FINAL PROGRESS REPORT

FORMALDEHYDE AND OTHER POLLUTANTS FROM OZONE REACTIONS IN VENTILATION SYSTEMS

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LIST OF TERMS AND ABREVIATIONS

ASHRAE	American Society of Heating, Refrigerating and Air Conditioning Engineers
BASE	Building Assessment Survey and Evaluation Study
BC	Black Carbon
BRS	Building-related Symptoms
Cal EPA	California Environmental Protection Agency
CP	Cotton/Polyester Blend
DNPH	Dinitrophenylhydrazine
E	Emission rate for a sample of filter media
E_{FA}	Aldehyde emission rate per unit filter face area
FG	Fiberglass
FTIR	Fourier Transform Infrared Spectrometry
GC/MS	Gas Chromatography / Mass Spectrometry
HPLC	High Performance Liquid Chromatography
HVAC	Heating, Ventilation and Air Conditioning
IAQ	Indoor Air Quality
IC	Ionic Chromatograpy
ICPMS	Inductively Coupled Plasma Mass Spectrometry
LBNL	Lawrence Berkeley National Laboratory
LOD	Limit of Detection
ORs	Odd Ratios
PAH	Polycyclic Aromatic Hydrocarbon
$PM_{2.5}$	Particulate Matter of < 2.5 micrometers
PO	Polyolefin
POAK	Port of Oakland
ppb	Part-per billion
PS	Polyester/Synthetic
PTR-MS	Proton Transfer Reaction Mass Spectrometry
Q_{FA}	Outdoor air flow rate per unit filter face area
R	Ratio of filtration surface media to filter face area
RH	Relative Humidity
S	Surface of filtration media
SBS	Sick Building Syndrom
SVOC	Semi-volatile Organic Compound
US EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
WHO	World Health Organization
WRA	Work-related Asthma
ΔC	Steady-state aldehyde indoor concentration increase

ABSTRACT

Title: Formaldehyde and other pollutants from ozone reactions in ventilation systems
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Final Report Abstract:

Formaldehyde is a harmful pollutant emitted by several sources in the indoor work environment. In office buildings provided with heating, ventilation and air conditioning (HVAC) systems, chemical reactions of atmospheric ozone or water vapor with filtration media may contribute to the formation of formaldehyde and other pollutants of concern. Understanding these reaction mechanisms and assessing their overall contributions to indoor pollutant levels will allow for an efficient control of those sources.

We investigated chemical reactions on the surface of filters used in HVAC systems that lead to the formation of indoor pollutants. Specific Aims of the study were 1) to identify key constituents of particle-loaded HVAC filters that may react with ozone to generate indoor pollutants, 2) to establish the reaction rates and mechanisms that lead to the formation of pollutants, assessing the effect of filter moisture content on pollutant yield, and 3) to evaluate the overall impact on the indoor work environment. This project involved the experimental study of reactions of ozone and water vapor with used and unused filtration media under controlled conditions in a laboratory setting. Different types of filters were used to compare across a wide range of materials. Tested filters were installed and retrieved from two buildings in the Berkeley/Oakland area under different types of environments with prevalence of vegetation and urban pollution, respectively.

Chemical analysis revealed the presence of mineral dust, black carbon, polymeric species and semivolatile organic compounds (SVOCs) on the surface of used filters, with variations associated to the different local environments at each site. We identified precursors and byproducts of ozone chemistry on filter surfaces. Our results confirmed that reaction with ozone and with water vapor (hydrolysis) as air flows through particle filters can constitute a small, albeit measurable, source of formaldehyde and other indoor pollutants. The effect of moisture was observed at 50% relative humidity (RH) and increased significantly at 80% RH. High formaldehyde levels were observed when humidified air passed through fiberglass filters, yielding estimated indoor concentration increases of up to 4 – 6 $\mu g/m^3$. These values are comparable with typical formaldehyde levels in office buildings, suggesting that hydrolysis of filter constituents in some cases may become a significant source under high relative humidity conditions.

SECTION 1 – SUMMARY

1.1. KEY FINDINGS

The results of this study confirmed that reaction with ozone and with water vapor (hydrolysis) as air flows through particle filters may constitute a source of formaldehyde and other indoor pollutants. In comparison with other sources, filters make likely a relatively small, albeit measurable, contribution. The amount of ozone reacted was higher when the filters were loaded with particles and when the air was humidified. Chemical analysis of the dust and particles (“filter cake”) deposited in used filters revealed the presence of inorganic species (mineral dust), black carbon, polymeric species and semivolatile organic compounds (SVOCs). More than 110 individual SVOCs were identified, and attributed to different indoor and outdoor sources, or identified as byproducts of oxidation. Filters from a building at Lawrence Berkeley National Laboratory showed significantly different composition than filters retrieved from a building at the Port of Oakland, due to their very different local environments.

A key finding of this study is the formation of formaldehyde when humidified air passed through some filter types in the absence of ozone, suggesting that hydrolysis of filter constituents or additives may be a significant formaldehyde source. At least one series of fiberglass filters with different levels of tackifier (impaction oil) coating proved to be a substantial source of indoor formaldehyde when the filter was subjected to high humidity conditions. The largest increases of indoor formaldehyde concentrations under humidified air in the absence of ozone were estimated based on the highest steady-state formaldehyde emission rate measured on fiberglass filter media at high face velocity (0.5 m/s). In laboratory tests, initial formaldehyde concentrations increases across the filter after 24 hours of operation were between 5.3 and 13 ppb, and steady-state formaldehyde concentrations increased across the filter by up to 4.2 $\mu g/m^3$ and 6.0 $\mu g/m^3$ after 10 days, when the filter was exposed to room temperature air at 50% RH and 80% RH, respectively. Such increases in formaldehyde emission rates with RH in the absence of oxidative conditions (e.g., ozone) suggests that formaldehyde is formed as a byproduct of the hydrolysis of filter additives. High formaldehyde emissions measured from filters that do not contain tackifiers indicate that these additives are not the source of the formaldehyde. Instead, the data suggest that formaldehyde is most likely emitted from hydrolysis of other additives such as polymers and fiber binders. Our results also suggest that water vapor may be the limiting reactant of hydrolysis under the operating air flow regimes. Formaldehyde emission rates increased roughly in proportion to the air velocity, indicating that the reactants participating in the hydrolysis process are not significantly depleted when the system operates at high face velocity.

While the main findings of this study are supported by the experimental data, there are limitations and questions that will need additional investigation. Some experimental variables need to be explored further, such as the effect of cyclic temperature changes, a wider range of air velocities, the frequency and duration of periods of high humidity, and the role of condensed water impinging on the filter surface. In addition, only a limited number of filters from a few manufacturers were employed in this study.

1.2. TRANSLATION OF FINDINGS

In commercial buildings, the supply airstream (mixture of outdoor and return air) upstream of heating and cooling coils is the most common location for particle filters. For recirculated indoor air, if indoor RH is often maintained near 50%, the filter will be exposed to the same level of humidity. On the other hand, many HVAC systems now use an airside economizer, which increases the outdoor air beyond the minimum ventilation requirements, often to 100% of the total supply airflow, during moderate weather when it is suitable for "free" cooling. When the system is operating under the economizer mode, it is possible for the filter to be periodically exposed to RH as high as 80% under humid climate conditions. Assuming no or little effect of the lower outdoor air temperatures on formaldehyde emission rates, the indoor formaldehyde concentration increases were estimated to be as high as 4 to 6 $\mu g/m^3$. These values are of the same order of magnitude of typical indoor formaldehyde levels in office buildings, suggesting that hydrolysis of filter additives may constitute a significant source under high relative humidity conditions. These high emissions were estimated to last over a period of 50 to 100 days after filter installation. Filters are usually changed every 120 to 190 days, but often the HVAC system operates only about half of the time. Hence, formaldehyde emissions from such filter types may be a persistent significant source of indoor formaldehyde levels in buildings over much of the filter deployment period (typically 3 to 6 months). Additionally, we showed in this study that the emissions of formaldehyde from soiled filters were higher than their clean counterpart, possibly due to added moisture retained by dust and particles ("filter cake").

1.3. OUTCOMES AND IMPACT

We identified chemical processes that lead to the formation of volatile oxygenated indoor pollutants under the range of humidity conditions commonly observed in HVAC systems. This information was incorporated into a model to predict the daily generation of formaldehyde under typical operating conditions for HVAC systems. The information generated in this study will contribute to providing the basis for assessing contributions of ozone-driven chemistry and other chemical reactions to indoor pollutant exposure levels. This information is vital to designing and implementing methods to mitigate exposure to pollutants generated indoors. In particular, this study may facilitate the identification of filtration media containing critical precursors of formaldehyde formation, assist the design of improved HVAC systems and filters that minimize the release of harmful chemical indoors, and identify improvements in building air handling practices.

SECTION 2: SCIENTIFIC REPORT

2.1. BACKGROUND

2.1.1. Formaldehyde, indoor air quality and occupational health

Asthma and allergies affect 6% and 20% of the 89 million US workers in nonagricultural, nonindustrial indoor settings, respectively. More than 20% also report nonspecific acute effects of indoor work exposures or conditions – including “sick building syndrome”, SBS – with a frequency higher than weekly. The estimated productivity losses due to building-related symptoms are between 20 and 70 \$B yr^{-1} (Mendell et al, 2002). For asthma, epidemiological studies have found a correlation between symptoms and indoor VOCs, particularly formaldehyde (Mendell et al, 2007, Wieslander et al, 1997; Norback et al, 1995; Delfino, 2002). Changes in nasal lavage fluids after formaldehyde inhalation suggested non-specific proinflammatory properties (Pazdrak et al, 1993). Additional concern about chronic exposures to indoor formaldehyde arises from its listing by the US EPA as a probable human carcinogen (group B1, US EPA, 1999) and its classification by the World Health Organization as a known human carcinogen (Cogliano et al, 2005). Formaldehyde is an ubiquitous indoor pollutant: mixing ratios measured in 100 office buildings as part of the BASE study (US EPA, 2003; Girman et al, 1995) were in the range 0 – 50 ppb, with a mean of 10.9 ppb, a median of 9.0 ppb and a standard deviation of 1.2 ppb. 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). Indoor formaldehyde levels often exceed the recommended exposure limit (REL) for an 8 – 10-hour average exposure and/or ceiling of 0.02 mg m^{-3} (16 ppb) (NIOSH, 1997). Formaldehyde is emitted by various indoor materials such as cabinetry and wooden building products (Hodgson et al, 2002) and is generated in reactions of gas-phase alkenes with indoor ozone and OH radicals (Fan et al, 2003). The same indoor chemical reactions generate a large number of ultrafine aerosol particles. Formaldehyde and acetaldehyde were the most abundant carbonyls (60 – 70 % of the total) collected in indoor and personal samples as part of a large study of residential indoor, outdoor and personal air (RIOPA). In that study, due largely to the influence of indoor sources, indoor carbonyl concentrations provided a better prediction of personal exposures to aldehydes than outdoor concentrations measured simultaneously (Liu et al, 2006; Weisel et al, 2005).

The current indoor exposure scenarios are likely to worsen in the near future, as various alternatives for adaptation to climate change suggest modifying building designs to cope with higher temperature and enhanced need for summer cooling (EEA, 2004). Those modifications will likely include increased use of air conditioning and, to save energy, lower air exchange rates. Furthermore, tighter building envelopes and reduced air exchange are tools to improve energy efficiency in the built environment, but may also lead to overall higher indoor air pollutant concentrations. Local conditions such as the "urban heat island effect", particularly in large metropolitan regions, can also lead to higher demand in air conditioning use. In addition, expanding urbanization and changes in land use patterns may contribute to increased surface-level ozone concentrations, as predicted for certain areas in the Northeastern US (Civerolo et al, 2007).

In spite of the widely appreciated health problems associated with formaldehyde and other airborne oxygenated species, there remains a critical gap in our ability to identify and eliminate the most important sources of these toxic and irritant VOCs from the indoor work environment. This study intended to identify a potentially significant source of formaldehyde and other indoor air toxics - ozone reactions on HVAC filters - and quantified its overall contribution to workplace air. We also provide insight on the chemical processes leading to the formation of these indoor pollutants. By obtaining a quantitative understanding of this major source of formaldehyde and other indoor pollutants and aerosols, we will be able to successfully implement specific engineering solutions to improve air quality in the indoor work environment. We provide basic chemical information that can assist in the improvement of building air handling practices and in the development of new filtration media that reduce or eliminate emission of toxic secondary pollutants. We intended to address priority research needs outlined by the NORA Indoor Environment Team, including the identification and quantification of pollutant sources and rates of emission, and the identification of strategies that reduce or prevent indoor chemical and particulate pollutants of concern (Mendell et al, 2002). We also addressed priority research needs identified at the 2004 Workshop "Indoor Chemistry and Health", conceived and sponsored by NIOSH/NORA, where indoor surface chemistry was recognized as a gap in our current understanding of how indoor pollutants interact (Weschler and Wells, 2004). Ozone surface chemistry on HVAC filters was specifically identified by Weschler (2004) as a key process affecting indoor air quality. Work reported at the 10th International Conference on Indoor Air Quality and Climate ("Indoor Air 2005", Beijing, China), the Healthy Buildings 2006 Conference (Lisbon, Portugal), the first workshop on Interfacial Chemistry in Indoor Environments (Berkeley, July 2007) and at the ASHRAE IAQ Conference (Baltimore, October 2007) indicated also that ozone chemistry on HVAC filters was an emerging topic attracting growing interest in the scientific community (Hyttinen et al, 2005; Bekö et al, 2005; Zhao et al, 2007; Fadeyi et al 2006; Hyttinen et al 2006b; Hyttinen et al, 2007). A summary of the Berkeley meeting was published as a feature article in *Environ. Sci. Technol.* by G. Morrison (2008).

The NIOSH Worker Health Chartbook (NIOSH, 2004) recognizes work-related asthma (WRA) as the most common occupational respiratory disease reported in several developed countries. WRA is asthma that is caused or made worse by exposures in the workplace. Population-based estimates suggest that 15%–23% of new-onset asthma cases in adults are work related. Four States (California, Massachusetts, Michigan, and New Jersey) maintained WRA surveillance programs during a 7-year period (1993–1999), observing that by occupation, the highest percentage of cases occurred among operators, fabricators, and laborers (33 %), followed by managerial and professional specialty (20 %), and technical, sales, and administrative support jobs (19%). Agents frequently associated with WRA were miscellaneous chemicals (20 %), cleaning materials (12 %) and indoor pollutants (10 %), among others. The clear links between exposure to airborne pollutants in the workplace and health effects highlight the need for a more complete description of indoor pollutant sources, dynamics and fate in the work environment.

Recent data have emerged indicating that formaldehyde and other VOCs, or their sources, increase the risks of asthma and allergy outcomes. Mendell (2007) reviewed the relevant scientific literature from studies performed in sets of homes. This review determined that most but not all studies have found moderate to strong increases in respiratory and allergic health effects among children in homes with higher concentrations of selected VOCs or SVOCs, including formaldehyde and some types of phthalates (softening agents for some plastics), or in homes with larger amounts of some VOC or SVOC sources, particularly particleboard (a formaldehyde source), plastics, and recent paint. The evidence of increased asthma or allergy outcomes or respiratory effects in association with high formaldehyde levels was particularly striking. As documented by Mendell (2007), higher indoor concentrations of formaldehyde or presence of particleboard were associated with the following outcomes:

- diagnosed asthma (Rumchev et al., 2002, Krzyzanowski et al., 1990, Jaakkola et al., 2004);
- diagnosed chronic bronchitis (Krzyzanowski et al., 1990);
- increased exhaled nitric oxide, a marker of airway inflammation elevated for asthmatics (Franklin et al., 2000);
- increased wheeze (Jaakkola et al., 2004, Venn et al., 2003);
- respiratory symptoms (Garrett et al., 1999), but not in two other studies (Quackenboss et al., 1989; Krzyzanowski et al., 1990);
- adverse effects on lung function in two studies (Krzyzanowski et al., 1990, Quackenboss et al., 1989), but not in one additional study (Franklin et al., 2000);
- atopy and increasing severity of sensitization (Garrett et al., 1999) and allergy (Jaakkola et al., 2004).

Some of the studies documented increased risks when formaldehyde exceeded concentrations as low as 16 and 24 parts per billion. Such concentrations are common indoors and may originate to a significant extent from ozone reactions on filters, according to recently published data (Hyttinen et al, 2006a; Hyttinen et al, 2007).

A review by the California Environmental Protection Agency (California EPA, 2007) considered a broader set of evidence, e.g., studies of workers and animals, in homes and environmental chambers, as well as research on toxicological mechanisms. It also identified a linkage between formaldehyde and increases in asthma-like respiratory symptoms, which is the basis for the proposed 7 ppb (8 hour) guideline. Health Canada (2006) has also established a 40 ppb (8 hour) target to prevent formaldehyde-related respiratory symptoms in children. There is clear evidence that formaldehyde can provoke sensory irritation symptoms, although, the associated concentration thresholds are uncertain. Some related guidelines for preventing sensory irritation symptoms are in the 75-100 ppb range for exposures on 1-hour or less (Health Canada 2006, World Health Organization (2000), California EPA (1999, 2000). The California EPA (2007) established a 44 ppb (1 hour) guideline to prevent eye irritation symptoms. There is also evidence that formaldehyde and some other indoor VOCs increase risks of cancer. In 1996 and again in 2006, the International Agency for Research on Cancer of the World Health Organization (2006) concluded that formaldehyde is a human carcinogen. The National Institute for Occupational Safety and Health (NIOSH, 1992) established a 16 ppb (8 hour) guideline for formaldehyde based on the evidence of increased nasal cancer risks. In a recent analysis by Loh (2007), the cancer risk from non-occupational formaldehyde exposures was estimated to be approximately one in 10000, which is well above the level usually considered acceptable for outdoor air pollutants (one in a millon).

2.1.2. Indoor ozone chemistry as a source of formaldehyde and poor IAQ.

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. In a review published in *Environ. Health Perspectives*, Weschler (2006) described multiple associations between outdoor ozone and both morbidity and mortality, and concluded that these are likely due to indoor exposures to ozone and ozone-initiated products. Occupational exposure to ozone-related indoor pollutants in mechanically ventilated buildings affects administrative, managerial, professional, janitorial and sales personnel working in office buildings, teachers and school staff, health care professionals and retail store employees, among others. Office settings are the workplace for a broad range of professions, as the US economy experienced major transformations from a manufacturing base to one where ‘white collar’ professions and service jobs dominate. In addition, certain subsets of the working population face higher risks due to inherently higher susceptibility to asthma exacerbation after exposure to air toxics and aerosols (Weisel, 2002; Peden, 2002) or from working in a geographical region with particularly high ambient ozone levels (e.g., the Los Angeles or Houston areas). Other subsets of workers at higher risks of exposure to ozone-related secondary pollutants (although not directly linked to reactions in HVAC systems) include cleaning personnel who spend time in close proximity to chemicals emitted by cleaning products such as terpenoids, that are highly reactive with ozone (Nazaroff and Weschler, 2004;

Destaillats et al, 2006a); and flight crews, due to frequent high in-flight ozone levels (Spengler et al, 2004; Weschler et al, 2007; Strøm-Tejsen et al, 2007). Hence, the proposed study addresses health problems that affect many workers in a range of occupations.

Ozone is produced photochemically in the troposphere primarily by photolysis of NO_2 (Finlayson-Pitts and Pitts, 2000). Although it is highly reactive, the atmospheric lifetime of ozone is long enough to allow for its transport to the indoor environment, where it reacts at rates that are similar to or higher than ventilation removal rates. Weschler (2000) reviewed available information on simultaneous indoor-outdoor (I/O) ozone measurements, finding that in most cases I/O ratios were between 0.2 and 0.7. In addition, the I/O ratios were inversely proportional to surface removal rates. Grøntoft and Raychaudhuri (2004) showed a wide range of ozone deposition velocities on various surface materials. Gypsum board and carpet, two prevalent indoor surfaces, were among the materials with higher deposition rates, in the range 0.06-0.14 cm s^{-1} (equivalent to air exchange rates of 3 to 7 h^{-1}). In a related study with the same materials, Grøntoft et al (2004) observed increasing ozone deposition rates with increasing relative humidity, suggesting the important role of aqueous surface films in the ozone uptake process. Ozone reactions on indoor surfaces generate gas-phase and aerosol secondary emissions. Morrison and Nazaroff (2002) observed that the emission rates of aldehydes from carpets increased markedly when samples were exposed to ozone. In contact with ozone, other building materials (rubber adhesive, wood board) generated sub-micron particles in the range 0.01 – 1 μm (Aoki et al, 2005).

2.1.3. HVAC filters and indoor air quality.

HVAC systems are present in commercial buildings, hospitals, schools, industrial facilities and in a large fraction of the residential building stock in the US. These systems are fitted with filters to remove airborne particles from incoming outdoor air (outdoor air is often not provided in residences) and from recirculated indoor air. Air filtration reduces considerably the burden of airborne particulate matter, thus improving indoor air quality while protecting the fan, motor, heat exchangers and other HVAC hardware. A significant portion of air supplied by an HVAC system often includes recirculated indoor air to reduce energy costs for heating and air conditioning. Typical HVAC filters do not remove volatile organic compounds (VOCs) and other gas phase pollutants, and may become instead a source of airborne pollutants. A number of studies have shown an association between HVAC filters, particularly used filters on which particles have accumulated, and lowered perceived air quality. 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). HVAC filters are also substrates for microbiological growth (Noris et al, 2011).

