), 5307–5316.

Lamble, S. P., Corsi, R. L., & Morrison, G. C. (2011). Ozone deposition velocities, reaction probabilities and product yields for green building materials. *Atmos Environ, 45*, 6965-6972.

Lappalainen, S., Salonen, H., Salmi, K., & Reijula, K. (2013). Indoor air particles in office buildings with suspected indoor air problems in the Helsinki area. *Int J Occcup Med Env, 26*(1), 155-164.

Lee, K., Vallarino, J., Dumyahn, T., Ozkaynak, H., & Spengler, J. D. (1999). Ozone decay rates in residences. *JAPCA J Air Waste Ma*, *49*(10), 1238-1244.

Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Seinfeld, J. H. (2006a). Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes. *J Geophys Res-Atmos*, *111*(D7).

Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., & Seinfeld, J. H. (2006b). Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes. *J Geophys Res-Atmos*, *111*(D17).

Leungsakul, S., Jaoui, M., & Kamens, R. M. (2005). Kinetic mechanism for predicting secondary organic aerosol formation from the reaction of d-limonene with ozone. *Environ Sci Technol*, *39*(24), 9583–9594.

Levy, J. I., Carrothers, T. J., Tuomisto, J. T., Hammitt, J. K., & Evans, J. S. (2001). Assessing the public health benefits of reduced ozone concentrations. *Environ Health Persp, 109*(12), 1215-1226.

Lin, C.-C., & Chen, H.-Y. (2014). Impact of HVAC filter on indoor air quality in terms of ozone removal and carbonyls generation. *Atmos Environ, 89*, 29-34.

Logue, J. M., McKone, T. E., Sherman, M. H., & Singer, B. C. (2011). Hazard assessment of chemical air contaminants measured in residences. *Indoor Air*, *21*(2), 92–109.

Logue, J. M., Price, P. N., Sherman, M. H., & Singer, B. C. (2012). A Method to Estimate the Chronic Health Impact of Air Pollutants in US Residences. *Environ Health Persp*, *120*(2), 216–222.

Loh, M. M., Levy, J. I., Spengler, J. D., Houseman, E. A., & Bennett, D. H. (2007). Ranking cancer risks of organic hazardous air pollutants in the United States. *Environ Health Persp*, *115*(8), 1160–1168.

Long, C.M., Suh, H.H., & Koutrakis, P. (2000). Characterization of indoor particle sources using continuous mass and size monitors. *JAPCA J Air Waste Ma, 50*(7), 1236-1250.

Lopez, A.D., Mathers, C.D., Ezzati, M., Jamison, D.T., Murray, C.J.L. (2006). Global burden of disease and risk factors. Washington D.C.: Oxford University Press.

Lvovsky, K., Hughes, G., Maddison, D., Ostro, B., & Pearce, D. (2000). *Environmental Costs of Fossil Fuels* (Environment Department Papers No. Paper No. 78) (pp. 1–104). Washington, DC: World Bank.

Marlet, C., & Lognay, G. (2011). Monoterpenes: sources and implications in the indoor air quality. *Biotechnol Agron Soc*, *15*(4), 611–622.

Massolo, L., Rehwagen, M., Porta, A., Ronco, A., Herbarth, O., & Mueller, A. (2010). Indoor-Outdoor Distribution and Risk Assessment of Volatile Organic Compounds in the Atmosphere of Industrial and Urban Areas. *Environ Toxicol*, *25*(4), 339–349.

McConnell, R., Berhane, K., Gilliland, F., London, S. J., Islam, T., Gauderman, W. J., Avol, E., Margolis, H. G., & Peters, J. M. (2002). Asthma in exercising children exposed to ozone: a cohort study. *Lancet*, *359*(9304), 386-391.

Meng, Y. Y., Rull, R. P., Wilhelm, M., Lombardi, C., Balmes, J., and Ritz, B. (2010). Outdoor air pollution and uncontrolled asthma in the San Joaquin Valley, California, *J Epidemiol Commun H, 64*, 142-147.

Michel, A. E., Usher, C. R., & Grassian, V. H. (2003). Reactive uptake of ozone on mineral oxides and mineral dusts. *Atmos Environ, 37*, 3201-3211.

