Lawrence Berkeley National Laboratory

Lawrence Berkeley National Laboratory

Title

Secondary Pollutants from Ozone Reaction with Ventilation Filters and Degradation of Filter Media Additives

Permalink

https://escholarship.org/uc/item/57k8k6x0

Author

Destaillats, Hugo

Publication Date

2011-07-01

eScholarship.org Powered by the California Digital Library
University of California

ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

Secondary pollutants from ozone reactions with ventilation filters and degradation of filter media additives

H. Destaillats, W. Chen, M.G. Apte, N. Li, M. Spears,
J. Almosni, G. Brunner, J. Zhang, W.J. Fisk

Environmental Energy Technologies Division

March 2011

Disclaimer

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory is an equal opportunity employer.

Secondary pollutants from ozone reactions with ventilation filters and degradation of filter media additives

Hugo Destaillats[1,2*], W. Chen[3#], Michael G. Apte[1], Nuan Li[3], Michael Spears[1], Jeremie Almosni[1], Gregory Brunner[4], Jianshun (Jensen) Zhang[3], William J. Fisk[1]

[1] Indoor Environment Department, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
[2] School of Sustainable Engineering and the Built Environment, Arizona State University AZ USA
[3] Building Energy and Environmental Systems Laboratory, Syracuse University, Syracuse, NY, USA.
[#] Current affiliation: California Department of Public Health, Richmond, CA, USA
[4] United States Environmental Protection Agency, Washington DC, USA.

Indoor Environment Department
Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720

March 2011

This research was supported by the U.S. Environmental Protection Agency through interagency agreement DW-89-92224401 with the U.S. Department of Energy under Contract DE-AC02-05CH11231. Additional support was provided by the National Institute for Occupational Safety and Health (NIOSH) through grant number OH008891-01A2. PTR-MS experiments were conducted at Syracuse University's Building Energy and Environmental Systems Laboratory with equipments funded by the New York Strategically Targeted Academic Research Center in Environmental Quality Systems (NYSTAR-EQS). Conclusions in this paper are those of the authors and not necessarily those of the U.S. Environmental Protection Agency or the U.S. Department of Energy.

Secondary Pollutants from Ozone Reaction with Ventilation Filters and Degradation of Filter Media Additives

Hugo Destaillats[1,2,*], Wenhao Chen[3,#], Michael G. Apte[1], Nuan Li[3], Michael Spears[1], Jérémie Almosni[1], Gregory Brunner[4], Jianshun (Jensen) Zhang[3], William J. Fisk[1]

[1] Indoor Environment Department, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
[2] School of Sustainable Engineering and the Built Environment, Arizona State University AZ USA
[3] Building Energy and Environmental Systems Laboratory, Syracuse University, Syracuse, NY, USA.
[#] Current affiliation: California Department of Public Health, Richmond, CA, USA
[4] United States Environmental Protection Agency, Washington DC, USA.

**Corresponding email: HDestaillats@lbl.gov*

Abstract

Prior research suggests that chemical processes taking place on the surface of particle filters employed in buildings may lead to the formation of harmful secondary byproducts. We investigated ozone reactions with fiberglass, polyester, cotton/polyester and polyolefin filter media, as well as hydrolysis of filter media additives. Studies were carried out on unused media, and on filters that were installed for 3 months in buildings at two different locations in the San Francisco Bay Area. Specimens from each filter media were exposed to ~150 ppbv ozone in a flow tube under a constant flow of dry or humidified air (50% RH). Ozone breakthrough was recorded for each sample over periods of ~1000 min; the ozone uptake rate was calculated for an initial transient period and for steady-state conditions. While ozone uptake was observed in all cases, we did not observe significant differences in the uptake rate and capacity for the various types of filter media tested. Most experiments were performed at an airflow rate of 1.3 L/min (face velocity = 0.013 m/s), and a few tests were also run at higher rates (8 to 10 L/min). Formaldehyde and acetaldehyde, two oxidation byproducts, were quantified downstream of each sample. Those aldehydes (m/z 31 and 45) and other volatile byproducts (m/z 57, 59, 61 and 101) were also detected in real-time using Proton-Transfer Reaction - Mass Spectrometry (PTR-MS). Low-ppbv byproduct emissions were consistently higher under humidified air than under dry conditions, and were higher when the filters were loaded with particles, as compared with unused filters. No significant differences were observed when ozone reacted over various types of filter media. Fiberglass filters heavily coated with impaction oil (tackifier) showed higher formaldehyde emissions than other samples. Those emissions were particularly high in the case of used filters, and were observed even in the absence of ozone, suggesting that hydrolysis of

additives, rather than ozonolysis, is the main formaldehyde source in those filters. Emission rates of formaldehyde and acetaldehyde were not found to be large enough to substantially increase indoor concentrations in typical building scenarios. Nevertheless, ozone reactions on HVAC filters cannot be ignored as a source of low levels of indoor irritants.

1. Introduction

Chemical reactions involving ozone of outdoor origin and indoor materials are known to be sources of formaldehyde and other irritant gas-phase oxidation products in the indoor environment. Heating, ventilation and air conditioning (HVAC) systems are commonly found in offices, health care facilities, schools, and other buildings in the U.S. Particulate matter and sorbed chemicals from outdoor and indoor origin are collected on the surface of particle filters installed in HVAC systems, and are susceptible to ozone oxidation reactions. These filters, which are typically fabricated from fine fiberglass or synthetic media fibers, provide one of the first major surfaces at which outdoor ozone can react during its transit into the indoor environment. Hence, reactions on filters may become a potentially significant source of secondary pollutants from ozone-initiated chemistry.

Used HVAC particle filters have been shown to be a sensory pollutant source, decreasing perceived indoor air quality (IAQ) and sometimes are associated with increased building-related health symptoms (BRS), also called sick building syndrome, or SBS symptoms (Hyttinen et al. 2006; Hyttinen et al. 2007; Beko et al. 2008). Reactions of ozone with organic compounds present on the filter surfaces have been assumed to be an important factor contributing to the sensory pollution from particle filters. Previous studies have reported that particle filters could remove a fraction of ozone from the air stream (Zhao et al, 2007) and sensory ratings of the air exiting filters are diminished when the air entering the filter contains ozone (Clausen 2004). As for reaction products, although production of formaldehyde and other carbonyl compounds has been reported to correlate to the ozone removal rate for dusty and sooty fiberglass filters (Hyttinen et al. 2006), systematic studies on how the production of secondary pollutants is influenced by environmental conditions such as relative humidity, filter media types and particle loading are limited. Other sources of pollutants from HVAC filters may be degradation of binders and additives. Emissions of aldehydes from filters incubated under extreme high humidity conditions was also reported (Schleibinger and Rüden, 1999). In this

study, integrated and real-time measurements of secondary pollutants at trace levels are carried out to help elucidate the nature and dynamics of ozone-HVAC filter interactions and to identify sources associated with degradation of filter media.

Associations between outdoor ozone and both morbidity and mortality are likely linked to indoor exposures to ozone and ozone-initiated products (Weschler 2006). Some epidemiological studies have also found a correlation between asthma and BRS and indoor pollutants, particularly formaldehyde (Norback et al. 1995; Wieslander et al. 1997; Delfino 2002; Mendell 2007). Additional concern about chronic exposures to indoor formaldehyde arises from its listing as a probable (Group B1) human carcinogen by the U.S. Environmental Protection Agency (EPA) (USEPA 1999a), and as a Group 1 human carcinogen by the by the World Health Organization International Agency for Research on Cancer (Cogliano et al. 2005, WHO 2006). Formaldehyde is ubiquitous indoors, with levels measured in 100 U.S. office buildings in the U.S. EPA's Building Assessment Survey and Evaluation (BASE) study in the range of 0 – 42 ppb, with a mean of 13 ppb, and a median of 12 ppb (USEPA 2003; USEPA 2010). These results are consistent with formaldehyde concentrations measured in 190 North American residences, with a median of 17 ppb and 90th percentile of 37 ppb (Hodgson and Levin 2003). Formaldehyde and acetaldehyde were the most abundant carbonyls (60 – 70 % of the total) detected in indoor and personal samples in the Relationships of Indoor, Outdoor and Personal Air (RIOPA) study (Weisel et al. 2005; Liu et al. 2006). Indoor formaldehyde levels often exceed the recommended exposure limit (REL) for an 8 to 10-hour average exposure and/or ceiling of 0.02 mg m^{-3} (16 ppb) (NIOSH 1997). Formaldehyde is emitted primarily by various indoor materials such as cabinetry and wooden building products (Hodgson et al. 2002). It is also emitted by office equipment (Destaillats et al. 2008) and is generated together with other volatile aldehydes in reactions of terpenoids with indoor ozone and OH radicals (Destaillats et al. 2006). The same reactions generate high levels of ultrafine aerosol particles (Coleman et al. 2008).

The goal of this study was to better understand chemical processes related to building air filtration and ozone in light of recent findings suggesting a strong association of synthetic filters with increased reporting of BRS at work particularly when outdoor ozone levels are elevated (Apte et al. 2008; Buchanan et al. 2008). The findings from those prior analyses suggest an easy and practical means of reducing BRS – avoiding synthetic filters; however, without mechanistic evidence it is premature to make such a recommendation. The results presented here further contribute to building a scientific foundation for guidance on building filtration methods.

2. Experimental Methods

2.1. Selection, handling, deployment and storage of HVAC filters

A group of filters reflecting a subset of the filters reported in the EPA BASE study of 100 U.S. office buildings was used in this work. Filter media included fiberglass (FG), polyester (PE), cotton/polyester blends (CP) and polyolefin (PO); some of these materials were coated with various levels of tackifier by the manufacturers. Tackifiers, also referred to as impaction oils, are provided as adhesives to help retain particles that impinge upon the filter media. A description of filters used in this study is presented in Table 1-S (Supplementary Material). A subset of filters in this study was installed in the ventilation systems of two office buildings at the Lawrence Berkeley National Laboratory (LBNL) for a period of 3 months. Another set of filters was installed in the HVAC system of a building at the Port of Oakland (POAK). Particles in the outdoor air in these locations was primarily influenced by vegetation (LBNL) and diesel emissions from trucks and freeway traffic (POAK). One of the LBNL buildings did not recirculate indoor air, while HVAC systems of the other LBNL building and the POAK building operated with significant recirculation of indoor air (>50%).

Used and unused filters were wrapped with aluminum foil and stored at room temperature under 40-60% RH before exposure to ozone and analysis. Aluminum foil used to wrap the samples was oil-free and inert towards ozone. Specimens for each experiment consisted of 47-mm diameter disks that were cut from representative sections of each filter (surface area = 1.7×10^{-3} m^2). Given the different nature and thickness of each filter material, samples of the same horizontally-projected surface area had relatively different masses in the range 100 – 550 mg (Table 2-S, Supplementary Material). No significant mass change was recorded after exposure to ozone. All mass determinations were carried out at ambient laboratory relative humidity.