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. When HVAC systems supply only outdoor air, the ozone concentrations at the filters will approximately equal the outdoor air concentrations (up to 50-100 ppbv in U.S. cities with elevated ozone), which are much higher than typical indoor air concentrations (5-30 ppbv). However, when a mixture of outdoor and recirculated indoor air is filtered, the ozone concentration at the filters is between the outdoor ozone concentration and the lower indoor ozone concentration. Ozone was shown to react with filter materials and with particles and dust deposited on their surface, leading to decreases in ozone concentrations and emission of a low to moderate level of oxidation byproducts (Hyttinen et al, 2006; Hyttinen et al, 2007; Zhao et al, 2007).

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, tackifiers and other additives. Emissions of aldehydes from filters incubated under extreme high humidity conditions was also reported. 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.

HVAC systems can have a strong effect on outdoor-to-indoor ozone transport. A survey of 43 residences showed that the I/O ratio was 68 ± 18 % in homes without air-conditioning, but less than 10 % in homes with air conditioning in use (Lee et al, 1999). This is a clear indication of the major role that HVAC systems may play in the uptake of outdoor ozone and its conversion to oxidation products and aerosol particles that are then introduced into the indoor environment. Based on this evidence, we hypothesize that ozone reactive deposition in mechanically ventilated buildings is taking place predominantly on the surface of particle-laden HVAC filters, the first major surface encountered by ozone during its transit indoors. Zhao et al (2007) estimated that filters contributed from 22% to 95% of total ozone removal in HVAC systems. Several studies have shown that loaded HVAC filters contributed to the degradation of perceived air quality, SBS symptoms and performance of office work (Pasanen et al, 1994; Clausen et al, 2002; Clausen, 2004). Hyttinen et al (2003) observed the reaction of ozone with particle-laden filters used during a year in office buildings. Ozone removal was ~5 % during winter tests and ~11 % in the summer, a period with higher relative humidity. Extent of ozone removal was affected also by the nature of the particles collected on filters, with up to 25-30% continuous abatement by sooty filters (Hyttinen et al, 2006a). Formaldehyde concentrations downstream of the filters were higher than upstream values. In subsequent studies, the same authors reported the formation of formic acid along with formaldehyde (Hyttinen et al, 2005). Up to 11% of ozone removed participated in the production of formaldehyde, suggesting that this reaction may be a significant contributor to indoor formaldehyde levels (Hyttinen et al, 2006a).The creation/growth of ultrafine particles during similar experiments was attributed to desorption of low volatility oxidation products generated in ozone reactions with filter material (Bekö et al, 2005), and to the reaction of ozone with sorbed reactive VOCs such as terpenoids (Fadeyi et al, 2006). Bekö et al (2003) evaluated the ozone removal efficiency of particle-laden HVAC filters, observing that an initial efficiency of 55 % dropped to ~ 5 % within an hour. However, upon successive exposures to ozone after a 24-48 h period in contact with clean air, the removal efficiency returned to essentially the same initial value, suggesting that slow processes (diffusion, chemical reactions) regenerated the ozone uptake capacity of the particles captured by the filter. The same effect was observed by Zhao et al (2007), who suggested that ozone reactivity is limited by internal diffusion of reactive species from the interior of particles. Formaldehyde and other detected byproducts are not only of concern due to their own toxicity, but also because their presence indicates co-emission of other short-lived irritants of concern (Weschler, 2006).

One of the main challenges associated with this study was obtaining a good chemical characterization of the material captured by HVAC filters –the filter cake, in order to better understand ozone reactions with dirty filters. A recent study provided preliminary characterization of HVAC filter dust, showing the presence of a complex organic mixture (Hyttinen et al, 2006b; Hyttinen et al, 2007). Variability in the chemical composition can be expected not only among different geographical locations but also within the same region or city, as particles collected by building ventilation systems are also influenced by nearby local sources such as truck traffic, construction activity and wood burning, in addition to regional PM. However, certain components of urban particulate matter such as Diesel PM and ammonium sulfate are ubiquitous, and can be expected to constitute a significant fraction of the studied systems. Sawant et al (2004) observed that organic carbon (OC) was the largest contributor to $PM_{2.5}$ in 20 Southern California residences (40-60% of the total mass) and 7 schools (26%), and that HVAC systems were efficient at filtering $PM_{2.5}$ from outdoor air. Using a dilution source sampling system, Kleeman et al (2000) observed that organic carbon comprised roughly half of the mass of particles from Diesel vehicles and most of the mass of PM from gasoline-powered vehicles. Diesel particles contributed from 10 to 75 % of the optically active PM in urban areas (Lloyd and Cackette, 2001). Metts et al (2005) quantified ozone removal by Diesel PM collected on Teflon filters, observing elimination of 6 wt% ozone by the aerosol particles. Major organic constituents of Diesel particles able to react with ozone or with OH radicals –formed upon O_3 decomposition– include high molecular weight alkanes, carboxylic acids and polycyclic aromatic hydrocarbons (PAH) (Schauer et al, 1999) Organic coatings on crustal or mineral particles could alter their heterogeneous chemistry: Usher et al (2003) observed that SiO_2 particles coated with a C_8-alkene displayed 40 % higher reactivity towards ozone than untreated SiO_2. However, coating with a C_8-alkane had the opposite effect. PM from biomass combustion also contains classes of organic compounds that react with ozone and OH (Schauer et al 2001).

A large fraction of indoor air is typically recirculated by the HVAC system, particularly during extreme outdoor temperatures and high humidity. Recirculation can trap suspended dust and semivolatile chemicals present in indoor air by allowing the SVOCs to sorb onto the surfaces of particle-laden HVAC filters. The filter cake presents ever-increasing surface area to the airstream. Several classes of SVOCs that are used indoors are also very reactive towards ozone, particularly terpenoids from cleaning products, air fresheners and scented oils. Hyttinen et al (2001) identified terpenes, carboxylic acids and aldehydes as the main VOCs desorbed from dust collected on air filters. Phthalate esters from plasticizers were the most prevalent indoor SVOCs that were detected in large quantities in dust (Rudel et al, 2003). Phthalate esters on HVAC surfaces may also be susceptible to oxidation (Howard et al, 1991).

2.1.4. Formaldehyde formation through hydrolysis of polymeric filter additives.

While ozone-driven oxidation on filter surfaces has been the initial focus of this study, we observed also that some filter types were a source of formaldehyde even in the absence of ozone and deposited dust. Those emissions likely originate in reactions involving the decomposition of additives present in the filter media in the presence of water vapor. Filter fibers are often coated with binders, adhesives and tackifiers that preserve the integrity of the media and improve filtration efficiency. The main constituents of tackifiers are glycols, polyethylene, nonylphenylethers, hydroxypoly oxyethelene and ethylene oxide (based on manufacturers' description). Often, adhesives and binders for nonwoven filtration media include formaldehyde-based polymeric resins in their formulation. The functional groups present in these filter additives may undergo reaction with water to give rise to a variety of decomposition products such as formaldehyde, acetaldehyde and association products such as higher glycols and polymers.

Based on preliminary observations described in this report, we measured formaldehyde emission rates from clean HVAC filters in the absence of ozone. Filters were exposed to various relative humidity (RH) levels, with different face velocities of air flowing through the filter media. The measured formaldehyde emission rates were then used to estimate the impacts on indoor formaldehyde levels under model scenarios.

2.1.5. Earlier contributions by our group

2.1.5.1. Statistical evaluation of the BASE study data

The BASE study (US EPA, 2003; Girman et al, 1995) included 100 non-complaint buildings selected randomly as representative of the US office building stock. Extensive indoor and outdoor environmental monitoring was performed from 1994 to 1998. We compared a subset of the BASE data for indoor VOC levels with average and maximum outdoor O_3 concentrations. Notably, no significant ($p < 0.05$) relationships were found for any VOC except formaldehyde, which was significantly correlated with maximum O_3 levels. Table 1 presents data that we analyzed recently, showing a clear correlation between peak outdoor O_3 and indoor formaldehyde, but not between outdoor O_3 and a variety of other common indoor VOCs. The formaldehyde I/O ratio was 4.1, indicating that indoor sources predominated.

Table 1: Correlation of indoor VOC concentration and outdoor ozone concentration for 100 buildings included in the US EPA BASE study.

Indoor VOC	Average outdoor ozone		Maximum outdoor ozone	
	R value	p-value	R value	p-value
α-pinene	0.01	0.96	0.09	0.36
Benzene	-0.19	0.06	-0.14	0.15
d-limonene	-0.02	0.82	-0.04	0.70
Ethyl acetate	0.11	0.28	0.09	0.36
Formaldehyde	0.18	0.07	***0.30***	***0.0025***
Naphthalene	-0.11	0.29	-0.03	0.76
Octane	-0.09	0.36	-0.11	0.27
Styrene	-0.12	0.22	-0.04	0.69
Tricloroethylene	0.15	0.14	0.09	0.38

Outdoor ozone also correlated with outdoor formaldehyde concentrations for average outdoor ozone (R = 0.34; p = 0.0006), and for maximum outdoor ozone (R = 0.43; p < 0.0001). The net indoor formaldehyde contribution, calculated as the difference between indoor and outdoor formaldehyde concentration, is positively correlated with outdoor ozone for both average outdoor ozone (R = 0.19; p = 0.06) and maximum outdoor ozone (R = 0.17; p = 0.09). These values suggest the possibility that the strong association of outdoor ozone with indoor formaldehyde is due to indoor chemistry. These data support our hypothesis that ozone-initiated chemistry is one of the major sources of formaldehyde in the indoor work environment. Furthermore, higher outdoor ozone levels were not correlated with enhanced depletion of gas-phase reactive terpenoids such as α-pinene and d-limonene. This additional observation suggests that formaldehyde is produced in surface reactions that consume most outdoor ozone before it reaches the bulk of the indoor air, possibly during its transit through the HVAC system.

Acetaldehyde and acetone, other carbonyls that can be generated in ozone-initiated reactions, were measured in a subset of buildings, showing a significant correlation with peak outdoor ozone similar to that described above for formaldehyde (Apte et al, 2008). Outdoor ozone can only contribute to increases in indoor formaldehyde to a minor extent, based on a study of 354 US residences, in which the median indoor/outdoor formaldehyde concentration ratio was 3.1, indicating the preeminence of indoor sources (Liu et al, 2006).

A subset of 34 buildings from the BASE study was analyzed to determine the separate and joint associations of filter medium -polyester/synthetic (PS) or fiberglass (FS)- and outdoor ozone concentration (above/below the median, 67.6 $\mu g/m^3$) with building related symptoms (BRS). Using logistic regression models and general estimating equations, we estimated odds ratios (ORs) and 95% confidence intervals for the association of filter medium, ozone, and filter medium*ozone with BRS. Relative to FG+low ozone, PS alone or high ozone alone each were significantly ($p<0.05$) associated only with fatigue/difficulty concentrating (ORs = 1.93, 1.54, respectively). However, joint exposure to both PS+high ozone, relative to FG+low ozone, had significant associations with lower and upper respiratory, cough, eye, fatigue, and headache BRS (ORs ranged from 2.26-5.90). Joint ORs for PS+high ozone for lower and upper respiratory and headache BRS were much greater than multiplicative, with interaction p-values < 0.10. Attributable risk proportion (ARP) estimates indicate that removing both risk factors might, given certain assumptions, reduce BRS by 26%-62%. These findings suggest adverse health consequences from chemical interactions between outdoor ozone and PS filters in buildings. (Buchanan et al, 2008).

These studies suggested 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), and suggested an easy and practical means of reducing BRS – avoiding synthetic filters. They also provided additional rationale for this study, as more information on chemical processes is needed to make recommendations.

2.1.5.2. Indoor ozone chemistry

Our group identified several indoor sources of formaldehyde, including materials such as cabinetry and wooden building products (Hodgson et al. 2002), office equipment (Destaillats et al. 2008) and reactions of terpenoids with indoor ozone and OH radicals (Destaillats et al. 2006a). The same reactions generate high levels of ultrafine aerosol particles (Coleman et al. 2008). Kinetics and mechanisms of ozone-induced reactions taking place in the gas-phase and on surfaces were studied using bench-scale and real-size environmental chambers (Destaillats et al, 2006b; Singer et al, 2006). We investigated the reaction of ozone with volatile components emitted by cleaning products and air fresheners at realistic indoor concentrations. Gas-phase concentrations of reactive terpenoids and oxidation products were measured once the system reached steady-state flow conditions. We observed that formaldehyde was the most prevalent secondary pollutant generated in these reactions, with yields of 20-30% with respect to ozone consumed under most conditions. Acetaldehyde, acetone, glycolaldehyde, formic acid and acetic acid were also detected when emissions from two of the cleaning products were exposed to ozone. Immediately after mixing of reactants, a scanning mobility particle sizer detected particle nucleation events that were followed by a significant ultrafine particle growth, at rates of 2 – 5 nm/min. The production of secondary gaseous pollutants and particles depended primarily on the ozone level and was influenced by other parameters such as the air exchange rate. We also measured OH radical concentrations in the range 0.04 – 200 x 10^5 molecules cm^{-3} (Destaillats et al, 2006a).

Reactions similar to those in the gas-phase described above were also observed when ozone interacted with surface-bound chemicals. When the same household products were applied directly on a glass plate allowing for complete evaporation of their volatile components, exposure of the dry residue to ozone yielded formaldehyde and other gas- and particle-phase oxidation products. (Destaillats et al, 2006a).This result is a clear indication that terpenoids with low-volatility such as α-terpineol and other terpene alcohols (that are commonly present in the formulation of cleaning products and air fresheners) have the potential to sorb to indoor surfaces and to react with ozone long after their original emission. Chemicals sorbed to indoor surfaces or HVAC filters can have long indoor residence times (from several hours to weeks) largely exceeding typical air exchange rates. In those conditions, ozone can react not just with very reactive chemicals (like the terpenoids mentioned above) but also with many other organic species that are typically considered non-reactive in the gas-phase. For example, in an independent study (Destaillats et al, 2006b) we evaluated the reactivity of nicotine sorbed to model surfaces towards ozone using a similar chamber design. In the presence of moderate ozone levels (14 – 40 ppb), nicotine present in the surface of Teflon or cotton surfaces reacted with ozone at rates that were competitive with its desorption rate. When surface nicotine reacted with ozone in the absence of water (i.e., dry air), its gas phase levels decreased with respect to desorption values measured in the absence of ozone by one order of magnitude after 100 hours of exposure and by two orders of magnitude after a week. By contrast, when ozone was introduced in humid air (70% RH), the surface reaction was completely inhibited and the desorption curve was similar to that recorded in the absence of ozone. This dramatic inhibition of O_3 reactions was attributed to the presence of water in the surface, since cotton increased 7 %wt due to water uptake at 70 % RH. However, humidity effects were not observed when the reaction took place on hydrophobic Teflon surfaces. These results show that water uptake by surfaces is a critical factor to consider when ozone reacts with surface materials or sorbed species. We identified the principal stable byproducts of ozone-nicotine reaction as formaldehyde, N-methyl formamide, nicotinaldehyde and cotinine.

2.2. SPECIFIC AIMS

Our *long-term research goals* are to contribute to understanding indoor chemical processes that yield harmful chemicals and aerosols and to reduce workers' exposure to these pollutants. The *objective* of this study was to provide fundamental information on reactions of ozone with dust, particulate matter and semivolatile chemicals deposited on HVAC filters, as well as with filter media itself, in order to identify chemical processes leading to formation of formaldehyde and other indoor pollutants of concern. Our *central hypothesis* has been that reaction of ozone with particulate matter and chemicals deposited on HVAC filters produces significant amounts of irritating and toxic gas-phase oxidation products and secondary organic aerosols that flow into the indoor work environment. The *rationale* for the proposed research is that understanding the reaction mechanisms and assessing the overall contribution of ozone chemistry on loaded HVAC filters to indoor pollutant levels will facilitate the development of approaches to eliminate or mitigate this indoor pollution source.

Work was carried out primarily at the Indoor Environment Group (formerly Department) of Lawrence Berkeley National Laboratory (LBNL). Experiments were also carried out with colleagues from Syracuse University (Prof. J. Zhang's group) and from the California Department of Public Health (Dr. K. Kumagai and Dr. W. Chen). Our research team included chemists, engineers and public health professionals. The specific aims originally proposed for this study were:

Specific Aim #1: *Identify key constituents of particle-loaded HVAC filters that react with ozone to generate volatile indoor pollutants and secondary organic aerosols.* Our working hypothesis, based upon strong preliminary data, was that various organic constituents of the carbonaceous organic fraction of atmospheric particles, particles of indoor origin captured by the filters due to air recirculation, compounds sorbed to aerosol particles, and possibly certain components of the filter matrix can react with ozone and OH radicals generated by ozone decomposition to yield volatile oxidation products and secondary aerosols.

Specific Aim #2: ***Establish the reaction rates and mechanisms that lead to the formation of gas-phase and particulate pollutants, and assess the effect of filter moisture content on pollutant yield*.** Our working hypothesis, also based upon our strong preliminary results, was that two principal mechanisms operate: direct ozonation and radical oxidation. The effect of high moisture content in the air was a critical parameter to investigate.

Specific Aim #3: ***Evaluate the overall impact of ozone chemistry with particle-loaded HVAC filters on the indoor work environment*.** Our working hypothesis was that these reactions constitute major sources of harmful volatile chemicals and ultrafine organic aerosol in indoor workplaces.

The reported research is *innovative* because it identified surface reactions as a potentially significant source of indoor pollutants, in contrast to the focus on gas-phase chemistry placed by a majority of studies. Data from this study will be used to assess the contributions of ozone surface chemistry and other reactions to indoor pollutant exposure levels. We identified chemical processes that lead to the formation of volatile oxygenated indoor pollutants under the range of humidity conditions commonly observed in HVAC systems. This information was incorporated into a model to predict the daily generation of formaldehyde under typical operating conditions for HVAC systems. The primary *impact* of this study will be providing information vital to designing and implementing methods to mitigate exposure to pollutants generated indoors. In particular, this study may facilitate the identification of filter materials that may contain critical precursors of formaldehyde formation, designing of HVAC systems that minimize the release of harmful chemicals indoors, and improvement of building air handling practices.

2.3. METHODOLOGY

2.3.1. Specific Aim #1: *Identify key constituents of particle-loaded HVAC filters that react with ozone to generate volatile indoor pollutants and secondary organic aerosols.*

2.3.1.1. 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 (Destaillats et al, 2011). 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 2. 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 were 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 3). No significant mass change was recorded after exposure to ozone. All mass determinations were carried out at ambient laboratory relative humidity. Additional details on filter selection, deployment and handling are provided in Destaillats et al (2011).

Table 2: 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 3: 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

2.3.1.2 Chemical analysis of filter cake

2.3.1.2.1. Thermal analysis of evolved carbon

Filter dust was analyzed using evolved gas analysis as described by Hadley et al (2008) to obtain total, elemental (black) and organic carbon. Filter specimens of 2”x2” were cut, and dust was obtained using vacuum suction techniques. A 47 mm quartz filter was conditioned at 100 ^{o}C, pre-weighed and fitted into an open filter holder. The filer holder was connected to laboratory vacuum system and dust from filters was collected on the quartz filter by applying uniform vacuum across the filter surface. Both the quartz filter and the HVAC filter were pre-weighed and post-weighed to determine the mass of filter cake collected.

2.3.1.2.2. Identification of organic species in solvent extracts by gas chromatography/mass spectrometry (GC/MS)

A 2”x2” piece of each of the HVAC filter specimen was cut and weighed. The HVAC filter cake was extracted by sonicating this specimen in 20 ml of 40:40:20 hexanes/acetone/dichloromethane mixture for a period of 20 minutes. The HVAC filter was then removed from the solvent and air dried. The mass of the extracted filter was weighed over a period of 1 hour till the weight stabilized. The mass of filter cake extracted was estimated as the difference in the weights of the filter specimen before and after extraction. Extracts were filtered through Teflon filters (Millipore FHUP 0047, 2µm) to remove any suspended solids. The masses of solid residuals were determined by weighing the Teflon filters before and after filtration. 10 ml of this extract was saved for gas chromatographic analysis. The remaining 10 ml was evaporated (Turbovap) to 0.5 ml and analyzed using gas chromatography with mass selective detection.

The GC-IT-MS/MS analyses were performed on a Varian 3800 gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA) equipped with a CP8400 autosampler, Model 4000 ion trap mass detector, GC/MS Workstation v. 6.6 software, and VF-5ms column (30-m length, 0.25-mm ID, 0.25-µm film, Varian part No. CP8944). The injector was operated in splitless mode for dilute samples and split mode for concentrated samples. The injector temperature was set at 250 ^{o}C and helium was used as the carrier gas, operated at a constant flow rate of 1 mL min^{-1}. The chromatographic oven was programmed to a three step temperature ramp initially starting at 40 ^{o}C for 2 min, then ramped to 200 ^oC at the rate of 20 ^oC min^{-1} and held for 5 min at 200 ^oC and eventually ramped to 320 ^oC at 40 ^oC min^{-1} and held for 5 minutes. The total run time was 30 minutes. The MS was turned off for the initial 3 minutes to account for solvent delay and was operated under full scan (40 – 400 m.z) using electron ionization (EI) mode at 70 eV. Supelco polynuclear aromatic hydrocarbons mix (Supelco #47543 U) and individual standards were used for quantification and identification was made through the NIST GC/MS library when individual standards were not available.

2.3.1.2.3. Characterization of surface-bound species by Fourier Transform Infrared Spectrophotometry (FTIR)

Filter cake was deposited on 4 cm^2 ZnSe crystal view cell enclosed by a quartz window and analyzed for functional groups using an attenuated total reflectance (ATR) –FTIR spectrophotometer (Nicolet Magna 760) with a MCT-A detector and a KBr beamsplitter in the range 4000-650 cm^{-1}.

