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Impacts of a Clay Plaster on Actual and Perceived Indoor Air Quality

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Impacts of a Clay Plaster on Actual and Perceived Indoor Air Quality

by

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Dedication

To my Izzy.

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Abstract

Impacts of a Clay Plaster on Actual and Perceived Indoor Air Quality

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Passive removal materials (PRMs) are building materials or furnishings that can effectively control indoor pollution without substantial formation of chemical byproducts and without energy penalty. To assess clay wall plaster as an effective 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 18 to 23 human subjects assessed air quality in twin 30 m³ chambers using a continuous acceptability scale. Air samples were collected immediately prior to panel assessment to quantify concentrations of C₅ to C₁₀ saturated n-aldehydes and two aromatic aldehydes that are commonly produced by reaction of ozone with 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. 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.

Ozone deposition and byproduct emissions of the clay wall plaster were also assessed using 48 liter stainless steel chambers. Clay plaster applied to gypsum wallboard that had been exposed in a test house (U-Test House) for one year effectively removed 88% of the ozone, and emitted high aldehyde concentrations when exposed to high purity air that did not increase when the material was exposed to ozone. The outcome of these experiments leads to speculation that the clay plaster adsorbed contaminants in the test house and then re-emitted them upon exposure to clean air in the small chambers.

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Introduction

Increasing levels of tropospheric ozone have been related to numerous adverse effects on humans, including decreases in short-term lung function (Mudway and Kelly, 2000; Levy et al., 2001), increased rates of asthma symptoms in infants (Triche et al., 2006), and increases in morbidity and both non-traumatic mortality and cardiopulmonary death rates (Bell et al., 2005; Bell et al., 2006; Jackson et al., 2010). 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 (Weschler, 2006). In addition, many sources of ozone exist indoors, including laser printers, photocopiers, and ion generators (Britigan et al., 2006; Destailats et al., 2008; Lee et al., 2001; Waring et al., 2008). 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 (Simoni et al., 1998; Williams et al., 2000; Weschler, 2006).

Ozone reacts with numerous chemicals in indoor environments, and 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 (Weschler, 2000). At low building air exchange rates, the time for these reactions to occur and the residence times of reaction products increase (Sarwar et al., 2003). Consequently, cumulative molar intake of ozone byproducts can be as high as twice the intake of unreacted ozone (Weschler, 2006), and therefore decreases in indoor ozone concentrations are an important part of reducing total population exposure to both ozone and ozone reaction products.

Indoor ozone concentrations can be lowered by treating building intake air with activated carbon (Shair, 1981; Shields et al., 1999), using fibrous activated carbon filters in HVAC systems, or alternatively by strategically placing ozone-scavenging materials indoors (Kunkel et al., 2010). The latter approach, i.e., application of passive removal materials (PRMs), should involve coverage of large surface areas, appear aesthetically acceptable, and not contribute to formation of ozone reaction products.

Clay may be a promising PRM. It has the advantage of possible application over large interior surfaces, e.g., as a wall plaster. Lamble et al. (2011) measured ozone deposition velocities and reaction byproducts of nineteen “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 already gained acceptance as a building material for human habitation; 1/3 of the world’s population now lives in earthen structures (Minke, 2006).

In this study, a clay wall plaster tested by Lamble et al. (2011) was explored to ascertain whether it 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 carpet. This was accomplished by surveying perceived air quality (PAQ) during single-blind experiments, and quantifying C₅-C₁₀ aliphatic aldehyde concentrations inside walk-in chambers containing combinations of carpet and clay wall plaster in the presence and absence of ozone.

Separate experiments on the clay wall plaster were also conducted in a system of four parallel 48 L stainless steel chambers that were equipped to measure ozone deposition velocities and concentrations of C₅-C₁₀ aldehydes. Clay wall plaster specimens had been prepared and stored unsealed in the UTest house for one year prior to

experiments. Transport-limited deposition velocities and reaction probabilities were determined using a clay plaster specimen coated with an aqueous solution of potassium iodide.

Experimental Methods

LABORATORY CHAMBER EXPERIMENTS

Material Preparation

The clay wall plaster specimens were prepared, covered with plastic, and stored in the UTest house for one year before testing. Specimen preparation consisted of mixing the dry clay plaster with water and powdered mineral pigment according to supplier directions, applying sanded water-based primer to paper-backed gypsum wallboards, and then troweling the clay onto the wallboards in two layers.

For the small chamber experiments, 48cm x 30cm pieces were cut to cover the majority of the chamber floors. Each sample was 1.3cm thick, and the exposed gypsum on the sides was covered by wrapping Teflon[®] tape around each sample to minimize ozone uptake to the gypsum. Three samples were cut; the top surface of one sample was coated with aqueous potassium iodide (KI) and left to dry, and the other two samples were unaltered. The KI-coated sample served to determine the transport-limited deposition velocity in the chambers (v_t) and the reaction probability of ozone with the clay plaster (γ).

Experimental Chamber System

The materials were tested in a parallel four-chamber system connected to a UV ozone generator (Perma Pure Zero-AirTM, Model ZA-750-10) and humidifier (Figure 1). Each stainless steel chamber had a volume of 48 liters and had been electro polished three months prior to experiments. Two perforated stainless steel tubes inside each chamber, one for providing inlet air and one for venting air, ensured uniform mixing of air over the materials. All tubing in the system was flexible ¼-in OD PFA, and tube fittings and valves were either PFA or stainless steel (Swagelok).

Laboratory air was supplied to the system using a compression pump (Thomas, Model 607CA220) after passing through two Teflon[®] PFA filter tubes packed with activated carbon (AC) mat to prevent compounds in lab air from reacting with ozone in the system. A portion of the air then bubbled through a Teflon[®] PFA (Savillex 120 ml column components, 1-1/2" MNPT) tube filled with distilled water, and remixed with the non-humidified air. The amount of air allowed to bubble through the humidifier was adjusted using a needle valve, and the relative humidity and temperature of the conditioned air were monitored using a QTrak probe (TSI QTrak). The humidified air then split, with a portion flowing through the ozone generator, and the rest bypassing the generator. The amount of air allowed to bypass the generator – effectively, inversely proportional to the chamber inlet ozone concentration – was adjusted with a needle valve. After ozonation and remixing with the bypassed air, the mixed air passed through the mass flow controllers (MFCs) (Aalborg GCF17) and then into the chambers. An automatic 6-port selector valve (VICI[®], EMT2VLSC6MWE2), with sampling lines to each chamber outlet, the inlet air line, and laboratory air line, allowed for constant monitoring of ozone concentrations. Ozone concentrations were monitored with a single UV-cell ozone monitor (2B Technologies, Model 202). System air was exhausted through tubing fed into a neighboring laboratory hood.

The entire system was placed in a walk-in hood with walls and ceiling insulated with two layers of R-4, 3/4-inch polystyrene foam sheathing (Owens Corning Foamular Sheathing) and foil tape to seal the joints and edges. In this setting, the system could be operated at controlled elevated temperatures using an electric space heater.

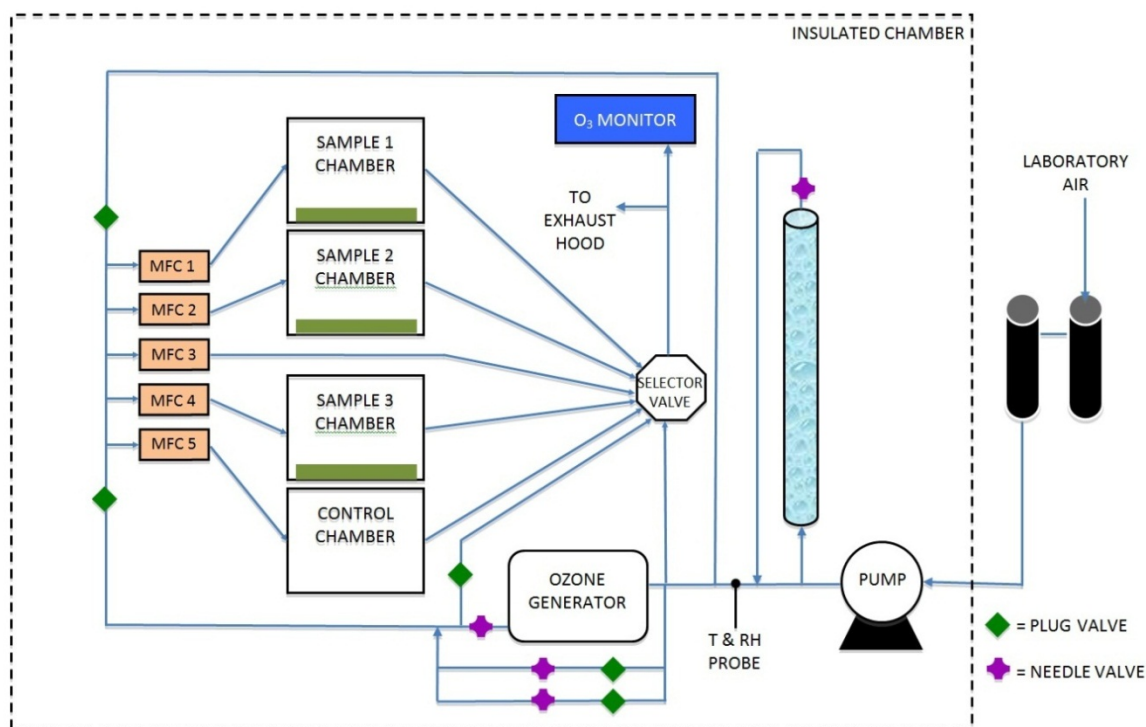


Figure 1: Diagram of small chamber system

Chamber Preparation

Before the experiment, all four chambers were treated with a heat gun that provided air at 538°C to the chamber surfaces (Milwaukee®). The chambers were then scrubbed and rinsed with KimWipes (Kimtech, Kimberly-Clark®) and distilled water, followed by methanol. Finally, the chambers were sealed and conditioned at 1500 ppb ozone for 2 hours to passivate any remaining reaction sites.

The ozone monitor filter was replaced and the monitor was calibrated before experiments. An Ozone Calibration Source (2B Technologies, Model 306) was used to calibrate the ozone monitor according to manufacturer protocol. The AC mat in the tube filter at the system intake was also replaced with fresh AC mat.

To ensure a constant air temperature within the insulated hood, a thermostat was programmed to switch on or off an electric space heater; however, no heating was

necessary for these experiments since the air temperature within the hood was roughly constant at 25°C. Relative humidity of the air in the system was maintained at $50 \pm 5\%$.

After ozone concentrations in the chambers decayed sufficiently, the inlet flows to the chambers were set to approximately 1050 ml min^{-1} by adjusting the MFCs and verifying the flows with a bubble flow calibrator (Gilian Gilibrator-2, Sensidyne®). Clay samples were then placed in the chambers and allowed to equilibrate over night with temperature and relative humidity. One empty chamber containing a length of Teflon® tape equal to the amount wrapped around one of the specimens served as the control chamber.

Experimental Procedure

On the day of the experiment, the ozone recording software and selector valve were activated. Before introducing ozone into the chambers, duplicate air samples were collected for one hour from the outflows of the control chamber and the two chambers with non-KI-coated clay samples. Duplicate air samples were also collected from the inlet of the control chamber. The air samples were collected on conditioned glass GC injection port liners (SiSS, open liners, tapered/frit, 3 mm I.D.) packed with Tenax-TA and glass wool fibers on both ends. Air was pulled through ozone scrubbers (P/N 505285, Sigma-Aldrich, Inc.) connected directly upstream of the glass liners using pumps (AP Buck, VSS-1) that had been calibrated to a flow rate of $43 \pm 2 \text{ mL min}^{-1}$. This flow rate and sample volume had been previously verified as sufficient via breakthrough tests using the same glass liners and adsorbent (Morrison & Corsi, 2010). Prior to sampling, the packed glass liners were cleaned and conditioned using a 200 mL min^{-1} flow of N_2 (Airgas, Inc.) at 330°C for 2 hours in a gas chromatograph oven (Hewlett-Packard 5890).

Ozone scrubbers were also conditioned in the gas chromatograph oven using a 200 mL min⁻¹ flow of N₂ at 60°C for 24 hours.

A bubble flow meter was used to calibrate the sample pumps before each sampling period, and was also used to confirm the sampling flow rates by measuring the chamber outlet flow to the ozone monitor. Before and after sampling, each glass liner was placed in a stainless steel tube that was sealed on each end with stainless steel fittings (Swagelok), and kept in a hermetically sealed glass jar packed with activated carbon mat.

After pre-ozone sampling, the plug valves were switched to inject ozone into the chambers. The inlet concentration was held at 248 ± 3 ppb and 50 ± 5% RH. After three hours of ozonation – enough time to achieve steady-state ozone concentrations in the chambers – duplicate air samples were collected for one hour from the chamber outlets (except the KI chamber) and from the control chamber inlet. During the experiment, duplicate samples of the laboratory air were collected near the system intake.

All collected air samples were analyzed for eight heavy aldehydes (C₅-C₁₀ saturated n-aldehydes, benzaldehyde, tolualdehyde) within one hour of collection by zero-path thermal desorption (ATAS Optic 2) followed by gas chromatography (column: RESTEK, Rxi-5Sil MS; 30 m, 0.25 mm ID; 0.5 µm film thickness) with flame ionization detection (TD/GC/FID). A 15:1 split ratio in the injector was used for GC analyses. The initial injector temperature of 60°C was ramped to 305°C at a rate of 10°C s⁻¹, followed by 20.67 minutes of thermal desorption of the glass liners. The initial oven temperature of 50°C was held for two minutes, and then ramped to 300°C at 15°C min⁻¹, and finally held at 300°C for two minutes.

Three-point calibration curves were generated using stock solutions containing pure chemicals purchased from Fisher Scientific, Inc. (pentanal, 97%, hexanal, 98%, heptanal, 95%, octanal, 99%, nonanal, 95%, decanal, 98%, benzaldehyde, 99%,

tolualdehyde, 97%). Calibration curves for each chemical are provided in Appendix A. The stock solution was made by dissolving heavy aldehydes (80 μL total) in 25 mL of methanol (CHROMASOLV[®], $\geq 99.9\%$). Subsequent 1:10 and 1:100 dilutions of the stock solution were made to complete the three-point calibration curve. Using a clean syringe, a volume of 1 μL was pulled from each dilution and injected into separate adsorbent tubes. Each tube was then purged with a 200 mL min^{-1} flow of high purity grade N_2 for 20 minutes before GC analysis.

Data Analysis

The ozone deposition velocity to each material was determined numerically by modeling each chamber. In order to model ozone behavior in each chamber, the following non-steady-state mass balance was employed:

$$\frac{dC}{dt} = \lambda C_{in} - \lambda C - v_{d,ch} \frac{A_{ch}}{V_{air}} C - v_{d,m} \frac{A_m}{V_{air}} C \quad \text{Eq. (1)}$$

where C is the ozone concentration inside the chamber, λ is the air exchange rate of the chamber, C_{in} is the inlet ozone concentration, $v_{d,ch}$ is the ozone deposition velocity for the chamber surfaces, $v_{d,m}$ is the ozone deposition velocity for the tested material, A_{ch} is the surface area of the chamber surfaces not covered by the test material, A_m is the horizontally projected surface area of the test material, V_{air} is the volume of air inside the chamber, and t denotes time. Equation 1 was discretized and solved for $v_{d,ch}$ or $v_{d,m}$. A time step of nine minutes was used and each deposition velocity was taken to be an average over that time step.