2.2. Experimental setup

Filter samples were placed inside an all-Teflon flow tube, connected to the ancillary system through Teflon-lined Tygon tubing, to minimize ozone loss in the system. Air containing a known level of ozone and humidity was split into two streams, one of which was directed to the flow tube containing the filter sample, while the other (bypass) was used as a reference. The

ozone level was controlled with an ozone generator (UVP, Upland, California) upstream of the filter, and the humidity was adjusted by circulating part of the incoming airflow through a humidifier to obtain RH = 50% ± 10%. The ozone level was measured at 5-min intervals, alternatively downstream of the filter and at the bypass line, using a photometric monitor (API 400). A multiplexing valve was used to switch automatically from the filter to the reference. Gas phase samples were collected through ports located downstream of the exposed filters and on the reference line. The experimental setup was operated under room temperature, in the range 21-24 ^{o}C. System temperature and RH, as well as ozone concentration, were recorded continuously (APT logging system, The Energy Conservatory, Minneapolis, MN). The experimental setup is shown in Figure 1-S (Supplementary Material).

2.3. Ozone breakthrough curves

Used and unused HVAC filters were exposed to air containing inlet ozone levels of ~150 ppbv (measured with a precision of ± 5 ppbv) for periods of 800 to 1200 min. High ozone concentrations were used to maximize the chances to detect reaction byproducts formed in relatively low levels. For each sample, two separate experiments were performed, using dry and humidified air respectively. The airflow through the filters was typically 1.3 L/min, corresponding to face velocities of 0.013 m/s (2.56 ft/min). We recorded ozone breakthrough curves by measuring ozone levels, $[O_3]$, downstream of the filter and in the reference line (equivalent to upstream ozone levels), at 5-minute intervals. The difference in ozone concentration measured downstream of the filter and the average of the reference periods immediately before and after each sample was recorded as $\Delta[O_3]$. We also performed a few experiments at a higher airflow rate, corresponding to a face velocity of 0.093 m/s (or 18.3 ft/min), to approach conditions that are closer to HVAC usual operation conditions (although still roughly one order of magnitude lower than typical face velocities).

2.4. Determination of integrated aldehyde emissions

We collected volatile carbonyls formed in the oxidation of filter media and particles deposited on the filters, downstream of the flow tube following a established procedure that has been described previously (USEPA 1999b). Dinitro phenylhydrazine (DNPH)-impregnated silica gel cartridges (# WAT047205, Waters, MA) were preceded by an ozone scrubber (# WAT054420, Waters, MA) to collect ozone-free aldehyde samples. The ozone removal capacity

of the scrubbers was verified under the experimental conditions. A new scrubber was used in each individual test to avoid possible artifacts associated with ozone breakthrough. The flow through the sampler was measured immediately before starting and at the end of each sampling period, and was used, together with the sampling duration, to determine the volume of air sampled with experimental uncertainty below ± 3%. The samplers were extracted with 2-mL acetonitrile aliquots, and analyzed by HPLC with UV detection (Agilent 1200). Formaldehyde and acetaldehyde were quantified with a calibration curve prepared with authentic standards of the DNPH hydrazone derivatives. The average formaldehyde concentration in reactants blanks was determined to be 0.02 ± 0.05 μg/m^3; and the average acetaldehyde concentration in the reactants blanks was 0.04 ± 0.05 μg/m^3. In both cases, values correspond to the average of five determinations, and the experimental error was determined as one standard deviation.

2.5. PTR-MS measurements

A sub-set of filter media samples was further tested using Proton-Transfer Reaction – Mass Spectrometry (PTR-MS) (Lindinger et al. 1998; Wisthaler and Weschler 2010), with a primary focus of monitoring and identifying trace level organic pollutants formed in heterogeneous reactions between ozone and HVAC filters in real-time. The instrument sampled downstream of the flow tube at 85 mL min^{-1}, and was used in full scan mode in the mass-to-charge ratio (m/z) range of m/z 20 to m/z 200. The PTR-MS was calibrated immediately prior to the experiments using toluene, acetaldehyde and formaldehyde standards generated with permeation tubes at a rate of ~400 ng min^{-1}. In the case of formaldehyde, due to the high sensitivity of the PTR-MS signal to relative humidity, two calibrations were performed using dry air and 50% RH. Humidity did not affect the other calibrations.

3. Results and Discussion

3.1. Ozone uptake by HVAC filters

Figure 1 illustrates a typical ozone breakthrough curve under humidified air, performed on a polyolefin filter used in the POAK building. The red curve corresponds to ozone concentration in the bypass (reference), and the curve in blue to ozone concentration downstream of the flow tube. Each data point is the average of a 5-min measurement. The

change in ozone concentration, $\Delta[O_3]$, can be calculated from the difference between those two curves. The green curve represents the percent change in ozone, $\%\Delta[O_3]$, calculated as

$$\%\Delta[O_3] = \frac{\Delta[O_3]}{[O_3]_{ref}} \times 100 \qquad (1)$$

with respect to inlet (*i.e.*, reference) ozone concentration, $[O_3]_{ref}$. This experimental approach allowed for precise $\Delta[O_3]$ determinations, even in the presence of fluctuations due to airflow or ozone generation instabilities. In the absence of filter media (initial quenching period), Figure 1 shows a very good match between temporal variations in bypass and sample ozone levels. The breakthrough curves obtained in this study were very similar to those reported by Zhao et al (2007) for synthetic and fiberglass filter media over the same time interval.

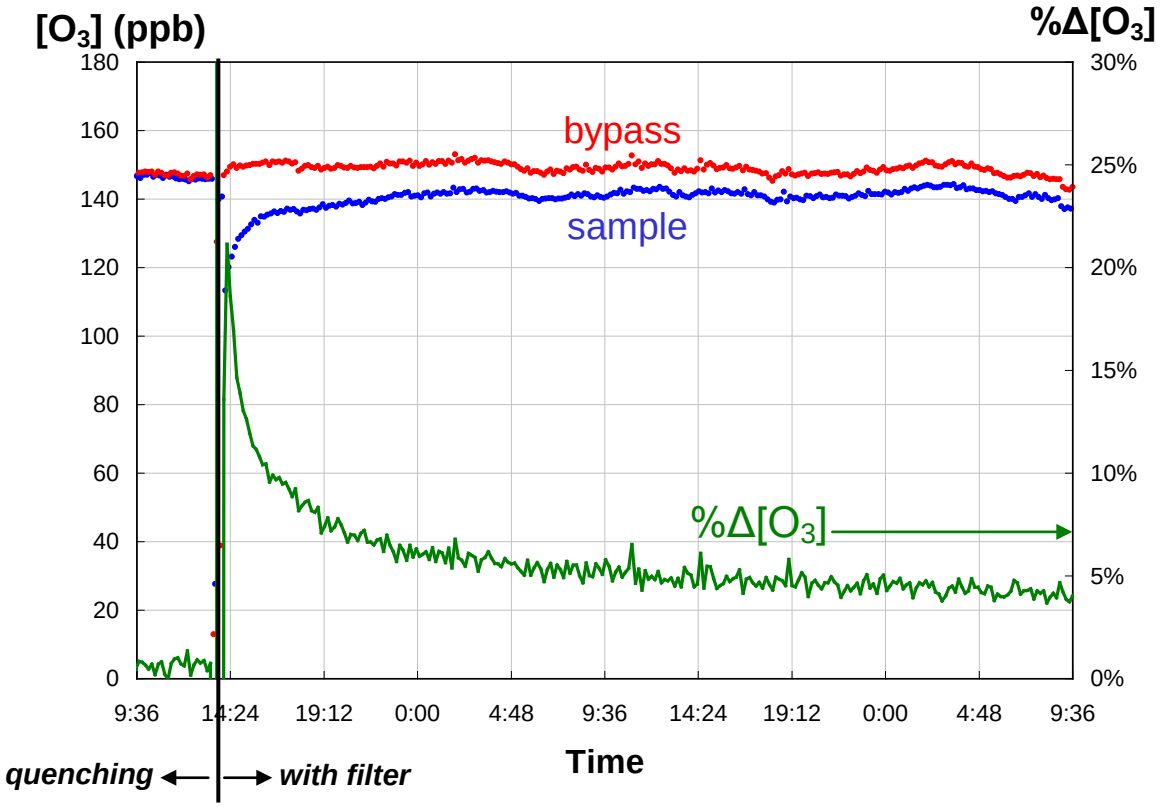


Figure 1: Ozone breakthrough curve for polyolefin filter media used in the POAK building, exposed to 150 ppb ozone under humidified air.

Results from ozone breakthrough curves such as that shown in Figure 1 were fit to an exponential function:

$$\Delta[O_3] = A \cdot \exp(-Bt) + \Delta[O_3]_{ss} \qquad (2)$$

which allowed for determination of the time at which outlet ozone concentration approached steady state (t_{ss}), the average ozone concentration change $\Delta[O_3]_{initial}$ with respect to inlet concentrations, corresponding to the initial transient period ($t < t_{ss}$), and $\Delta[O_3]_{ss}$, the ozone concentration change corresponding to the steady state period ($t > t_{ss}$). The value of t_{ss} in each experiment was established as the time at which the fitted $\Delta[O_3]$ was 5% higher than $\Delta[O_3]_{ss}$, in the range $59 < t_{ss}$ (min) < 552 for unused filters, and $64 < t_{ss}$ (min) < 1266 for used filters. These parameters are illustrated schematically in Figure 2-S (Supplementary Material). Fitted values corresponding to unused and used filters are reported in Tables 3-S and 4-S (Supplementary Material), respectively. Tables 3-S and 4-S also include the mass of ozone consumed during the initial period (in μg), and the rate of ozone consumption in the steady-state regime (in μg h^{-1}). This information was used to determine the mass of ozone consumed during a 24-h period of continuous exposure in each case, as illustrated in Figure 2 for fiberglass and polyester filters. The choice of a 24-h exposure period allowed us to capture the full transient period in all cases and compare all filters under controlled conditions. A diurnal cycling with 12 – 15 hours of ozone exposure may lead to higher ozone removal due to regeneration of filter capacity for ozone uptake (Zhao et al, 2007). The mass of ozone uptake during the initial period was obtained directly from Tables 3S and 4S, and the uptake of ozone between t_{ss} and $t = 24$ h was calculated using the rate of ozone uptake at steady-state. Highest ozone uptake was observed for fiberglass filters with a heavy tackifier coating, particularly for the used filters. Although those were also the heavier unused filter samples (Table 2-S), mass differences alone do not account for the much higher ozone uptake. The presence of a heavy coating of impaction oil, and accumulated particles in the cases for the used filters, are likely major factors leading to higher ozone uptake. The used polyester filter media, treated with a medium application of the same impaction oil, also exhibited also a high ozone uptake rate both under humidified and dry air conditions, with a significant contribution of the steady-state period, which indicates that the pollutants accumulated in this media may be a moderate but constant source of other indoor

pollutants originated in ozone chemistry. Thus for both the fiberglass and polyester media, pollutants trapped in the filter media may be more important for ozone reactions than the filter media itself. In Figures 3-S and 4-S (Supplementary Material), similar results are plotted for cotton/polyester and for polyolefin media, respectively. For nearly all filter media, initial ozone reactivity was higher than under steady-state conditions, suggesting that the most reactive constituents present on the surface of the filter media were rapidly eliminated by reaction with ozone. Nevertheless, when a 24-h period is considered, ozone removal during the steady-state period is also significant in many cases, suggesting a steady-state condition in which the ozone removal rate is matched by the diffusion rate of reactive compounds to the exposed surface. Used, particle-loaded, filters presented significantly higher ozone uptake than unused filters of the same type, particularly when exposed to humidified air. In filters used in the POAK building we observed significant ozone uptake for most filter media, likely due to the carbonaceous nature of the material collected on the filter surfaces (Hyttinen et al. 2006).