2.3.1.2.4. Identification and quantification of inorganic species by Ion Chromatography (IC)

Filter dust was analyzed to quantifiy anions (Cl^-, F^-, SO_4^{2-}, NO_3^-, NO_2^-, Br^-) in the filter cake. Filter dust was collected on Teflon filters (Millipore FHUP 0047, 2µm) using the same methods as described in Section 2.3.1.2.1. The collected filter cake was dissolved by sonicating in 15 ml of high purity deionized 18 **Ω** milliQ water (Dionex). The extract was filtered through Teflon filter (Millipore FHUP 0047, 2µm) and analyzed using Ion Chromatography (IC, Dionex IC2000). A calibration curve for each anion was prepared prior to the analysis using standards to estimate the concentration of anions present in the samples.

2.3.1.2.5. Identification and quantification of inorganic species by Inductively Coupled Plasma Mass Spectrometry (ICPMS)

The elemental composition of macro and trace constituents the filter dust was analyzed using a Perkin Elmer DRCII Inductively Coupled Plasma – Mass Spectrometer (ICP–MS). To measure the concentrations of trace impurities such as rare earths the instrument was used in DRC (Dynamic Reaction Cell) mode using ammonia as reaction gas to remove interferences. Other elements were analyzed in standard mode. Gallium was used as an internal standard. Dust samples were weighed out in Savillex PFA digestion beakers using a high precision balance (0.1 mg resolution) and digested on 130°C hotplate for two days using 10:1 HF:HNO_3. Samples were then dried down and re-dissolved in 6M HCl. All work was done in a cleanroom. Samples were further prepared for analysis by spiking each sample with internal standard (^{6}Li, ^{45}Sc, ^{71}Ga, ^{89}Y, ^{103}Rh, ^{115}In, ^{169}Tm) and diluting with 2% (v/v) ultra high purity nitric acid. All samples were prepared gravimetrically.

Samples were then analyzed on a Perkin Elmer SCIEX Elan DRC II ICP-MS using a multi-element method. Dynamic Reaction Cell (DRC) mode was used for K, Ca, V, Ti, Fe, Mn, Co, Cu, Zn and Se –using NH_3 as reaction gas. P and As were analyzed as PO and AsO at masses 47 and 91 using DRC mode with oxygen as a reaction gas. All other elements were analyzed in standard mode. Several reference materials were also analyzed at the same time to verify the validity of the custom in-lab-made standard. (NIST 1643e Trace Elements in water; SPEX CertiPrep CL-CRDL-1; Inorganic Ventures IV-ICPMS-71B).

2.3.2. Specific Aim #2: *Establish the reaction mechanisms and rates leading to the formation of gas-phase and particulate pollutants, and the effect of filter moisture content on pollutant yield*.

2.3.2.1. Experimental approach

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. The experimental setup is shown in Figure 1. (Destaillats et al, 2011). Air containing known levels 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).

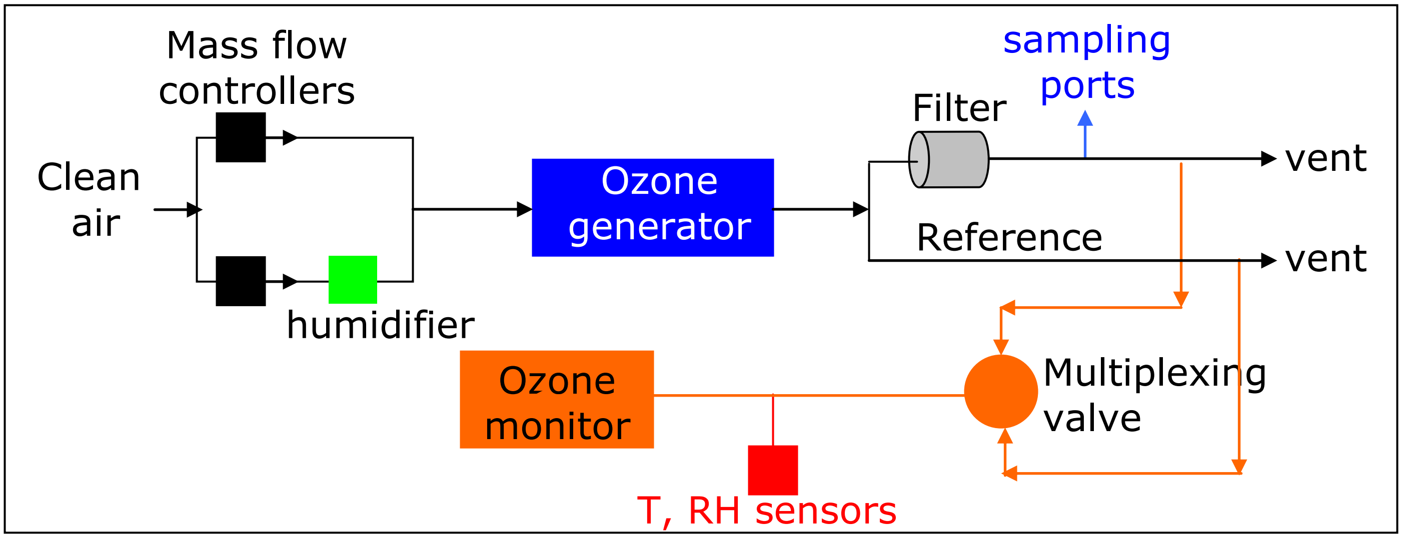


Figure 1: Experimental setup

Experiments evaluating the effect of RH on formaldehyde emissions in the absence of ozone were performed in a similar system using two groups of commercially available HVAC filters from different brand names and models (Table 2). One group contained four types of fiberglass filters, all from the same filter manufacturer, with different levels of tackifier coatings (none-, lightly-, medium-, and heavily-coated). The other group contained three types of polyester filters, all from distinct filter manufacturers, two with tackifier coatings. The filters employed in these tests were all unpleated panel or pad filters, 2.5 to 5.0 cm thick, without a filter frame. Sample coupons were cut from unused filters and tested over a wide range of RH conditions (from 15% to 85% RH). Bench-scale experiments were performed at two different face velocities: a low velocity of 0.013 m/s, and a high velocity of 0.5 m/s, typical of velocities through the media of pleated filters in real HVAC applications. Experiments were short term (24 – 96 hours) or long term (168 to 720 hours). Table 4 shows the summary of the experimental matrix describing filter types and test conditions. The air then passed through the flow tube reactor containing a filter coupon of 47-mm diameter (geometric surface area = 1.7×10^{-3} m^2) at a flow rate of 1.4 ± 0.1 L/min. With this flow rate, the velocity of the air entering the filter sample was approximately 0.013 m/s which is 3% of a typical 0.5 m/s velocity of air passing through the filter media in a deployed pleated air filter and even less than 3% of the typical air velocity through an unpleated filter. The experiments took place at room temperature in the range of 22 - 27 °C. Four different RH settings of (20 ± 5)%, (50 ± 5)%, (65 ± 5)% and (80 ± 5)% were employed. For all tests, the background formaldehyde concentration in the supply air was checked first before installing the filter coupon. The filter coupon was then quickly installed and continuously exposed to the air flow.

For experiments performed at higher velocity, we used a different experimental system described in Sidheswaran et al (2012). Briefly, clean air was circulated through a humidifier and a dilution stream of dry air used to achieve the desired RH. The temperature and RH were monitored downstream of the filter using a calibrated APT logging system (Automated Performance Testing, TEC, Minneapolis). A 10-cm^2 filter sample was cut out from the filter and placed inside the holder in the flow system. Air samples were collected through sample ports located upstream and downstream of the filter holder. The air flow rate was 30 L/min resulting in a velocity of 0.5 m/s. Three different RH settings of (20 ± 5)%, (50 ± 5)% and (80 ± 5)% were employed. Initial samples were collected at the end of 24 hours, and long term tests were conducted for a period of up to 240 hours.

Table 4: Experimental matrix describing filter types and test conditions. S = short term test with a minimum test period of 24 h and a maximum test period of 96 h; L = long term test, with a minimum test period of 168 h and a maximum test period of 720 h.

Filter	Description	v = 0.013 m/s				v = 0.5 m/s		
		20 % RH	50 % RH	65 % RH	80% RH	20% RH	50% RH	80% RH
F1	Fiberglass media with heavy tackifier coating	S	S	L	L*	S	L	L
F2	Fiberglass media with medium tackifier coating	S	S		S			
F3	Fiberglass media with light tackifier coating	S	S		S *			
F4**	Fiberglass media without tackifier		S	S	L*			L
P1	Polyester media without tackifier				S			S
P2	Polyester media withtackifier coating				S			S
P3	Polyester media with tackifier coating							S

* *replicate tests have been conducted*
** *additional tests at v =0.05 m/s and 1 m/s were also conducted for F1 and F4.*

2.3.2.2. 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 of detecting 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).

2.3.2.3. Determination of integrated aldehyde emissions

We collected volatile carbonyls formed by 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 (US EPA 1999). 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 and analyzed by HPLC with UV detection (Agilent 1200). Formaldehyde and acetaldehyde were quantified with a calibration curve prepared from authentic standards of the DNPH hydrazone derivatives. The average formaldehyde concentration in blank samples was determined to be 0.02 ± 0.05 $\mu g/m^3$; and the average acetaldehyde concentration in the blanks was 0.04 ± 0.05 $\mu g/m^3$. In both cases, values correspond to the mean of five determinations, and the experimental error was determined as one standard deviation from the mean.

2.3.2.4. 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 over the mass-to-charge ratio (m/z) range of 20 to 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, calibrations were performed using dry air and air with 50% RH. Humidity did not affect the other calibrations.

2.3.3. Specific Aim #3: *Evaluate the overall impact of ozone chemistry with particle-loaded HVAC filters on the indoor work environment*.

The expected increases in indoor aldehyde concentrations were estimated from the emission rates determined in this study at the low air flow rates with humidified air (Destaillats et al, 2011). 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

$$\Delta C = \frac{E_{FA}}{Q_{FA}} \qquad (1)$$

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 $\mu g/(m^2 s)$, 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:

$$E_{FA} = \frac{E}{S} R \qquad (2)$$

where E is the emission rate for a sample of filter media 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 $m^3/s\text{-}m^2$. 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 (US EPA 2008).

2.4. RESULTS AND DISCUSSION

2.4.1. Specific Aim #1: *Identify key constituents of particle-loaded HVAC filters that react with ozone to generate volatile indoor pollutants and secondary organic aerosols.*

2.4.1.1. Analysis of evolved carbon

Figures 2-4 show the carbon thermograms obtained from evolved gas analysis (in oxygen) of filter cake collected from POAK and LBNL for CP, FG and PE filter types, respectively. It should be noted that the thermograms show two or three distinct peaks evolving at different temperatures. Each peak was deconvoluted and integrated as a Gaussian distribution to obtain the concentration of the each carbon component. The first peak evolving around 300 C is due to the volatilization of lighter organic compounds such as SVOCs from outdoor particles and plasticizers, phthalates, and poly-aromatics from indoor sources; the second peak around 450 ^{o}C is the evolution of “brown carbon” that comprises higher molecular weight organic compounds from inefficient combustion of vehicle exhaust, and polymeric material from biogenic sources and/or atmospheric processing, ,; the third peak around 550 ^{o}C represents the combustion of black carbon (BC), also known as elemental carbon (EC).

Figures 2-4 also show the percentage distribution of SVOC, brown carbon, BC and metal ions in the filter cake. The BC levels in filter cake retrieved from POAK were higher than the levels found at LBNL. The main source of BC in the San Francisco Bay Area is diesel exhaust from on-road engine emissions and maritime traffic associated with shipping port activities. The BC found at LBNL was significantly lower due to Diesel traffic. For all three filter types the SVOC and brown carbon peaks were large compared to the BC peak for the filter cake obtained from LBNL. The mass fractions of inorganic species were smaller from filters loaded at LBNL, compared to those found on POAK filters.

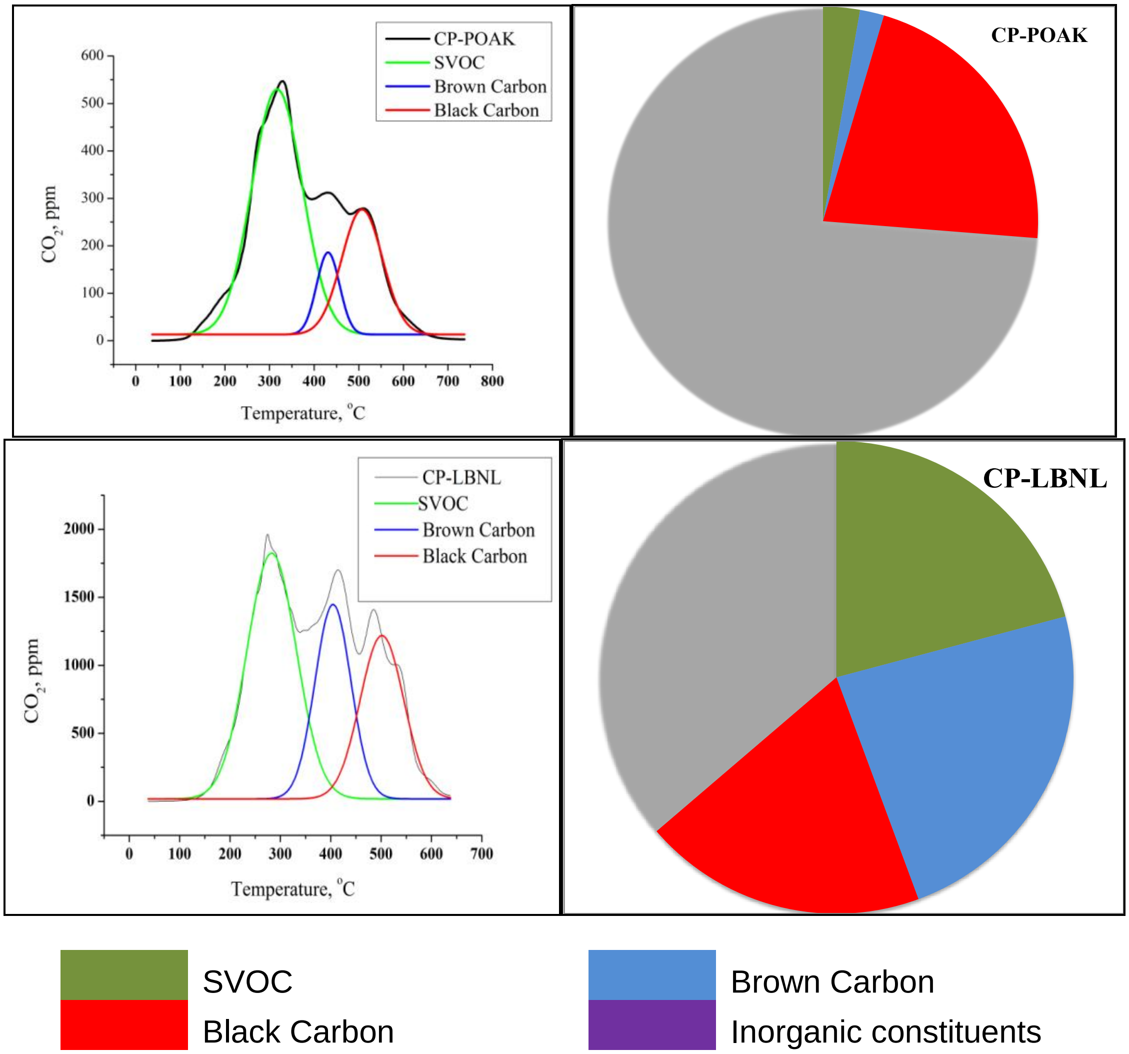


Figure 2. Thermal evolution of carbonaceous constituents of filter cake (left) and the corresponding mass balance (right) for CP filters exposed at LBNL and POAK.

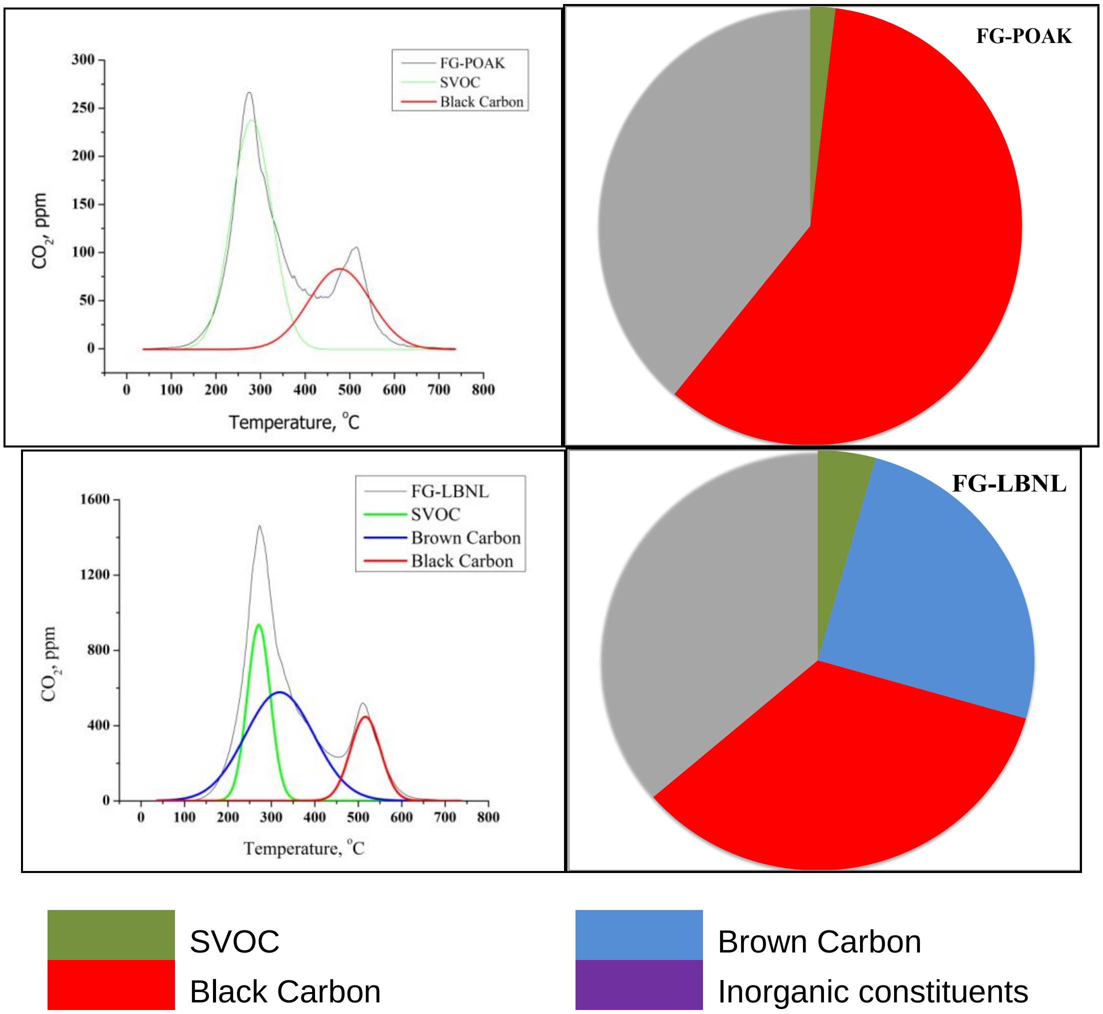


Figure 3. Thermal evolution of carbonaceous constituents of filter cake (left) and the corresponding mass balance (right) for FG filters exposed at LBNL and POAK.

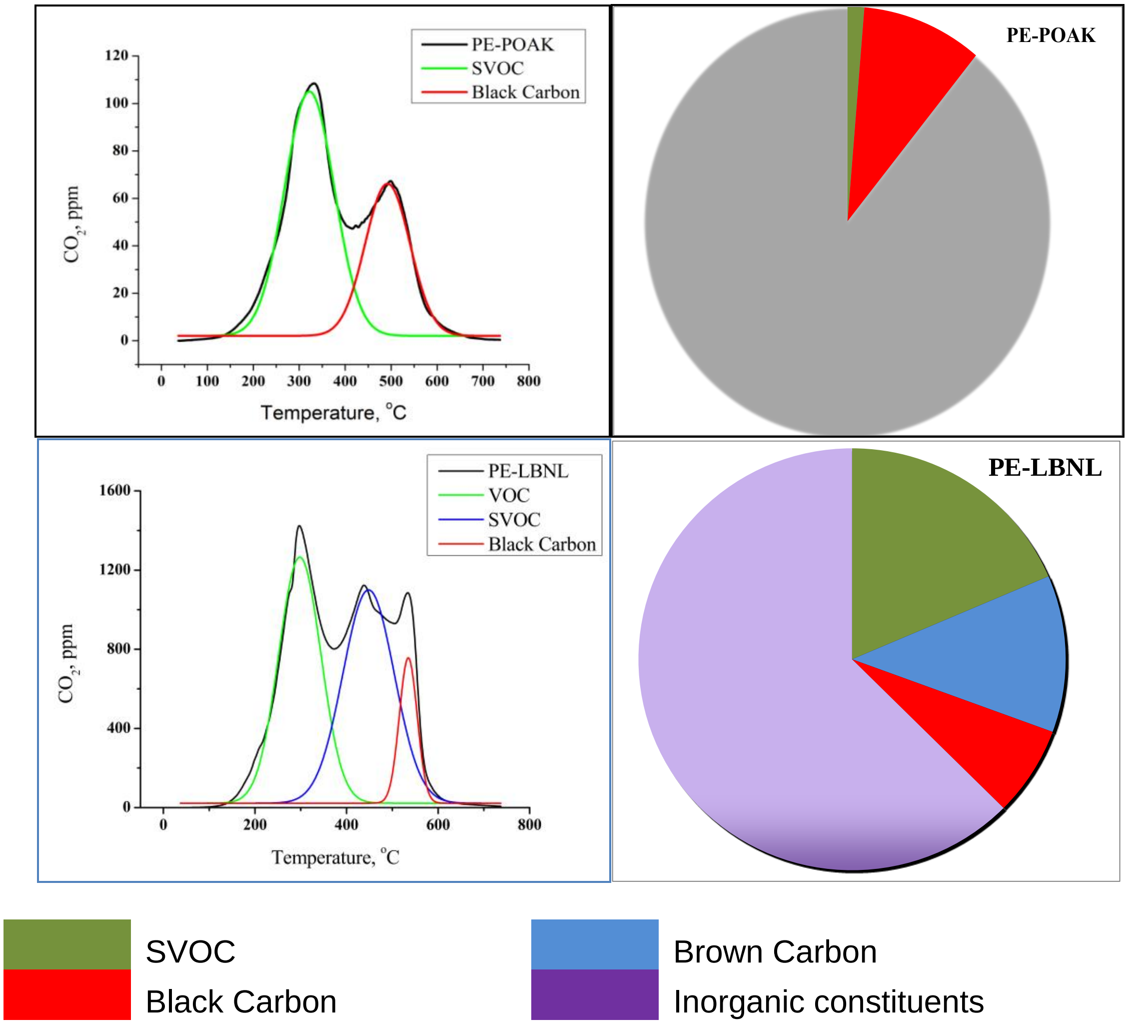


Figure 4. Thermal evolution of carbonaceous constituents of filter cake (left) and the corresponding mass balance (right) for PE filters exposed at LBNL and POAK.