Ozone deposition velocity (v_d) is defined as the mass flux of gaseous ozone to a surface (e.g., $\mu\text{g m}^{-2} \text{h}^{-1}$), normalized by the local ozone concentration in air (e.g., $\mu\text{g m}^{-3}$), and therefore, v_d essentially describes the rate at which ozone is removed by a surface

(Cano-Ruiz, 1993). Both fluid mechanics near the surface and chemical reactivity of the surface material with ozone influence v_d . For the assumption of laminar airflow parallel to a flat surface, deposition velocity can be modeled as follows:

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v_b \rangle} \quad \text{Eq. (2)}$$

where v_t is the transport-limited deposition velocity, γ is the reaction probability, and $\langle v_b \rangle$ is the Boltzmann velocity, which for ozone at 20°C is 362 m s⁻¹. Equation 2 states that the total resistance to deposition, $\frac{1}{v_d}$, is equal to the sum of the transport resistance, $\frac{1}{v_t}$, and the reaction resistance, $\frac{4}{\gamma \langle v_b \rangle}$ (for more extensive background, see Cano-

Ruiz, 1993). The transport-limited deposition velocity is dependent solely on fluid mechanics and not on the properties of the surface material, and therefore deposition velocities reported for experiments conducted under different flow conditions cannot be meaningfully compared without additional knowledge of the transport-limited deposition velocities and experimental air temperatures, i.e., to determine $\langle v_b \rangle$.

For this study, v_t was determined from the KI-coated clay sample. By coating the material surface with KI, which has a high reaction probability for ozone, the third term in Equation 2 could be neglected, and the measured v_d would equal v_t . By knowing v_t , the reaction probability of the clay plaster was able to be determined. Reaction probability is a coefficient, defined as the ratio of the surface removal rate of pollutant molecules to the collision rate of pollutant molecules with the surface. Instead of comparing combinations of v_d , v_t , and temperature for various materials, the reaction probabilities more conveniently indicate the materials that most effectively remove ozone from the air.

PERCEIVED AIR QUALITY ANALYSES

Materials

Carpet was purchased from a distributor in Denmark and aired out in a separate chamber for three weeks prior to experiments. 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. 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. The total areas of carpet and clay on each rack were 14 m² and 10.6 m², respectively.

Test Chambers and Ozone Generation

Experiments were performed in 30 m³ stainless-steel chambers described by Albrechtsen (1988). Each chamber was equipped with a piston flow type ventilation system that provided 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 piston-type 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. 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 PAQ events (Figure 2).

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 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).

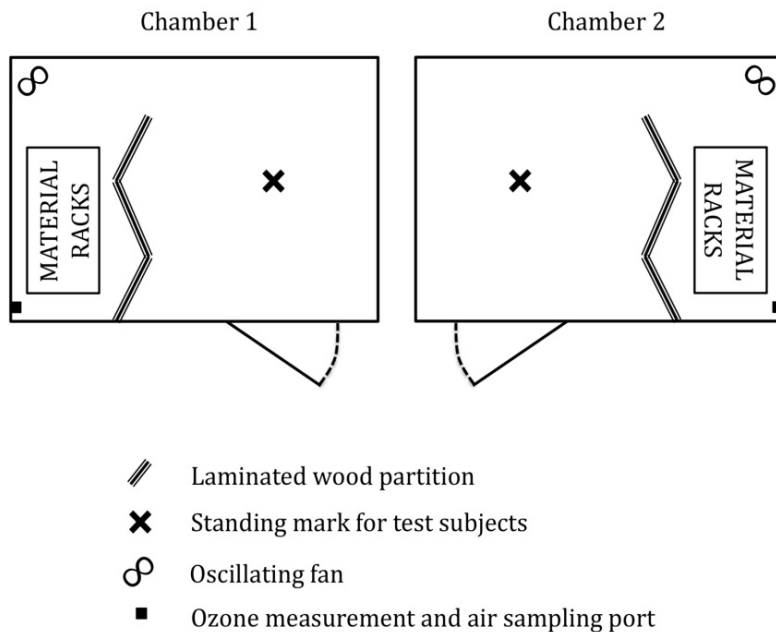


Figure 2: Layout of test chambers¹

¹ Diagram credit: Clément Cros

Air Sampling

Immediately before panelists arrived on a given day, air samples were collected through ports in the chamber walls to be analyzed for C₅ to C₁₀ n-aldehydes, benzaldehyde and tolualdehyde. These aldehydes are commonly observed reaction products of ozone with carpet (Cros et al., 2011; Morrison and Nazaroff, 2002; Nicolas et al., 2007), are themselves odorous 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). The samples were collected on large-volume glass GC injection liners (SISS, open liners, tapered, frit, 3 mm I.D.) containing Tenax-TA (Supelco Inc., 80/100 mesh). A flow rate of $48 \pm 3 \text{ ml min}^{-1}$ was drawn through the sorbent tubes by sampling pumps (model VSS-1, A.P. Buck Inc.) with low flow adapters. 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 AC mat. At the end of the experimental program, the jar was packed in ice and shipped to The 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). 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. Sample tubing was threaded through sample ports in the wall for this purpose. 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.

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 3), 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 (Table 1). 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.

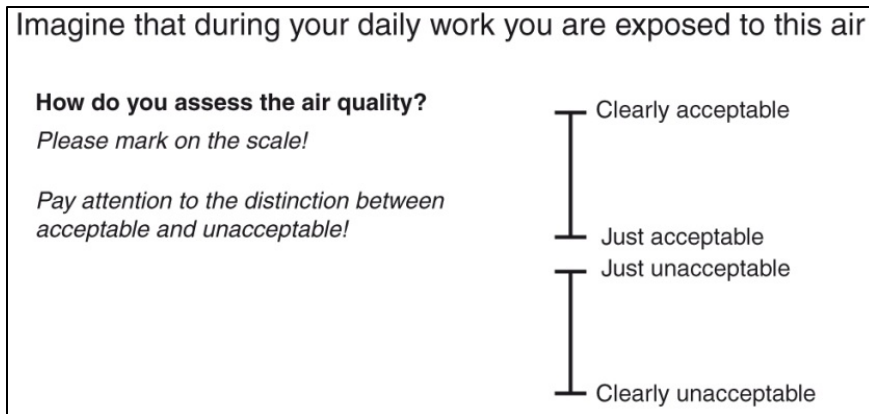


Figure 3: Perceived air quality assessment scale

Table 1: Material and ozone configurations in test chambers

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

Ozone 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.

Results and Discussion

LABORATORY CHAMBER RESULTS

Ozone Deposition Velocity

Time-averaged ozone deposition velocities to the three clay samples and to the control chamber are shown in Figure 4. The deposition velocity to control chamber walls was small relative to deposition velocities to clay specimens. Both clay samples 1 and 2 increased ozone deposition inside the chambers to similar extents, and the clay sample coated with KI more than doubled ozone deposition relative to the uncoated clay samples. Figure 5 shows the ozone concentrations in the four chambers, as well as the inlet concentration during the 6.5-hour exposure period.

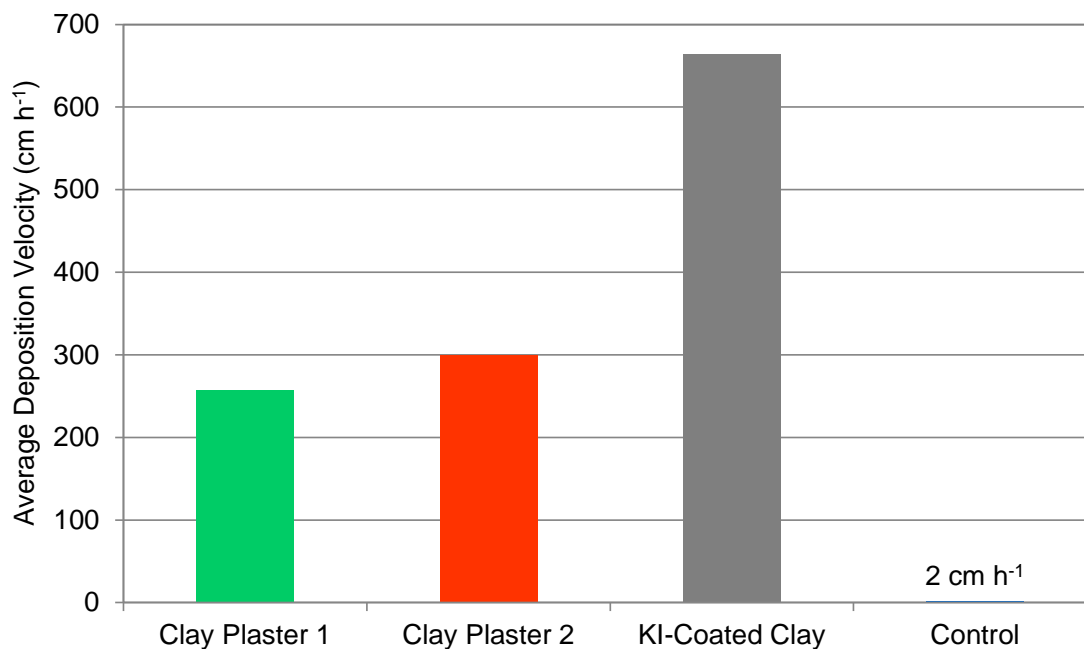


Figure 4: Time-averaged ozone deposition velocities to materials and control chamber

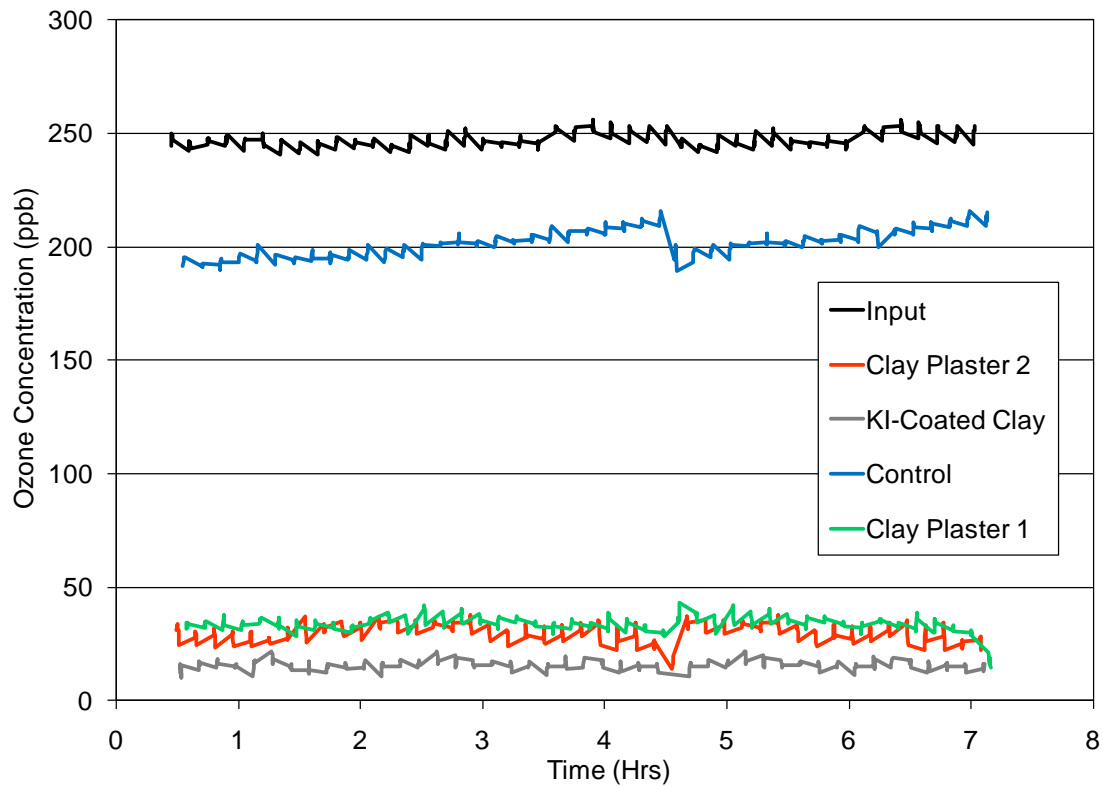


Figure 5: Input and output ozone concentrations for laboratory experiments

Reaction probabilities of several building materials with ozone at temperatures and relative humidity similar to those used in this study are listed in Table 2, along with the reaction probability determined for the clay plaster in this study. Reaction probabilities are shown in increasing magnitude. As shown in Table 2, the clay plaster tested in this study had a mean γ similar to that of materials known to be reactive with ozone, such as perlite ceiling tiles and cloth impregnated with activated carbon. The clay plaster tested in this study had a slightly lower reaction probability compared to the clay plaster tested by Lamble (2011), which could be explained by difference in age of the specimens; Lamble tested freshly made specimens.

Table 2: Ozone reaction probabilities (γ) of common and/or green building materials

Material	γ	Temperature & RH	Reference
Hard dense stone	1.80×10^{-8}	22 °C, 50%	a
Untreated, aged hard wood	5.60×10^{-7}	22 °C, 50%	a
Floor tile, recycled	1.02×10^{-6}	25 °C, 50%	h
Clay floor tile, non-glazed	1.02×10^{-6}	25 °C, 50%	h
Marmoleum floor tile	1.19×10^{-6}	25 °C, 50%	h
Brick	1.30×10^{-6}	22 °C, 50%	a
Latex-painted wall	1.70×10^{-6}	23 °C, 50%	b
Fine concrete	1.90×10^{-6}	22 °C, 50%	a
Bamboo flooring, finished	1.95×10^{-6}	25 °C, 50%	h
Untreated, fresh soft wood	2.40×10^{-6}	22 °C, 50%	a
Cork wall tile	2.45×10^{-6}	25 °C, 50%	h
Wood flooring, renewable	2.48×10^{-6}	25 °C, 50%	h
Concrete with sealer	2.70×10^{-6}	25 °C, 50%	c
Latex paint on gyp. board, flat, low-VOC	2.70×10^{-6}	25 °C, 50%	h
Collagen-based paint on gyp. board, eggshell	3.15×10^{-6}	25 °C, 50%	h
Latex painted brick, weathered 2 months	3.54×10^{-6}	33 °C, 34%	g
Brick, weathered 4 months	4.81×10^{-6}	33 °C, 31%	g
Latex paint, ozone treated	5.00×10^{-6}	20 °C, 50%	e
Rayon fabric wall covering	5.30×10^{-6}	25 °C, 50%	h
Recycled tire floor tile	7.52×10^{-6}	25 °C, 50%	h
Soft porous stone	7.90×10^{-6}	22 °C, 50%	a
Coarse concrete	8.90×10^{-6}	22 °C, 50%	a
Eurostone-perlite ceiling tile	1.02×10^{-5}	25 °C, 50%	h
Clay wall plaster on gyp. board, non-sealed	1.50×10^{-5}	25 °C, 50%	f
Activated carbon cloth	1.80×10^{-5}	22 °C, 50%	d
Concrete, weathered 4 months	2.10×10^{-5}	33 °C, 33%	g
Clay wall plaster on gyp. board, non-sealed	2.20×10^{-5}	25 °C, 50%	h
Limestone, weathered 4 months	2.85×10^{-5}	33 °C, 32%	g
Carpet, recycled	3.00×10^{-5}	25 °C, 50%	h
Mineral fiber ceiling tile, recycled	4.20×10^{-5}	25 °C, 50%	h
Gypsum board, paper-backed	4.25×10^{-5}	25 °C, 50%	h
Clay-based paint on gyp. board	5.65×10^{-5}	25 °C, 50%	h
Acoustic wall panel, recycled	8.30×10^{-5}	25 °C, 50%	h
New brick	2.20×10^{-4}	20 °C	d
Old brick	2.20×10^{-4}	20 °C	d

a. Grontoft, 2004; b. Morrison, 2010; c. Poppendieck, 2007; d. Simmons, 1990; e. Ryan, 1992; f. this study; g. Poppendieck et al., 2011; h. Lamble, 2011

Byproduct Concentrations

Concentrations of total heavy aldehydes (C_5 - C_{10} saturated n-aldehydes, benzaldehyde and tolualdehyde) measured in laboratory air, inflow to the control chamber, and chamber outflows before and during ozone exposure are plotted in

Figure 6. Duplicate samples of lab air were taken only once during the middle of the experiment, as the assumption was made that lab air concentrations would be relatively low and would not vary considerably; experiments were conducted in the evening during a weekend when no other employees were present in the lab. Inlet air was sampled only from the control chamber, due to time and equipment constraints. However, the air supplied to the chambers was split from a common line and then passed through the MFCs and a short length of Teflon[®] tubing; therefore, the air supplied to the control chamber should have had the same composition as the air supplied to the other chambers. Since all four chambers underwent the same cleaning and conditioning prior to the experiment, the assumption was also made that the concentrations measured in the control chamber would be similar to those in the other chambers if no materials were inside them.