Missia, D. A., Demetriou, E., Michael, N., Tolis, E. I., & Bartzis, J. G. (2010). Indoor exposure from building materials: A field study. *Atmos Environ*, *44*(35), 4388–4395.

Moriske, H. J., Ebert, G., Konieczny, L., Menk, G., & Schondube, M. (1998). Concentrations and decay rates of ozone in indoor air in dependence on building and surface materials. *Toxicol Lett*, *96-7*, 319-323.

Morrison, G. C., & Nazaroff, W. W. (2000). The rate of ozone uptake on carpets: experimental studies. *Envion Sci Technol, 34*(23), 4963-4968.

Morrison, G. C., & Nazaroff, W. W. (2002). Ozone interactions with carpet: Secondary emissions of aldehydes. *Environ Sci Technol, 36*(10), 2185-2192.

Morrison, G. C., Ping, Z., Wiseman, D. J., Ongwandee, M., Chang, H., Portman, J., & Regmi, S. (2003). Rapid measurement of indoor mass-transfer coefficients. *Atmos Environ, 37*(39-40), 5611-5619.

Morrison, G. C., Zhao, P., & Kasthuri, L. (2006). The spatial distribution of pollutant transport to and from indoor surfaces. *Atmos Environ*, *40*(20), 3677–3685.

Mudway, I. S., & Kelly, F. J. (2000). Ozone and the lung: a sensitive issue. Molecular Aspects of Medicine, *21*(1-2), 1-48.

Nazaroff, W.W., Gadgil, A.J., & Weschler, C.J. (1993). Critique of the use of deposition velocity in modeling indoor air quality. In *Modeling Indoor Air Quality and Exposure*, ASTM STP 1205, N.L. Nagda, 1993, American Society for Testing and Materials, Philadelphia, 81-104.

Nazaroff, W. W., & Singer, B. C. (2004). Inhalation of hazardous air pollutants from environmental tobacco smoke in US residences. *J Expo Anal Env Epid*, *14*, S71–S77.

Nazaroff, W. W., & Weschler, C. J. (2004). Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmos Environ, 38*(18), 2841-2865.

Nazaroff, W. W., Coleman, B. K., Destaillats, H., Hodgson, A. T., Liu, D.-L., Lunden, M. M., Singer, B. C., & Weschler, C. J. (2006). Indoor Air Chemistry: Cleaning Agents, Ozone and Toxic Air Contaminants (No. California Air Resources Boad Contract No. 01-336). Lawrence Berkeley National Laboratory.

Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R.C., Goldstein, A. H. (2006). Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons. *Environ Sci Technol*, *40*(7), 2283–2297.

Nicolas, M., Ramalho, O., & Maupetit, F. (2007). Reactions between ozone and building products: Impact on primary and secondary emissions. *Atmos Environ, 41*, 3129-3138.

Nomura, A., & Jones, C. W. (2013). Amine-functionalized porous silicas as adsorbents for aldehyde abatement. *ACS Applied Materials & Interfaces, 5*(12), 5569-5577.

Nomura, A., & Jones, C. W. (2014). Enhanced formaldehyde-vapor adsorption capacity of polymeric amine-incorporated aminosilicas. *Chem-Eur J*, *20*(21), 6381-6390.

Nomura, A., & Jones, C. W. (2015). Airborne aldehyde abatement by latex coatings containing amine-functionalized porous silicas. *Ind Eng Chem Res, 54*(1), 263-271.

Norris 1999

Nunes, F. M. N., Veloso, M. C. C., Pereira, P., & De Andrade, J. B. (2005). Gas-phase ozonolysis of the monoterpenoids (S)-(+)-carvone, (R)-(-)-carvone, (-)-carveol, geraniol and citral. *Atmos Environ*, *39*(40), 7715–7730.

Oberdorster, G., Elder, A., Finkelstein, J., Frampton, M., Hopke, P., Peters, A., Utell, M. (2010). *Assessment of Ambient UFP Health Effects:Linking Sources to Exposure and Responses in Extrapulmonary Organs* (No. EPA Grant R827354). University of Rochester.