2.4.1.2. Identification and quantification of organic constituents

Chromatographic analysis of the extracts yielded a total of more than 100 compounds that were identified and listed in the Appendix (Table 1-S and 2-S). The organics found included linear alkanes, alkenes, aldehydes, ketones, aromatics, phthalates, sulfur- and nitrogen-substituted organics, polycyclic aromatic hydrocarbons (PAHs), organophosphates, organic acids, esters, ethers and ethoxides. Identification of compounds was predominantly performed using the NIST mass spectral library database (NIST MS v2.0, 2008), and some compounds were confirmed with standards available commercially. The compounds were classified into five broad categories based on the possible sources, and equation 3 shows how their abundances were estimated from the peak areas on chromatograms, as naphthalene equivalents:

$$C_i = \left(\frac{\left(A_{N-i} \times m_s + C_o\right)}{6}\right) \Big/ \left(\frac{M_{fd} - M_f}{20}\right) \qquad (3)$$

where C_i is the concentration of compound i (µg/g-dust), $A_{N\text{-}i}$ is the area equivalent of the compound in terms of naphthalene area, m_s is the slope and C_o is the intercept of the naphthalene calibration curve, M_{fd} is the mass of filter with dust before sonicating it in solvent and M_f is the mass of the filter and the insoluble suspended portion of the dust after sonication in solvent.

Source category “Indoor” encompasses compounds that are know to be released from indoor sources such as electronics, furniture, bioeffluents, etc. Source category “Urban pollution” encompasses compounds that are associated with vehicular exhausts and those that have possible anthropogenic sources. Source category “Reaction products” refers to possible oxidation and polymerization byproducts formed on filter surfaces due to surface reactions. Source category “Indoor/Outdoor” encompasses compounds that are found in both indoor and outdoor air, and for which source apportionment could not be unequivocally established. Source category “Vegetation” refers to compounds from biogenic sources (in outdoor air). Figure 5 illustrates a general distribution of sources for fiberglass (FG) filters collected in POAK and LBNL. In Figures 6-11 we also report the identity and amount of each chemical functionality found in POAK and LBNL filters, classified by source. Zheng et al. (2000) found that solvent extraction of ambient particulate matter from Hong Kong urban air contained 46-80% fatty acids, 10-34% alkanes, 4-21% alkanols and 1-6% PAHs. A semi-quantitative analysis of our filter extraction results also shows a similar pattern, although no PAHs were observed. It should be noted that various compounds observed in these filters have unsaturated double bonds and reactive sites in their molecular structure. This can facilitate ozone reactions on filter surfaces and explain the absence of some reactive species (such as PAHs) present at low levels, compared to the ambient particulate matter. It was also found that the organics present in the filters were different at each location. The filters retrieved from LBNL contained more organics of biogenic origin compared to the ones obtained from POAK, which showed pollutants associated with motor vehicle emissions.

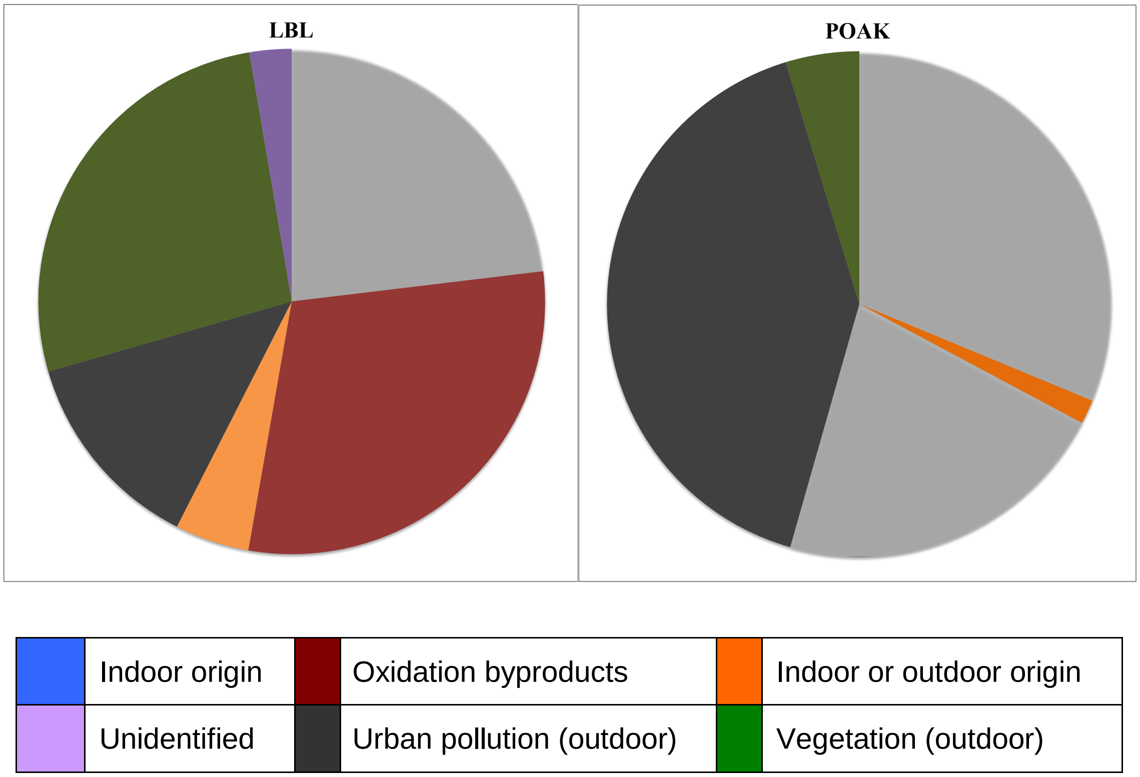


Figure 5. Source apportionment for organic compounds identified from GC-MS analysis of filter type FG-LBL and FG-POAK

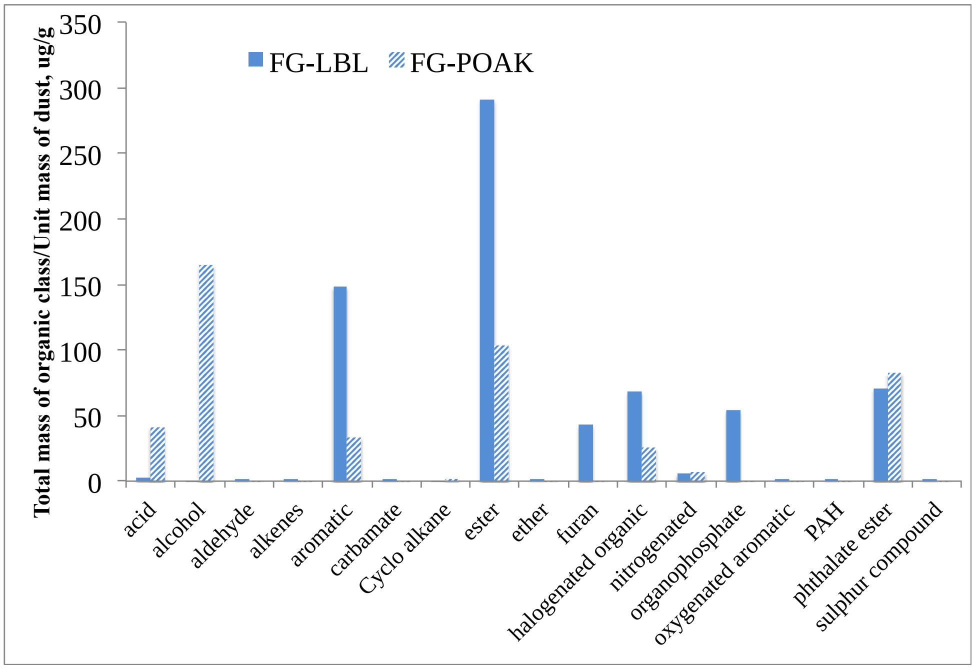


Figure 6. Principal chemical functionalities present in the fraction assigned to pollutants of indoor origin.

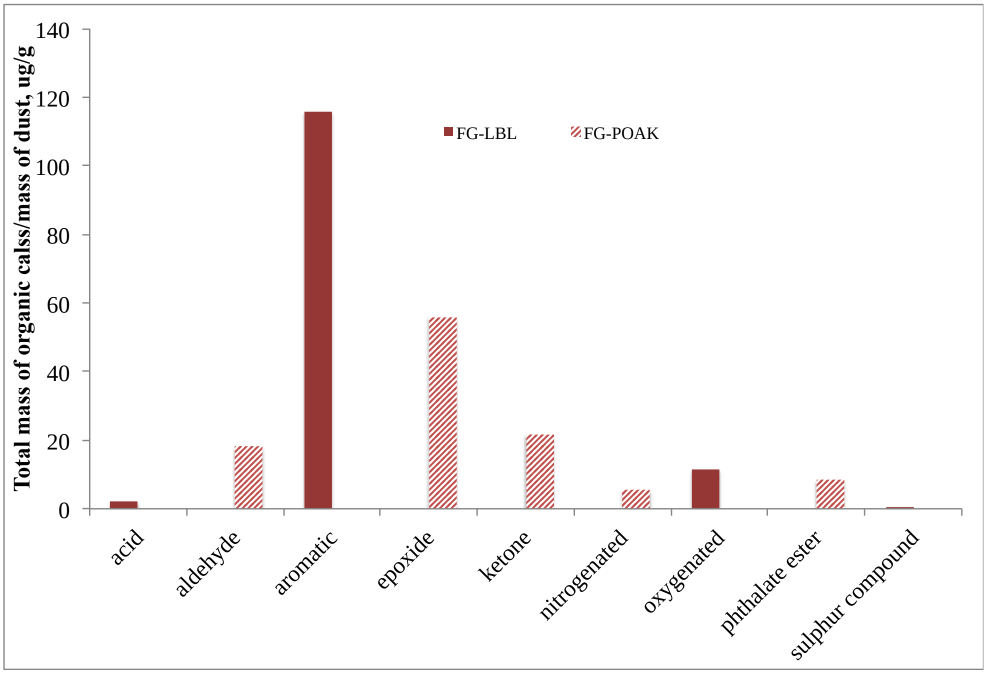


Figure 7. Principal chemical functionalities present in the fraction assigned to secondary byproducts of ozone chemistry.

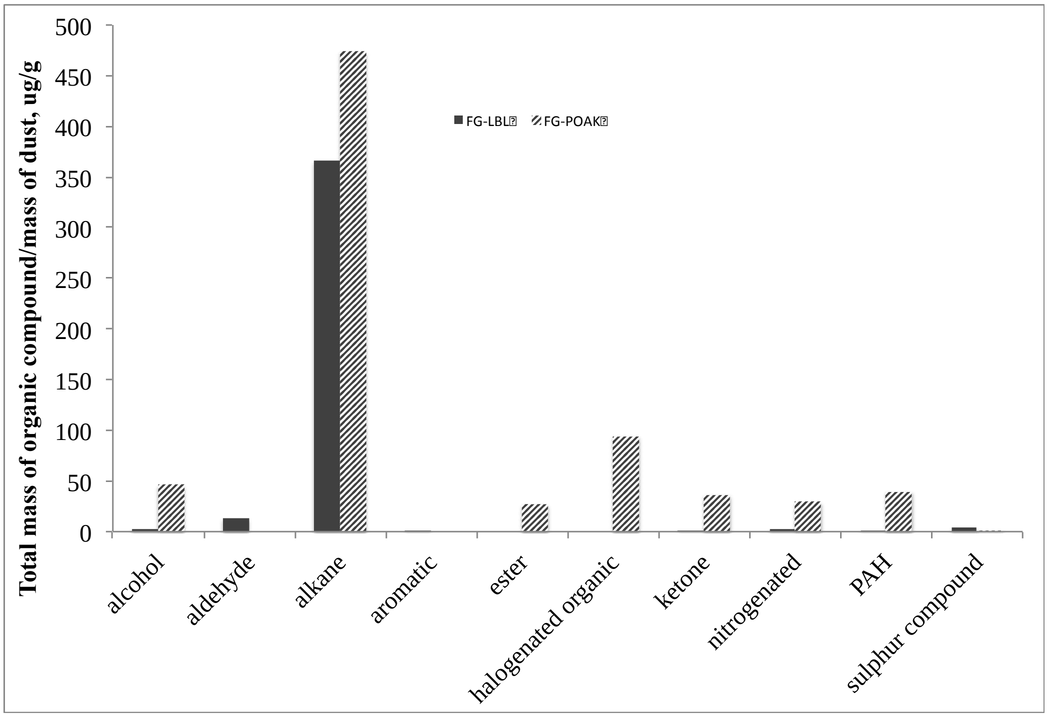


Figure 8. Principal chemical functionalities present in the fraction assigned to outdoor pollutants originated in urban pollution (anthropogenic).

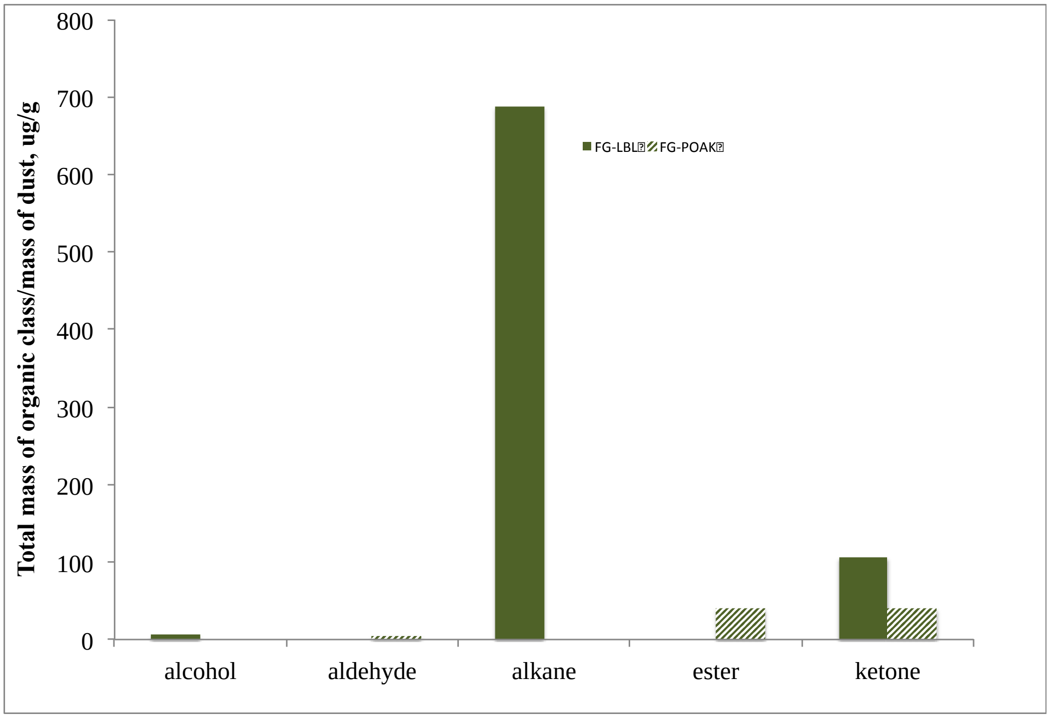


Figure 9. Principal chemical functionalities present in the fraction assigned to outdoor pollutants originated in emissions from vegetation (biogenic).

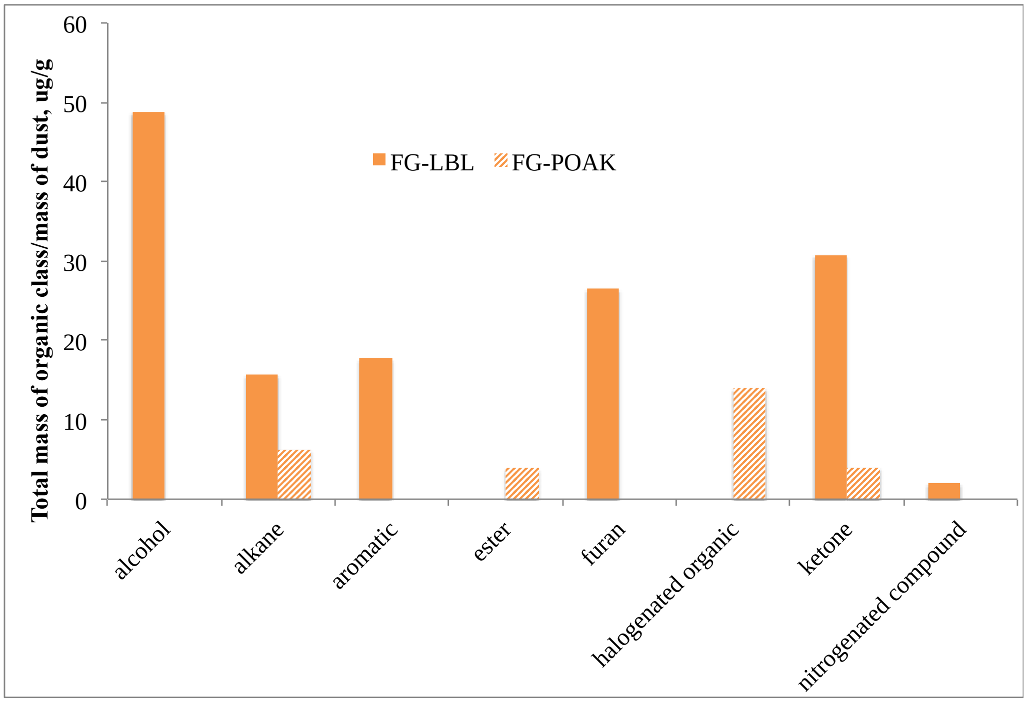


Figure 10. Principal chemical functionalities present in the fraction assigned to pollutants of both indoor and outdoor origin.

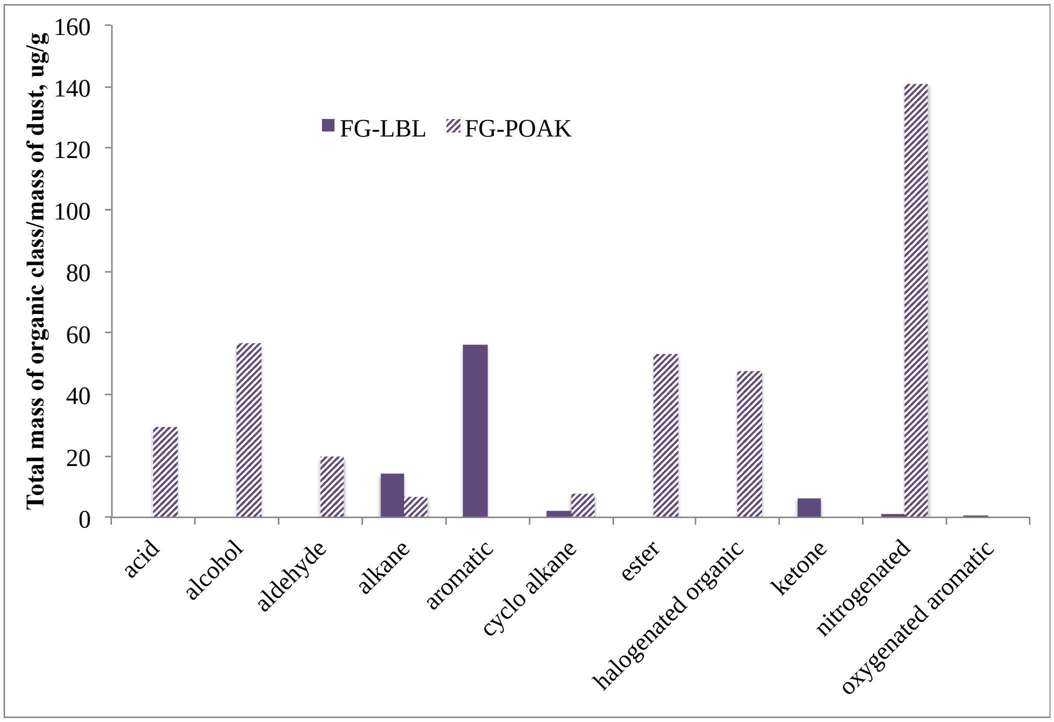


Figure 11. Principal chemical functionalities present in the fraction assigned to pollutants of unidentified origin.