Lower total aldehyde concentrations were observed in both clay chambers 1 and 2 after three hours of exposure to 250 ppb ozone compared to pre-ozone concentrations (19% average decrease of total byproducts). Total byproduct levels in the inlet air also decreased by 28% during ozonation, while levels in the control chamber slightly increased by 17% during ozonation, but remained near typical system background levels. The most prevalent compounds in the two clay chambers were hexanal (C₆), heptanal (C₇), octanal (C₈), and nonanal (C₉) both before and during ozonation (Figure 6). High mean concentrations of pentanal (C₅) were also measured in the lab air, inlet air, and in the chambers before and during ozonation. Pentanal was shown to be present and persistent in the laboratory air that enters the chambers, as 67% of the mean concentration of lab air was attributed to C₅. In the week prior to the experiment, duplicate air samples were collected from an empty chamber after it had been cleaned and conditioned, and C₅ was found to comprise 77% of the mean total heavy aldehyde

concentration. Due to its ubiquity throughout the experimental system and the high error on the standard tube (Appendix D), C₅ data have been omitted from the final calculations and graphs for these experiments, but are provided in Appendix C.

Some of the C₆ emitted from the clay specimens likely originated from the test house, where previous experiments observed high concentrations of C₆ compared to the other aldehydes sampled from the background air (see Appendix B). As mentioned earlier, the clay specimens were made one year before the experiments, and stored unsealed under painter’s plastic in the test house. It is possible that compounds emitted by materials and humans in the test house adsorbed to the clay plaster both during and after it was applied to the wallboard.

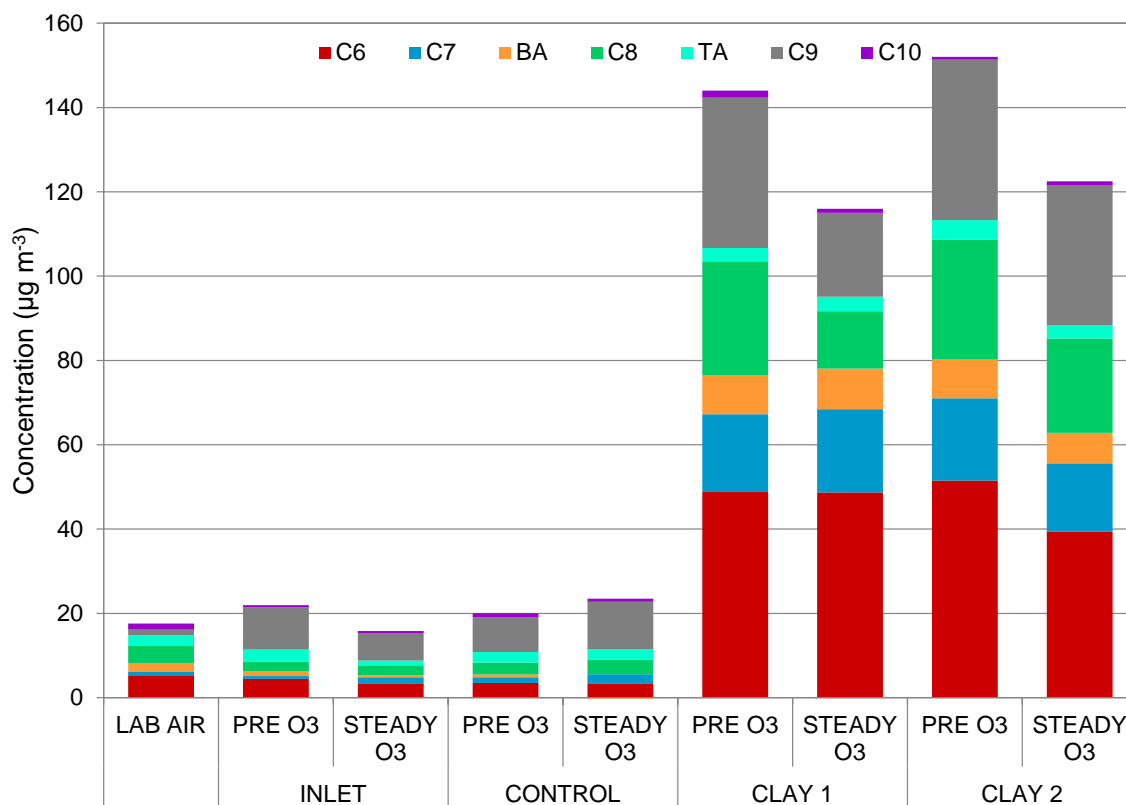


Figure 6: Measured byproduct concentrations before and during ozonation (mean of duplicates; BA = benzaldehyde, TA = o-tolualdehyde)

PERCEIVED AIR QUALITY RESULTS

Ozone Removal

The steady-state ozone concentrations for the pair of experiments involving an empty chamber with ozone injection were 73 and 77 ppb. For the same ozone injection rate of 9.6 mg hr^{-1} , the steady-state ozone concentrations for two experiments for 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 E). 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} . A similar ozone deposition velocity of 11.5 m h^{-1} was measured in the UTest house for clay plaster on gypsum wallboard that was prepared from the same batch as that studied at DTU (Appendix B). These values are higher than the range of transport-limited deposition velocities observed in an apartment with fans ($2 - 4 \text{ m h}^{-1}$); however, near an air supply register the value was 18.7 m hr^{-1} (Morrison et al., 2006).

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.

PAQ Survey and Air Samples

The results of all PAQ experiments are presented as box plots in Figure 7. 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) PAQ. In comparing the two chambers on a given day, significantly different PAQ results ($\alpha = 0.05$, Wilcoxon signed-rank test) were observed on days when clay was tested with ozone (days 7 and 8, $p = 0.0001$) or when clay was tested with both ozone and carpet (days 3 and 4, $p = 0.017$). The addition of clay on days 3 and 4 improved PAQ, while addition of ozone on days 7 and 8 reduced PAQ. PAQ results were not significant when only ozone was studied (days 1 and 2, $p = 0.211$) or when clay and carpet were tested together in the absence of ozone (days 5 and 6, $p = 0.138$).

Aldehyde concentrations measured prior to sensory assessments are also shown in Figure 7. The dominant pollutant in chamber air was nonanal (C₉). Pentanal (C₅) and heptanal (C₇) 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 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). When exposed to ozone the clay plaster emitted fewer aldehydes than did the

carpet (Figure 7). The mean total aldehyde concentration in the chamber with clay and ozone was nine times lower than that in the chamber with carpet and ozone.

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 C₅ to C₁₀ aldehydes between the two chambers was only 8.6 $\mu\text{g m}^{-3}$, i.e., a few ppb. The median PAQ for the ozonated chamber was also 50% more favorable (less negative) than that for the chamber without ozone on day 2. While only one experiment, it is interesting that the small increase in carbonyls in chamber 1 may have led to a less acceptable PAQ than a chamber with far higher ozone concentration (chamber 2). However, it is possible that the contrasting PAQ results between days 1 and 2 were due to a malfunctioning door on chamber 1. Shortly after panelists began arriving to assess air quality on day 2 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 always sealed properly during 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 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., 2011; Morrison and Nazaroff, 2002; Weschler et al., 1992).

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 may have minimized any effects of ozone reactions with panelists themselves. Nevertheless, this does remain an area for future research.

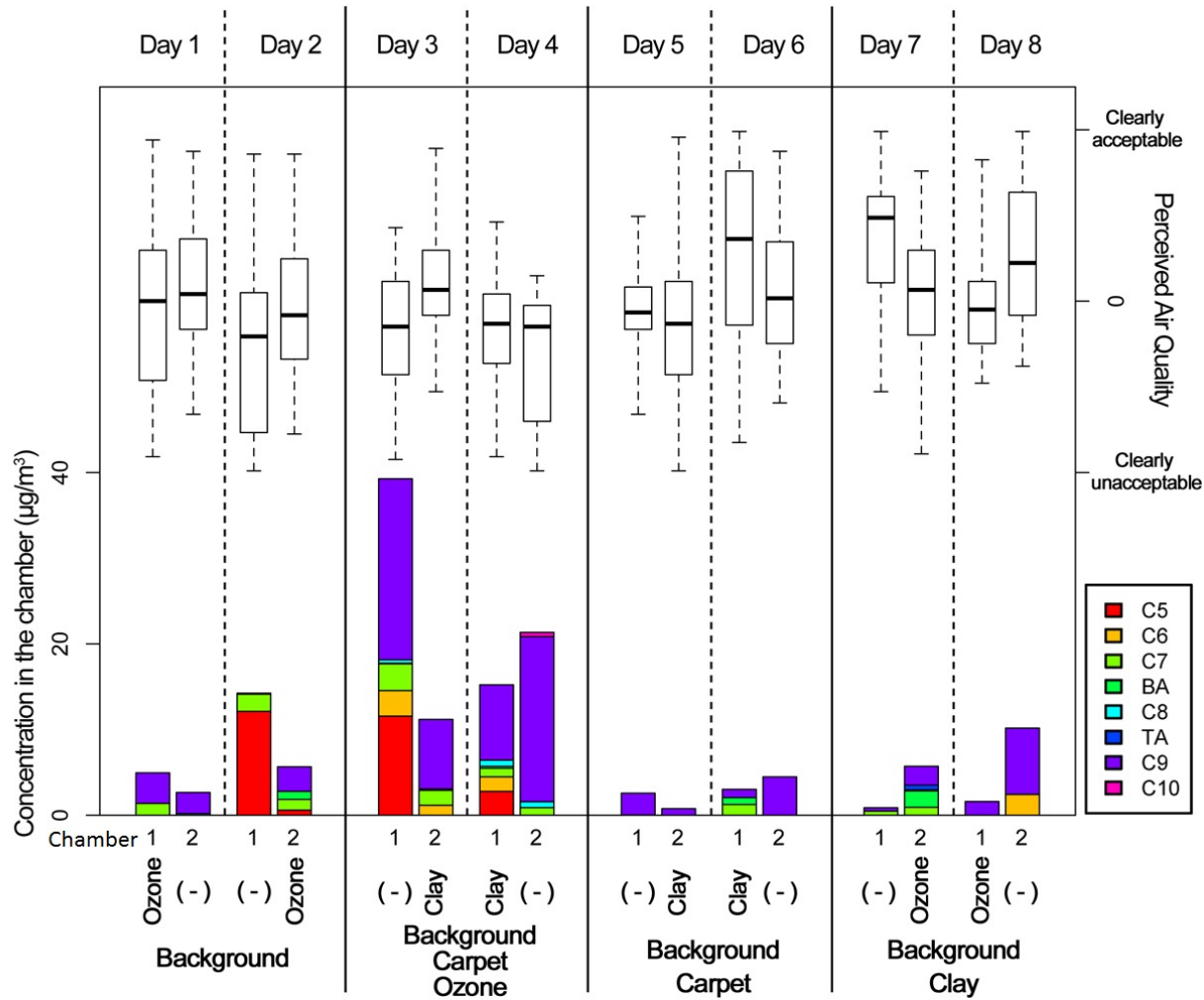


Figure 7: Perceived air quality and related aldehyde concentrations in test chambers (BA = benzaldehyde, TA = o-tolualdehyde)

Perception by Gender

Male and female PAQ results were also analyzed (Figure 8). 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 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 and studied 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.

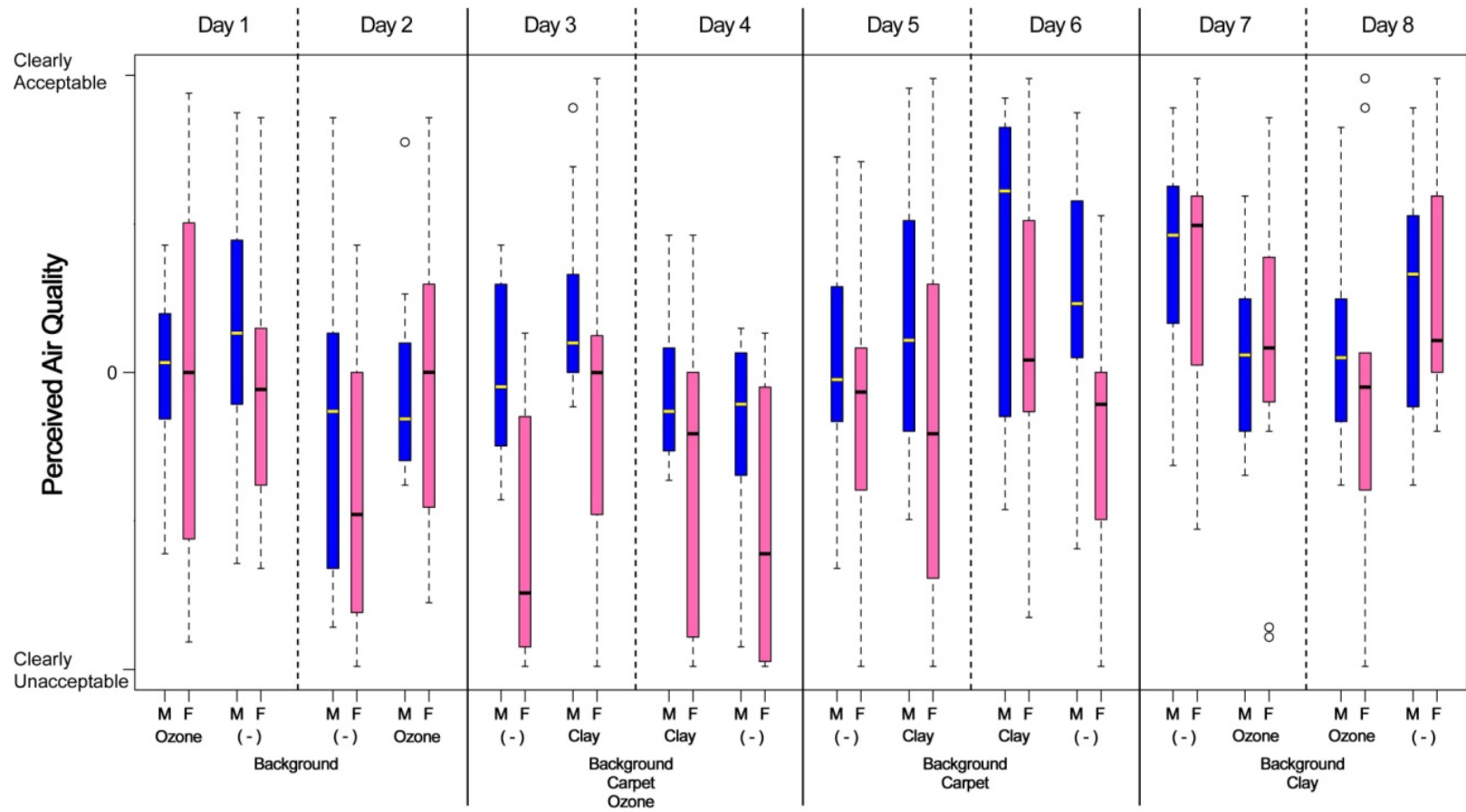


Figure 8: Comparison of male (M) and female (F) PAQ assessments. Circles indicate outliers.