Office of Environmental Health Hazard Assessment (OEHHA). (2008). *Air Toxics Hot Spots Program Risk Assessment Guidelines. Technical Support Document for the Derivation of Noncancer Reference Exposure Levels*. California Environmental Protection Agency.

Offermann, F., J. (2009). *Ventilation and Indoor Air Quality in New Homes* (No. CEC-500-2009-085). San Francisco, CA: California Air Resources Board and California Energy Commission, PIER Energy Related Environmental Research Program Collaborative Report.

Ostro, B. (1987). Air-Pollution and Morbidity Revisited - A Specification Test. *J Environ Econ Manag*, *14*(1), 87–98.

Ostro, B., & Rothschild, S. (1989). Air-Pollution and Acute Respiratory Morbidity - An Observational Study. *Environ Res*, *50*(2), 238–247.

Ourrad, H., Thevenet, F., Gaudion, V., and Riffault, V. (2015). Limonene photocatalytic oxidation at ppb levels: Assessment of gas phase reaction intermediates and secondary organic aerosol heterogeneous formation, *Appl Catal B-Environ, 168-169,* 183-194.

Pandrangi, L., & Morrison, G. C. (2009). Ozone interations with human hair: Ozone uptake rates and product formation. *Atmos Environ, 42*, 5079-5089.

Park, J.S., and Ikeda, K. (2006). Variations of formaldehyde and VOC levels during 3 years in new and older homes, *Indoor Air, 16*, 129-135.

Parodi, S., Vercelli, M., Garrone, E., Fontana, V., & Izzotti, A. (2005). Ozone air pollution and daily mortality in Genoa, Italy between 1993 and 1996. *Public Health*, *119*(9), 844-850.

Pekey, H., & Arslanbaş, D. (2008). The Relationship between indoor, outdoor and personal VOC concentrations in homes, offices and schools in the metropolitan region of Kocaeli, Turkey. *Water Air Soil Poll*, *191*(1), 113–129.

Persily, A., Musser, A., & Emmerich, S. J. (2010). Modeled infiltration rate distributions for U.S. housing. *Indoor Air*, *20*(6), 473–485.

Petrick, L. & Dubowski, Y. (2009). Heterogeneous oxidation of squalene film by ozone under various indoor conditions. *Indoor Air, 19*(5), 381-391.

Pope, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., & Thurston, G. D. (2002). Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *JAMA-J Am Med Assoc*, *287*(9), 1132–1141. doi:10.1001/jama.287.9.1132

Pope, C. A., Burnett, R. T., Turner, M. C., Cohen, A., Krewski, D., Jerrett, M., et al. (2011). Lung Cancer and Cardiovascular Disease Mortality Associated with Ambient Air Pollution and Cigarette Smoke: Shape of the Exposure-Response Relationships. *Environ Health Persp*, *119*(11), 1616–1621.

Popescu, R. S., Blondeau, P., Jouandon, E., Costes, J. C., & Fanlo, J. L. (2013). Elemental modeling of adsorption filter efficiency for indoor air quality applications. *Build Environ, 66*, 11-22.

Poppendieck, D., Hubbard, H., Ward, M., Weschler, C., & Corsi, R. L. (2007a). Ozone reactions with indoor materials during building disinfection. *Atmos Environ*, *41*(15), 3166-3176.

Poppendieck, D., Hubbard, H., Weschler, C., & Corsi, R. L. (2007b). Formation and emissions of carbonyls during and following gas-phase ozonation of indoor materials. *Atmos Environ, 41*(35), 7614-7626.

Ranciere, F., Dassonville, C., Roda, C., Laurent, A.-M., Le Moullec, Y., & Momas, I. (2011). Contribution of ozone to airborne aldehyde formation in Paris homes. *Sci Total Environ*, *409*(20), 4480–4483.

Rehwagen, M., Schlink, U., & Herbarth, O. (2003). Seasonal cycle of VOCs in apartments. *Indoor Air*, *13*(3), 283–291.

Rim. D., Gall, E. T., Maddalena, R. L., & Nazaroff, W. W. (2016). Ozone reaction with interior building materials: Influence of diurnal ozone variation, temperature and humidity. *Atmos Environ, 125*, 15-23.