2.4.1.3. FTIR analysis of insoluble filter cake constituents

Figure 12 illustrates FTIR spectra of the solvent insoluble fraction of the filter cake obtained from polyester media collected at each location. The differences in spectral signatures of the filter cake collected from two locations are clearly shown in the figure. The LBNL sample shows peaks corresponding to the possible presence of aliphatic hydrocarbons, olefins and aliphatic acids, while some of those features are not observed in the POAK samples. Figure 12 also includes photographs of each of the samples illustrating clearly the different color and texture of filter cake collected in each location on the same filter.

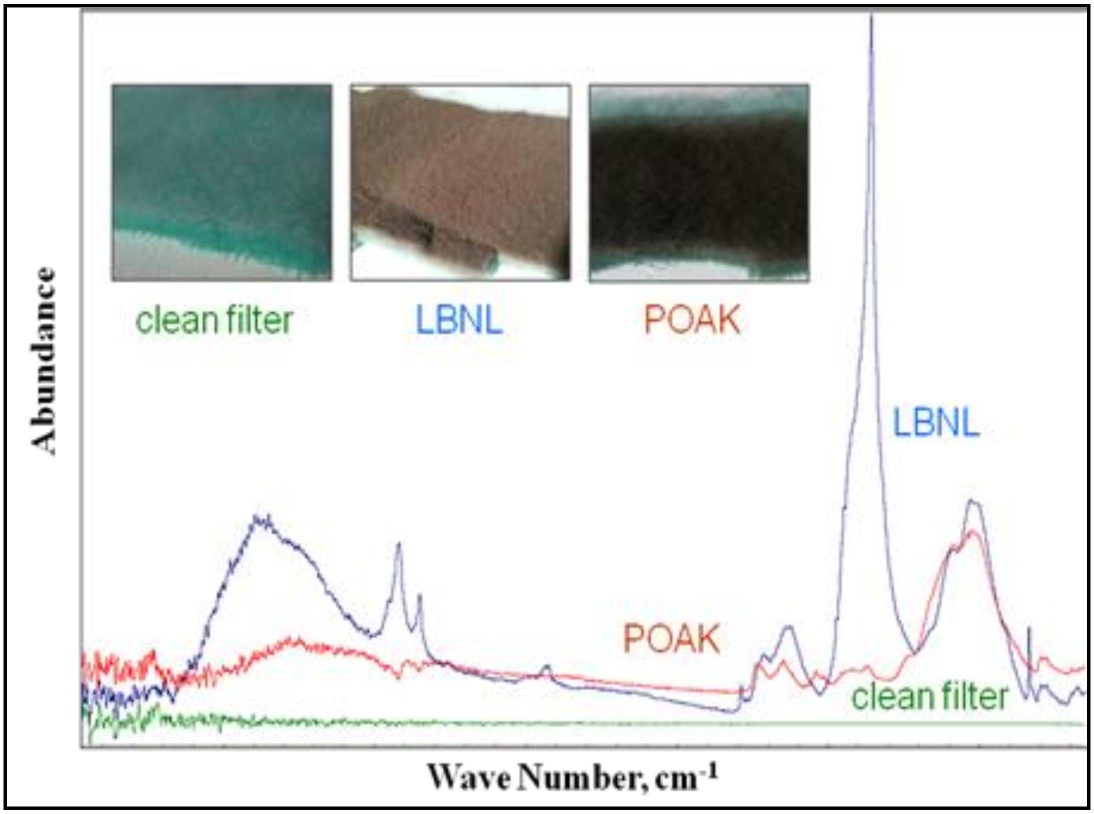


Figure 12: FTIR spectra of solvent insoluble filter cake obtained from polyester filter media (pictures inlay are the polyester media samples showing clean, LBNL and POAK deployed filters)

2.4.1.4. Characterization of inorganic constituents

Table 5 summarizes the concentration of inorganic species present in filter cake, determined by ion chromatography (Li, Na, Ca, K), and by inductively coupled plasma mass spectrometry (Al, Fe, Mg, Zn, Ti, Cu, Ba). These elements are associated with mineral dust collected by filtration media.

Table 5. Concentration of inorganic species present in filter cake (expressed in microgram per gram of filter cake).

	Polyester		Cotton Polyester		Fiberglass	
	LBNL	POAK	LBNL	POAK	LBNL	POAK
Li	0.04	0.15	0.04	0.08	0.02	0.03
Na	108	104	65.0	283	39.3	118
Al	50.8	64.8	16.9	69.0	21.0	35.1
Ca	44.1	60.1	21.3	70.0	20.7	38.0
Fe	41.5	57.8	13.6	79.6	24.7	34.8
Mg	23.3	30.9	13.6	52.2	14.1	21.1
K	15.6	22.6	7.37	26.9	7.85	12.2
Zn	4.87	8.39	2.53	31.6	6.55	8.36
Ti	2.41	3.59	0.85	3.32	1.12	1.77
Cu	2.20	3.88	0.71	2.97	1.05	1.47
Ba	1.31	1.67	0.45	2.12	0.66	0.83

2.4.2. Specific Aim #2: *Establish the reaction mechanisms and rates leading to the formation of gas-phase and particulate pollutants, and the effect of filter moisture content on pollutant yield*.

2.4.2.1. Ozone uptake by HVAC filters

Figure 13 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

$$\%\Delta[O_3] = \frac{\Delta[O_3]}{[O_3]_{ref}} \times 100 \qquad (4)$$

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 (Destaillats et al, 2011). In the absence of filter media (initial quenching period), Figure 13 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 (24 hr).

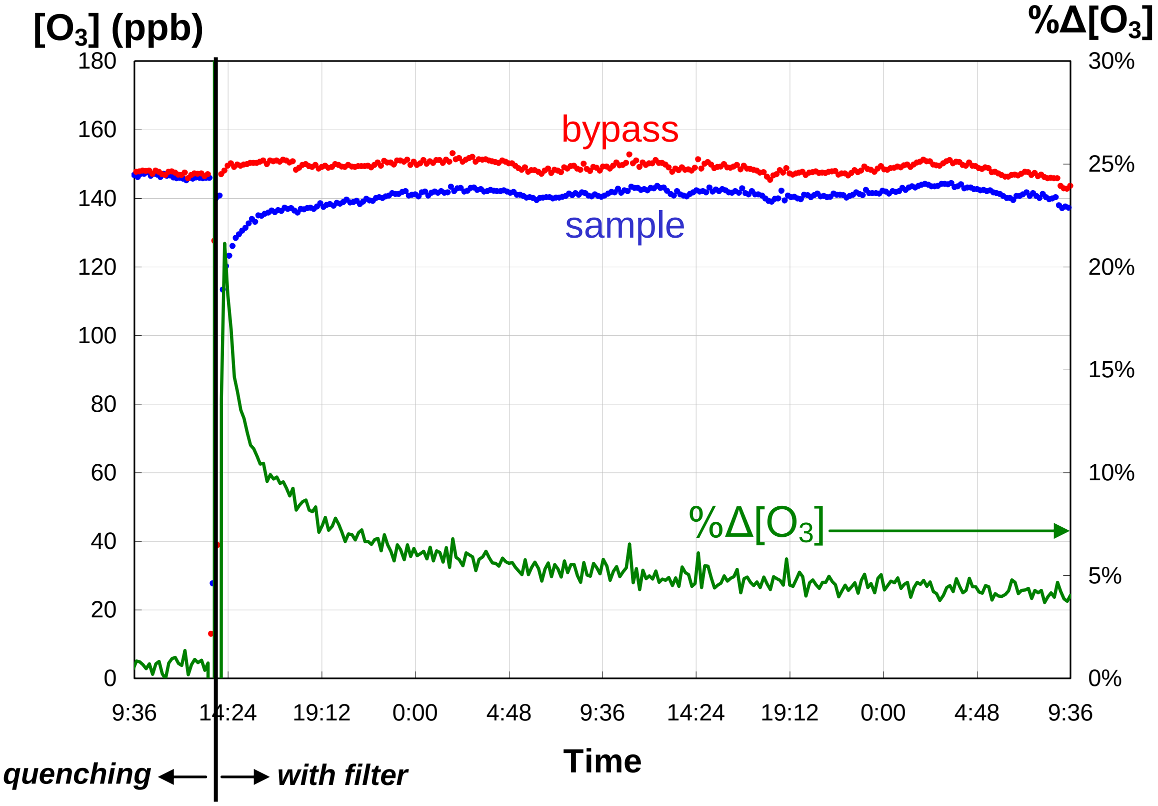


Figure 13: Ozone breakthrough curve for polyolefin filter media used in the POAK building, exposed to 150 ppb ozone under humidified air.

Results from ozone breakthrough curves such as that shown in Figure 13 were fit to an exponential function:

$$\Delta[\mathrm{O}_3] = A \cdot \exp(-Bt) + \Delta[\mathrm{O}_3]_{ss} \qquad (5)$$

which allowed for determination of the time at which outlet ozone concentration approached steady state (t_{ss}), the average ozone concentration change $\Delta[\mathrm{O}_3]_{\mathrm{initial}}$ 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 14.

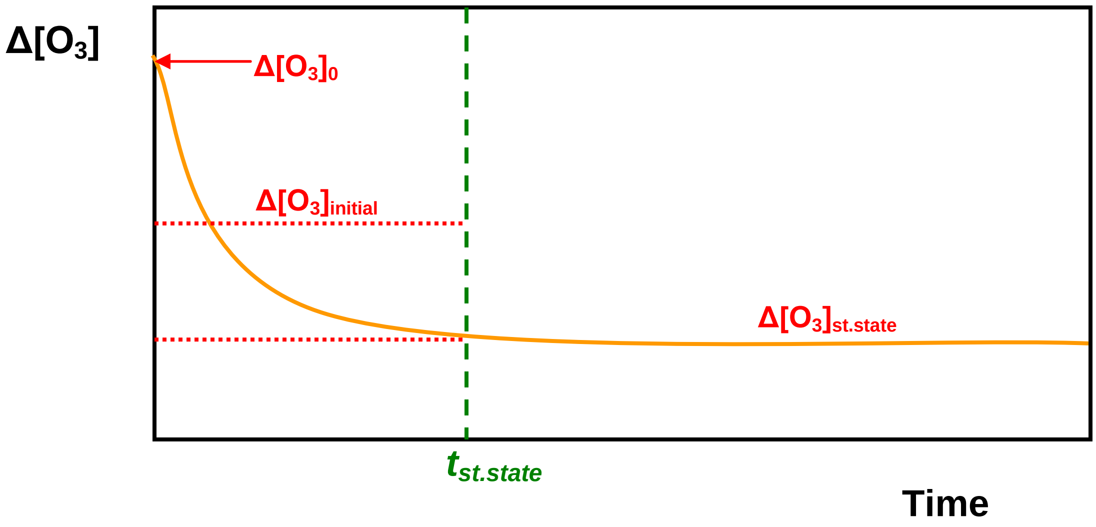


Figure 14: Schematic representation of an ozone breakthrough curve, showing the parameters obtained from fitting the experimental data.

Fitted values corresponding to unused and used filters are reported in Tables 6 and 7, respectively. Tables 6 and 7 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 15 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 6 and 7, 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), 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 16 and 17, 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).

Table 6: Experimental results obtained from ozone breakthrough curves for unused filters

Manufacturer/ Model	**Inlet ozone**	**RH**	$t_{st.state}$	**Δ[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.: Δ[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 7: Experimental results obtained from ozone breakthrough curves for used filters

Manufacturer/ Model	**Building**	**Inlet ozone**	**RH**	$t_{st.state}$	**Δ[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.: Δ[O$_3$] not detected; ozone concentration downstream of the filter was not significantly different from the reference
(a) with plastic backing

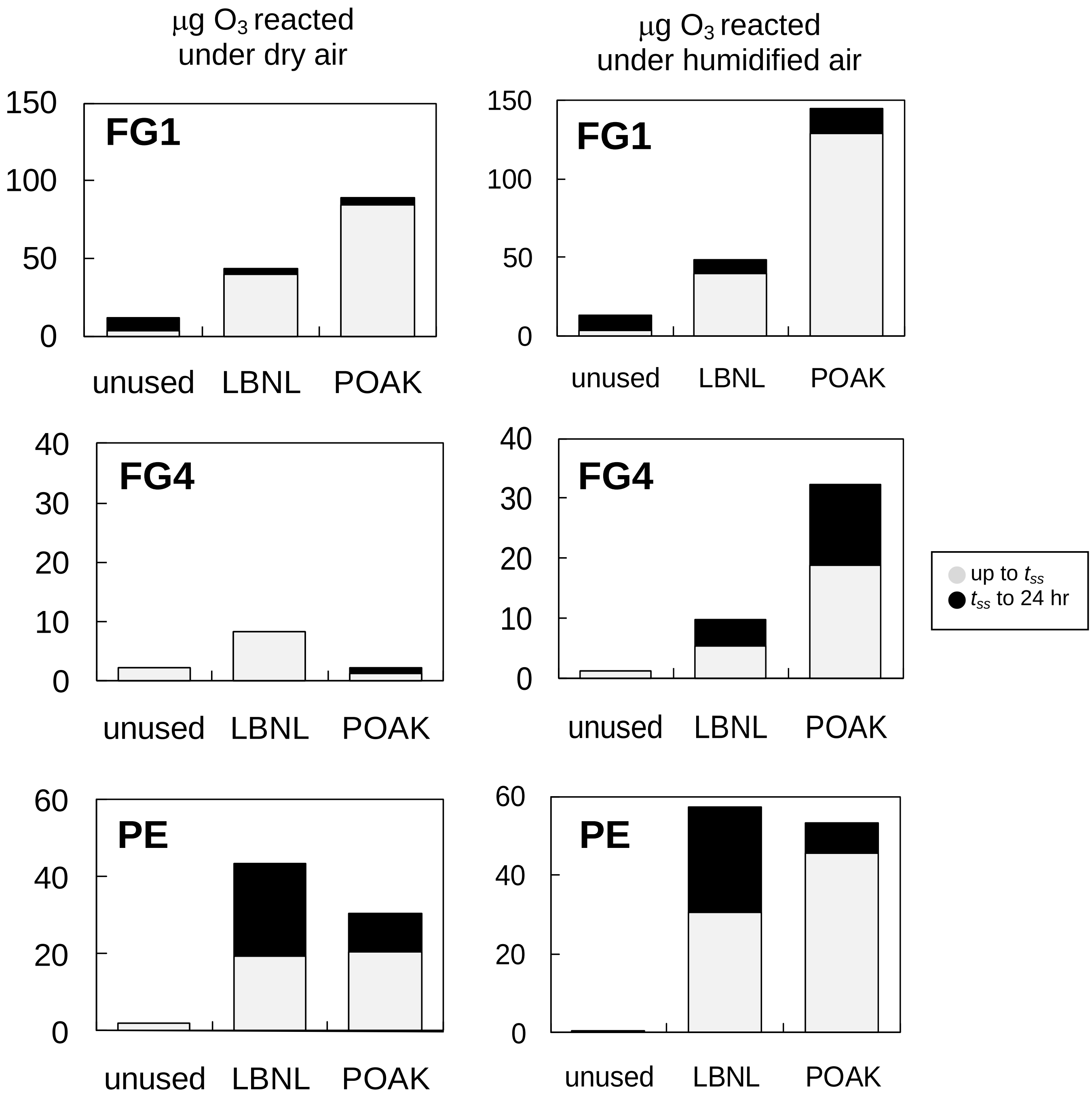


Figure 15: Ozone uptake in a 24-h period for two fiberglass filters and one polyester filter. FG1: fiberglass with heavy tackifier application; FG4: fiberglass with light tackifier application; PE: polyester with medium tackifier application and plastic backing. Plots are represented in each case to maximum scale, but it should be noted that significant differences exist between FG1 and other filters.

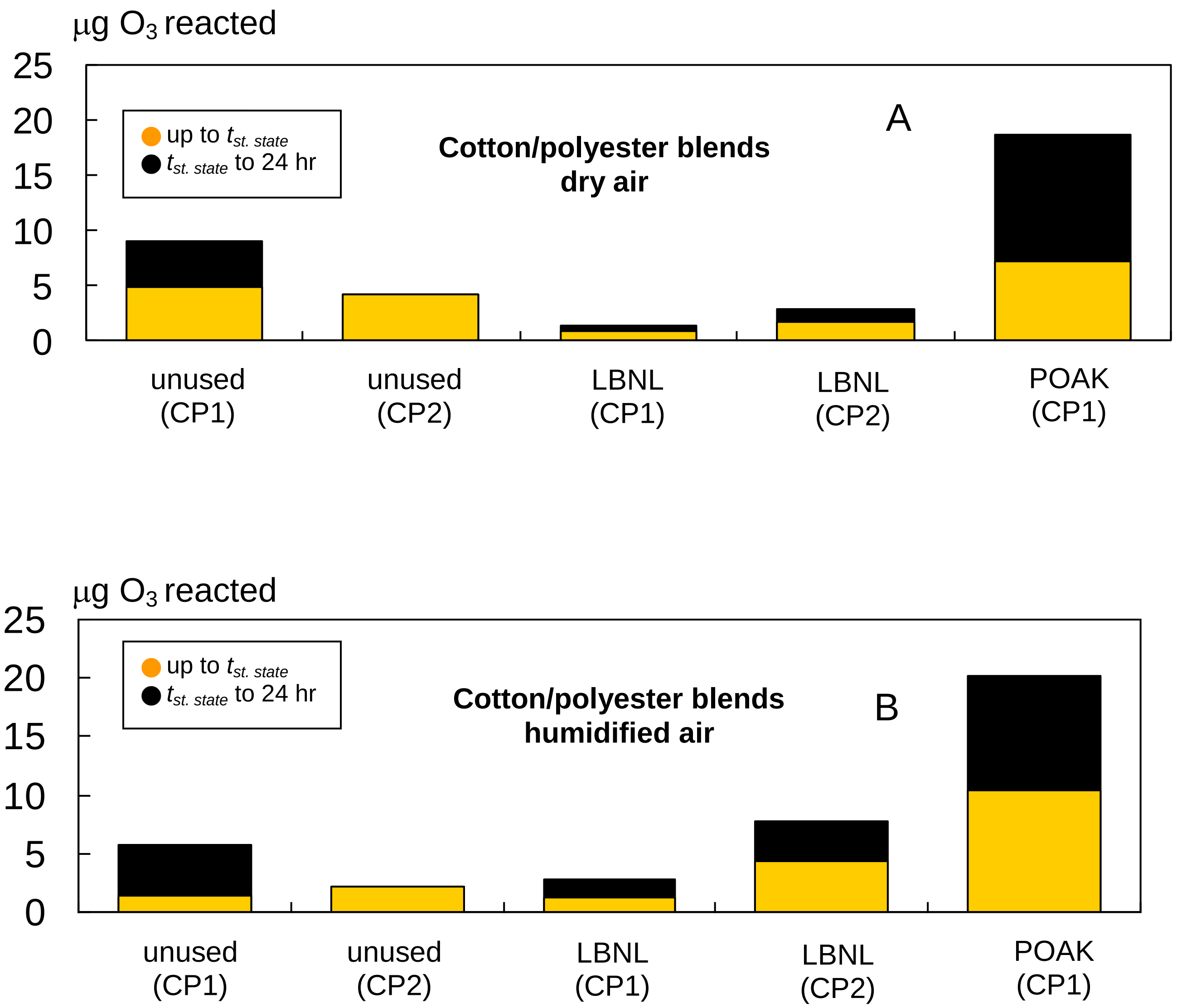


Figure 16: Ozone uptake in a 24-h period for cotton/polyester blend filters for (A) dry air and (B) humidified air.