Summary and Conclusions

Laboratory Chambers

Clay wall plaster specimens were placed inside stainless steel chambers and ozonated for several hours while chamber air was sampled for primary and secondary reaction byproducts. Reaction probabilities of ozone with the clay plaster were quantified based on the measured transport limited deposition velocity in the chambers. A few conclusions can be made from this study:

1. Clay plaster has a moderately high reactivity with ozone, relative to other common building materials,
2. Emissions of C₅ to C₁₀ aldehydes, benzaldehyde and tolualdehyde do not increase upon exposure of the clay plaster to ozone,
3. Based on the high primary and secondary byproduct concentrations in the chambers containing clay, and the fact that the specimens were left exposed for one year, clay plaster can potentially adsorb contaminants from indoor air, and desorb them when exposed to less contaminated air.

Perceived Air Quality

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, C₅ to C₁₀ saturated n-aldehydes and two aromatic aldehydes were also measured to characterize chamber air. Based on the results of this study, I conclude:

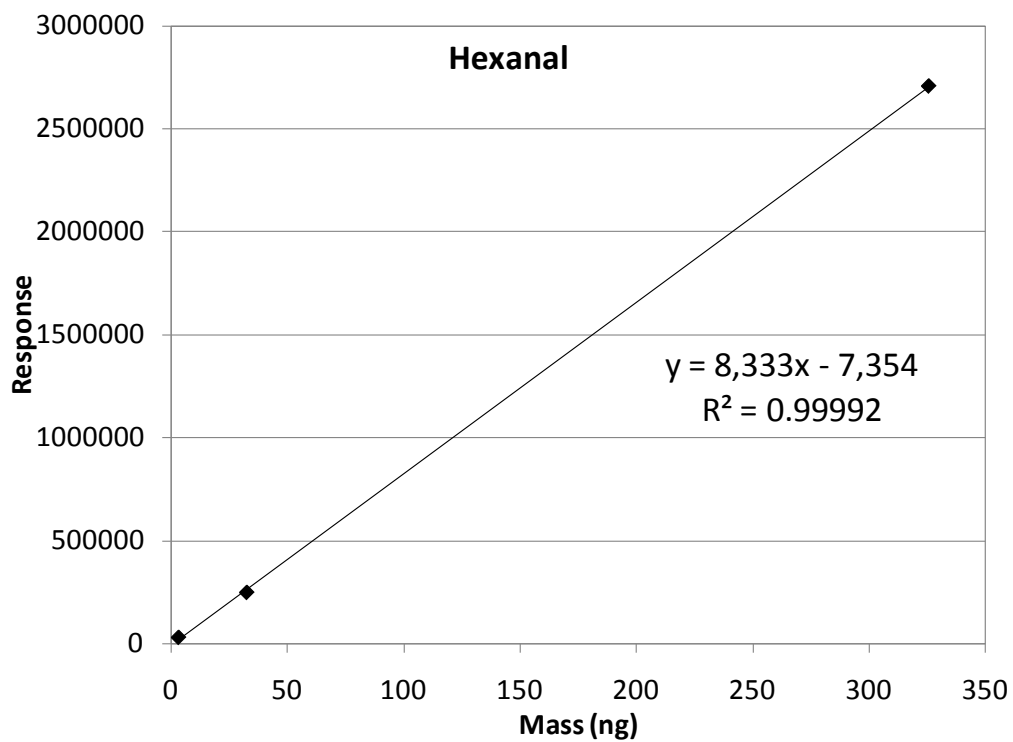
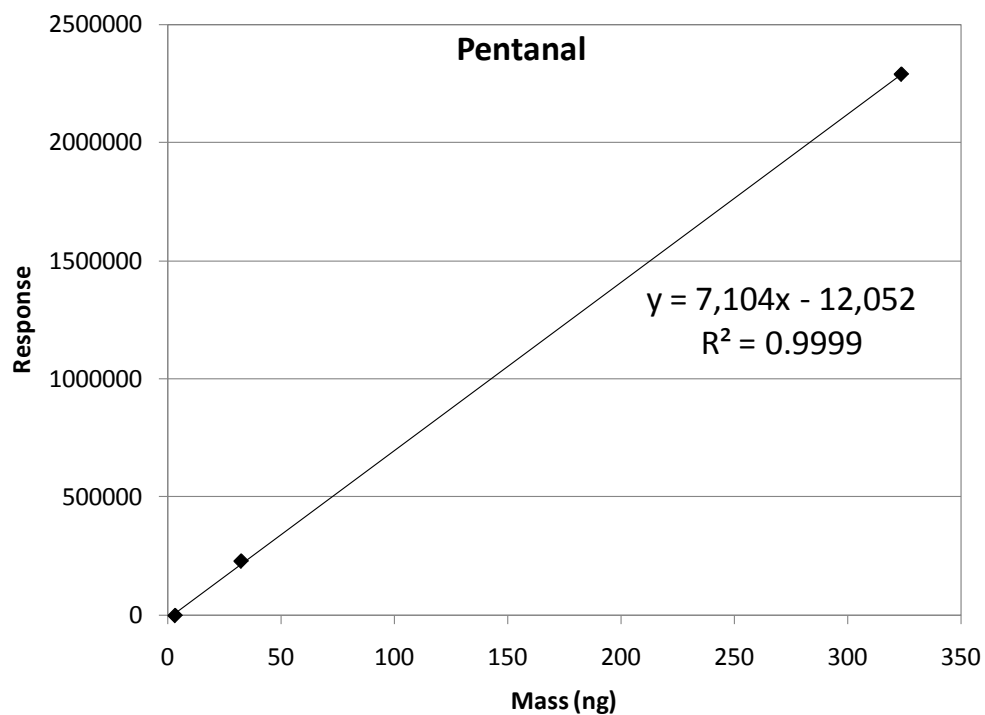
1. Reactions of ozone with carpet are associated with low PAQ,

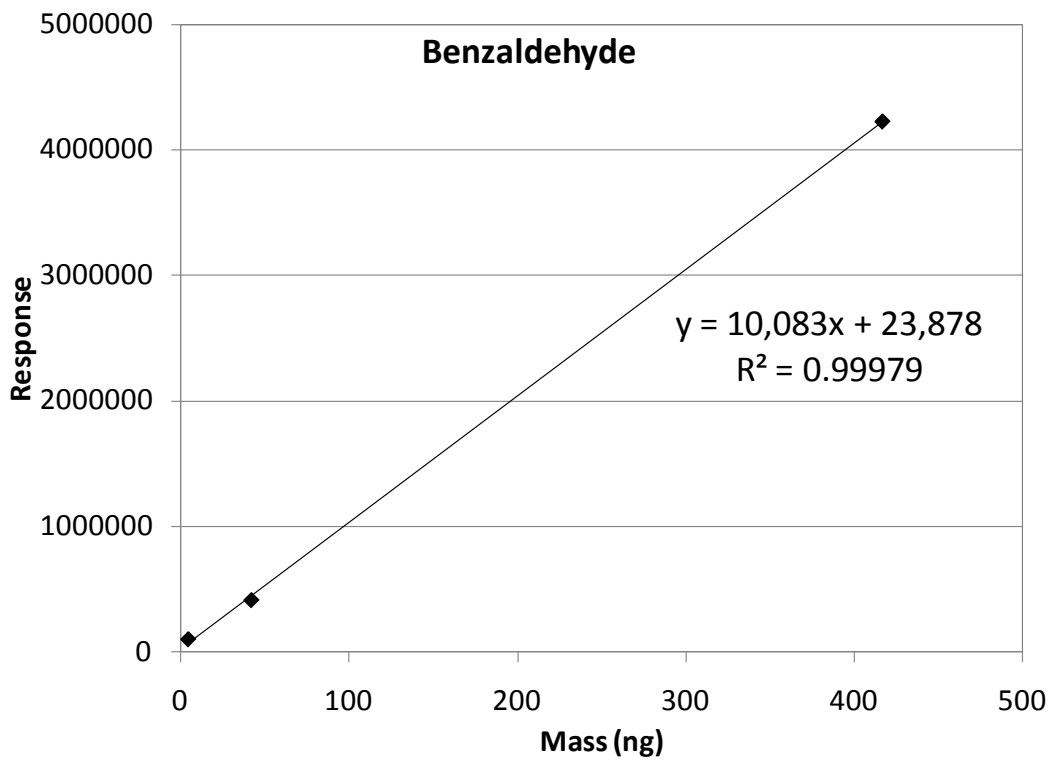
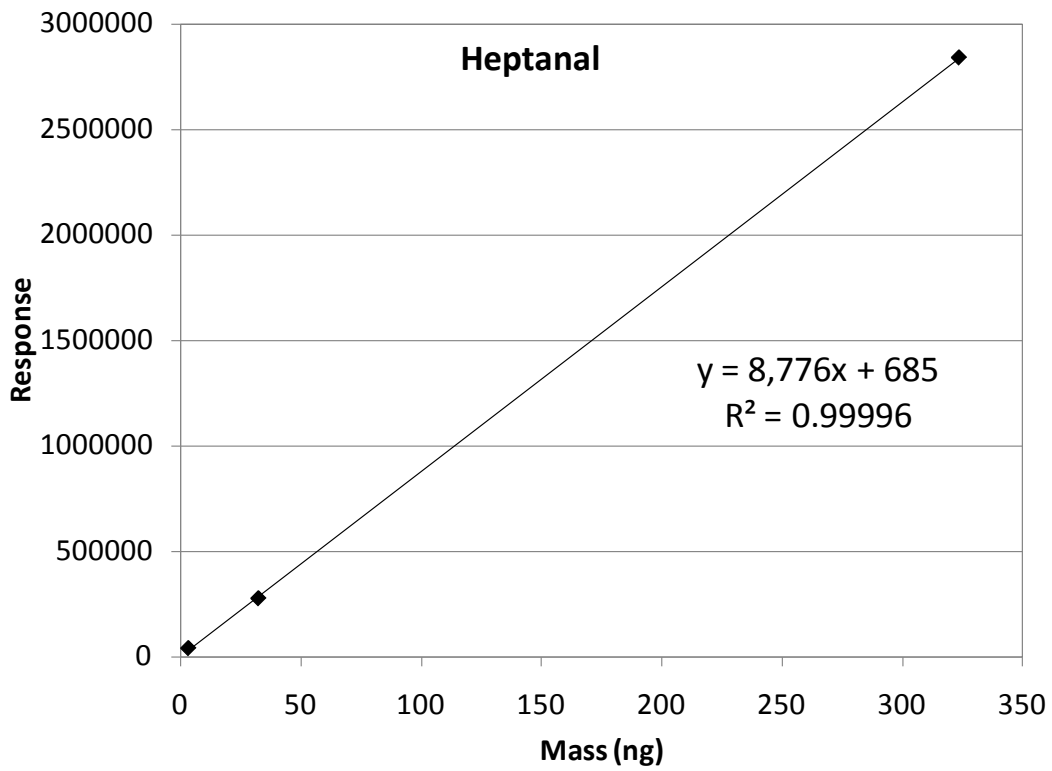
2. PAQ is inversely associated with the presence of C₅ to C₁₀ aldehydes and potentially other byproducts associated with ozone reactions with carpet,
3. Clay wall coverings can improve PAQ, particularly in the presence of ozone or ozone and carpet,
4. There are gender differences in PAQ for air exposed to carpet and/or clay in the presence or absence of ozone; females were more sensitive to differences in test conditions and were more inclined toward unacceptable rankings.

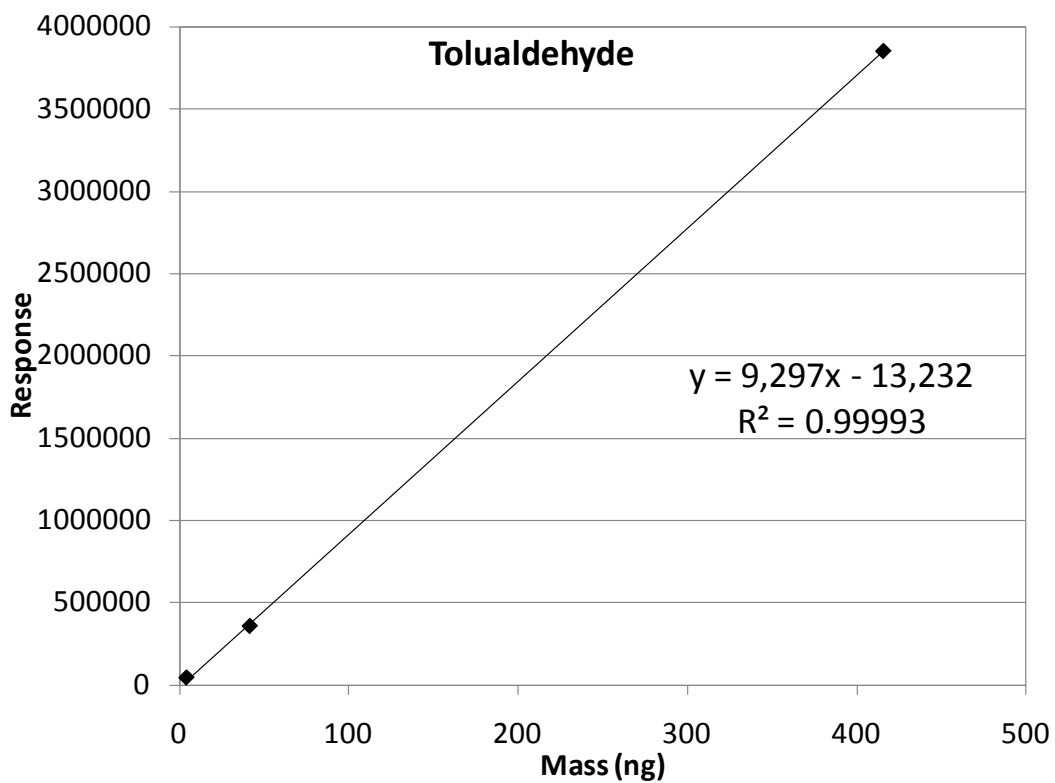
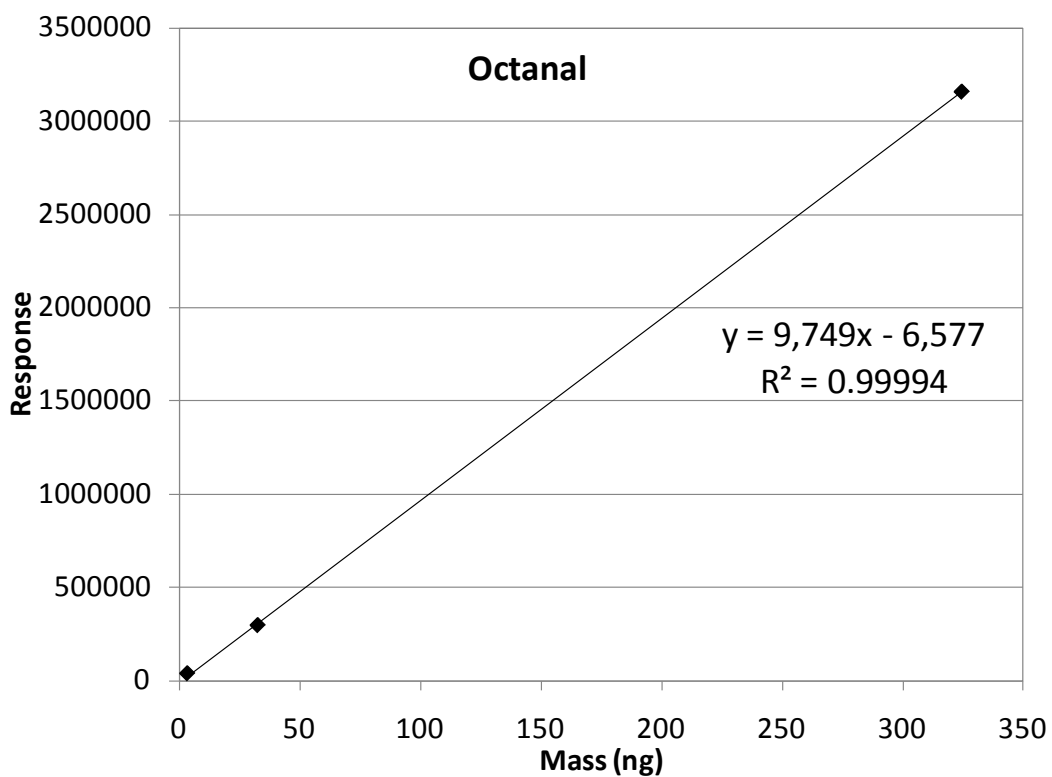
Additional research is needed to confirm the results presented herein with a broader base of panelists and with longer exposure times that would allow for extended PAQ and productivity assessments. Field tests involving the performance of clay as an air purifier are needed over extended time periods.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