Rohr, A. C., Weschler, C J., Koutrakis, P., & Spengler, J. D. (2003). Generation and quantification of ultrafine particles through terpene/ozone reaction in a chamber setting, *Aerosol Sci Tech, 37*, 65-78.

Rumchev, K., Spickett, J., Bulsara, M., Phillips, M. & Stick, S. (2004). Association of domestic exposure to volatile organic compounds with asthma in young children. *Thorax, 59,* 746-751.

Ryhl-Svendsen, M. (2011). Passive sorption of organic compounds on clay bricks. *INDOOR AIR 2011, The 12 International Conference on Indoor Air Quality and Climate,* Austin, TX, 5-11 June 2011, 6pp. (paper 383).

Sabersky, R., Sinema, D., & Shair, F. (1973). Concentrations, Decay Rates, and Removal of Ozone and Their Relation to Establishing Clean Indoor Air. *Environmental Science & Technology*, *7*(4), 347–353.

Sakr, W., Weschler, C. J., & Fanger, P. O. (2006). The impact of sorption on perceived indoor air quality. *Indoor Air, 16*, 98-110.

Sarnat, J. A., Schwartz, J., Catalano, P. J., & Suh, H. H. (2001). Gaseous pollutants in particulate matter epidemiology: Confounders or surrogates? *Environ Health Persp*, *109*(10), 1053–1061.

Sarnat, J. A., Brown, K. W., Schwartz, J., Coull, B. A., & Koutrakis, P. (2005). Ambient gas concentrations and personal particulate matter exposures - Implications for studying the health effects of particles. *Epidemiology*, *16*(3), 385–395.

Sarwar, G., Corsi, R., Kimura, Y., Allen, D., and Weschler, C.J. (2002). Hydroxyl radicals in indoor environments, *Atmos Environ, 36*, 3973-3988.

Sarwar, G., Corsi, R., Allen, D., and Weschler, C. (2003). The significance of secondary organic aerosol formation and growth in buildings: experimental and computational evidence, *Atmos Environ*, *37*, 1365-1381.

Sarwar, G., Olson, D. A., Corsi, R. L., and Weschler, C. J. (2004). Indoor fine particles: The role of terpene emissions from consumer products*, JAPCA J Air Waste Ma, 54*, 367-377.

Sarwar, G., and Corsi, R. (2007). The effects of ozone/limonene reactions on indoor secondary organic aerosols, *Atmos Environ, 41*, 959-973.

Sax, S. N., Bennett, D. H., Chillrud, S. N., Ross, J., Kinney, P. L., & Spengler, J. D. (2006). A cancer risk assessment of inner-city teenagers living in New York City and Los Angeles. *Environ Health Persp*, *114*(10), 1558–1566.

Schlink, U, Rehwagen, M., Damm, M., Richter, M., Borte, M., & Herbarth, O. (2004). Seasonal cycle of indoor-VOCs: comparison of apartments and cities. *Atmos Environ*, *38*(8), 1181–1190.

Schlink, U., Thiem, A., Kohajda, T., Richter, M., & Strebel, K. (2010). Quantile regression of indoor air concentrations of volatile organic compounds (VOC). *Sci Total Environ*, *408*(18), 3840–3851.

Schweizer, C., Edwards, R.D., Bayer-Oglesby, L., Gauderman, W.J., Ilaqua, V., Juhani Jantunen, M., Lai, H. K., Nieuwenhuijsen, M., & Künzli, N. (2007). Indoor time-microenvironment-activity patterns in seven regions of Europe. *J Expo Sci Env Epid, 17*(2), 170-181.

Sekine, Y., & Nishimura, A. (2001). Removal of formaldehyde from indoor air by passive type air-cleaning materials. *Atmos Environ*, *35*, 2001-2007.

Seppanen, O.A., & Fisk, W. (2006). Quantitative relations between indoor environmental quality and work performance or health. *HVAC&R Res, 12*(4), 957-973.