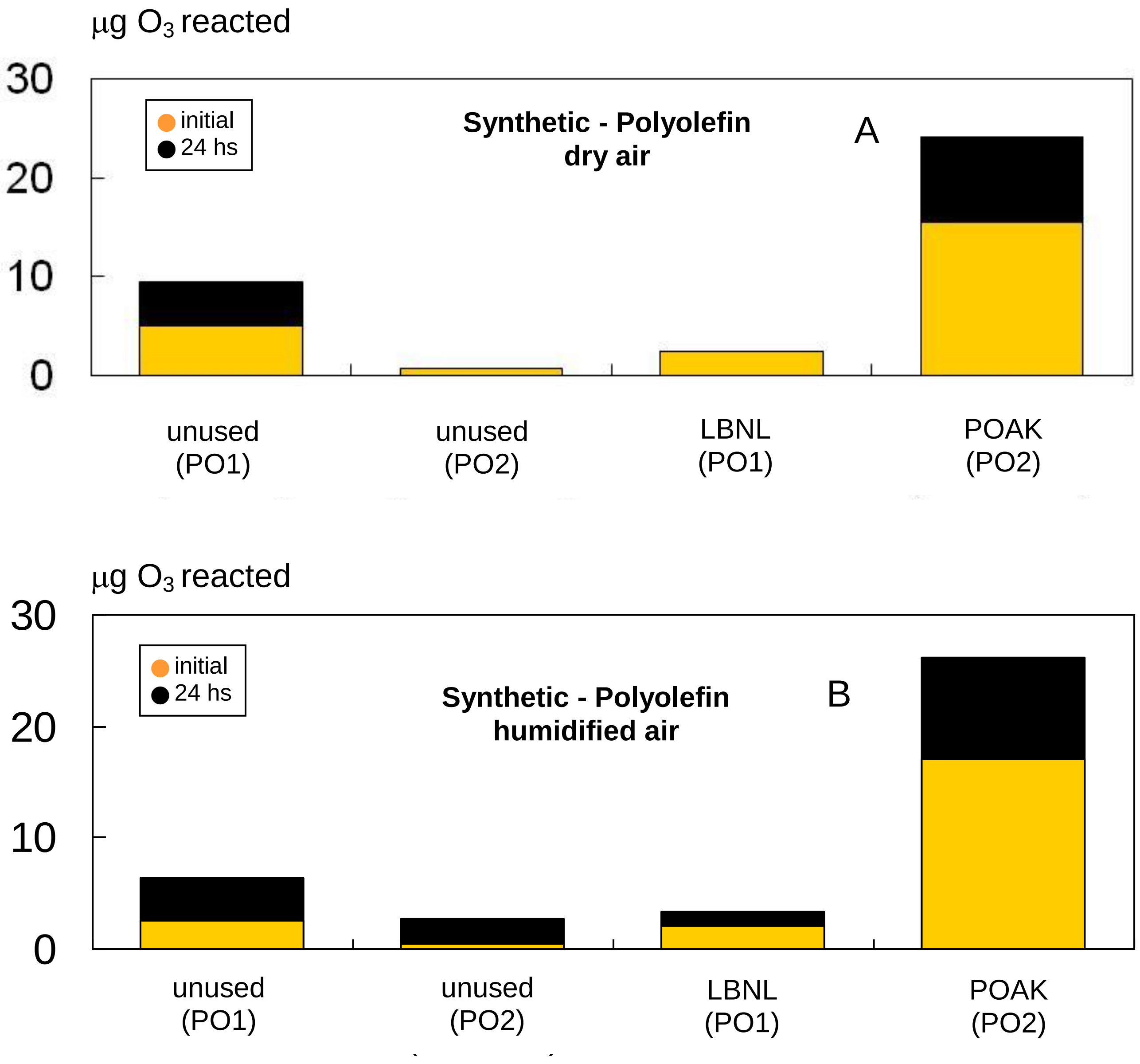


Figure 17: Ozone uptake in a 24-h period for polyolefin filters for (A) dry air and (B) humidified air.

2.4.2.2. 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 18. We report data for unused filters, as well as for particle-laden filters used over 3 months at LBNL and POAK buildings (Destaillats et al, 2011).

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 18. 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 18. 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.

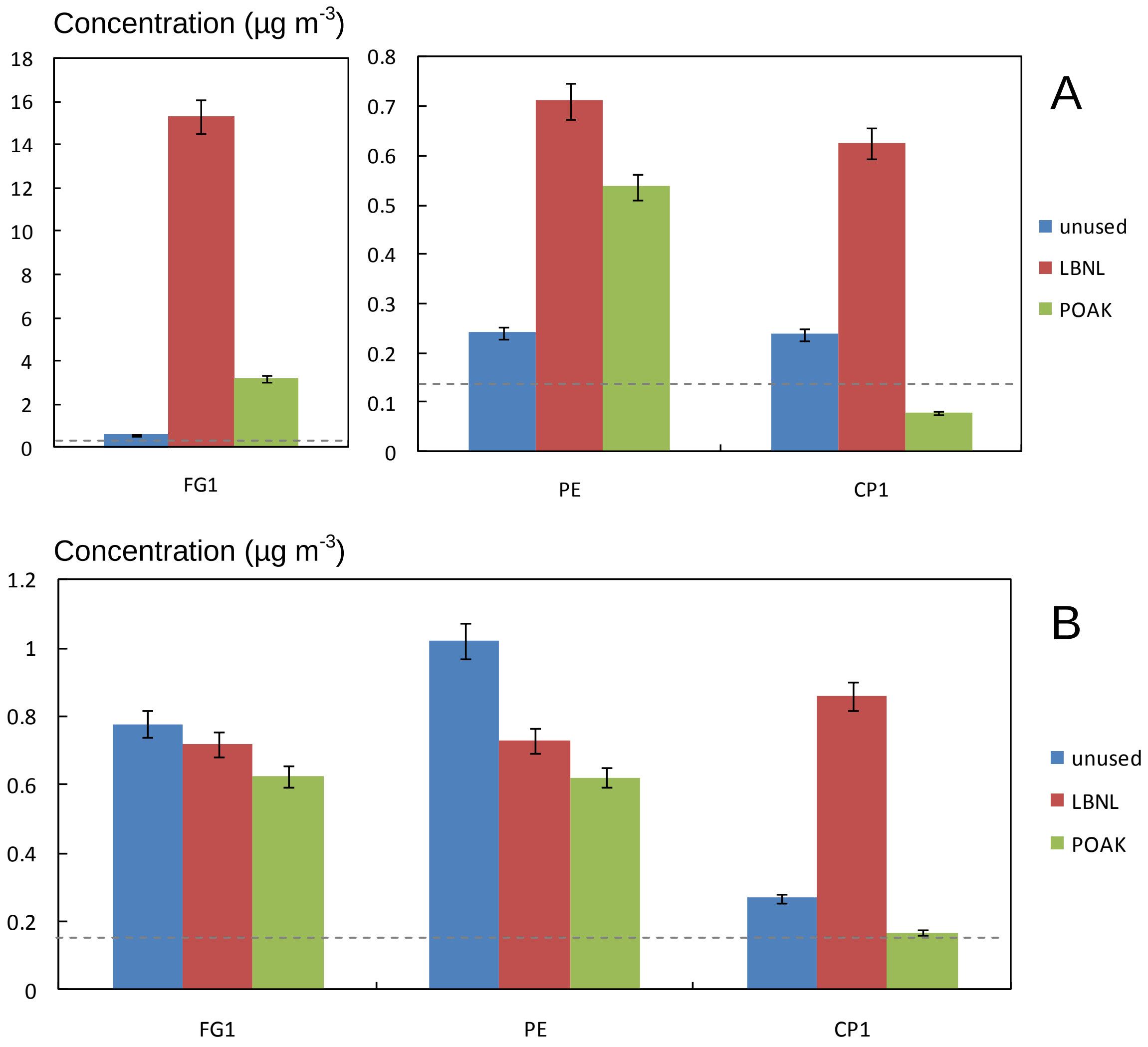


Figure 18: Aldehyde concentrations measured downstream of used and unused filters exposed to ozone. The filter media included fiberglass with heavy tackifier application (FG1), polyester with medium tackifier application (PE) and cotton/polyester blend without tackifier (CP1). Results are reported for (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 18-A and all other filters.

2.4.2.3. 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 19. Similar results from another fiberglass filter corresponding to another manufacturer (FG4) are shown in Figure 20. 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 19. Overall formaldehyde emissions were significantly lower, and we did not observe emission of formaldehyde in the absence of ozone in any case (Figure 20).

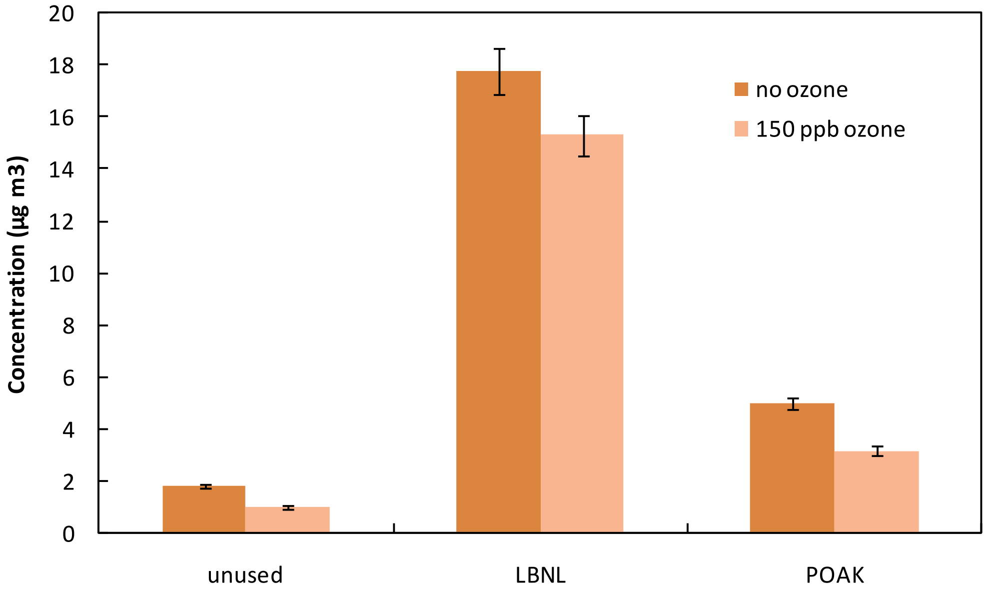


Figure 19: Formaldehyde concentrations measured downstream of FG1 filter media in the presence and absence of ozone, for experiments performed at 50% RH.

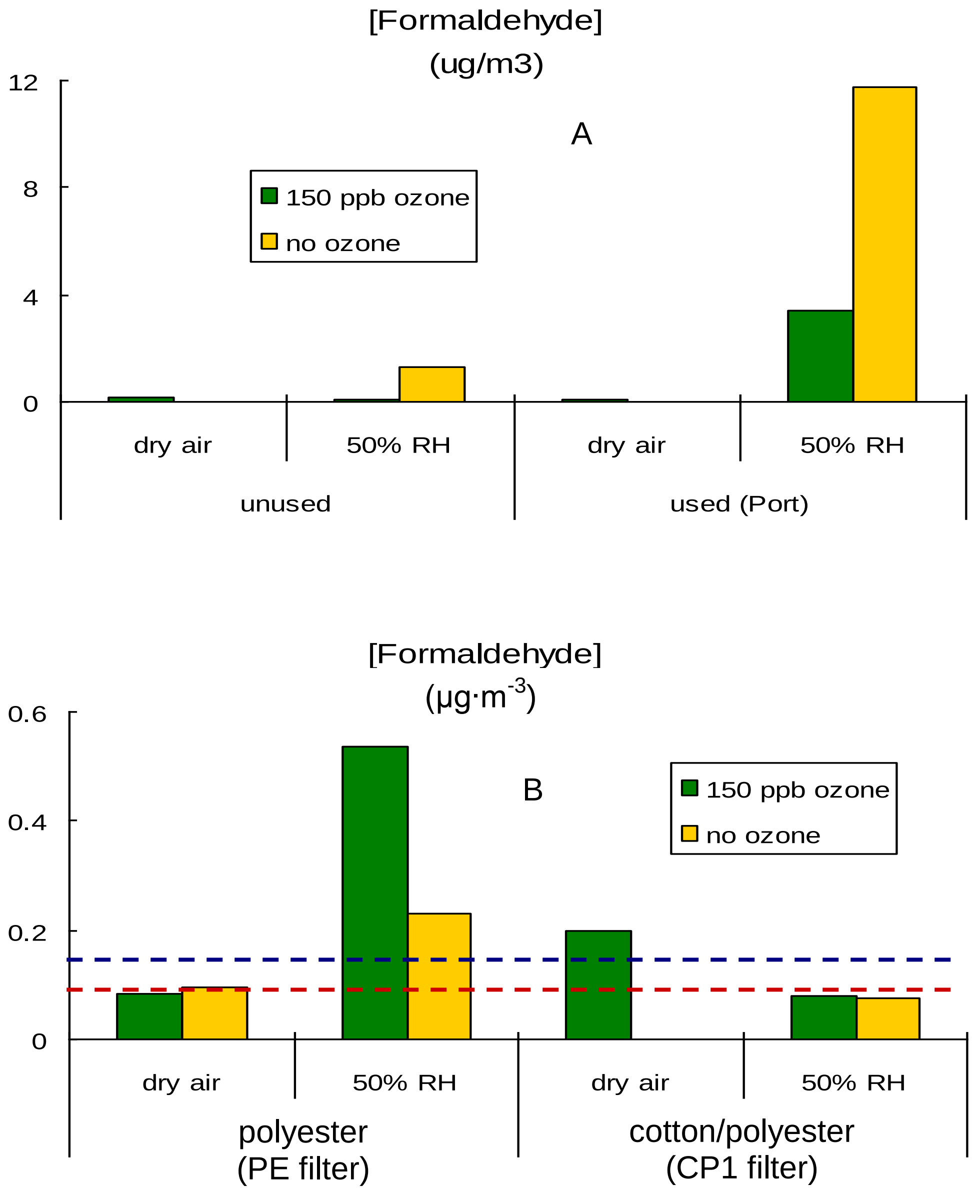


Figure 20: Formaldehyde concentrations measured downstream of A) fiberglass filter FG4 with light tackifier application; B) polyester filter PE with medium tackifier application and cotton/polyester filter CP1 without tackifier, used in the Port of Oakland under various experimental conditions.

2.4.2.4. 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 (Destaillats et al, 2011). Figure 21 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 8 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 18 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 19, 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 8: 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

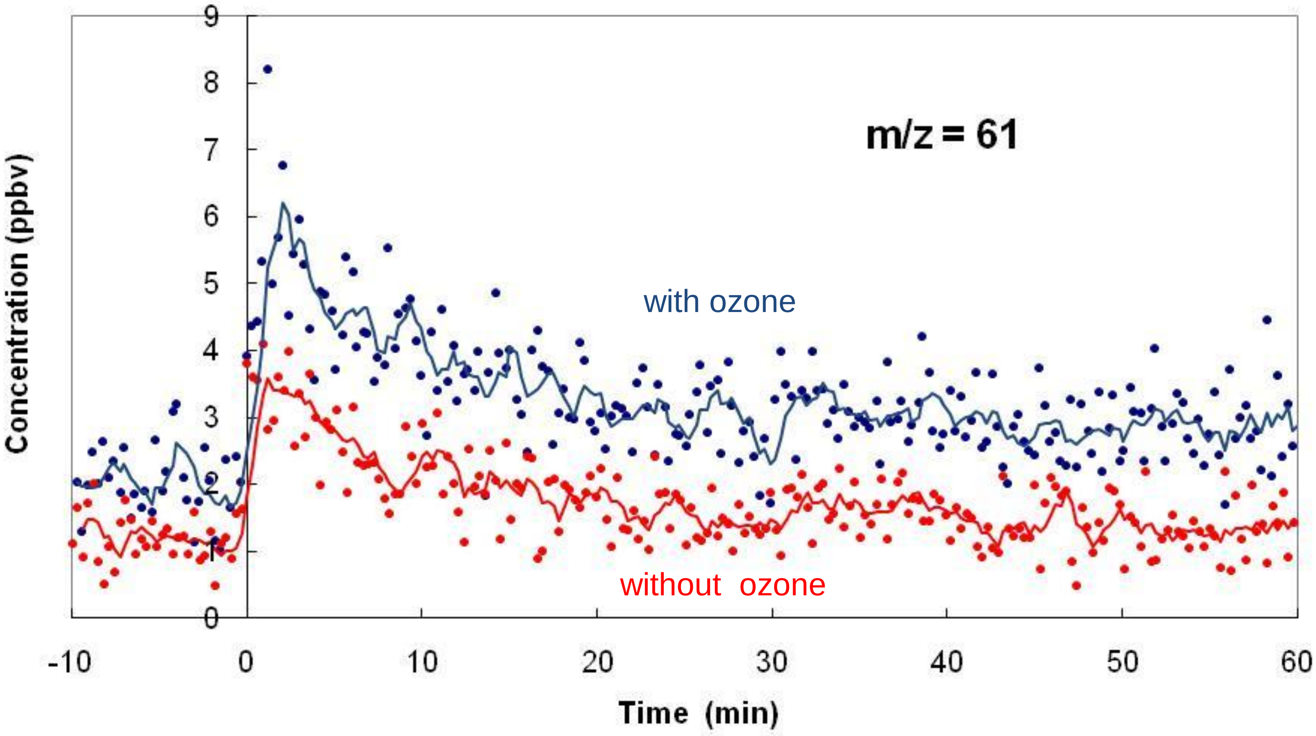


Figure 21: PTR-MS concentration profiles corresponding to m/z 61 for the filter PO1, in the absence and the presence of ozone, humidified air conditions.

2.4.2.5. Effect of the face velocity on ozone reactions

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 1.7×10^{-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 22. In both cases, we represent the $\%\Delta[O_3]$ value as a function of the air volume circulated through the filter.

Table 9: 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 9, 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.

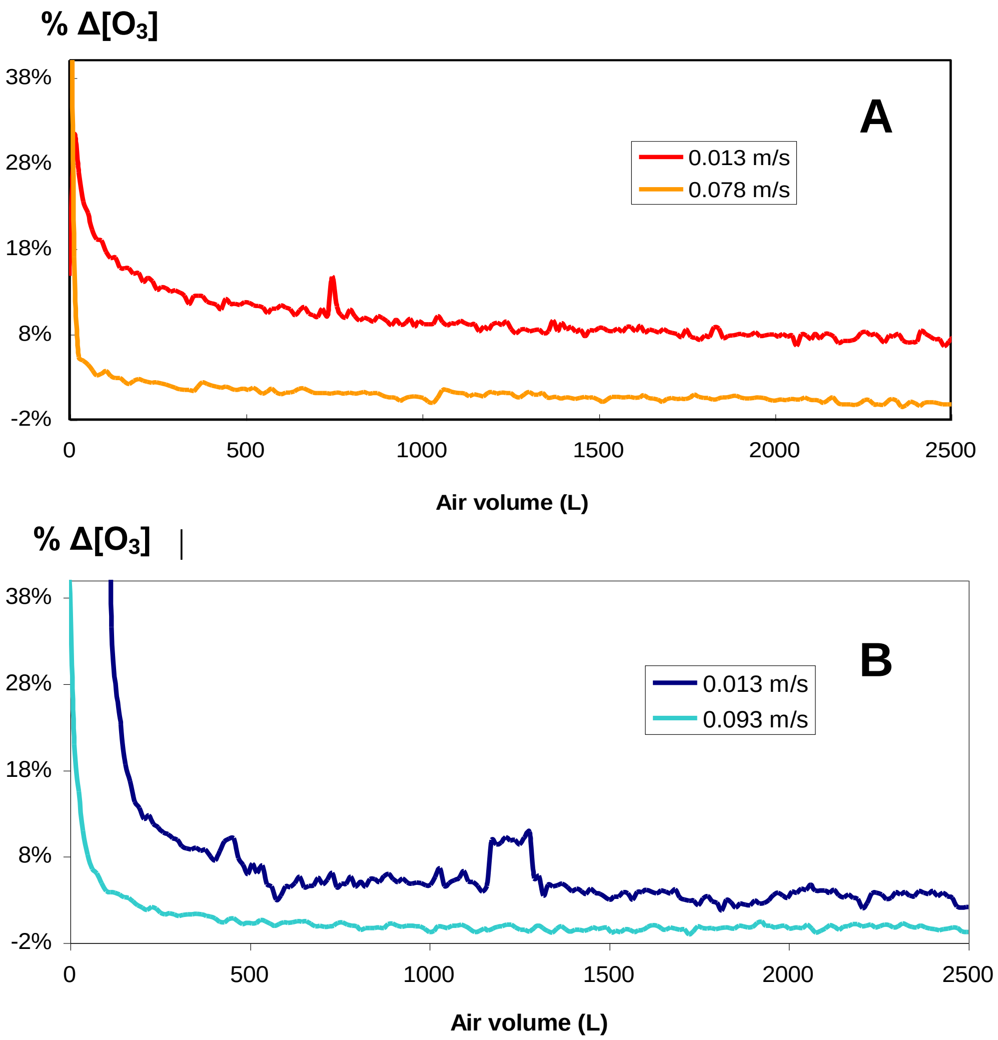


Figure 22: Ozone breakthrough curves for the FG1 filter used in LBNL, exposed to 150 ppb ozone at two different flow conditions under A) humidified air, and B) dry air.

2.4.2.6. Tests performed in the absence of ozone to evaluate the hydrolysis of filter additives

Table 10 summarizes formaldehyde concentration changes Δ[F] across the filter media, defined as

$$\Delta[F] = [F]_d - [F]_u \qquad (6)$$

where $[F]_d$ and $[F]_u$ are the concentrations downstream and upstream the filter, respectively. The reported concentrations are based on the integrated air samples taken between 24 and 48 hours of the exposure. Duplicate samples were taken for about 50% of the experiments and, in these cases, the average of the measurements ± one standard deviation are reported. Upstream (background) formaldehyde concentrations were below 0.9 µg/m^3. Results of experiments with an indoor RH of approximately 20% are not reported in Table 10 because the measured downstream concentrations were similar to upstream (background) and the formaldehyde emission could be regarded as negligible.

In addition to replicate measurements for each filter coupon, tests were conducted for filters F1, F3 and F4 at 80% RH using a different new filter coupon, and results for the second determination are also reported in Table 10 in parenthesis. It can be seen that the concentration variations among different coupons of the same filter type were in general larger than that of replicate measurements taken with the same filter coupon, which may be caused by the material inhomogeneity of filter media.

Figure 23 shows the formaldehyde concentration measured downstream of filter as a function of time for the long-term tests at low face velocity conducted for filters F1 and F4. Results indicate that the formaldehyde emission decreased moderately over time. For example, the formaldehyde emission at the end of one month was still over 70% of that measured between 24 and 48 hr exposure for filter F1 under 80% RH.