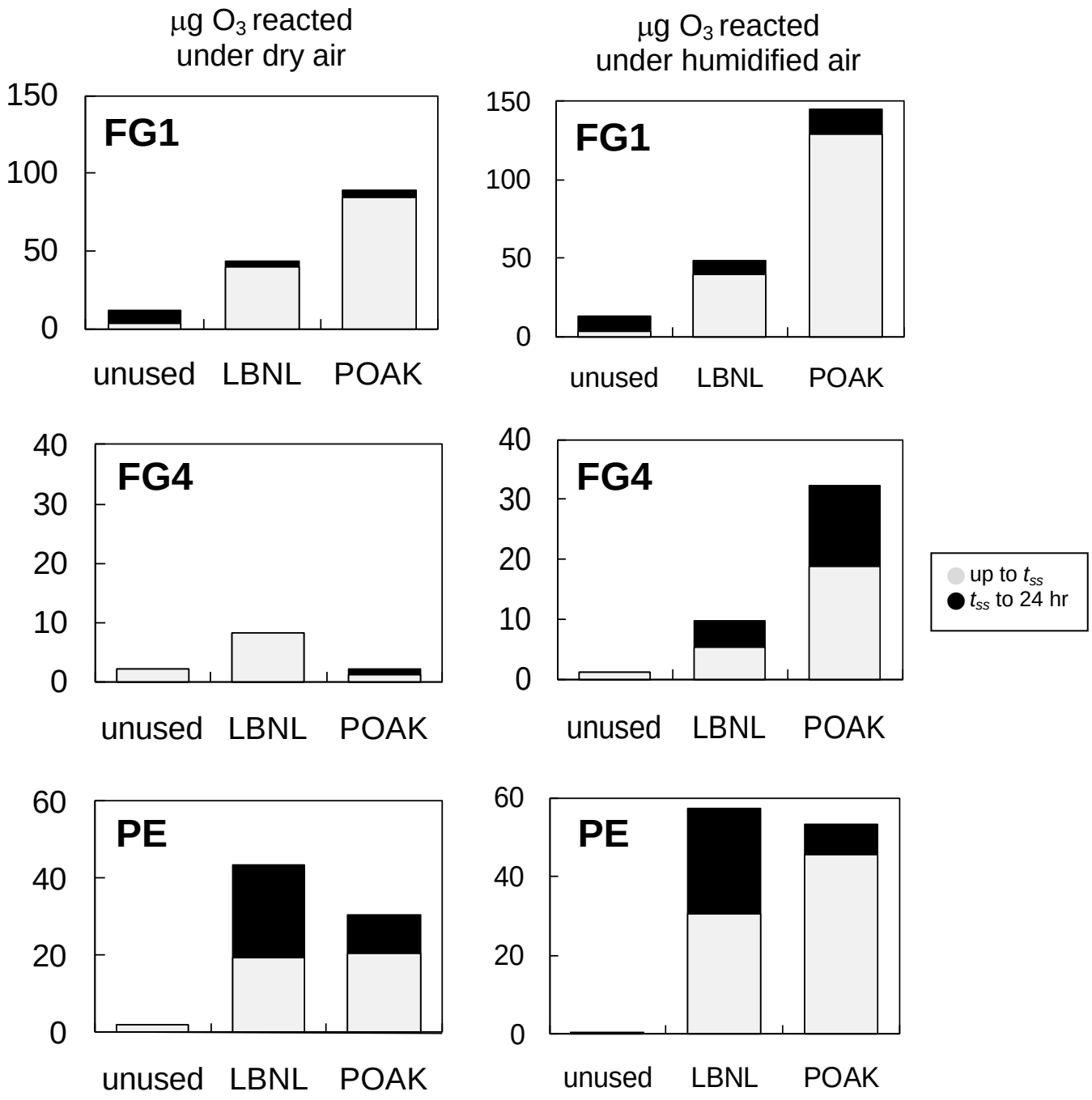


Figure 2: Ozone uptake in a 24-h period for two fiberglass filters and one polyester filter. FG1: fiberglass with heavy tackifier application; FG4: fiberglass with light tackifier application; PE: polyester with medium tackifier application and plastic backing. Plots are represented in each case to maximum scale, but it should be noted that significant differences exist between FG1 and other filters.

3.2. Determination of integrated aldehyde emissions

Integrated formaldehyde and acetaldehyde levels determined downstream of three different filter media exposed to ozone in humidified air (inlet ozone levels = 140 to 165 ppbv, air RH ~ 50%) over periods of ~1000 min are shown in Figure 3. We report data for unused filters, as well as for particle-laden filters used over 3 months at LBNL and POAK buildings.

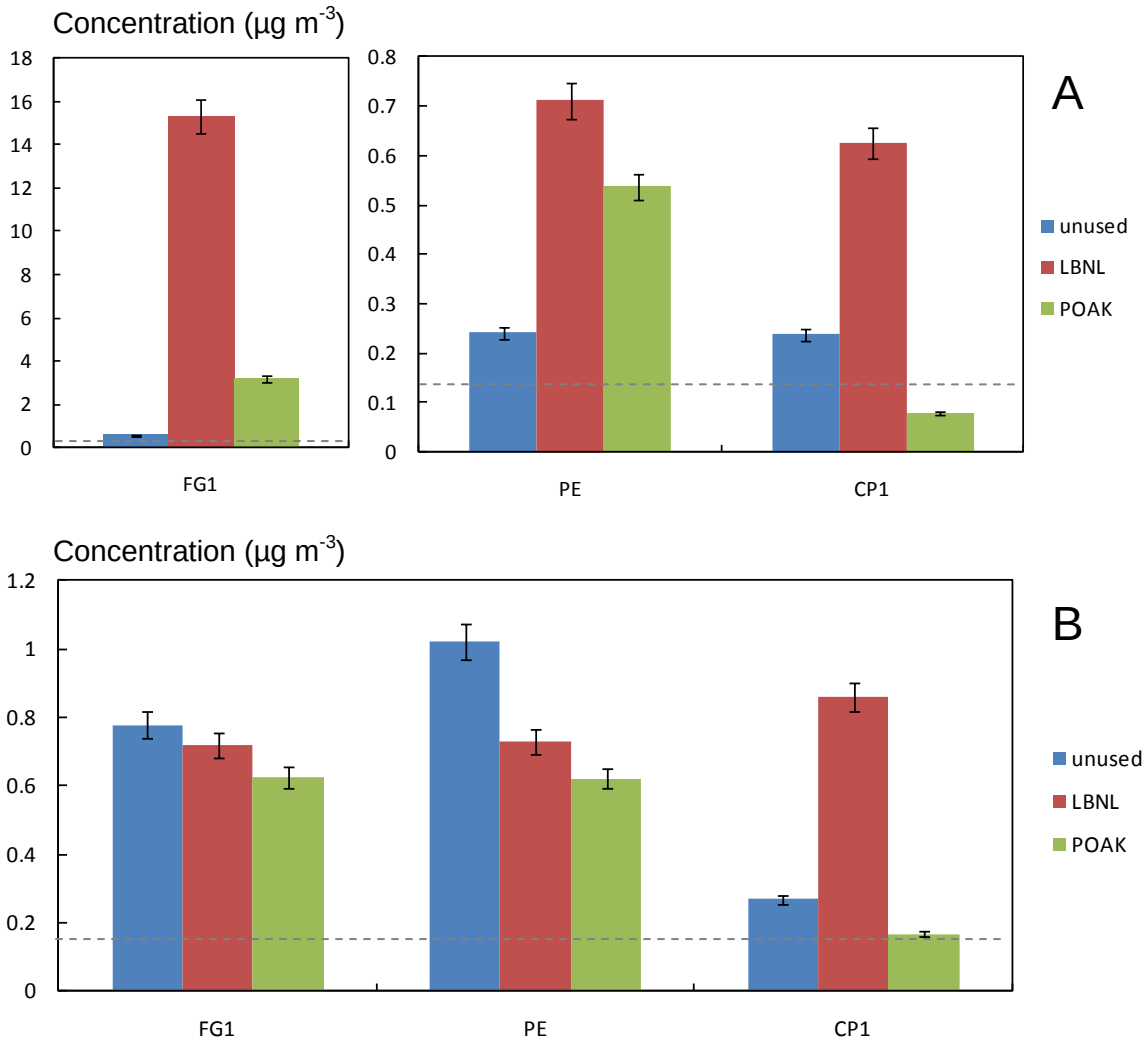


Figure 3: Aldehyde concentrations measured downstream of used and unused filters exposed to ozone. The filter media included fiberglass with heavy tackifier application (FG1), polyester with medium tackifier application (PE) and cotton/polyester blend without tackifier (CP1). Results are reported for (A) formaldehyde and (B) acetaldehyde. Limits of detection are indicated with dashed lines in each case. Plots are represented in each case to maximum scale, but it should be noted that significant differences exist between FG1 in Fig 3-A and all other filters.

Overall, downstream aldehyde concentrations were low in almost all cases. Similar experiments performed using dry air, yielded in all cases aldehyde concentrations near the limit of detection (LOD), and are therefore not included in Figure 3. For experiments under humidified air, aldehyde levels were between ~2 to ~6 higher than the LODs in most cases. Only the fiberglass filter media coated with tackifier exhibited much higher emissions, up to ~120 times higher than the LOD. The LODs were determined by collecting samples in the absence of filter media under otherwise identical conditions, and are indicated with dashed lines in Figure 3. High emissions of volatile aldehydes from fiberglass media are discussed in more detail below. For the other filter types, and assuming that emissions are exclusively due to reaction with ozone, we estimated formaldehyde and acetaldehyde molar yields (moles product formed per mole ozone consumed) in the range 10 to 70% of ozone reacted with unused filters, and in the range 1 to 20 % of ozone reacted with used filters.