Appendix A

Figure A1: Gas chromatograph calibration curves for small chamber experiments







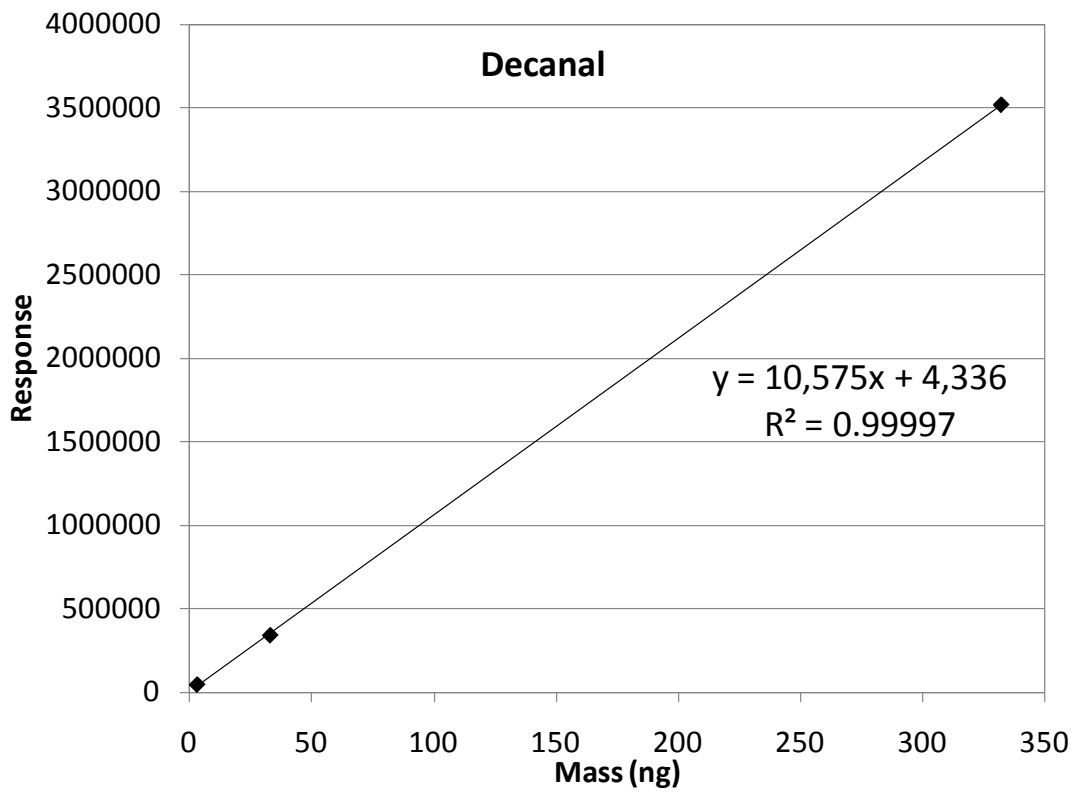
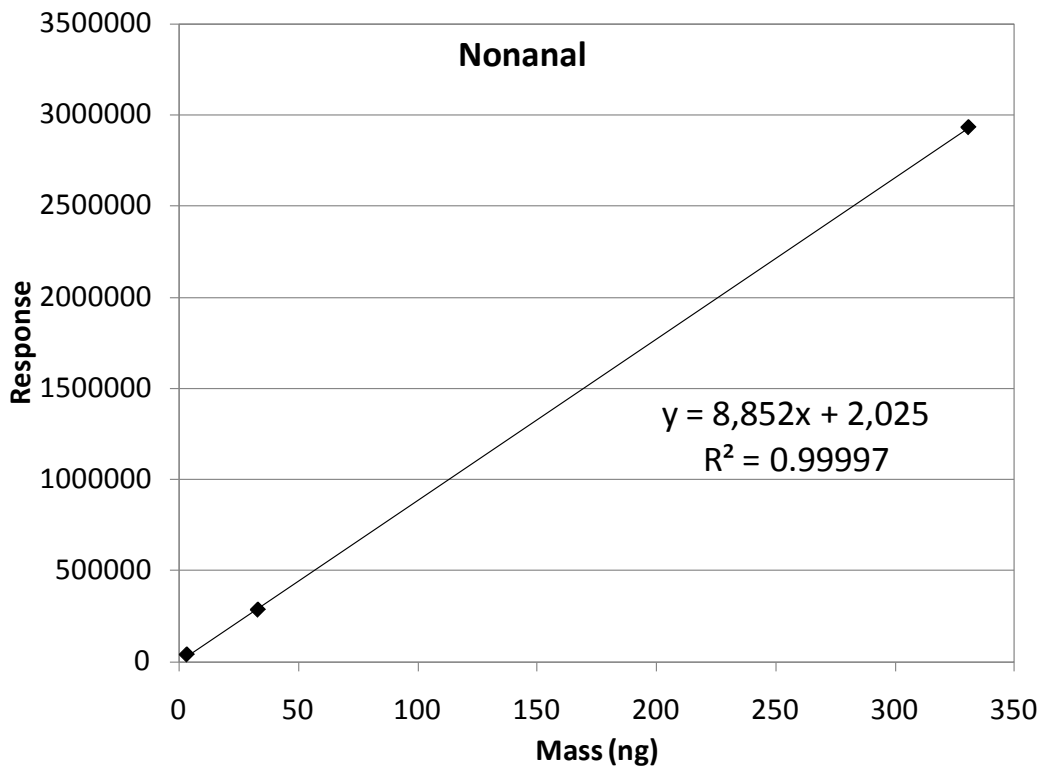
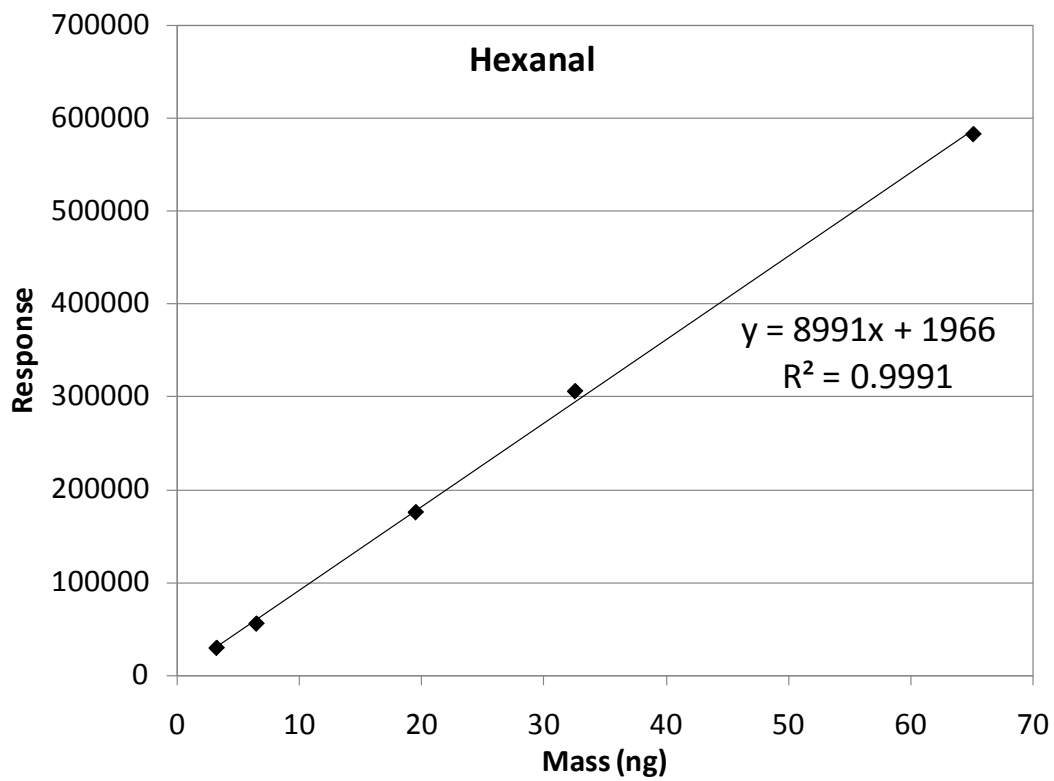
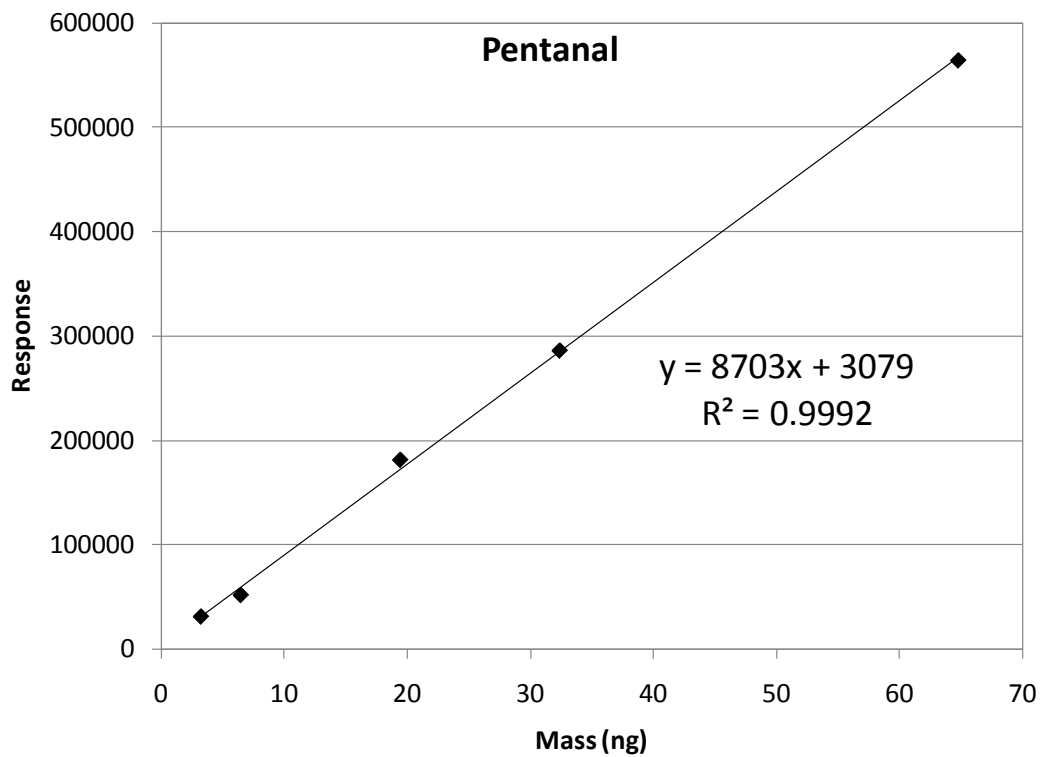
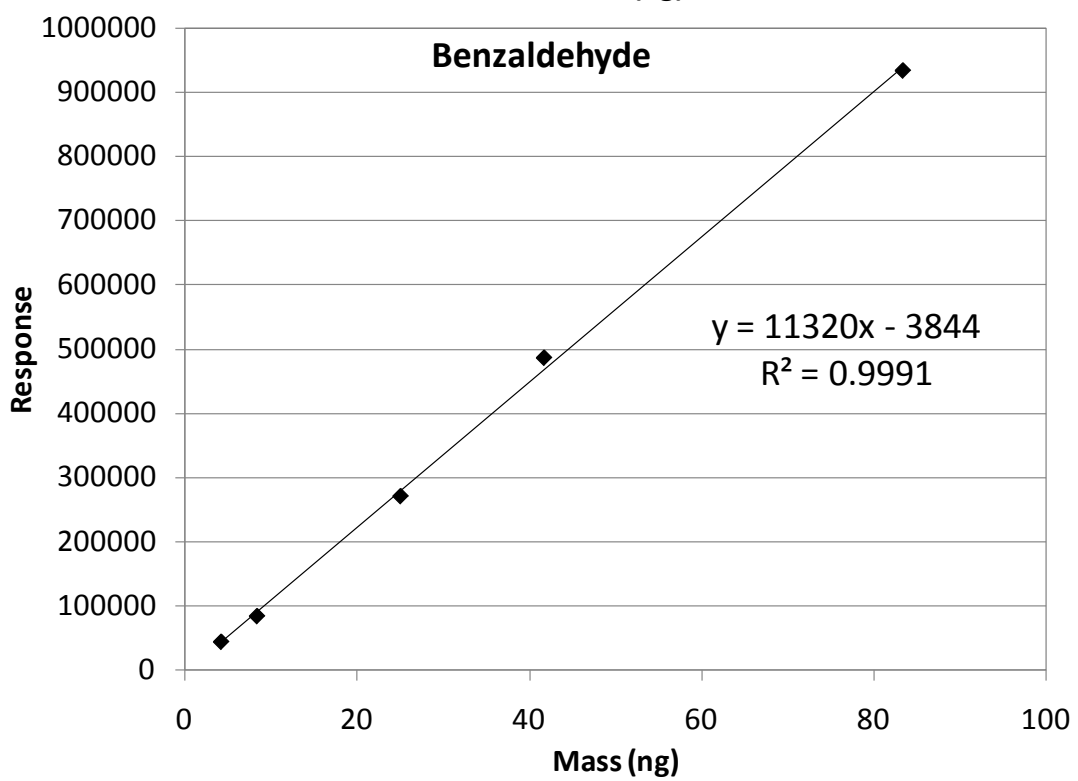
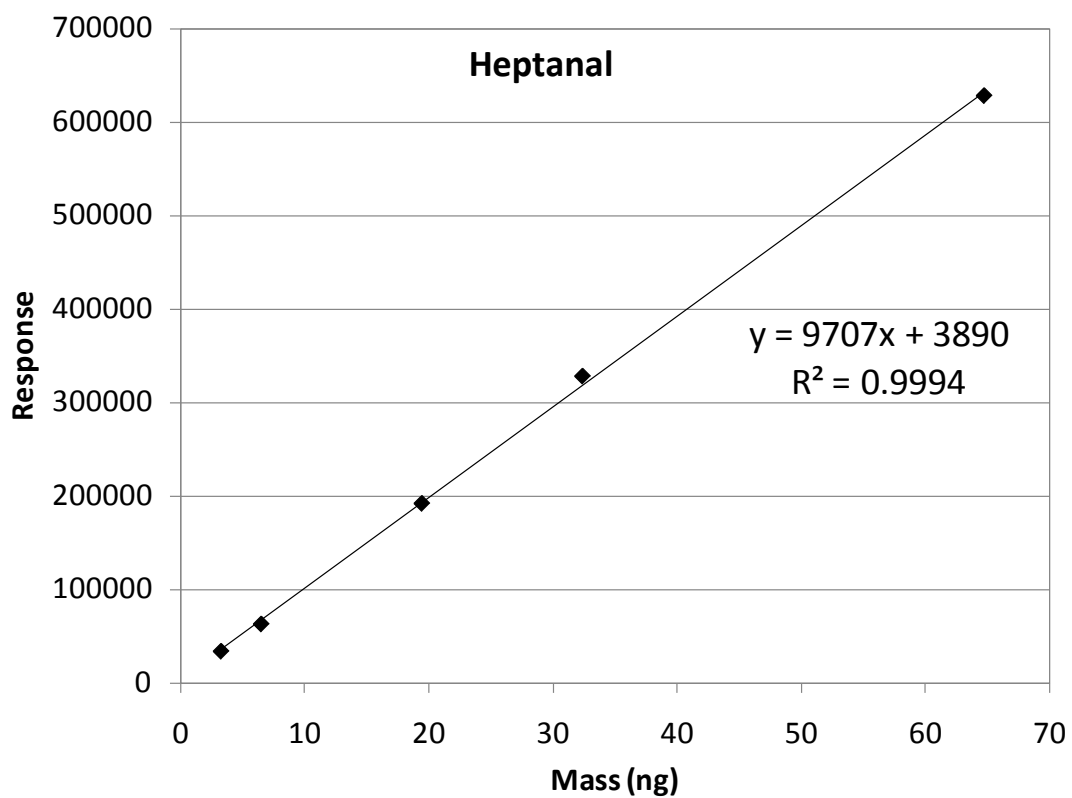
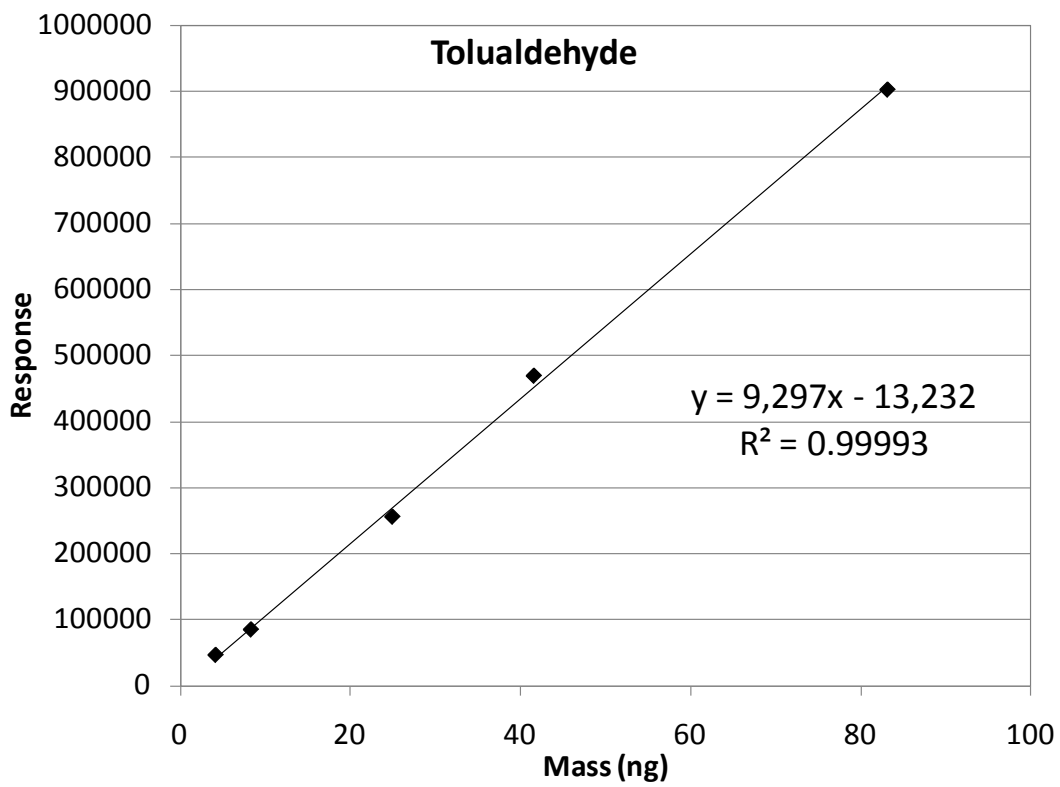
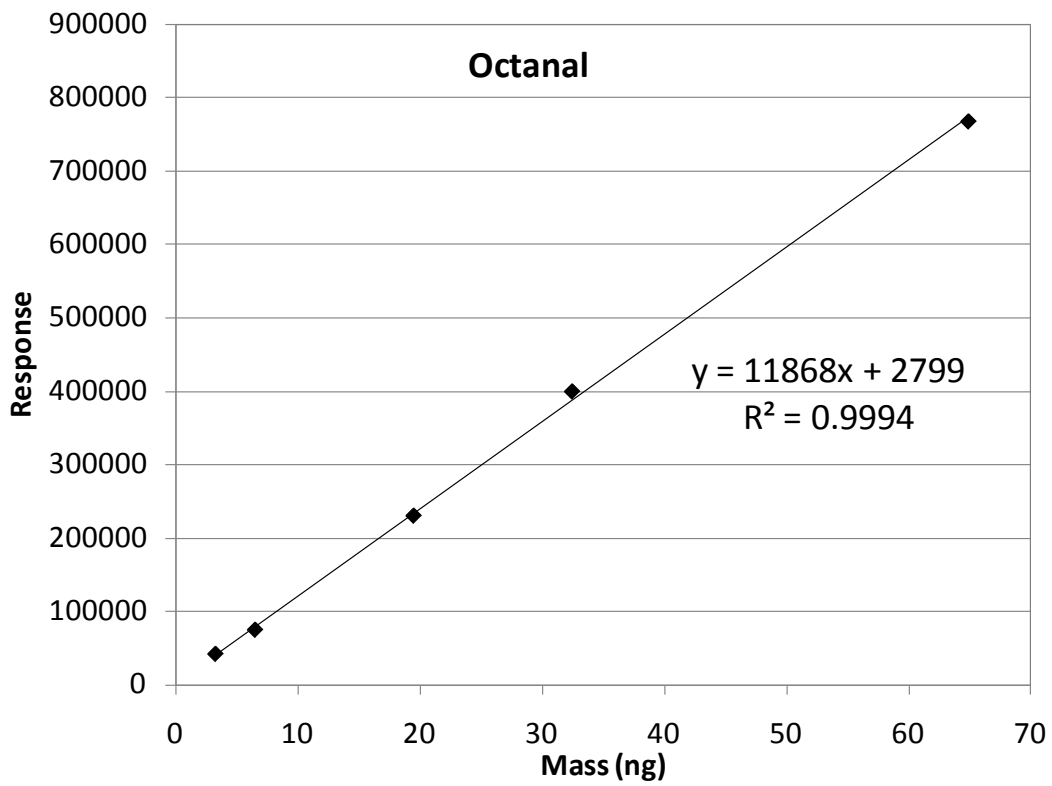
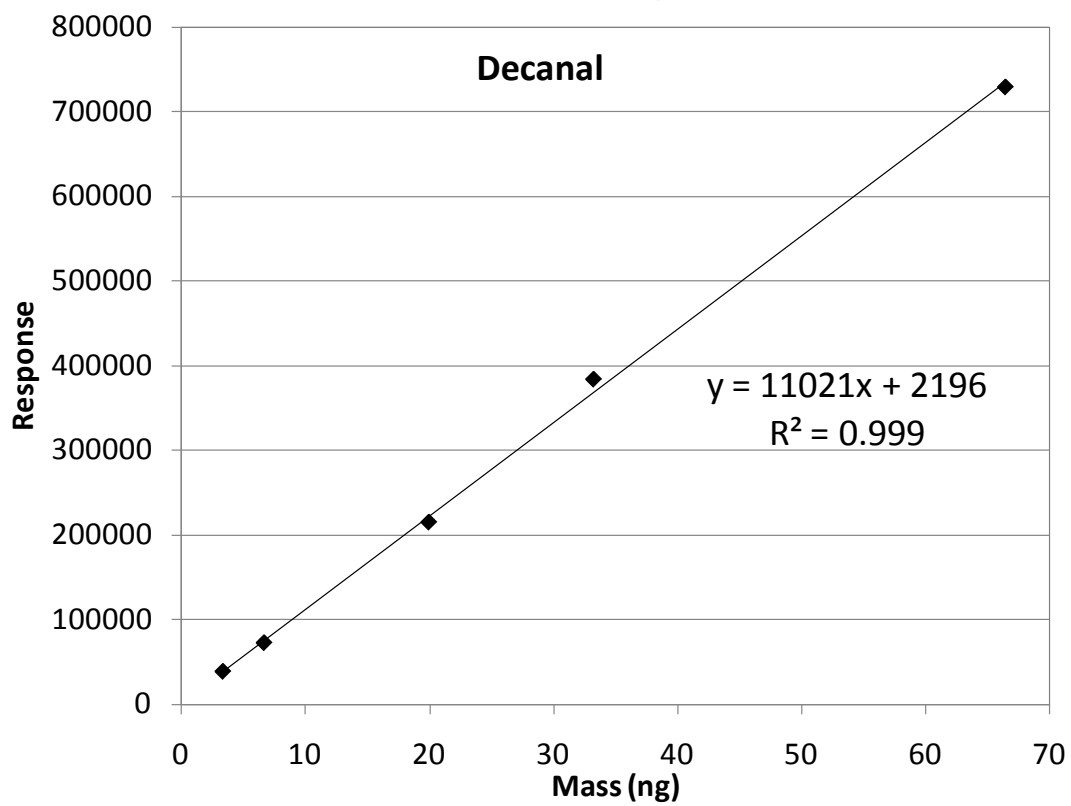
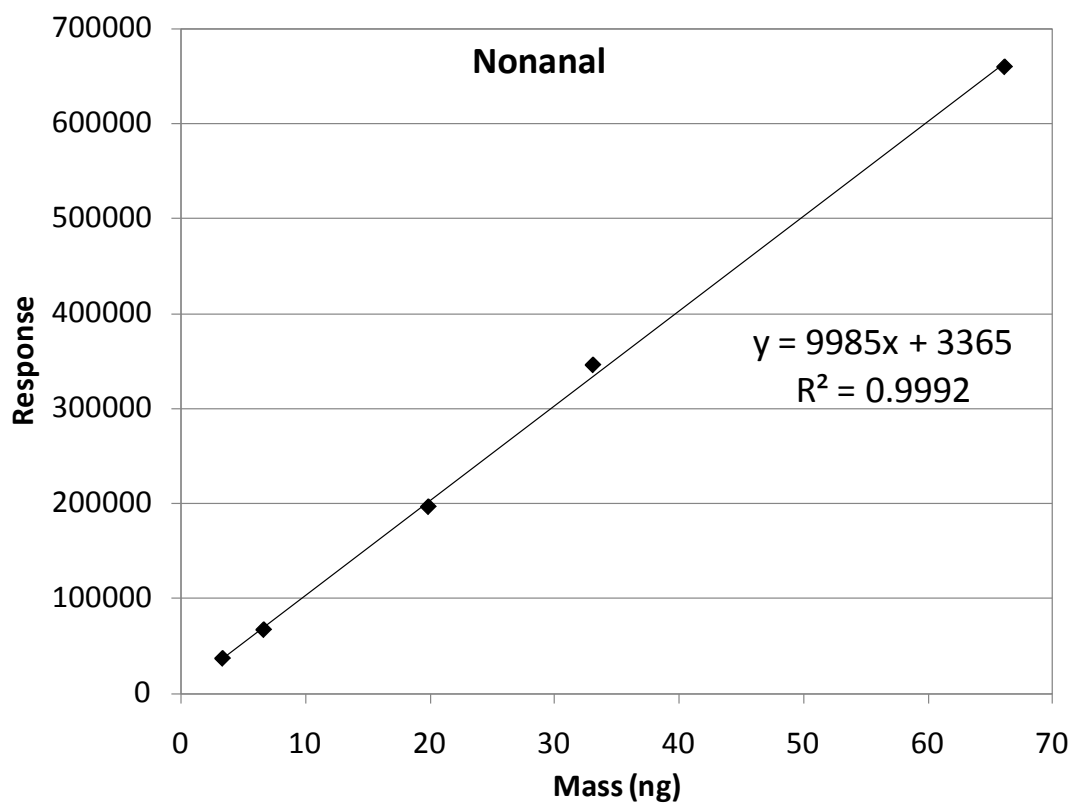