Table 10: Formaldehyde concentration changes Δ[F] across filters in low face velocity experiments (v = 0.013 m/s) based on air samples taken between 24 and 48 hours

Filter	Increase in formaldehyde concentration, Δ[F] (μg/m^3)		
	50 % RH	65 % RH	80 % RH
F1	0.4	2.0 ± 0.1	5.9 (8.2 ± 0.5)
F2	0.3		5.6
F3	0.3		6.4 (7.7 ± 0.1)
F4	5.2 ± 0. 1	9.3 ± 0.1	37.1 ± 0.5 (31.8 ± 0.6)
P1			1.3 ± 0.1-
P2			0.5 ± 0.1-

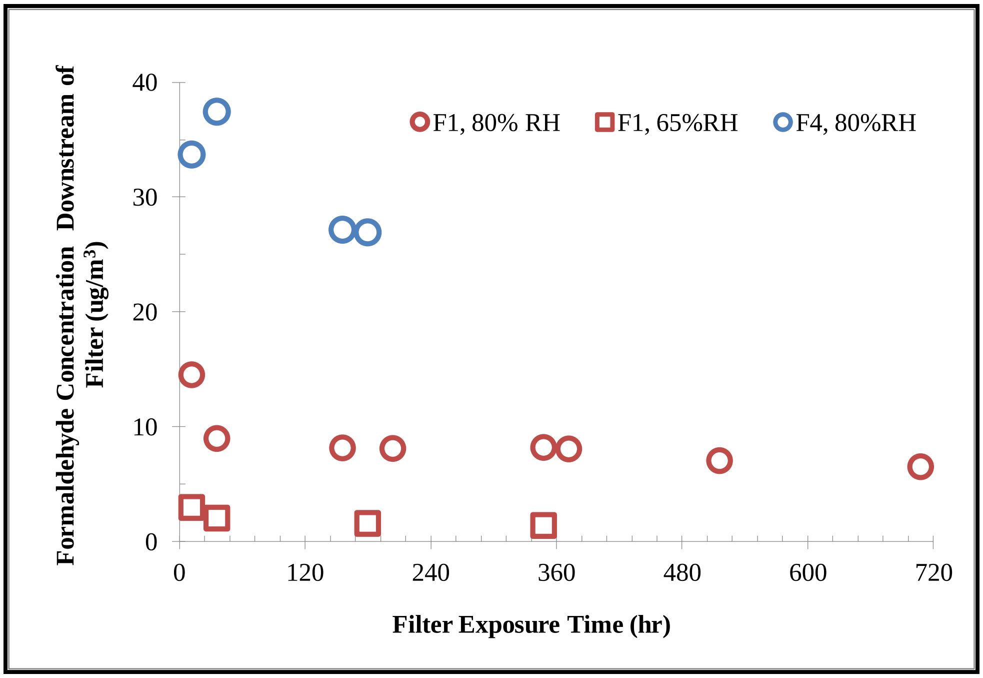


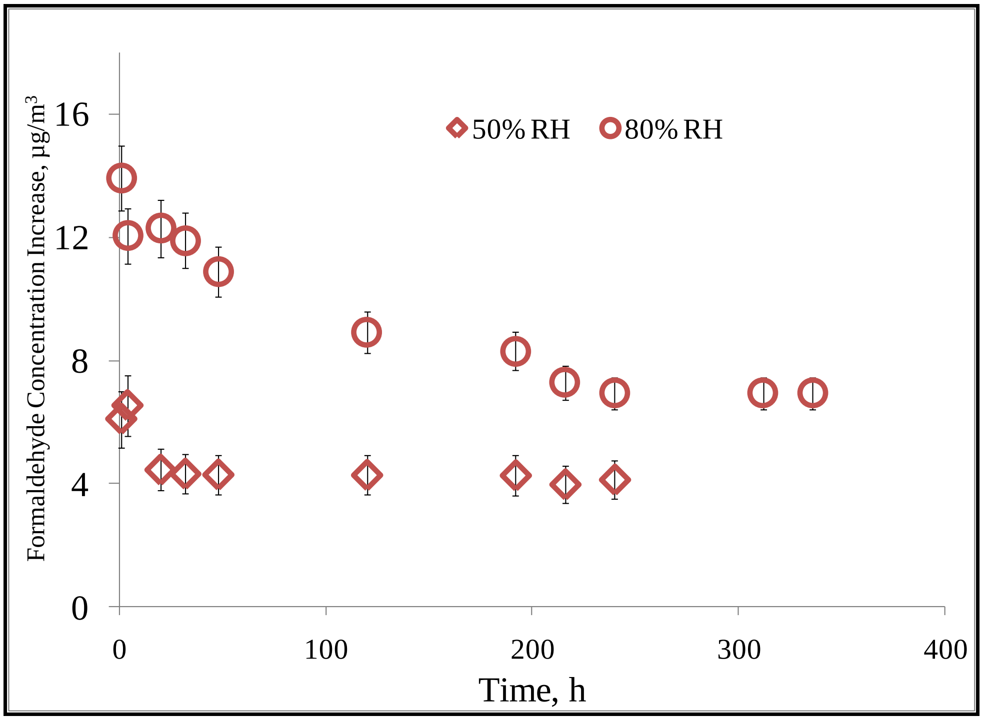
Figure 23: Formaldehyde downstream concentration vs. exposure time for filters F1 and F4 in low face velocity experiments (v = 0.013 m/s)

Fiberglass filters F1 (with heavy tackifier coating) and F4 (with no tackifier) and three polyester filters (P1-P3) were used to study formaldehyde emissions under high face velocity conditions (v = 0.5 m/s). Table 11 summarizes formaldehyde emission results for these filters. Similar to the findings of low velocity experiments, formaldehyde concentrations increased at higher RH. We report in each case the average of two 1-hour integrated samples taken during the experiment, subtracting the upstream concentration. The average background formaldehyde concentrations upstream of the filter were < 0.4 μg/m^3, and were subtracted from downstream values to determine emission rates. The experimental error in each case corresponds to one standard deviation.

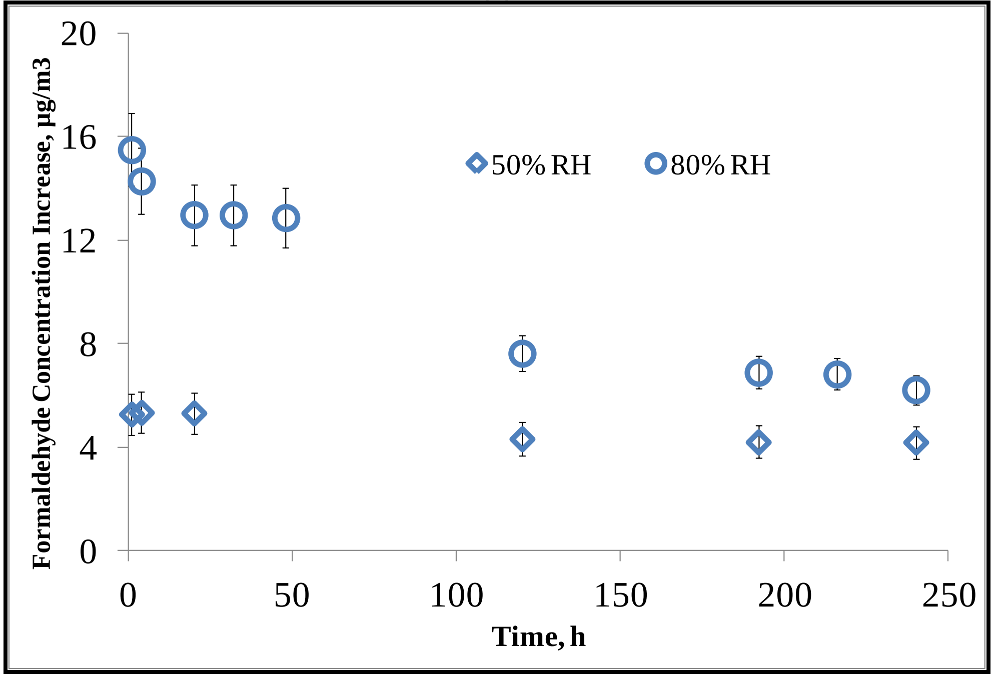
Independent tests were conducted with liquid samples of three different brands/models of tackifiers available commercially, applied to an inert substrate, and exposed to a flow of air at 80% RH. No significant formaldehyde emissions were observed leading to the conclusion that tackifiers do not take part in the hydrolysis reaction.

Table 11: Formaldehyde concentration changes Δ[F] across filters in high face velocity experiments (v = 0.5 m/s) at the end of 48 hours

Filter	Increase in formaldehyde concentration, Δ[F] (μg/m^3)		
	20 % RH	50 % RH	80 % RH
F1	1.2 ± 0.2	4.9 ± 0.6	10.8 ± 0.4
F4		4.3 ± 0.4	12.9 ± 0.7
P1			1.4 ± 0.3
P2			0.8 ± 0.2
P3			0.8 ± 0.3



(a)



(b)

Figure 24: Formaldehyde concentration increase downstream of filters (a) F1 and (b) F4 for different RH levels in experiments performed with high face velocity (v = 0.5 m/s) over a period of 10 days.

Figures 24(a) and (b) show the formaldehyde concentration measured downstream of filters F1 and F4 exposed to 50% and 80% RH as a function of time. It can be observed that initial formaldehyde concentrations decrease with time and approximately stabilize after ~100 hours of continuous exposure to the air flow.

Formaldehyde emissions from other types of filters P1, P2, and P3 were negligible after the first 24 hours. Table 11 shows the formaldehyde, concentrations observed downstream of the filters at the end of 24 hours. No significant emissions were observed from the polyester type filters, leading to the conclusion that fiberglass filter material type and construction may be the influencing factors in formaldehyde emissions at high humidity conditions.

2.4.3. Specific Aim #3: *Evaluate the overall impact of ozone chemistry with particle-loaded HVAC filters on the indoor work environment*.

2.4.3.1. Estimated impacts of ozone reactions with HVAC filters on indoor aldehyde concentrations

The expected increases in indoor aldehyde concentrations were estimated using equations 1 and 2, with the emission rates reported in Table 9 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. In Figure 25, 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 $\mu g/m^3$ for an *R* value of 1 as indicated by the single blue point in Figure 25. This could be predicted to increase to approximately 10 $\mu g/m^3$ (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 25 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.

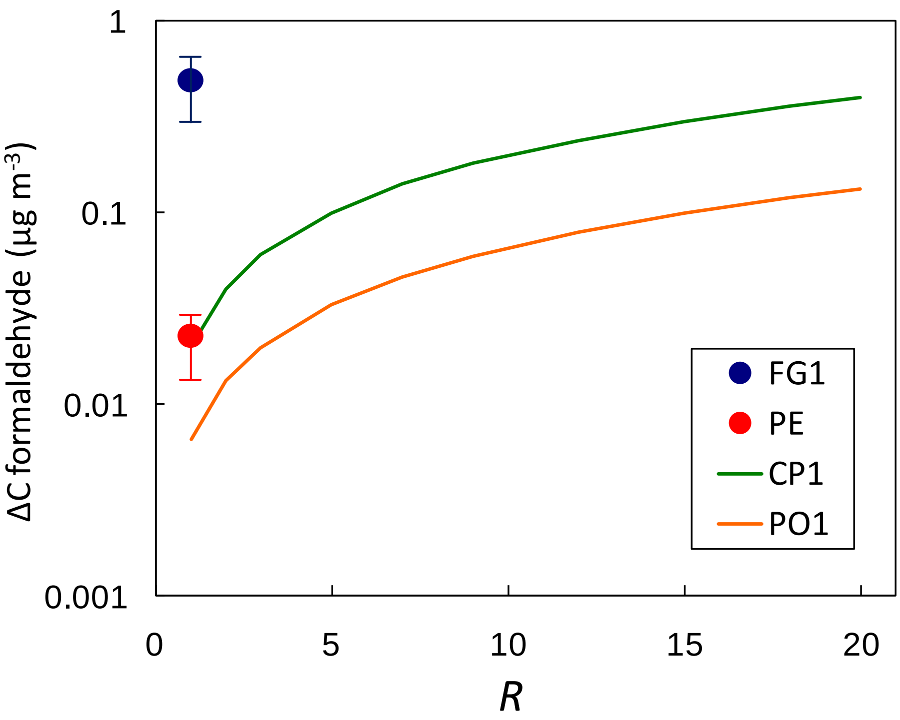


Figure 25: Estimated formaldehyde concentration increases at 50% RH, based on emission rates from filters used at LBNL, as a function of the ratio of filter media area to filter face area, *R*. FG1: fiberglass with heavy tackifier application; PE: polyester with medium tackifier application; CP1: cotton/polyester blend without tackifier; PO1: polyolefin without tackifier.

2.4.3.2. Estimated impacts of hydrolysis of HVAC filter additives in the absence of ozone on indoor aldehyde concentrations

The formaldehyde emission rate per unit filter face area, E_{FA} (in µg/h-m^2), for each experiment was calculated as

$$E_{FA} = (f \times \Delta[\mathrm{F}]) / S \qquad (7)$$

where f is the air flow rate (m^3/h) and S is the exposed filter face area (m^2). Figure 26 plots formaldehyde emission rate E_{FA} as a function of RH for the four fiberglass filters tested. For the filter media for which repeat tests were conducted, the average of replicates was used in Figure 26. Results indicate that the formaldehyde emission rate increased as the RH increased for all the four fiberglass filters regardless of tackifier loading, and that the effect was not linear. The formaldehyde emission rate at 80% RH increased about 5 – 7 times compared to that at 50% RH. The limited data measured at 50%, 65% and 80% RH for filter F1 and F4 indicated an approximate exponential increase in emission rate with RH as shown by the straight line fits on the semi-log plot (Figure 26). The strong dependence of formaldehyde emission rate on relative humidity suggests hydrolysis is likely the main mechanism causing formaldehyde emission from these filters. In addition, the formaldehyde emission rate from fiberglass filters with tackifier coatings (filters F1, F2 & F3) were similar regardless of the amount of tackifer coating for all RH levels, but was significantly lower than that from the otherwise identical fiberglass filter without tackifier. This finding implies that other additives (such as fiberglass binders), rather than the tackifier, are likely to be the main source of formaldehyde emission. This is further indicated by the fact that formaldehyde emission was much lower for all tackfier-coated polyester media even at 80% RH. Although high formaldehyde emission from fiberglass filter products have not been previously reported, formaldehyde emission from other fiberglass building products that use formaldehyde-based binders (such as fiberglass insulation) has been widely recognized and reported as a significant indoor source of formaldehyde (Salthammer et al., 2010).

In Figure 26, formaldehyde emission rates under high face velocity conditions are plotted as a function of RH for filter types F1 and F4 at the end of 24 h. It was observed that the emission rates were higher when the velocity was high, leading to downstream concentrations that were relatively similar under low and high velocity conditions. Under high velocity conditions, emission rates for F1 and F4 were comparable, in contrast with the results observed at low velocity.

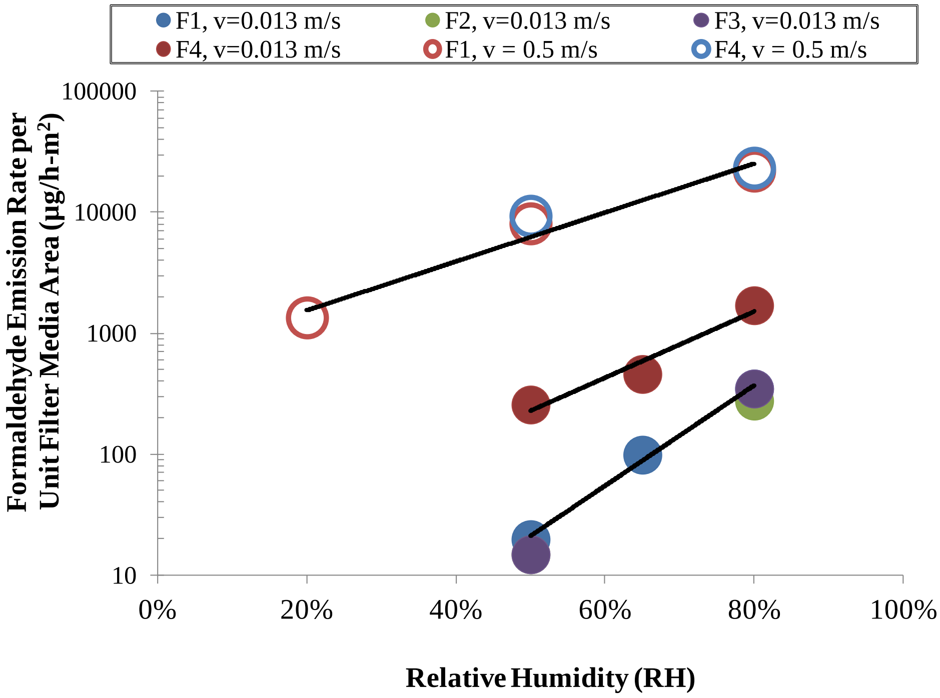


Figure 26: Formaldehyde emission rate as a function of RH in low (v = 0.013 m/s) and high (v = 0.5 m/s) face velocity experiments

Figure 27 shows in more detail the variation of formaldehyde emission rates with face velocity comparing the two types of filters F1 and F4. Figure 27(a) illustrates formaldehyde emissions rates for different face velocities at the end of 24 hours and Figure 27(b) shows results at the end of 240 hours. The emission rates at low face velocities for filter type F4 were about 3 times higher than the formaldehyde emission rate for filter type F1 (Figure 27(a), (b) and (d)). Hence, again the evidence indicates that the tackifier, present in filter F1 but not in F4, does not seem to be the main source of formaldehyde, and other additives (such as fiber binder resins) are likely the main source due to hydrolysis.

While filter F1 presents lower formaldehyde emission rates compared to filter F4 at low velocity, this difference is negligible at high velocity (Figure 27 (c) and Figure 27(e)). This phenomenon might be explained by mass transfer resistance associated with the presence of a tackifier coating on the surface of the fibers, or by the larger amount of water vapour delivered to the filters at high air velocity. At low air velocity, the reaction may be mass transfer limited or constrained by the small amount of water vapor delivered to the filter. At higher velocities these limitations are diminished. Instead, due to the absence of tackifier coating in filter F4, the reaction may be limited by the hydrolysis kinetics. An increase in velocity increases the mass transfer coefficient and decreases the resistance offered to the reaction on the filter surface. It should be noted that the y-axis on the plots shown in Figures 27 (a) – (e) are different.

One other experiment was conducted at a face velocity of 1 m/s for filter type F4 to estimate the dependence of face velocity on formaldehyde emissions from the filter surface. A formaldehyde concentration increase of 9.1 $\mu g/m^3$ was observed at the end of 24 hours. Figure 28 shows the emission rate as a function of face velocity. A logarithmic dependence of emission rate on face velocity at 80% RH was estimated and is also shown in Figure 28.

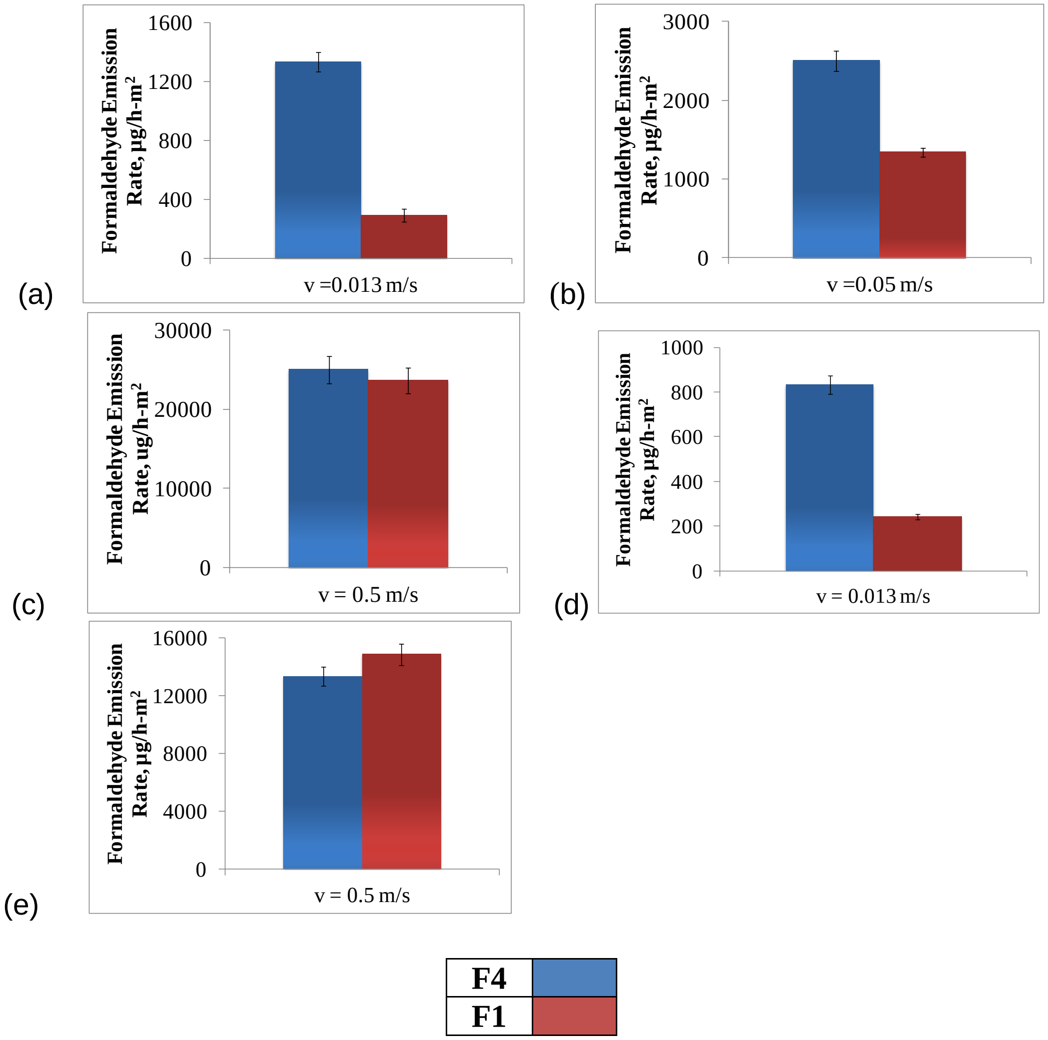


Figure 27: Formaldehyde emission rate from filter types F1 and F4 at different face velocities and RH of 80%: (a) at the end of 24 h for v = 0.013 m/s, (b) at the end of 24 h for v = 0.05 m/s, (c) at the end of 24 h for v = 0.5 m/s, (d) at the end of 240 h for v = 0.013 m/s, (e) at the end of 240 h for v = 0.5 m/s. Note that vertical axis scales vary among the plots.