Serrano-Trespalacios, P. I., Ryan, L., & Spengler, J. D. (2004). Ambient, indoor and personal exposure relationships of volatile organic compounds in Mexico City Metropolitan Area. *J Expo Sci Env Epid*, *14*, S118–S132.

Shair, F. H. (1981). Relating indoor pollutant concentrations of ozone and sulfur dioxide to those outside: economic reduction of indoor ozone through selective filtration of the make-up air, *ASHRAE Tran*, *87*, 116-139.

Shen, J.-H., Wang, Y.-S., Lin, J.-P., Wu, S.-H., & Horng, J.-J. (2014). Improving the indoor air quality of respiratory type of medical facility by zeolite filtering. *JAPCA J Air Waste Ma, 64*(1), 13-18.

Shields, H. C., Weschler, C. J., & Naik, D. (1999). Ozone removal by charcoal filters after continuous extensive use (5 to 8 years), In *Proceedings of the 8th International Conference on Indoor Air Quality and Climate* (Vol. 4, pp. 49-54).

Simmons, A. & Colbeck, I. (1990). Resistance of various building materials to ozone deposition. *Environ Sci Technol, 11*, 973-978.

Singer, B. C., Coleman, B. K., Destaillats, H., Hodgson, A. T., Lunden, M. M., Weschler, C. J., and Nazaroff, W. W. (2006). Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone, *Atmos Environ, 40*, 6696–6710.

Singh, B. P., Kumar, A., Singh, D., Punia, M., Kumar, K., & Jain, V. K. (2014). An assessment of ozone levels, UV radiation and their occupational health hazard estimation during photocopying operation. *J Hazard Mater, 275*, 55-62.

Slob, W. (1994). Uncertainty Analysis in Multiplicative Models. *Risk Analysis*, *14*(4), 571–576.

Smith, R. L., Xu, B., & Switzer, P. (2009). Reassessing the relationship between ozone and short-term mortality in U.S. urban communities. *Inhal Toxicol, 21*(Suppl 2), 37-61.

Stephens, B., Siegel, J. A., & Novoselac, A. (2011). Operational characteristics of residential and light-commercial air-conditioning systems in a hot and humid climate zone. *Build Environ*, *46*(10), 1972–1983.

Stephens, B., Gall, E. T., & Siegel, J. A. (2012). Measuring the penetration of ambient ozone into residential buildings. *Environ Sci Technol*, *46*(2), 929–936.

Tamas, G., Weschler, C.J., Bako-Biro, Z., Wyon, D.P., & Strom-Tejsen, P. (2006). Factors affecting ozone removal rates in a simulated aircraft cabin environment. *Atmos Environ, 40*(32), 6122-6133.

Taoda, H., Fukaya, M., Watanabe, E., & Tanaka, K. (2006). VOC Decomposition by photocatalytic wall paper. *Mater Sci Forum, 510-511*, 22-25.

Turner, M. C., Krewski, D., Pope, C. A., Chen, Y., Gapstur, S. M., & Thun, M. J. (2011). Long-term Ambient Fine Particulate Matter Air Pollution and Lung Cancer in a Large Cohort of Never-Smokers. *Am J Resp Crit Care*, *184*(12), 1374–1381.

USCB (U.S. Census Bureau). (2012). Households and Families: 2010. Retrieved August 20, 2013, from http://www.census.gov/prod/cen2010/briefs/c2010br-14.pdf

USCB (U.S. Census Bureau) (2013). AHS Main. Retrieved September 20, 2013, from http://www.census.gov/housing/ahs/

USEIA (U.S. Energy Information Administration). (2014). Commercial Building Energy Consumption Survey. Retrieved May 27, 2014, from http://www.eia.gov/consumption/commercial/

USEPA (2006a). *Air Quality Criteria for Ozone and Related Photochemical Oxidants* (No. EPA/600/R-05/004aF-cF). Washington, DC: U.S. Environmental Protection Agency.

USEPA (2006b). *Building Assessment Survey and Evaluation (BASE) Study* (No. 402-C-06-002). Washington, DC: U.S. Environmental Protection Agency.