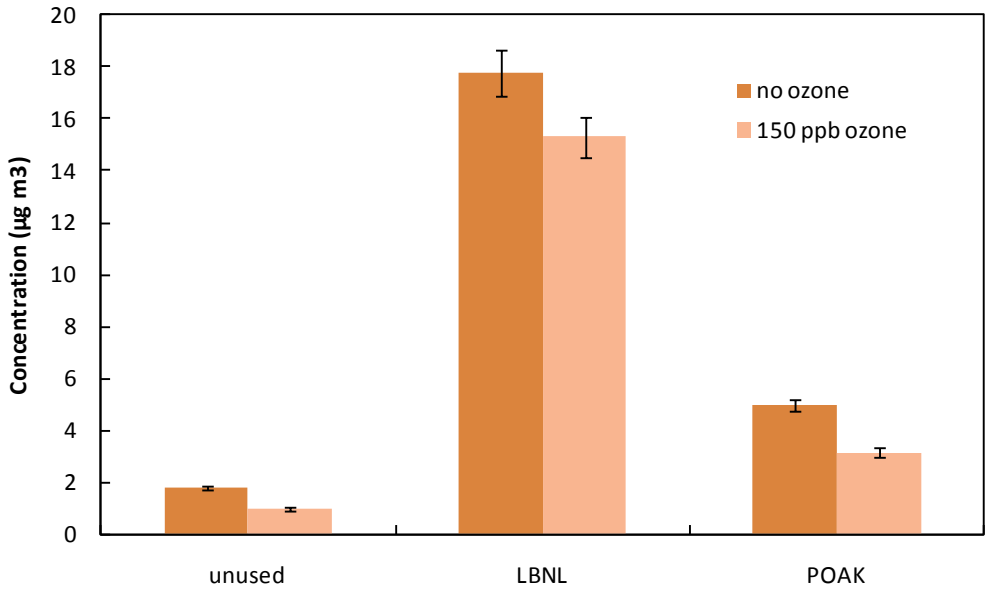


Figure 4: Formaldehyde concentrations measured downstream of FG1 filter media in the presence and absence of ozone, for experiments performed at 50% RH.

3.3. Formaldehyde emissions in the absence of ozone

In order to explore in more detail the high formaldehyde emissions from fiberglass HVAC media under humidified air, we performed additional experiments in the absence of ozone to investigate if those unusually high emissions were due to ozone chemistry or to other chemical processes. We observed that high levels of formaldehyde were present with humidified air even in the absence of ozone, but no significant emissions were observed in dry air. High formaldehyde emissions were detected with unused filters, but were significantly higher in the case of used filters. Results corresponding to a fiberglass media with a heavy tackifier application (FG1) are shown in Figure 4. Similar results from another fiberglass filter corresponding to another manufacturer (FG4) are shown in Figure 5(A)-S (Supplementary Material). In all cases, formaldehyde levels were slightly higher in the absence of ozone, as compared with the same sample exposed to ozone. These results suggest the presence of a source that emits formaldehyde through hydrolysis, rather than ozone-driven chemistry. The presence of filter cake (in used filters) may serve as a medium to accumulate water, thus enhancing the hydrolysis process. Possible sources of formaldehyde in the presence of moisture are binders, impaction oils or other additives that may be present on the filter surface. While our experiments did not allow for a closer examination of the effect of filter cake on the formaldehyde yields originating in hydrolysis of filter additives, future research should consider the role of acidity of various aerosols (such as acidic particles from urban pollution or alkaline tobacco smoke). The chemical composition of filter cake and aerosol mass loading of filters likely play an important role in the net emissions of formaldehyde due to hydrolysis reactions. In the case of polyester and cotton/polyester media, the effects of ozone and humidity on formaldehyde emissions are very different from those described for fiberglass media in Figure 4. Overall formaldehyde emissions were significantly lower, and we did not observe emission of formaldehyde in the absence of ozone in any case (Figure 5-S, Supplementary Material).

3.4 PTR-MS results

A subset of samples was analyzed by PTR-MS during the initial 1-h period of reaction with ozone and in the absence of ozone (control) under humidified air conditions. Figure 6-S (Supplementary Material) illustrates the time-resolved downstream concentration profiles obtained using a PO1 filter for a compound with m/z = 61 in the presence and absence of

ozone, representative of results obtained in these experiments. We observed PTR-MS signals for compounds with m/z = 31 (formaldehyde), 45 (acetaldehyde), 57, 59, 61 and 101. The compound with m/z 57 may be tentatively attributed to acrolein, a strong irritant. Other candidate analytes with similar MW are 1-butene and butylene, but formation of acrolein, an oxygenated molecule, is more likely. In the case of m/z 61, two possible candidates are glycolaldehdye and acetic acid. The compounds with m/z 59 and 101 have been attributed to acetone and 4-oxopentanal (4-OPA) respectively, two oxidation byproducts of squalene, a semivolatile organic compound that is ubiquitous indoors (Wisthaler and Weschler 2010).

We estimated downstream pollutant concentrations by subtracting background levels measured immediately before exposing each filter sample to ozone. Table 1 reports 1-h average levels for a subset of the filters studied and for each analyte. Concentrations were determined using the corresponding calibration curves for formaldehyde and acetaldehyde, and that of toluene for all other compounds (assuming that the PTR-MS response is not significantly different). For formaldehyde and acetaldehyde, levels as high as 20 and 5 ppbv were recorded, respectively. These initial 1-h emission levels are higher than those recorded in Figure 3 for integrated emissions of these compounds over longer periods (~15 h). In the PTR-MS experiments we also observed high emissions of formaldehyde from the FG1 filter in the absence of ozone, consistent with results shown in Figure 4, obtained with DNPH derivatization and HPLC analysis. For nearly all filters, m/z 61 and 101 were consistently detected, with levels recorded as high as 4 and 10 ppbv, respectively, suggesting the presence of other oxidation byproducts from ozone chemistry. Most acetone and 4-OPA levels were higher for used filters than for unused filters. Squalene, a skin oil constituent, is likely present in filter cake as a result of emissions from building occupants. However, non-zero levels observed in unused filters suggest that it may also originate (to a minor extent) in handling of the filters during manufacturing and packing operations, as well as during storage periods. While all experimental procedures were carried out using nitrile gloves to avoid contamination with operator's skin oils, it is impossible to completely eliminate background levels of squalene. In the case of m/z 57, low levels were detected downstream of FG1 filters for both used (POAK) and unused samples. Given the high irritancy of acrolein and other α,β-unsaturated carbonyls, these data suggest that at least for certain filters, reactions between ozone and the media may lead to formation of pollutants possibly associated with BRS.

Table 1: 1-h average downstream concentrations measured by PTR-MS (in ppbv)

	m/z 31		m/z 45		m/z 57		m/z 59		m/z 61		m/z 101	
	no O_3	with O_3	no O_3	with O_3	no O_3	with O_3	no O_3	with O_3	no O_3	with O_3	no O_3	with O_3
FG1 filter												
unused	5.3 ± 3.0	5.3 ± 4.6	n.d.	1.9 ± 1.6	n.d.	0.5 ± 0.8	n.d.	1.4 ± 1.3	n.d.	1.1 ± 1.3	n.d.	5.1 ± 3.0
POAK	12.2 ± 6.1	20.5 ± 7.6	3.5 ± 1.4	5.1 ± 2.1	n.d.	0.8 ± 0.8	n.d.	1.6 ± 1.2	3.0 ± 1.3	4.3 ± 1.6	n.d.	10.5 ± 3.5
PE filter												
unused	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.5 ± 1.6
POAK	n.d.	n.d.	1.9 ± 1.3	2.4 ± 2.1	n.d.	n.d.	n.d.	0.6 ± 2.0	1.9 ± 1.3	0.5 ± 2.4	n.d.	2.4 ± 2.4
PO1 filter												
unused	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7 ± 1.1	n.d.	n.d.	n.d.	2.7 ± 3.0
POAK	n.d.	1.5 ± 2.2	3.5 ± 1.6	3.5 ± 2.1	n.d.	n.d.	n.d.	1.5 ± 1.3	2.4 ± 1.3	2.7 ± 1.3	n.d.	6.2 ± 3.2
LNBL	3.0 ± 3.8	4.5 ± 3.8	1.9 ± 1.3	3.0 ± 2.1	n.d.	n.d.	n.d.	1.2 ± 1.2	1.6 ± 1.3	3.5 ± 1.9	n.d.	3.2 ± 2.4

3.5. Effect of the face velocity

Our experimental flow conditions corresponded to a face velocity of 0.013 m s^{-1}, which is much lower than typical values in HVAC systems. Due to experimental limitations, we could not run experiments with the high face velocities used during actual filter deployment without losing measurement sensitivity and precision. However, we carried out two tests at higher flows, to evaluate the effect of face velocity on both the ozone removal capacity and aldehyde emissions. For these tests, we selected the FG1 filter used in LBNL, which exhibited one of the highest values of ozone removal and aldehyde emissions (although high aldehyde emissions are attributed to hydrolysis of additives, rather than to ozonation). In all cases, we used the same filter sample surface area of 1.7 x 10^{-3} m^2, and airflow of 8 to 10 L.min^{-1}, which is ~1 order of magnitude higher than that used in the experiments described above. We observed that the rate of ozone removal at a lower flow was significantly higher than at the higher flow, particularly in the case of humidified air. This indicates that the higher residence time corresponding to the low flow condition allowed for a more complete ozone reaction, and hence our ozone removal percentages determined at the low face velocity condition could be seen as an upper limit. The ozone removal curves for this filter at both face velocity conditions under dry and humidified air are shown in Figure 7-S (Supplementary Materials). In both cases, we represent the $\%\Delta[O_3]$ value as a function of the air volume circulated through the filter.

Table 2: Aldehyde downstream concentrations and emission rates (*E*) for 1.7 x 10^{-3} m^2 samples of FG1 media at high and low airflow, with 150 ppb ozone.

	High Airflow		Low Airflow	
	Humidified	**Dry**	**Humidified**	**Dry**
Airflow (L min^{-1})	8.16	9.68	1.36	1.35
Face velocity (m s^{-1})	0.078	0.093	0.013	0.013
Concentration (µg m^{-3})				
Formaldehyde	1.96	0.014	15.3	0.13
Acetaldehyde	0.43	0.017	0.7	0.22
Emission rate *E* (µg h^{-1})				
Formaldehyde	0.96	8.0E-03	1.26	0.0108
Acetaldehyde	6.6E-04	2.7E-05	1.9E-04	4.7E-05

We collected aldehyde integrated samples downstream of the filters under the high flow condition, both in humidified and dry air. The results are reported in Table 2, and show that the emission rates (product of outlet concentration and flow rate) of both aldehydes were, in general, not significantly affected by the change in airflow, given the uncertainty in low aldehyde concentration measurements at high air flow rates. The data do suggest, however, an increase in acetaldehyde emission rate at high, relative to low, air flow rate with humidified air. The ratio of measured formaldehyde concentration under high and low airflow (1.96/15.3) was quite different from that of acetaldehyde (0.43/0.7). This is another indication that, in the FG1 filter, different emission mechanisms for formaldehyde and acetaldehyde are present, with rate controlling steps likely related to hydrolysis and ozone reaction, respectively.