Figure A2: Gas chromatograph calibration curves for PAQ experiments









Appendix B

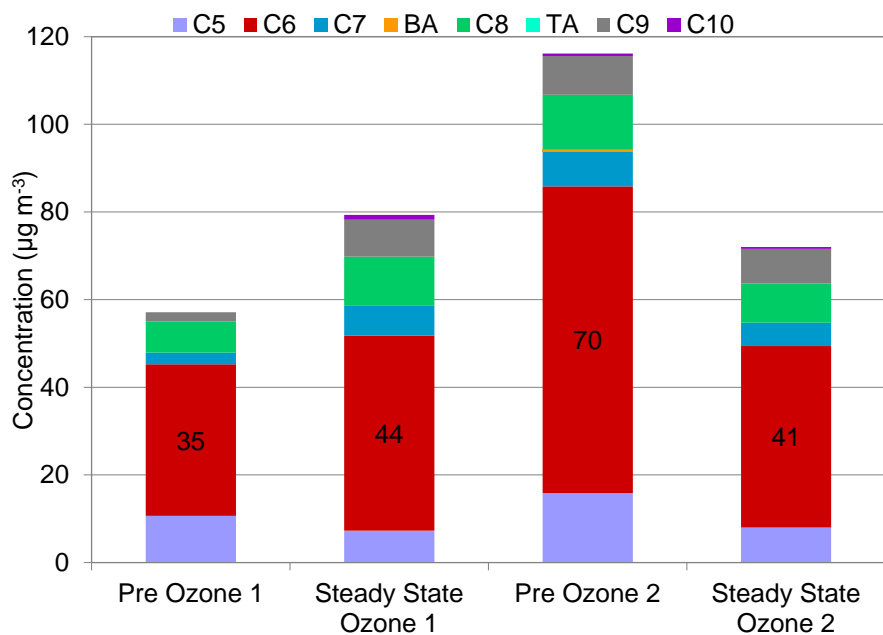


Figure B1: Aldehyde concentrations sampled from UT test house air (July 2010)