USEPA. (2010). *Quantitative Health Risk Assessment for Particulate Matter* (No. EPA-452/R-10-005). Research Triangle Park, NC. Retrieved from http://www.epa.gov/ttnnaaqs/standards/pm/data/20100209RA2ndExternalReviewDraft.pdf

USEPA. (2012c). Integrated Risk Information System (IRIS). Reports & Assessments. Retrieved November 15, 2012, from http://www.epa.gov/IRIS/

Usher, C. R., Michel, A. E., Stec, D., & Grassian, V. H. (2003). Laboratory studies of ozone uptake on processed mineral dust. *Atmos Environ, 37*, 5337-5347.

USSSA (U.S. Social Security Administration). (2013). Measures of Central Tendency for Wage Data. Retrieved December 18, 2013, from http://www.ssa.gov/oact/cola/central.html

Wainman, T., Zhang, J., Weschler, C. J., & Lioy, P. J. (2000). Ozone and limonene in indoor air: A source of submicron particle exposure. *Environ Health Persp, 108*(12), 1139-1145.

Wallace L, Williams R, Rea A, Croghan C. (2006). Continuous week-long measurements of personal exposures and indoor concentrations of fine particles for 37 health-impaired North Carolina residents for up to four seasons. *Atmos Environ, 40*(3), 399–414.

Wang, H., & Morrison, G. C. (2006). Ozone-initiated secondary emission rates of aldehydes from indoor surfaces in four homes. *Environ Sci Technol, 40*, 5263-5268.

Wang, H., & Morrison, G. (2010). Ozone-surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends. *Indoor Air, 20*(3), 224-234.

Wang, J., Engvall, K., Smedje, G., Norbäck, D. (2014a). Rhinitis, asthma and respiratory infections among adults in relation to the home environment in multi-family buildings in Sweden. *PLOS ONE, 9*(8), Article number e105125.

Wang, M., Zhang, P., Li, J., & Jiang, C. (2014b). The effects of Mn loading on the structure and ozone decomposition activity of MnOx supported on activated carbon. *Chinese J Catal, 35*(3), 335–341.

Wargocki, P., Wyon, D. P., Baik, Y. K., Clausen, G., & Fanger, P. O. (1999). Perceived air quality, sick buildings syndrome (SBS) symptoms and productivity in an office with two difference pollution loads. *Indoor Air, 9*, 165-179.

Wargocki, P., Bakó-Biró, Z., Clausen, G., & Fanger, P.O. (2002). Air quality in a simulated office environment as a result of reducing pollution sources and increasing ventilation. *Energ Buildings, 34*(8), 775-783.

Waring, M. S., Wells, J. R., & Siegel, J. A. Secondary organic aerosol formation from ozone reactions with single terpenoids and terpenoid mixtures. (2011). *Atmos Environ, 45*(25), 4235-4242.

Waring, M. S., & Siegel, J. A. (2011). The effect of an ion generator on indoor air quality in a residential room. *Indoor Air, 21*(4), 267–276.

Weisel, C. P., Zhang, J. (Jim), Turpin, B. J., Morandi, M. T., Colome, S., Stock, T. H., & Spektor, D. M. (2005). *Relationships of Indoor, Outdoor, and Personal Air (RIOPA) Part I. Collection Methods and Descriptive Analyses* (130 Part 1). Health Effects Institute.

Weschler, C. J., Brauer, M., & Koutrakis, P. (1992a). Indoor ozone and nitrogen-dioxide − a potential pathway to the generation of nitrate radicals, dinitrogen petaoxide, and nitric-acid indoors. *Environ Sci Technol, 26*(1), 179-184.

Weschler, C. J., Hodgson, A. T., & Wooley, J. D. (1992b). Indoor chemistry: Ozone, volatile organic compounds, and carpets. *Environ Sci Technol, 26*, 2371-2377.

Weschler, C.J., & Shields, H.C. (1996). Production of the hydroxyl radical in indoor air. *Environ Sci Technol, 30*(11), 3250-3258.

Weschler, C. J., & Shields, H. C. (1997). Measurements of the hydroxyl radical in a manipulated but realistic indoor environment. *Environ Sci Technol, 31*(12), 3719-3722.

Weschler, C. J., & Shields, H. C. (1999). Indoor ozone/terpene reactions as a source of indoor particles. *Atmos Environ, 33*(15), 2301-2312.