3.6. Estimated impacts on indoor aldehyde concentrations

The expected increases in indoor aldehyde concentrations were estimated from the emission rates provided in Table 2 for the FG1 filter and from calculations of emission rates based on the data collected from tests of other used filters from the LBNL buildings at the low air flow rates with humidified air. Assuming that all outdoor air passing through the air filter is distributed through the HVAC system, the steady-state indoor concentration increase (ΔC) was calculated from the equation

$$\Delta C = \frac{E_{FA}}{Q_{FA}} \qquad (3)$$

where E_{FA} is the aldehyde emission rate per unit filter face area (filter face area not necessarily equal to filter media area because the media may be pleated) in μg/(m^{2}s), and Q_{FA} is the outdoor air flow rate per unit filter face area in m^3/(m^{2}s). E_{FA} is calculated as follows:

$$E_{FA} = \frac{E}{S} R \qquad (4)$$

where E is the emission rate for a sample of filter media from Table 2 divided by 3600 (time units conversion factor). S is the media area of these filter samples (0.0017 m^2), and R is the ratio of filter media area to filter face area in a deployed filter. Examples values of R include: unity for a pad filter, 3 to 4 for a 5 cm thick pleated filter, 6 to 7 for a 10 cm thick pleated filter, and 19 for a 56 cm deep bag filter. Q_{FA} was estimated to equal 20% of the typical 2 m^3/s of airflow per 1 m^2 of filter face area, or 0.4 m^3/s-m^2. We assume that 20% outdoor air is mixed with 80% recirculated air. The calculations also assume an approximate 150 ppbv ozone concentration in outdoor air, essentially double the current 8-hour National Ambient Air Quality Standards (NAAQS) for ozone (USEPA 2008).

In Figure 5, we illustrate the expected indoor formaldehyde concentration increases for four of the studied filter media at 50% RH. The formaldehyde emission rates were obtained from the experiments with those filters used in LBNL buildings and exposed to ozone in humidified air at low airflows (approx 1.3 L/min). High formaldehyde emissions from the FG1 fiberglass filter media led to the highest predicted indoor concentration increases, approximately 0.5 μg/m^3 for an R value of 1 as indicated by the single blue point in Figure 5. This could be predicted to increase to approximately 10 μg/m^3 (8 ppbv) if the results were extrapolated to an R value of 19 under the current experimental conditions, which represent an extreme case based on the assumed parameters of filter media, surface area, face velocity, and inlet ozone concentration. The error bars in Figure 5 represent an estimated 20% uncertainty of the ΔC values, originating primarily in the uncertainty of emission rate determinations. The calculations are for illustration purposes -- in practice the filters available on the market with a specific filter media type may have only a few R values. Other filter samples, such as the polyester and cotton/polyester media, were estimated to increase the indoor formaldehyde concentration by 0.02 to 0.4 μg/m^3 in the presence of ozone, which are small increases relative to typical indoor formaldehyde

concentrations. The polyolefin filter media sample was estimated to increase the indoor formaldehyde concentration even less, ranging from less than 0.01 μg/m^3 to slightly above 0.1 μg/m^3.

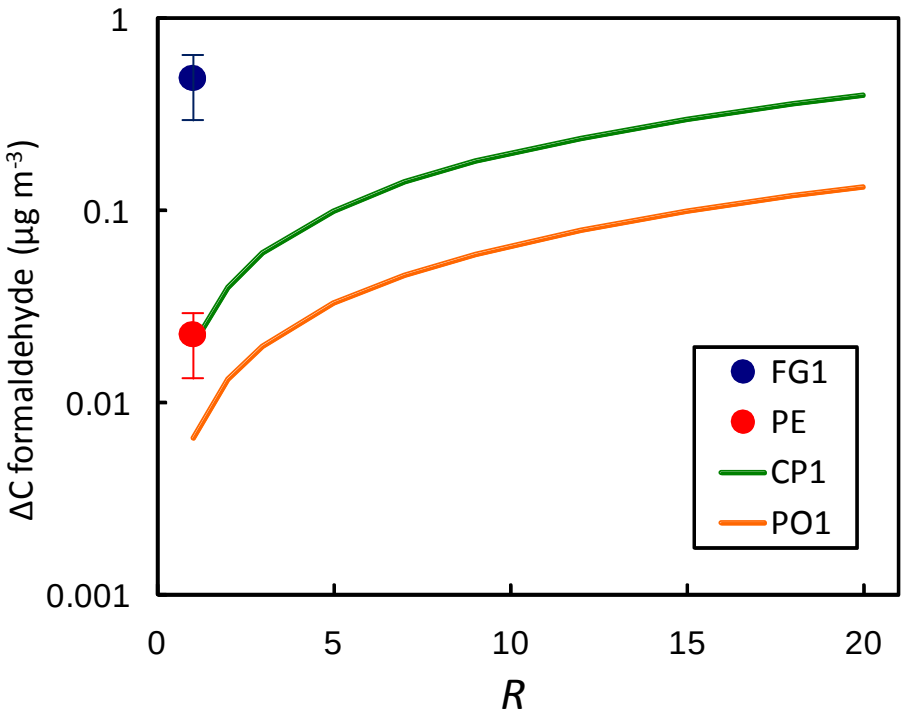


Figure 5: Estimated formaldehyde concentration increases at 50% RH, based on emission rates from filters used at LBNL, as a function of the ratio of filter media area to filter face area, *R*. FG1: fiberglass with heavy tackifier application; PE: polyester with medium tackifier application; CP1: cotton/polyester blend without tackifier; PO1: polyolefin without tackifier.

4. Summary

The results of this study confirm the presence of reactions with ozone and hydrolysis of additives as outdoor air flows through particle filters, which become a source of byproducts. In comparison with other indoor pollutant sources, filters are likely a relatively small albeit measurable contribution. The amount of ozone reacted is much higher when the filters are loaded with particles and when the air is humidified. The amount of ozone reacted is not clearly

related to the types of filter media, e.g., fiberglass versus synthetic. These results do not help to explain why polyester or synthetic filters in environments with elevated ozone were statistically associated with increases in sick building syndrome symptoms from earlier analyses of the EPA's BASE study data (Buchanan et al, 2008). The ozone reaction rates were often higher with filters coated with tackifier, suggesting ozone reaction with impaction oils, and accumulated particles for the cases with used filters (accumulation of particles may be enhanced by impaction oils).

While aldehydes are produced as humidified air containing ozone passes through filters, this study reports for the first time the formation of significant formaldehyde levels when humidified air passes through some of the filters (unused or particle-laden) in the absence of ozone, suggesting that hydrolysis of filter binder or tackifier additives may be a significant formaldehyde source. The estimated increases in indoor aldehyde concentrations are small relative to typical indoor aldehyde concentrations, except in a few cases in which formaldehyde emissions from filters were particularly higher and the results were extrapolated to other filter configurations. The results illustrate that very low levels of certain organic pollutants are being emitted upon contact with ozone in the presence of moisture, and detailed emission dynamics that can be captured in real-time with PTR-MS.

Two important caveats should be kept in mind before extrapolating these results to typical building conditions. First, flow conditions in these experiments were more than one order of magnitude lower than typical HVAC conditions, so results can be extrapolated to higher airflows only if reactions are not severely limited by mass transport. Secondly, HVAC systems typically operate under regimes in which new particles and volatile organic compounds (VOCs) are being simultaneously deposited on filters together with ozone, thus providing fresh supplies of reactive material with very large effective surface area. This study isolated one group of reactions of ozone with the filter media itself, additives (binders, tackifier), and with "recalcitrant" material deposited in used filter that have already been significantly depleted of its most reactive fraction by evaporation and oxidation under atmospheric conditions. Hence, while the low face velocities may lead to "worst-case" reactive conditions, the absence of reactive VOCs and particles in the air fed to the system may lead to lower emissions than those taking place under real-world conditions. Follow-on studies in our laboratory are currently incorporating the effect of added VOCs to assess their contribution to secondary pollutant formation in ozone reactions with HVAC filter media.

Acknowledgments

This research was supported by the U.S. Environmental Protection Agency through interagency agreement DW-89-92224401 with the U.S. Department of Energy under Contract DE-AC02-05CH11231. Additional support was provided by the National Institute for Occupational Safety and Health (NIOSH) through grant number OH008891-01A2. PTR-MS experiments were conducted at Syracuse University's Building Energy and Environmental Systems Laboratory with equipments funded by the New York Strategically Targeted Academic Research Center in Environmental Quality Systems (NYSTAR-EQS). Conclusions in this paper are those of the authors and not necessarily those of the U.S. Environmental Protection Agency or the U.S. Department of Energy. The authors acknowledge L.A. Gundel, M. Sidheswaran and M. Sleiman (LBNL) for helpful suggestions, T. Hotchi and D. Sullivan (LBNL) for experimental assistance and R. Patterson and M. Ringbom for facilitating access to HVAC air handling systems. We also thank anonymous reviewers for their helpful comments.

References

Apte, M. G., I. S. H. Buchanan and M. J. Mendell, 2008. Outdoor ozone and building-related symptoms in the BASE study. Indoor Air 18, 156-170.

Beko, G., G. Clausen and C. J. Weschler, 2008. Is the use of particle air filtration justified? Costs and benefits of filtration with regards to health effects. Building and Environment 43, 1647-1657.

Buchanan, I. S. H., M. J. Mendell, A. G. Mirer and M. G. Apte, 2008. Air filter materials, outdoor ozone and building-related symptoms in the BASE study. Indoor Air 18, 144-155.

Clausen, G., 2004. Ventilation filters and indoor air quality: a review of research from the International Centre for Indoor Environment and Energy. Indoor Air 14, Suppl. 7, 202-207.

Cogliano, V. J., Y. Grosse, R. A. Baan, K. Straif, M. B. Secretan and F. El Ghissassi, 2005. Meeting Report: summary of IARC Monographs on formaldehyde, 2-butoxyethanol and 1-tert-butoxy-2-propanol. Environmental Health Perspectives 113, 1205-1208.

Coleman, B. K., M. M. Lunden, H. Destaillats and W. W. Nazaroff, 2008. Secondary organic aerosol from ozone-initiated reactions with terpene-rich household products. Atmospheric Environment 42, 8234-8245.

Delfino, R. J, 2002. Epidemiologic evidence for asthma and exposure to air toxics: linkages between occupational, indoor and community air pollution research. Environmental Health Perspectives 110**,** Supp. 4, 573-589.

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

Destaillats, H., R.L. Maddalena, B.C. Singer, A.T. Hodgson and T.E. McKone, 2008. Indoor pollutants emitted by office equipment: a review of reported data and information needs. Atmospheric Environment 42, 1371-1388.

Hodgson, A. T., D. Beal and J. E. R. McIlyaine, 2002. Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house. Indoor Air 12, 235-242.