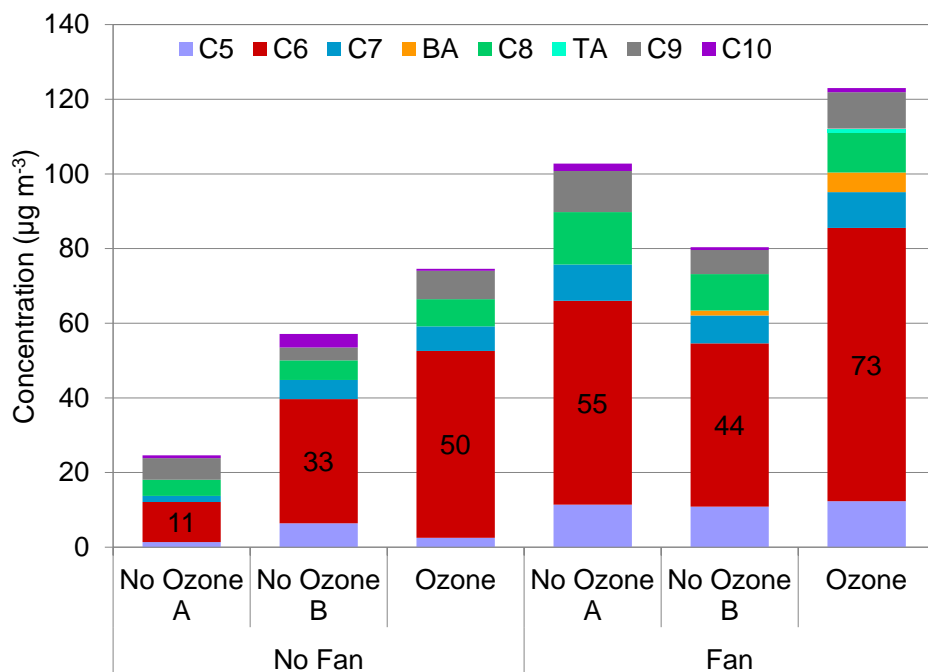


Figure B2: Aldehyde concentrations sampled from UT test house air (August 2009)

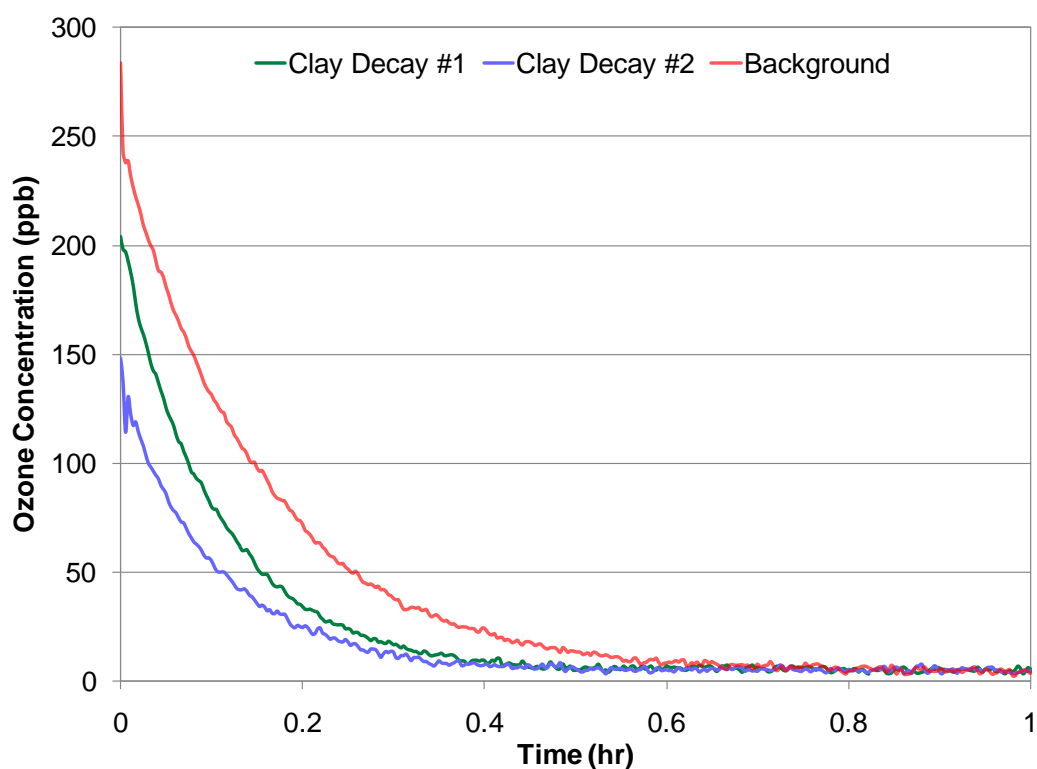


Figure B3: Ozone decay curves measured in (34.5 m³) small bedroom of UT test house using clay plaster applied to gypsum wallboard (July 2010)

Table B1: Experimental conditions and ozone deposition velocities to clay wall plaster during ozone decay tests in small bedroom of UT test house

Test Material	Background ¹	Clay Wall Plaster (Replicate 1)	Clay Wall Plaster (Replicate 2)
Date(s) of Experiment(s)	July 14 & 15, 2010	July 20, 2010	July 22, 2010
Temperature (°C) ²	28.7	27.4	27.2
Relative Humidity (%) ²	55	53	52
Surface Area : Volume (m ⁻¹)	1.8	0.2	0.2
AER (h ⁻¹) ³	1.9	1.9	1.0
Measured O ³ Decay (h ⁻¹)	4.4	5.5	6.5
Deposition Velocity (m h ⁻¹)	2.4	3.0	3.6
Corrected Deposition Velocity (m	2.4	9.6	13.4

¹Values for background are average of two replicates

²Time-average temperature and relative humidity recorded on HOBO data logger

³Air exchange rates determined from CO₂ decays from approx. 2400 ppm

Appendix C

Table C1: Small chamber pre-ozonation byproduct sampling data

Sample Label	Lab1	Lab2	In1	In2	C1Pre1	C1Pre2	C2Pre1	C2Pre2	ConPre1	ConPre2
Material	laboratory air		control inlet		clay plaster 1		clay plaster 2		control	
Pump Flow Rate (ccm)	41	44	46	45	39	42	42	43	40	43
Sample Duration (min)	60	60	60	60	60	60	60	60	60	60
Sample Volume (m ³)	0.00246	0.00264	0.00276	0.0027	0.00234	0.00252	0.00252	0.00258	0.0024	0.00258
Compound	GC Response									
C5	586240	709101	1521810	1206922	1287328	1653198	1364778	1417898	1220489	1223941
C6	109716	101947	125302	63417	836657	1133545	1075838	1098833	71177	59252
C7	17913	23035	12992	20511	335876	455307	440703	432701	20321	39484
BA	104368	45187	24985	82195	229492	268199	265060	255095	46040	35331
C8	85514	101205	74811	36091	530484	747164	705655	694362	60554	63431
TA	48333	45438	16812	101463	88454	25148	125817	68148	41885	45314
C9	29895	35214	344102	145260	656739	887728	895603	825879	180953	190186
C10	43382	42203	24595	12939	65006	27565	20616	24084	23256	31672
Compound	Mass (ng)									
C5	84.2	101.5	215.9	171.6	182.9	234.4	193.8	201.3	173.5	174.0
C6	14.1	13.1	15.9	8.5	101.3	136.9	130.0	132.7	9.4	8.0
C7	2.0	2.6	1.4	2.3	38.2	51.8	50.1	49.2	2.2	4.4
BA	8.0	2.1	0.1	5.8	20.4	24.3	23.9	23.0	2.2	1.2
C8	9.5	11.1	8.4	4.4	55.1	77.3	73.1	71.9	6.9	7.2
TA	6.6	6.3	3.2	12.3	10.9	4.1	15.0	8.8	5.9	6.3
C9	3.2	3.8	38.6	16.2	74.0	100.1	100.9	93.1	20.2	21.3
C10	3.7	3.6	1.9	0.8	5.7	2.2	1.5	1.9	1.8	2.6
Compound	Conc. (µg/m3)									
C5	34	38	78	64	78	93	77	78	72	67
C6	6	5	6	3	43	54	52	51	4	3
C7	1	1	1	1	16	21	20	19	1	2
BA	3	1	0	2	9	10	10	9	1	0
C8	4	4	3	2	24	31	29	28	3	3
TA	3	2	1	5	5	2	6	3	2	2
C9	1	1	14	6	32	40	40	36	8	8
C10	2	1	1	0	2	1	1	1	1	1

Table C2: Small chamber steady-state ozone byproduct sampling data

Sample Label	InO31	InO32	C1O31	C1O32	C2O31	C2O32	ConO31	ConO32
Material	control inlet		clay plaster 1		clay plaster 2		control	
Pump Flow Rate (ccm)	45	41	42	45	39	48	44	43
Sample Duration (min)	55	55	60	60	60	60	60	60
Sample Volume (m ³)	0.002475	0.002255	0.0024	0.0025	0.0028	0.0032	0.0025	0.0025
Compound	GC Response							
C5	952042	647968	945447	1263812	981051	1109409	896092	644185
C6	57907	61914	884998	1074732	874367	1072599	39308	85885
C7	19468	38970	382075	464077	379480	468157	40535	55324
BA	65409	10958	238665	280417	203873	281123	20599	16724
C8	47221	43602	594595	21576	582949	705209	78541	73727
TA	12007	13481	77946	49027	82518	62110	48540	42017
C9	128095	147478	825900	12682	796543	957036	250429	246154
C10	16836	15639	36712	20244	31355	39167	31557	16371
Compound	Mass (ng)							
C5	135.7	92.9	134.8	179.6	139.8	157.9	127.8	92.4
C6	7.8	8.3	107.1	129.8	105.8	129.6	5.6	11.2
C7	2.1	4.4	43.5	52.8	43.2	53.3	4.5	6.2
BA	4.2	-1.2	21.3	25.5	17.9	25.5	0.0	0.0
C8	5.5	5.2	61.7	2.9	60.5	73.0	8.7	8.2
TA	2.7	2.9	9.8	6.7	10.3	8.1	6.7	6.0
C9	14.2	16.4	93.1	1.2	89.8	107.9	28.1	27.6
C10	1.2	1.1	3.1	1.5	2.6	3.3	2.6	1.1
Compound	Conc. (µg/m3)							
C5	55	41	57	72	50	50	51	38
C6	3	4	45	52	38	41	2	5
C7	1	2	18	21	16	17	2	3
BA	2	-1	9	10	6	8	0	0
C8	2	2	26	1	22	23	3	3
TA	1	1	4	3	4	3	3	2
C9	6	7	39	0	32	34	11	11
C10	0	0	1	1	1	1	1	0

Table C3: Small chamber flow rates at beginning and end of experiment

Chamber Inlet Flow (ccm)	Bubble Flowmeter Sample Number							Average Flow (ccm)	Standard Deviation (ccm)
START	1	2	3	4	5	6	7		
Clay Plaster 1	1057	1054	1058	1055	1058	1062	1054	1057	3
Clay Plaster 2	1054	1053	1045	1052	1047	1048	1053	1050	4
Clay Plaster KI	1050	1053	1043	1051	1054	1054	1054	1051	4
Control	1053	1054	1054	1054	1053	1053	1055	1054	1
FINISH	1	2	3	4	5	6	7	Average Flow (ccm)	Standard Deviation (ccm)
Clay Plaster 1	1054	1054	1042	1055	1058	1063	1056	1055	6
Clay Plaster 2	1052	1047	1046	1042	1057	1050	1056	1050	5
Clay Plaster KI	1060	1057	1053	1056	1062	1061	1057	1058	3
Control	1048	1063	1080	1057	1053	1054	1044	1057	12

Table C4: Material and control chamber dimensions and effective air exchange rates

Material	Height (cm)	Length (cm)	Width (cm)	Air Volume (L)	Non-Specimen Area (cm ²)	Material Area (cm ²)	Flow rate (L h ⁻¹)	λ (h ⁻¹)
Clay Plaster 1	1.3	48.3	30.5	46.5	7062	1473	63.4	1.36
Clay Plaster 2	1.3	48.3	30.5	46.5	7062	1473	63.0	1.35
Clay Plaster KI	1.3	48.3	28.0	46.7	7177	1352	63.3	1.36
Control	25.0	51.4	37.7	48.4	8331	8331	63.3	1.31

Appendix D

Table D1: Verification of standards for small chamber experiments

Compound	Expected Mass (ng)	Actual Mass (ng)	Difference (%)
C5	32.38	41.3	27.7
C6	32.56	35.1	7.9
C7	32.36	34.4	6.4
BA	41.66	41.6	0.0
C8	32.44	34.4	6.2
TA	41.56	44.3	6.5
C9	33.08	34.5	4.4
C10	33.2	34.6	4.3

Table D2: 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

Appendix E

Table E1: Perceived air quality analysis byproduct sampling data

Day of Experiment	Condition in Chamber	Chamber	Mass (ng)							
			C5	C6	C7	BA	C8	TA	C9	C10
1	BG+O3	1	0	0	4.052	0	0	0	10.5	0
1	BG	2	0	0	0	0	0.531	0	7.286	0
2	BG	1	36.734	0	6.082	0.337	0	0	0	0
2	BG+O3	2	1.674	0	3.545	2.654	0	0	8.081	0
3	BG+CA+O3	1	16.91	5.846	8.577	0.395	0.523	0	67.855	0
3	BG+CA+O3	1	48.641	11.104	9.27	0	1.82	0	52.618	0
3	BG+CA+CL+O3	2	0	3.355	5.03	0	0.48	0	23.355	0
4	BG+CA+CL+O3	1	15.408	5.253	0	1.258	2.929	0	28.073	0
4	BG+CA+CL+O3	1	0	3.995	5.398	0	1.016	0	20	0
4	BG+CA+O3	2	0	0	2.553	0	1.98	0	55.452	1.474
5	BG+CA	1	0	0	0	0	0	0	10.435	0
5	BG+CA	1	0	0	0.162	0	0	0	4.16	0
5	BG+CA+CL	2	0	0	0	0	0	0	2.155	0
6	BG+CA+CL	1	0	0	3.621	2.308	0	0	2.795	0
6	BG+CA	2	0	0	0	0	0	0	13.452	0
7	BG+CL	1	0	0	0.982	0	0	0	0.126	0
7	BG+CL	1	0	0	1.832	0	0	0	2.138	0
7	BG+CL+O3	2	0	0	2.602	5.396	0.332	1.595	6.199	0
8	BG+CL+O3	1	0	0	0	0	0	0	4.516	0
8	BG+CL	2	0	7.286	0	0	0.018	0	23.211	0

Note on abbreviations: BG = background; O3 = ozone; CA = carpet; CL = clay wall plaster

Day of Experiment	Condition in Chamber	Chamber	Pump Flow Rate (ccm)	Concentration ($\mu\text{g m}^{-3}$)							
				C5	C6	C7	BA	C8	TA	C9	C10
1	BG+O3	1	49	0	0	1.38	0	0	0	3.57	0
1	BG	2	49	0	0	0	0	0.18	0	2.48	0
2	BG	1	51	12.12	0	2.01	0.11	0	0	0	0
2	BG+O3	2	47	0.59	0	1.26	0.94	0	0	2.87	0
3	BG+CA+O3	1	48	5.87	2.03	2.98	0.14	0.18	0	23.56	0
3	BG+CA+O3	1	47	17.25	3.94	3.29	0	0.65	0	18.66	0
3	BG+CA+CL+O3	2	48	0	1.16	1.75	0	0.17	0	8.11	0
4	BG+CA+CL+O3	1	46	5.58	1.90	0	0.46	1.06	0	10.17	0
4	BG+CA+CL+O3	1	45	0	1.48	2.00	0	0.38	0	7.41	0
4	BG+CA+O3	2	48	0	0	0.89	0	0.69	0	19.25	0.51
5	BG+CA	1	49	0	0	0	0	0	0	3.55	0
5	BG+CA	1	45	0	0	0.06	0	0	0	1.54	0
5	BG+CA+CL	2	47	0	0	0	0	0	0	0.76	0
6	BG+CA+CL	1	48	0	0	1.26	1	0	0	0.97	0
6	BG+CA	2	50	0	0	0	0	0	0	4.48	0
7	BG+CL	1	47	0	0	0.35	0	0	0	0.04	0
7	BG+CL	1	49	0	0	0.62	0	0	0	0.73	0
7	BG+CL+O3	2	47	0	0	0.92	1.91	0.12	0.57	2.20	0
8	BG+CL+O3	1	47	0	0	0	0	0	0	1.60	0
8	BG+CL	2	50	0	2.43	0	0	0.01	0	7.74	0