Weschler, C. (2000). Ozone in indoor environments: Concentration and chemistry. *Indoor Air, 10*(4), 269-288.

Weschler, C. J. (2006). Ozone's impact on public health: Contributions from indoor exposures to ozone and products of ozone-initiated chemistry. *Environ Health Persp, 114*, 1489-1496.

Weschler, C. J., Wisthaler, A., Cowlin, S., Tamás, G., Strøm-Tejsen, P., Hodgson, A. T., et al. (2007). Ozone-initiated chemistry in an occupied simulated aircraft cabin. *Environ Sci Technol, 41*(17), 6177-6184.

Wheeler, A.J., Xu, X.H., Kulka, R., You, H.Y., Wallace, L., Mallach, G., Van Ryswyk, K., MacNeill, M., Kearney, J., Rasmussen, P. E., Dabek-Zlotorzynska, E., Wang, D., Poon, R., Williams, R., Stocco, C., Anastassopoulos, A., Miller, J. D., Dales, R., & Brook, J. R. (2011). Windsor, Ontario exposure assessment study: Design and methods validation of personal, indoor, and outdoor air pollution monitoring. *J Air Waste Manage, 61*(3), 324-338.

Wilson, M.J.G. (1968). Indoor air pollution, *Proc R Soc London, Ser A, 307*(1489), 215-221.

Wisthaler, A., & Weschler, C. J. (2010). Reactions of ozone with human skin lipids: sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. *P Natl Acad Sci USA, 107*, 6568-6575.

Wolkoff, P., Clausen, P. A., Larsen, K., Hammer, M., Larsen, S. T., & Nielsen, G. D. (2008). Acute airway effects of ozone-initiated d-limonene chemistry: Importance of gaseous products. *Toxicol Lett*, *181*(3), 171–176.

Wolkoff, P., & Nielsen, G. D. (2010). Non-cancer effects of formaldehyde and relevance for setting an indoor air guideline. *Environ Int*, *36*(7), 788–799.

Yang, Q. Y., Chen, Y., Shi, Y. L., Burnett, R. T., McGrail, K. M., & Krewski, D. (2003). Association between ozone and respiratory admissions among children and the elderly in Vancouver, Canada. *Inhal Toxicol*, *15*(13), 1297-1308.

Youssefi, S., & Waring, M. S. (2012). Predicting secondary organic aerosol formation from terpenoid ozonolysis with varying yields in indoor environments. *Indoor Air*, *22*(5), 415–426.

Yu, J.-W., Christiansson, J., & Neretnieks, I. (1993). Modeling of a passive adsorption sheet to purify indoor air. *Indoor Air*, *3*(4), 310-314.

Zhang, L., Tang, X., Rothman, N., Vermeulen, R., et al. (2010). Occupational Exposure to Formaldehyde, Hematotoxicity, and Leukemia-Specific Chromosome Changes in Cultured Myeloid Progenitor Cells. *Cancer Epidem Biomar*, *19*(1), 80–88.

Zheng, X. Y., Ding, H., Jiang, L. N., Chen, S. W., Zheng, J. P., Qiu, M., Zhou, Y. X., Chen, Q., and Guan, W. J. (2015). Association between air pollutants and asthma emergency room visits and hospital admissions in time series studies: A systematic review and meta-analysis, *PLoS ONE, 10*, e013814

# VITA

Erin Kennedy Darling was born in West Virginia in 1987 and grew up in Colorado, Georgia, Texas, and Louisiana. She is a 2005 alum of the Academy of The Sacred Heart in Grand Coteau, Louisiana. Upon returning to Texas, she began undergraduate studies in Civil Engineering. During her final two semesters, she worked as an undergraduate research assistant with Dr. Corsi's group. After graduating with a Bachelor of Science in Civil Engineering in May 2009, she immediately transitioned to the Environmental and Water Resources Engineering Master's program, continuing to research under the guidance of Dr. Corsi. She obtained a Master of Science in Engineering in August 2011.

Address:    irreverint@gmail.com

This manuscript was typed by Erin Kennedy Darling