Hodgson, A. T. and H. Levin, 2003. Volatile organic compounds in indoor air: a review of concentrations measured in North America since 1990. Berkeley, California, Lawrence Berkeley National Laboratory**:** LBNL Report 51715.

Hyttinen, M., P. Pasanen, M. Bjorkroth and P. Kalliokoski, 2007. Odors and volatile organic compounds released from ventilation filters. Atmospheric Environment 41, 4029-4039.

Hyttinen, M., P. Pasanen and P. Kalliokoski, 2006. Removal of ozone on clean, dusty and sooty supply air filters. Atmospheric Environment 40, 315-325.

Lindinger, W., A. Hansel and A. Jordan, 1998. On-line monitoring of volatile organic compounds at pptv levels by means of Proto-Transfer-Reaction Mass Spectrometry (PTR-MS). Medical applications, food control and environmental research. International Journal of Mass Spectrometry and Ion Processes 173, 191-241.

Liu, W. L., J. F. Zhang, C. P. Weisel, B. J. Turpin, M. T. Morandi, S. Colome, T. H. Stock and L. Korn, 2006. Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States. Atmospheric Environment. 40, 2202-2214.

Mendell, M. J., 2007. Indoor residential chemical emissions as risk factors for respiratory and allergic effects in children: a review. Indoor Air 17, 259-277.

NIOSH, 1997. National Institute for Occupational Safety and Health. Pocket Guide to Chemical Hazards. US Department of Health and Human Services, Center for Disease Control and Prevention Cincinnati, OH. http://www.cdc.gov/niosh/npg/npgd0293.html.

Norback, D., E. Bjornsson, C. Janson, J. Widstrom and G. Boman, 1995. Asthmatic symptoms and volatile organic compounds, formaldehyde and carbon dioxide in dwellings. Occupational and Environmental Medicine 52, 388-395.

Schleibinger, H., Rüden, H., 1999. Air filters from HVAC systems as possible source of volatile organic compounds (VOC) – laboratory and field assays. Atmospheric Environment 33, 4571-4577.

USEPA, 1999a. Integrated risk information system (IRIS) on formaldehyde. . National Center for Environmental Assessment. Office of Research and Development Washington DC**.** http://www.epa.gov/iris/subst/0419.htm.

USEPA, 1999b. Compendium Method TO-11A - Determination of formaldehyde in ambient air using adsorbent cartridge followed by HPLC [active sampling methodology]. Office of Research and Development - US Environmental Protection Agency, Cincinnati, OH.

USEPA, 2003. A standardized EPA protocol for characterizing indoor air quality in large office buildings. Washington DC.

USEPA, 2008. Code of Federal Regulations, Title 40, Part 50. National Ambient Air Quality Standards. Washington DC. www.epa.gov/air/criteria.html.

USEPA, 2010. BASE Study – Volatile Organic Compound Master List http://www.epa.gov/iaq/base/voc_master_list.html.

Weisel, C. P., J. Zhang, B. J. Turpin, M. T. Morandi, S. Colome, T. H. Stock, D. M. Spektor, L. Korn, A. Winer, S. Alimoktari, J. Kwon, K. Mohan, R. Harrington, R. Giovanetti, W. Cui, M. Afshar, S. Maberti and D. Shendell, 2005. Relationship of indoor, outdoor and personal air (RIOPA) study: study design, methods and quality assurance/control results. Journal of Exposure Analysis and Environmental Epidemiology 15, 123-137.

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.

WHO, 2006. World Health Organization International Agency for Research on Cancer, IARC monographs on the evaluation of carcinogenic risks to humans. Volume 88 formaldehyde, 2-butoxyethanol, 1-tert-butoxypropan-2-ol. Summary of data reported and evaluation. http://monographs.iarc.fr/ENG/Monographs/vol88/volume88.pdf.

Wieslander, G., D. Norback, E. Bjornsson, C. Janson and G. Boman, 1997. Asthma and the indoor environment: the significance of emission of formaldehyde and volatile organic compounds from newly painted indoor surfaces. Int. Arch. Occup. Environ. Health 69, 115-124.

Zhao, P., Siegel, J.A. and Corsi, R.L., 2007. Ozone removal by HVAC filters. Atmospheric Environment 41, 3151-3160.

Wisthaler, A. and C. J. Weschler (2010). "Reactions of ozone with human skin lipids: sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air." Proceedings of the National Academy of Sciences of the United States of America 107, 6568-6575.

Supplementary Material

Secondary Pollutants from Ozone Reactions with Ventilation Filters and Degradation of Filter Media Additives

Hugo Destaillats[1,2,*], Wenhao Chen[3], Michael G. Apte[1],
Nuan Li[3], Michael Spears[1], Jérémie Almosni[1],
Gregory Brunner[4], Jianshun (Jensen) Zhang[3], William J. Fisk[1,*]

[1] Indoor Environment Department, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.
[2] School of Sustainable Engineering and the Built Environment, Arizona State Univ., AZ, USA.
[3] Building Energy and Environmental Systems Laboratory, Syracuse University, Syracuse, NY, USA.
[4] United States Environmental Protection Agency, Washington DC, USA.
**Corresponding email: HDestaillats@lbl.gov*

Table 1-S: HVAC filters used in this study

Designation	Panel or Roll	Media Coating	Thickness
Fiberglass			
FG1	Panel	Impaction oil (heavy application) [(a)]	2”
FG2	Panel	Impaction oil (medium application) [(a)]	2”
FG3	Panel	Impaction oil (light application) [(a)]	2”
FG4	Panel	Adhesive	2”
FG5	Panel	Bonding resin[(b)]	2”
Polyester			
PE	Roll	Impaction oil (medium application) [(a)]	1”
Cotton/polyester blend			
CP1	Panel	None	2”
CP2	Panel	None	2”
Polyolefin			
PO1	Panel	None	2”
PO2	Panel	Electrostatically charged	2”

(a) "high", "medium" and “light” application are nominal classifications which don't necessarily correlate linearly with the amount of oil present on the surface.

(b) per manufacturer literature, the bonding resin is to provide rigidity and resistance to media compression.

Table 2-S: Mass of selected filter specimens used in this study (± one standard deviation).

Filter	Mass of specimen (mg)
FG1	550 ± 70
FG4	330 ± 20
PE	450 ± 30
CP1	120 ± 10
PO1	105 ± 10

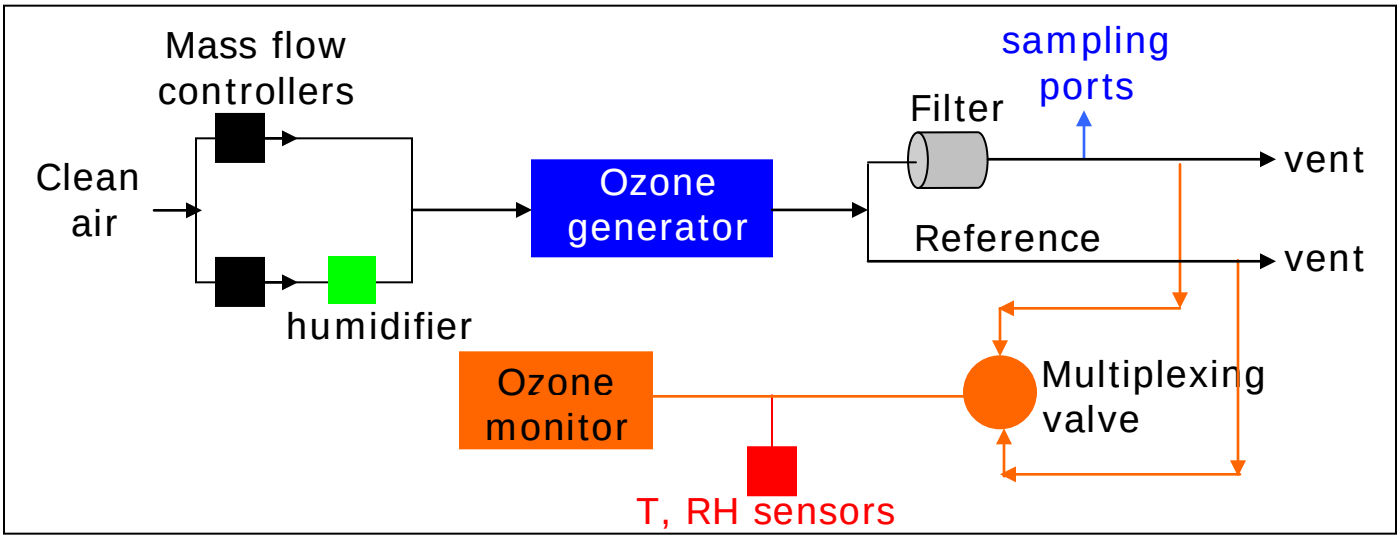


Figure 1-S: Experimental setup

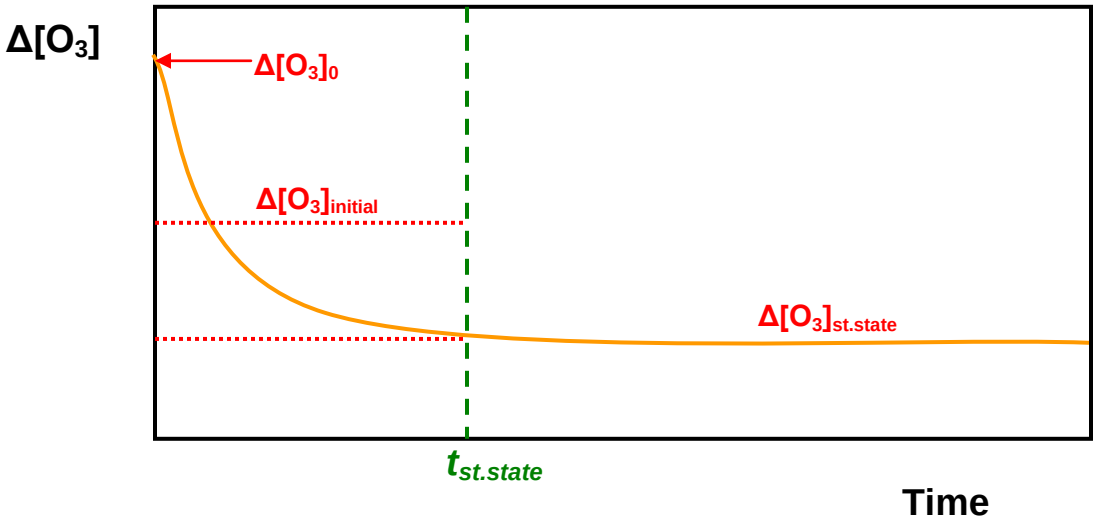


Figure 2-S: Schematic representation of an ozone breakthrough curve, showing the parameters obtained from fitting the experimental data.