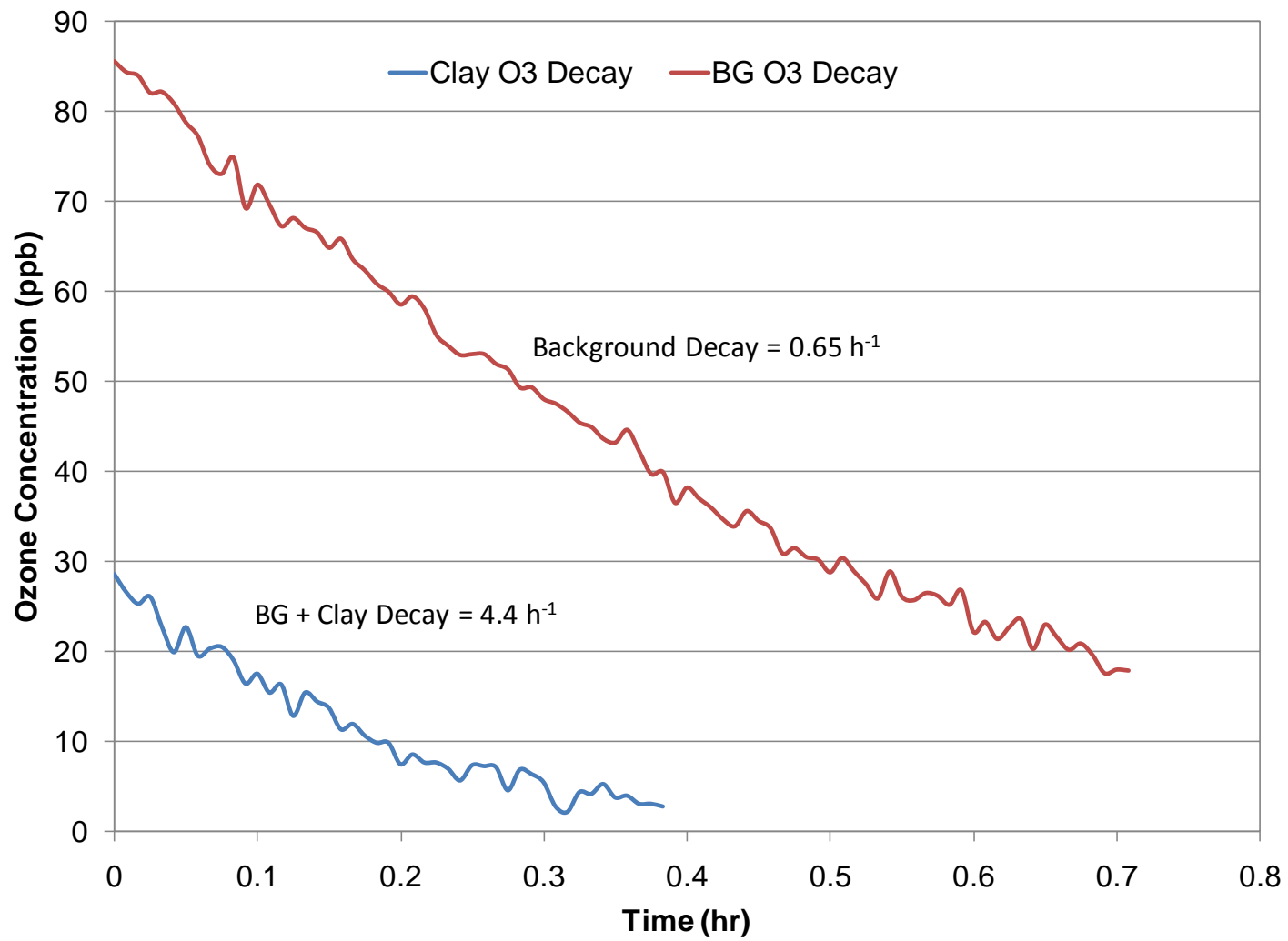


Figure E2: Ozone decay curves for clay plaster and chamber surfaces used in perceived air quality analyses

Appendix F

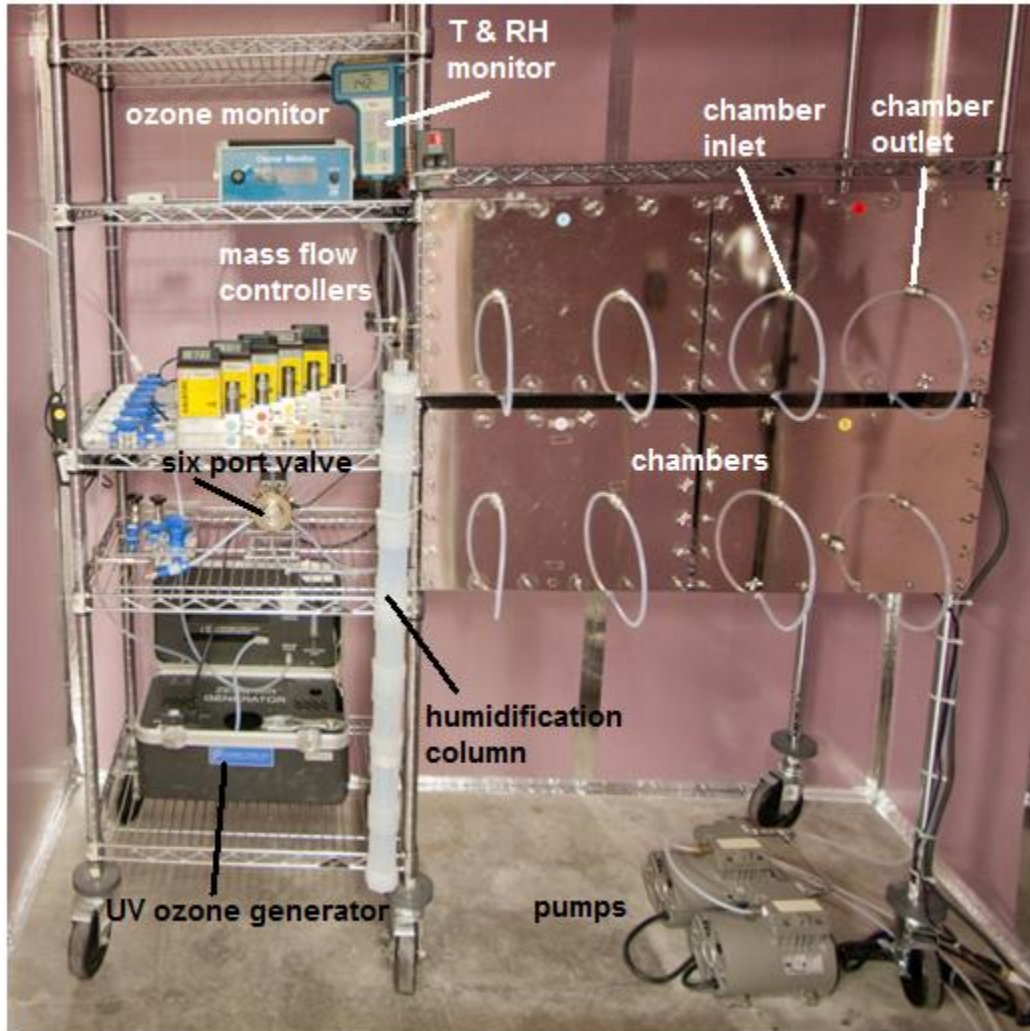


Figure F1: Small chamber system for measuring ozone deposition velocities and material emissions²

² Photo credit: Dustin Poppendieck



Figure F2: Configuration of clay plaster specimens on metal racks for PAQ analyses



Figure F3: Configuration of carpet and clay plaster specimens on metal racks for PAQ analyses

References

- Albrechtsen, O. (1988). Twin climatic chambers to study sick and healthy buildings. *Proceedings of Healthy Buildings*, 3, pp. 25-30. Stockholm.
- 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.
- 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. *Environmental Health Perspectives*, 114(4), 532-536.
- Britigan, N., Alshawa, A., & Nizkorodov, S. A. (2006). Quantification of ozone levels in indoor environments generated by ionization and ozonolysis air purifiers. *J. Air Waste Manage. Assoc.*, 56, 601-610.
- Cano-Ruiz, J. A., Kong, D., Balas, R. B., & Nazaroff, W. W. (1993). Removal of reactive gases at indoor surfaces: combining mass transport and surface kinetics. *Atmospheric Environment*, 27A(13), 2039-2050.
- Cros, C., Morrison, G. C., Siegel, J. A., & Corsi, R. L. (2011). Long-term performance of passive removal materials for removal of ozone from indoor air. *Indoor Air* (accepted for publication).
- Doty, R. L., & Cameron, E. L. (2009). Sex differences and reproductive hormone influences on human odor perception. *Physiology & Behavior*, 97, 213-228.
- Filleul, L., Cassadou, S., Medina, S., Fabres, P., Lefranc, A., Eilstein, D., et al. (2006). The relation between temperature, ozone, and mortality in nine French cities during the heat wave of 2003. *Environmental Health Perspectives*, 114(9), 1344-1347.
- Fisk, W. J. (2000). Health and productivity gains from better indoor environments and their relationship with building energy efficiency. *Annu. Rev. Energy Env.*, 25, 537-566.
- Gall, E., Darling, E., Siegel, J., Morrison, G., & Corsi, R. (2011). Primary and secondary emissions from green building materials: Large chamber experiments.

- Proceedings of the 12th International Conference on Indoor Air Quality and Climate, Indoor Air 2011.* Austin.
- Girman, J. (2011). Research needed to address climate change impacts on indoor air quality. *Proceedings of the 12th International Conference on Indoor Air Quality and Climate, Indoor Air 2011.* Austin.
- Jackson, J. E., Yost, M. G., Karr, C., Fitzpatrick, C., Lamb, B. K., Chung, S. H., et al. (2010). Public health impacts of climate change in Washington State: projected mortality risks due to heat events and air pollution. *Climatic Change, 102*(1-2), 159-186.
- 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. *Building and Environment, 45*(2), 445-452.
- Lam, Y. F., Fu, J. S., Wu, S., & Mickley, L. J. (2011). Impacts of future climate change and effects of biogenic emissions on surface ozone and particulate matter concentrations in the United States. *Atmospheric Chemistry and Physics, 11*, 4789-4806.
- Lamble, S., Morrison, G., & Corsi, R. (2011). 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.
- Lee, S. C., Lam, S., & Fai, H. K. (2001). Characterization of VOCs, ozone, and PM10 emissions from office equipment in an environmental chamber. *Building and Environment, 36*(7), 837-842.
- Levy, J. I., Corrothers, T. J., Tuomisto, J. T., Hammitt, J. K., & Evans, J. S. (2001). Assessing the public health benefits of reduced ozone concentrations. *Environmental Health Perspectives, 109*, 1215-1226.
- Minke, G. (2006). *Building with earth: Design and technology of a sustainable architecture.* Basel, Switzerland: Birkhauser.

- Morrison, G. C., & Nazaroff, W. W. (2002). Ozone interactions with carpet: secondary emissions of aldehydes. *Environmental Science & Technology*, *36*(10), 2185-2192.
- Morrison, G. C., Zhao, P. Z., & Kasthuri, L. (2006). The spatial distribution of pollutant transport to and from indoor surfaces. *Atmospheric Environment*, *40*, 3677-3685.
- Morrison, G., & Corsi, R. L. (2010). *Development and implementation of a new protocol for testing the air quality implications of green building materials*. Retrieved June 28, 2011, from USGBC: U.S. Green Building Council: <https://www.usgbc.org/ShowFile.aspx?DocumentID=9131>
- Mudway, I. S., & Kelly, F. J. (2000). Ozone and the lung: a sensitive issue. *Mol. Aspects Med.*, *21*(1-2), 1-48.
- Nicolas, M., Ramalho, O., & Maupetit, F. (2007). Reactions between ozone and building products: impact on primary and secondary emissions. *Atmospheric Environment*, *41*, 3129-3138.
- Pandurangi, L., & Morrison, G. C. (2009). Ozone interactions with human hair: ozone uptake rates and product formation. *Atmospheric Environment*, *42*, 5079-5089.
- Poppendieck, D., Darling, E., McDonald-Buller, E., Kimura, Y., & Corsi, R. (2011). *Dry deposition of ozone to built environment surfaces: volume i experimental*. University of Texas at Austin, Center for Energy and Environmental Resources.
- Sarwar, G., Corsi, R., Allen, D., & Weschler, C. (2003). The significance of secondary organic aerosol formation and growth in buildings: experimental and computational evidence. *Atmospheric Environment*, *37*, 1365-1381.
- 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 Transactions*, *1*, 116-139.
- Shields, H. C., Weschler, C. J., & Naik, D. (1999). 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.
- Simoni, M., Biavati, P., Carrozzi, L., Viegi, G., Paoletti, P., Matteucci, G., et al. (1998). The Po River Delta (North Italy) indoor epidemiological study: home

- characteristics, indoor pollutants, and subjects' daily activity pattern. *Indoor Air*, 8(2), 70-79.
- Triche, E. W., Gent, J. F., Holford, T. R., Belanger, K., Beckett, W. S., Naeher, L., et al. (2006). Low-level ozone exposure and respiratory symptoms in infants. *Environmental Health Perspectives*, 114(6), 911-916.
- Wainman, T., Zhang, J., Weschler, C. J., & Liroy, P. J. (2000). Ozone and limonene in indoor air: a source of submicron particle exposure. *Environmental Health Perspectives*, 108(12), 1139-1145.
- Wargocki, P. (2004). Sensory pollution sources in buildings. *Indoor Air, Supplement 7*, 82-91.
- 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.
- Waring, M. S., Siegel, J. A., & Corsi, R. L. (2008). Ultrafine particle removal and generation by portable air cleaners. *Atmospheric Environment*, 42(20), 5003-5014.
- 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. *Environmental Health Perspectives*, 114, 1489-1496.
- Weschler, C. J., Hodgson, A. T., & Wooley, J. D. (1992). Indoor chemistry: ozone, volatile organic compounds, and carpets. *Environmental Science & Technology*, 26, 2371-2377.
- 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. *Environmental Science & Technology*, 41(17), 6177-6184.
- Williams, R., Creason, J., Zweidinger, R., Watts, R., Sheldon, L., & Shy, C. (2000). Indoor, outdoor, and personal exposure monitoring of particulate air pollution: the

Baltimore elderly epidemiology-exposure pilot study. *Atmospheric Environment*, 34(24), 4193-4204.

Wisthaler, A., & Weschler, C. J. (2009). Reactions of ozone with human skin lipids: sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. *P. Natl. Acad. Sci. USA*, 107, 6568-6575.

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