Table 3-S: Experimental results obtained from ozone breakthrough curves for unused filters

Manufacturer/ Model	Inlet ozone	RH	$t_{st.state}$	$\Delta[O_3]$		Mass of 0_3 reacted	
				Initial	St.State	Initial	St.State
	(ppb)	(%)	(min)	(ppb)	(ppb)	(µg)	(µg h^{-1})
Fiberglass							
FG1[(a)]	161± 9	0	529	11.9	3.43	3.24	0.53
FG1[(a)]	147± 7	52	422	13.3	3.61	3.02	0.56
FG2	137 ± 16	0	237	4.88	n.d.	2.16	n.d.
FG2	144 ± 6	52	193	6.37	n.d.	1.94	n.d.
FG3[(a)]	146 ± 9	0	552	13.6	5.81	8.26	0.90
FG3[(a)]	151± 6	53	106	13.1	4.54	3.11	0.70
FG4	145 ± 6	0	209	1.93	n.d.	2.80	n.d.
FG4	144 ± 5	52	72	4.65	n.d.	1.21	n.d.
FG5	180 ± 3	0	160	2.85	n.d.	1.17	n.d.
FG5	162 ± 1	68	122	7.50	n.d.	2.41	n.d.
Polyester							
PE [(b)]	148 ± 3	0	228	4.36	0.49	2.98	0.08
PE [(b)]	154 ± 7	59	263	2.71	n.d.	1.58	n.d.
PE [(c)]	165 ± 3	0	59	5.57	n.d.	2.11	n.d.
PE [(c)]	155 ± 3	57	145	4.54	n.d.	0.72	n.d.
Cotton/polyester blend							
CP1	141 ± 16	0	164	9.48	1.24	4.81	0.20
CP1	145 ± 4	54	119	7.10	1.29	1.33	0.20
CP2	153 ± 13	0	168	3.06	n.d.	4.16	n.d.
CP2	145 ± 5	54	93	7.35	n.d.	2.24	n.d.
Polyolefin							
PO1	136 ± 6	0	100	4.45	1.25	4.97	0.20
PO1	145 ± 9	52	88	4.78	1.10	2.59	0.17
PO2	141 ± 7	0	91	3.34	n.d.	0.79	n.d.
PO2	145 ± 4	53	61	2.64	0.64	0.43	0.10

n.d.: $\Delta[O_3]$ not detected; ozone concentration downstream of the filter was not significantly different from the reference.
(a) these filters were tested more than once
(b) without plastic backing
(c) with plastic backing

Table 4-S: Experimental results obtained from ozone breakthrough curves for used filters

Manufacturer/ Model	Building	Inlet ozone	RH	$t_{st.state}$	$\Delta[O_3]$		Mass of 0_3 reacted	
					Initial	St.State	Initial	St.State
		(ppb)	(%)	(min)	(ppb)	(ppb)	(µg)	(µg h^{-1})
Fiberglass								
FG1	LBNL	161 ± 5	0	422	40.2	1.46	39.9	0.21
FG1	LBNL	171 ± 4	64	849	18.1	5.79	39.2	0.89
FG1	POAK	167 ± 3	0	1276	26.1	10.1	84.7	1.54
FG1	POAK	176 ± 12	55	1182	42.6	23.9	129.1	3.67
FG4	LBNL	162 ± 5	0	158	20.5	n.d.	8.28	n.d.
FG4	LBNL	150 ± 2	59	289	7.25	1.42	5.39	0.22
FG4	POAK	173 ± 2	0	189	6.37	0.32	1.04	0.05
FG4	POAK	146 ± 5	57	327	10.2	5.02	18.7	0.73
Polyester								
PE [(a)]	LBNL	171 ± 7	0	322	23.4	8.23	19.6	1.28
PE [(a)]	LBNL	160 ± 2	62	315	16.9	10.2	30.5	1.42
PE [(a)]	POAK	150 ± 2	0	502	15.8	4.20	20.5	0.65
PE [(a)]	POAK	144 ± 2	49	1146	15.3	9.60	45.7	1.51
Cotton/polyester blend								
CP1	LBNL	149 ± 13	0	104	3.34	0.18	0.81	0.02
CP1	LBNL	149 ± 2	60	93	5.18	0.48	1.24	0.07
CP1	POAK	168 ± 2	0	261	10.55	3.77	7.14	0.59
CP1	POAK	152 ± 2	47	492	8.15	4.03	10.33	0.62
CP2	LBNL	160 ± 4	0	192	3.58	0.43	1.62	0.06
CP2	LBNL	197 ± 1	55	64	26.64	0.97	4.40	0.15
Polyolefin								
PO1	LBNL	152 ± 2	0	201	4.55	n.d.	2.39	n.d.
PO1	LBNL	140 ± 2	51	175	4.51	0.38	2.09	0.06
PO2	POAK	161 ± 5	0	272	21.76	2.76	15.53	0.44
PO2	POAK	149 ± 2	54	501	12.98	3.66	17.06	0.58

n.d.: $\Delta[O_3]$ not detected; ozone concentration downstream of the filter was not significantly different from the reference
(a) with plastic backing

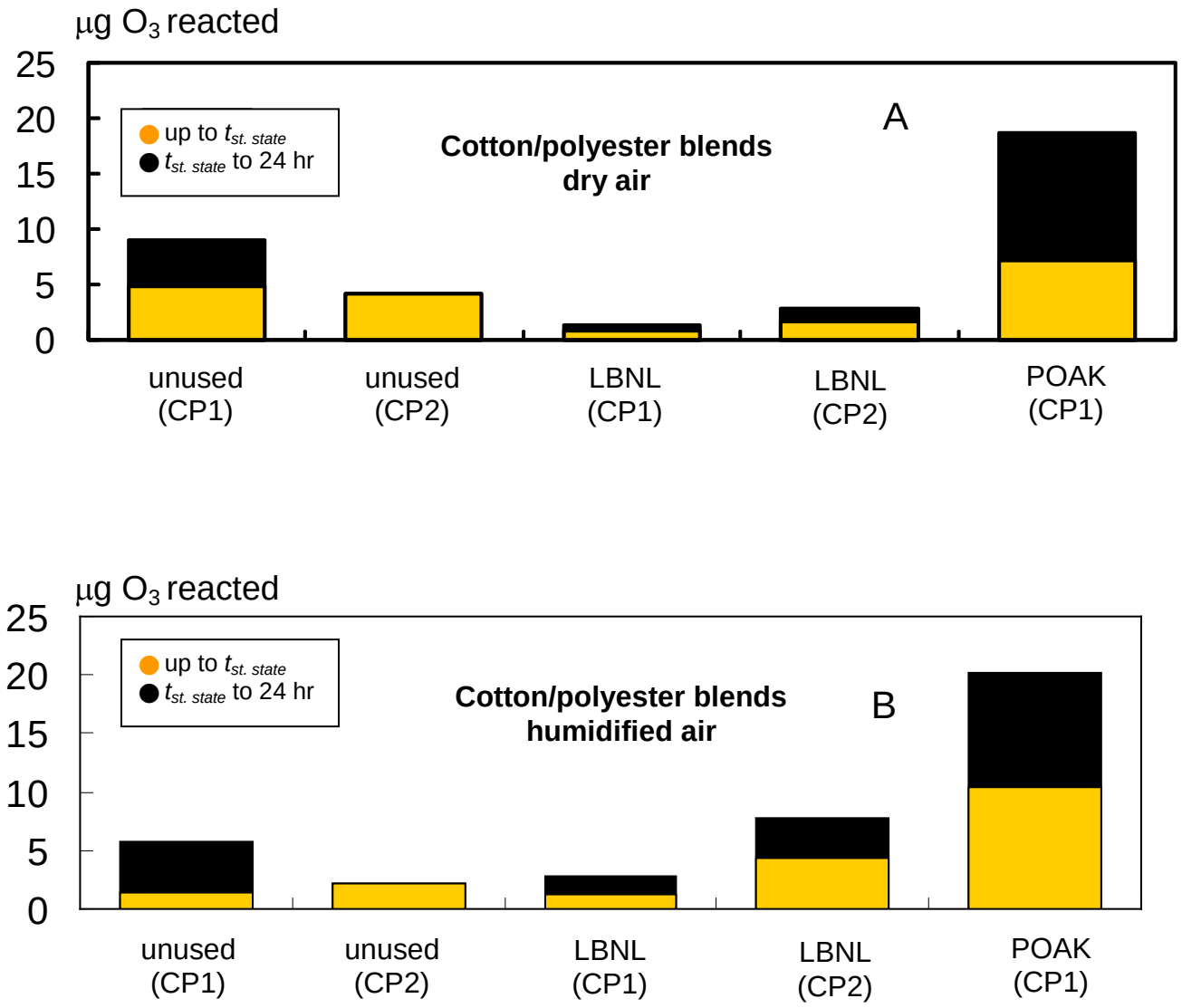


Figure 3-S: Ozone uptake in a 24-h period for cotton/polyester blend filters for (A) dry air and (B) humidified air.

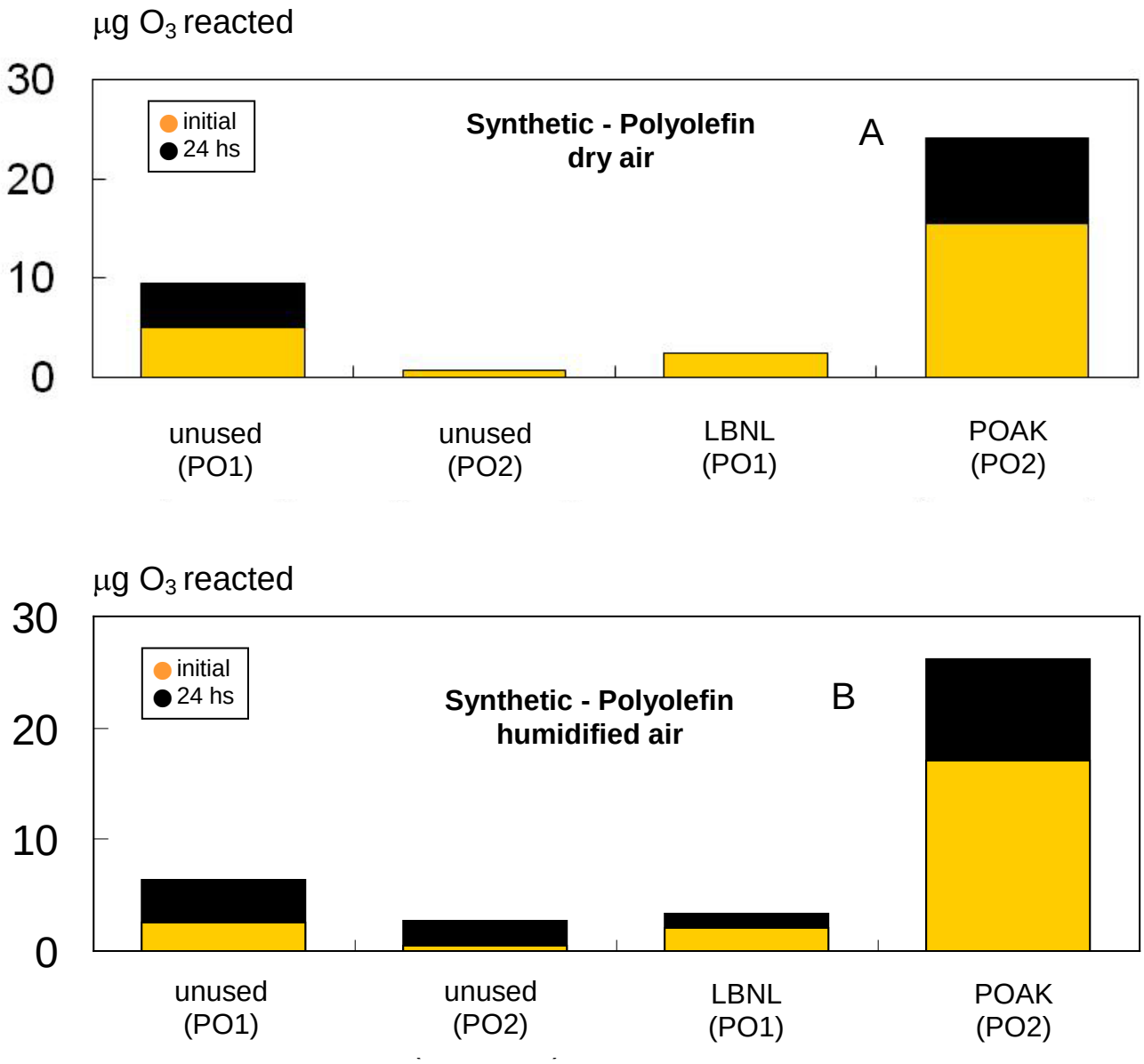
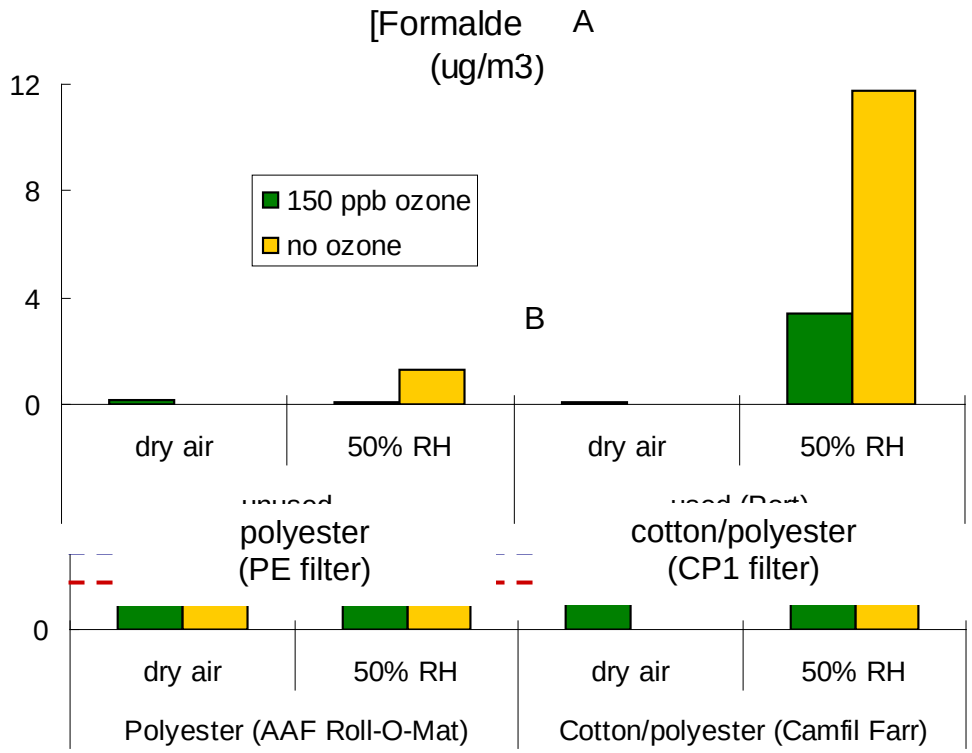


Figure 4-S: Ozone uptake in a 24-h period for polyolefin filters for (A) dry air and (B) humidified air.



Figur
tackif
witho
:h light
:r filter CP1

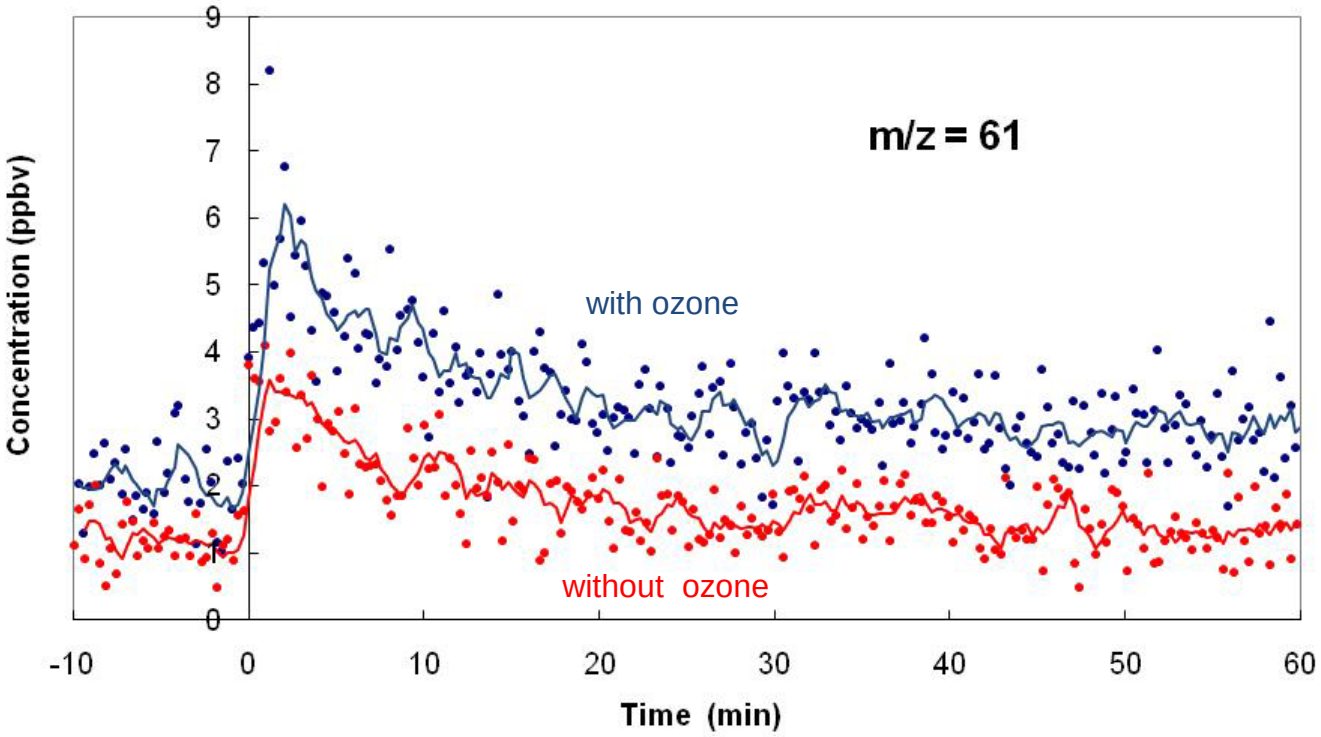


Figure 6-S: PTR-MS concentration profiles corresponding to m/z 61 for the filter PO1, in the absence and the presence of ozone, humidified air conditions.

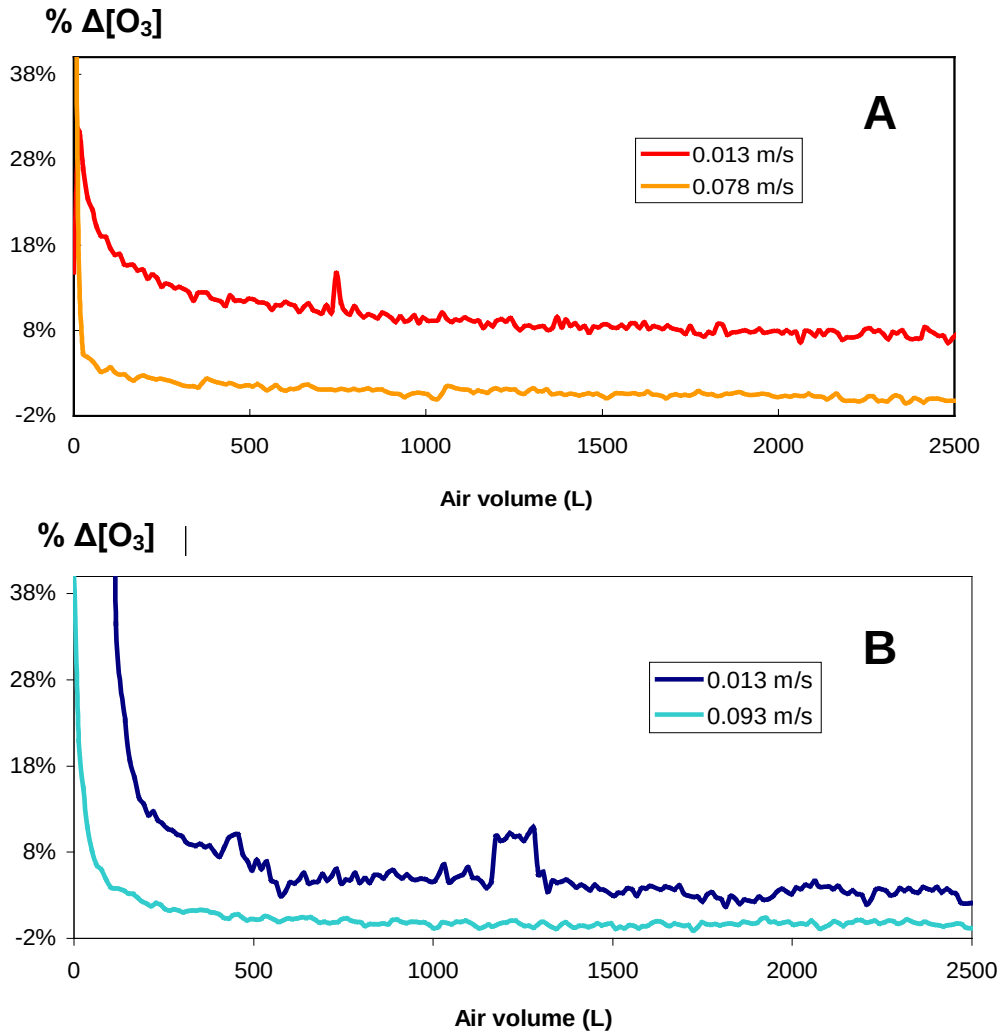


Figure 7-S: Ozone breakthrough curves for the FG1 filter used in LBNL, exposed to 150 ppb ozone at two different flow conditions under A) humidified air, and B) dry air.