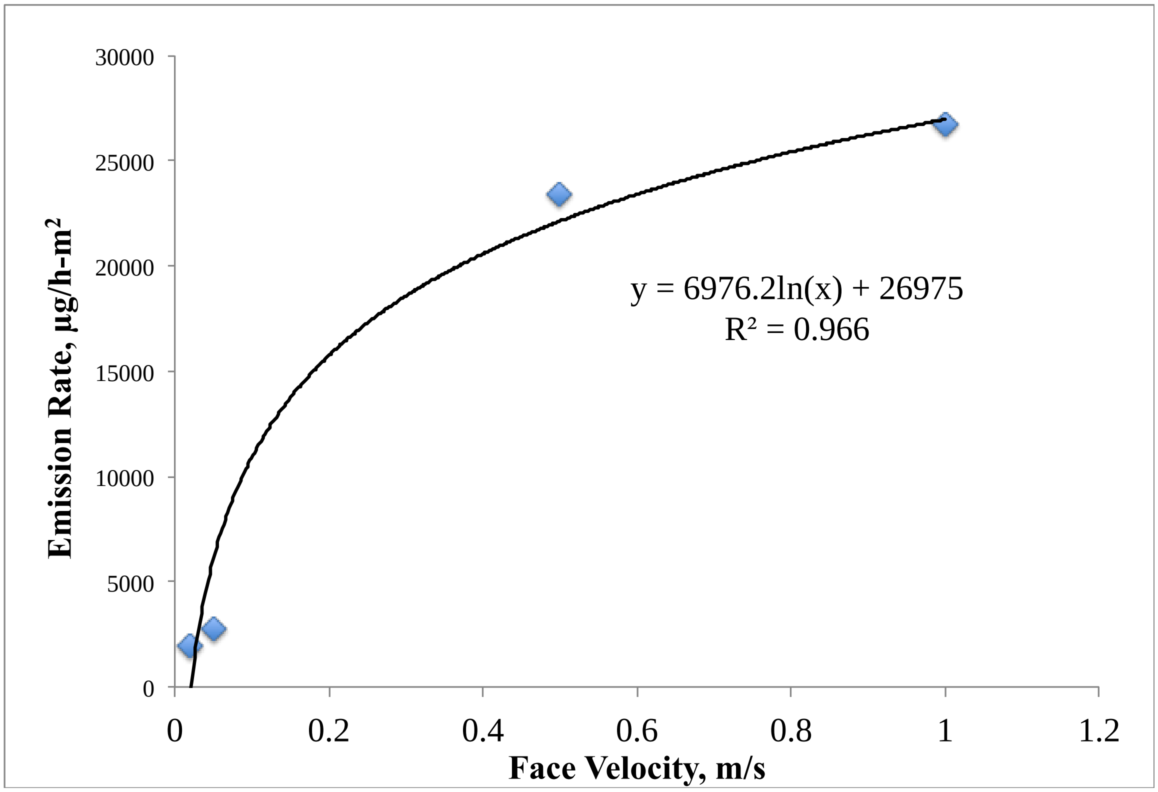


Figure 28: Emission rate as a function of face velocity for filter type F4 at 80% RH at the end of 24 hours.

2.5. CONCLUSIONS

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 formaldehyde and other 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 that detailed emission dynamics 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 some of our 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.

The largest possible increases of indoor formaldehyde concentrations due to hydrolysis of filter additives were estimated based on the highest steady-state formaldehyde emission rate measured among fiberglass filter media (F4) at high velocity (0.5 m/s). Assuming all outdoor air passes through the air filter, i.e., there is negligible outdoor air entry into the building via infiltration or other process that bypass the filter, and that formaldehyde emission rates from other sources are unaffected by the formaldehyde released from the filter, the steady-state indoor air formaldehyde concentration increase (ΔC) caused by the filter is equal to the concentration increase across the filter. Therefore, for an office building with filter(s) made of such fiberglass media installed, it is expected that the steady-state indoor formaldehyde concentration would increase by 4.2 $\mu g/m^3$ and 6 $\mu g/m^3$, as shown in Table 12, when the filter is exposed to room temperature air at 50% RH and 80% RH, respectively.

In commercial buildings, the supply airstream (mixture of outdoor and return air) upstream of heating and cooling coils is the most common location for particle filters. Much of the time, this mixed air is mostly recirculated indoor air. Since indoor RH is often maintained near 50%, under these conditions the RH at the filter will be near to 50% too. On the other hand, many HVAC systems now use an airside economizer, which increases the outdoor air beyond the minimum ventilation requirements, often to 100% of the total supply airflow, during moderate weather when it is suitable for "free" cooling. When the system is operating under the economizer mode, it is possible for the filter to be periodically exposed to RH as high as 80% under humid climate conditions. However, under these economizer-mode conditions the air temperature at the filters may be substantially less than room temperature. It is known that formaldehyde emission rates from manufactured wood products decrease with decreased air temperature. If the formaldehyde emission rates from filters decrease with air temperature, the formaldehyde concentration increases at the filter and the associated formaldehyde emission rates may be less than indicated in Table 12. Also, some economizers restrict the amount of outdoor air entry when the outdoor air is humid.

Table 12. Formaldehyde concentration increase across filter and emission rate for 1.0 x 10^{-3} m^2 samples of F4 media at high air velocity (v = 0.5 m/s).

RH (%)	Concentration Increase Across Filter (µg/m^3)		Emission Rate (mg/h-m^2)	
	At the end of 24 hrs	At the end of 240 hrs	At the end of 24 hrs	At the end of 240 hrs
50	5.3	4.2	10.7	9.3
80	13	6.0	23.4	12.5

In order to estimate the maximum duration of formaldehyde emissions from filters, the mass of polymers, binders and other extractable materials present on the filter F4 was determined by weighing filter samples before and after sonicating a sample in 20 ml of methylene chloride for 20 min. The mass of extracted material was determined by drying the solvent from the extracts after sonication. An average concentration of 58 g/m^2 was obtained for 5 filter samples. The mass of the extracts was estimated as 20% by weight of the filter material. Since average steady state formaldehyde emission rates of 9.3 and 12.5 mg/h-m^2 were estimated for 50% and 80% RH respectively, we can estimate a duration of formaldehyde emission between 50 and 100 days if we assume that ~ 25% of the extracted material can be hydrolyzed to formaldehyde. Filters are usually changed every 4-6 months, or 120 to 190 days, but often the HVAC system operates only about half of the time. These findings suggest that formaldehyde emissions from such filter types may be a persistent significant source of indoor formaldehyde levels in buildings over much of the filter deployment period (typically 3 to 6 months). Additionally, we showed in this study that the emissions of formaldehyde from soiled filters were higher than the clean counterpart, possibly due to added moisture retained by dust and particles ("filter cake").

At least one series of fiberglass filters made of same base media with different levels of tackifier coatings proved to be a substantial source of indoor formaldehyde when the filter was subjected to a high humidity. The increase in formaldehyde emission rates with RH in the absence of oxidative conditions (e.g., ozone) suggests that formaldehyde is formed as a byproduct of the hydrolysis of filter additives. High formaldehyde emissions measured from filters that do not contain tackifiers indicate that tackifiers are not the source of the formaldehyde. Instead, the data suggest that formaldehyde is most likely emitted from hydrolysis of other additives such as polymers and fiber binders. Our results also suggest that water vapor may be the limiting reactant of hydrolysis under the operating regime of these filters. Formaldehyde emission rates increased roughly in proportion to the air velocity, indicating that the reactants participating in the hydrolysis process are not significantly depleted when the system operates at high face velocity.

While the main findings of this study are robustly supported by the experimental data, there are limitations and questions that remain unanswered. Among the experimental variables not fully studied are the effect of temperature, of a wider range of air velocities, of the presence of dust and particles on the filter surface, the frequency and duration of periods of high humidity, the role of condensed water impinging on the filter surface. In addition, only a limited number of fiberglass filters from a few manufacturers were employed in this study.

2.6. PUBLICATIONS RESULTING FROM THIS GRANT

The following publications in peer-reviewed journals and conference proceedings have been supported by this grant:

2.6.1. Journal articles

1. Destaillats H; Chen W; Apte MG; Li N; Spears M; Almosni J; Brunner G; Zhang J; Fisk WJ. (2011) Secondary pollutants from ozone reaction with ventilation filters. *Atmos. Environ*. 45, 3561-3568.

2. Sidheswaran M.; Chen W; Chang A; Miller R; Cohn S; Fisk WJ; Sullivan D; Kumagai K; Destaillats H. Formaldehyde emissions from HVAC filters under different relative humidity conditions. *Submitted for publication*.

3. Sidheswaran M; Gundel L; Destaillats H. Composition of dust and particles deposited on HVAC filters. *In preparation*.

2.6.2. Conference proceedings

1. Chang A; Sidheswaran M; Miller R; Fisk WJ; Destaillats H; Chen W; Kumagai K. Effect of the relative humidity on formaldehyde emissions from HVAC filters. *10th International Healthy Buildings Conference (HB2012)*, Brisbane, Australia, July 2012.

2. Sidheswaran M; Williams RN; Gundel L; Lunden MM; Fisk WJ; Apte MG; Destaillats H. Characterization of reaction products and ultrafine particles from ozone-initiated chemistry on filters from ventilation systems of commercial buildings. *12th International Conference on Indoor Air Quality and Climate (Indoor Air 2011)*, Austin TX, USA, June 2011.

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APPENDIX

Table 1-S. Organic compounds extracted from filter cake in filters retrieved from an LBNL building.

CAS	Name	Source	Chemical functionality	RT	m/z of Parent Ion	Formula	MW
565-69-5	3-Pentanone, 2-methyl-	indoor/outdoor	ketone	2.55	71 m/z	C6H12O	100
104-61-0	2(3H)-Furanone, dihydro-5-pentyl-	insecticide	furan	2.61	85 m/z	C9H16O2	156
623-37-0	3-Hexanol	indoor/outdoor/perfume	alcohol	2.72	55 m/z	C16H14O	102
111-27-3	1-Hexanol	indoor/outdoor/perfume	alcohol	2.83	56 m/z	C6H14O	102
115-19-5	3-Butyn-2-ol, 2-methyl-	indoor/outdoor/pesticides	alcohol	2.95	69 m/z	C5H8O	84
695-53-4	Dimethadione	drug	nitrogenated compound	3.19	129 m/z (67)	C5H7NO3	129
123-42-2	2-Pentanone, 4-hydroxy-4-methyl-	indoor/outdoor	ketone	3.26	59 m/z (83)	C6H12O2	116
110-83-8	Cyclohexene	indoor/outdoor	cycloalkane	3.31	67 m/z	C6H10	82
6672-30-6	(R)-(+)-3-Methylcyclopentanone		cycloketone	3.38	69 m/z	C6H10O	98
302-66-9	1-Pentyn-3-ol, 3-methyl-, carbamate	bioeffluents	nitrogenated compound	3.44	83 m/z	C7H11NO2	141

100-41-4	Ethylbenzene	plasticizer/pertro chemical	aromatic	3.50	91 m/z	C8H10	106
79-06-1	2-Propenamide	cooking byproduct	carbamate	3.54	71 m/z	C3H5NO	71
95-47-6	o-Xylene	indoor/outdoor	aromatic	3.61	91 m/z	C8H10	106
123-38-6	Propanal	wood based flooring materials	aldehyde	3.83	58 m/z	C3H6O	58
100-42-5	Styrene	smoking/latex based carpet	aromatic	3.88	78 m/z	C8H8	104
79-29-8	Butane, 2,3-dimethyl-		alkane	4.15	71 m/z	C6H14	86
7326-46-7	2-Furanol, tetrahydro-2-methyl-	pest control	furan	4.15	71 m/z	C5H10O2	102
637-64-9	2-Furanmethanol, tetrahydro-, acetate	pest control	furan	4.15	71 m/z	C7H12O3	144
599-04-2	Pantolactone	cream/ personal products	furan	4.15	71 m/z	C6H10O3	130
79-34-5	Ethane, 1,1,2,2-tetrachloro-	fumigant or refrigerant?	halogenated alkane	4.24	83 m/z	C2H2Cl4	166
96-23-1	2-Propanol, 1,3-dichloro-	indoor reaction hydrolysis	halogenated alcohol	4.51	81 m/z	C3H6Cl2O	128
695-06-7	2(3H)-Furanone, 5-ethyldihydro-	emission from flooring materials	furan	4.63	85 m/z	C6H10O2	114
590-67-0	1-Methylcyclohexanol		cycloalkane	4.73	71 m/z (105)	C7H14O	114
1122-60-7	Cyclohexane, nitro-		nitrogenated compound	4.76	83 m/z	C6H11NO2	129
98-83-9	α-Methylstyrene	emissions from electronics	aromatic	4.95	118 m/z	C9H10	118
821-55-6	2-Nonanone	microbial VOC	ketone	5.41	58 m/z	C9H18O	142
112-25-4	Ethanol, 2-(hexyloxy)-		alcohol	5.77	85 m/z	C8H18O2	146
149-57-5	Hexanoic acid, 2-ethyl-	varnished paraquet	acid	6.31	73 m/z	C8H16O2	144

65-85-0	Benzoic Acid	emission tests of paints and building material	acid	6.82	77 m/z	C7H6O2	122
529-20-4	Benzaldehyde, 2-methyl-	emissions from polymers - plastics	aromatic	7.18	119 m/z	C8H8O	120
91-20-3	Naphthalene	emissions from fuel, tobacco smoke, use of mothballs, fumigants and deodorizers	PAH	7.23	128 m/z (119)	C10H8	128
85006-04-8	1,6-Octadiene, 5,7-dimethyl-, (R)-	perfume	alkenes	7.31	67 m/z	C10H18	138
934-32-7	1H-Benzimidazol-2-amine	pesticide	nitrogenated compound	7.50	133 m/z	C7H7N3	133
95-16-9	Benzothiazole	rubber emissions	nitrogenated compound	7.64	135 m/z	C7H5NS	135
112-05-0	Nonanoic acid	environment tobacco smoke, photooxidation of biogenic compounds with ozone	carboxylic aicd	7.82	60 m/z (99)	C9H18O2	158
96-80-0	N,N-Diisopropylaminoethanol	chemical indoor/outdoor	nitrogenated compound	8.24	72 m/z	C8H19NO	145
91-57-6	Naphthalene, 2-methyl-	cigarette smoke, wood smoke, tar, asphalt	PAH	8.31	142 m/z	C11H10	142
85-44-9	Phthalic anhydride	oxidation of naphthalene, also produced from plasticizer emissions	oxygenated aromatic	8.43	76 m/z	C8H4O3	148
3581-91-7	Thiazole, 4,5-dimethyl-	flavoring and perfume	nitrogenated compound	8.50	113 m/z	C5H7NS	113
2231-57-4	Carbonothioic dihydrazide		nitrogenated compound	8.73	106 m/z	CH6N4S	106
97-87-0	Propanoic acid, butyl ester	printed matter - emissions from printed publications, journals, books etc	ester	8.91	89 m/z	C8H16O2	144
83-32-9	Acenaphthene	traffic, wood burning, tar and bitumen based adhesives	PAH	9.06	154 m/z	C12H10	154

131-11-3	Dimethyl phthalate	plasticizer/pertro chemical	phthalate ester	9.58	163 m/z	C10H10O4	194
88-32-4	Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	pesticides, fragrants, insecticides,	oxygenated aromatic	9.62	165 m/z	C11H16O2	180
719-22-2	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	biomass fuel emissions	ketone	9.68	177 m/z	C14H20O2	220
527-84-4	Benzene, 1-methyl-2-(1-methylethyl)-	particle board emissions	aromatic	9.86	119 m/z	C10H14	134
532-27-4	Acetophenone, 2-chloro-	tear gas!!! And pharmaceutical intermediate	aromatic	10.51	77 m/z	C8H7ClO	154
115-86-6	Triphenyl phosphate	flame retardant	aromatic phosphate	10.63	325 m/z	C18H15O4P	326
84-66-2	Diethyl Phthalate	plasticizer/pertro chemical	phthalate ester	10.71	149 m/z	C12H14O4	222
101-84-8	Diphenyl ether	flame retardant	ether	12.23	170 m/z	C1210O	170
84-74-2	Dibutyl phthalate	plasticizer/pertro chemical	phthalate ester	13.01	149 m/z (205)	C16H22O4	278
	Phthalic acid, butyl hexyl ester	plasticizer/pertro chemical	ester	13.34	149m/z	C18H26O4	306
84-69-5	diisobutylphthalate	plasticizer/pertro chemical	phthalate ester	13.45	149 m/z (205)	C16H22O4	278
82304-66-3	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	oxidartion of	ketone	14.15	57 m/z (276)	C17H24O3	276

84-62-8	diphenyl phthalate	plasticizer/pertro chemical		14.19	225 m/z	$C_{20}H_{14}O_4$	318
502-69-2	2-pentadecanone-6,10,14,trimethyl	oxidation of phytol	ketone	14.32	43 m/z (268)	$C_{18}H_{36}O$	268
131758-71-9	(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	emissions from essential oil		16.12	91 m/z	$C_{22}H_{20}OS$	332
22532-16-7	Alpha-phenyl-alpha-tropylacetaldehyde tosylhydrazone			16.23	91 m/z	$C_{22}H_{22}N_2O_2S$	378
7614-93-9	1,3-Diphenyl-1-butene	dimerization reaction of styerene, plasticizer	aromatic	16.29	115 m/z	$C_{16}H_{16}$	208
1726-14-3	Benzene, 1,1'-(1-butenylidene)bis-	human source	aromatic	16.37	115 m/z	$C_{16}H_{16}$	208
	Thiocarbamic acid, N,N-dimethyl, S-1,3-diphenyl-2-butenyl ester	landfill leachat	thiozoles	16.42	207 m/z	$C_{19}H_{21}NOS$	311
1788-31-4	Dibenzyl ketoxime		oxime	16.61	91 m/z	$C_1H_{15}NO$	225
1460-59-9	Dibenzo[a,e]cyclooctene, 5,6,11,12-tetrahydro-			16.74	193 m/z	$C_{16}H_{16}$	208
1120-21-4	Undecane	Fuel emission	alkane	16.80	129 m/z	$C_{11}H_4$	156
106-21-8	1-Octanol, 3,7-dimethyl-	Fuel emission	alcohol	16.94	57 m/z (149)	$C_{10}H_{22}O$	158
150-86-7	Phytol	plant wax	alcohol	17.43	57 m/z	$C_{20}H_{40}O$	296
2432-90-8	Didodecyl phthalate	plasticizer/pertro chemical	phthalate ester	17.65	71 m/z	$C_{32}H_{54}O_4$	502

112-44-7	Undecanal	Fuel emission	aldehyde	17.93	149 m/z (72)	C11H22O	170
111-84-2	Nonane	Fuel emission	alkane	18.49	57 m/z	C9H20	128
481-21-0	Cholestane	Fuel emission	alkane	19.15	217 m/z	C27H48	372
53584-60-4	C2 7 20S 5α(H),14α(H),17α(H)-cholestane	Fuel emission	alkane	21.37	191 m/z	C29H50	398
53584-62-6	17α(H),21 β(H)-30-Norhopane	Fuel emission	alkane	24.28	191 m/z		
	22S-17α(H),21 β(H)-30,31 -Bishomohopane	Fuel emission	alkane	25.095	191 m/z		
498-07-7	levoglucosan	wood	cyclo alkane	27.81	60 m/z	C6H10O5	162
646-31-1	tetracosane	plant wax	cyclo alkane	29.34	57 m/z	C24H50	338
1604-34-8	6,10-dimethylundecane-2-one	plant wax	ketone	30.26	58 m/z	C13H26O	198
629-99-2	pentacosane	plant wax	alkane	31.52	57 m/z	C25H52	352
593-49-7	heptacosane	plant wax	alkane	33.47	57 m/z	C27H56	380

630-02-4	octacosane	plant wax	alkane	36.82	57 m/z	C28H58	394
	1,16-hentriacontaneione	plant wax	alkane	39.15	55 m/z	C31H62O	436
141-79-7	3-Penten-2-one, 4-methyl-	indoor/outdoor	ketone	2.7018	55 m/z	C6H12O	
124-18-5	Decane	indoor/outdoor	alkane	2.7494	71 m/z	C10H22	142
108-93-0	Cyclohexanol	carpets	cyclic alcohol	3.2946	67 m/z (80)	C6H12O	100
591-12-8	2(3H)-Furanone, 5-methyl-	reaction product of Xylene with OH radical	furan	3.5803	55 m/z	C5H6O2	98
79-01-6	Trichloroethylene	indoor/outdoor	chlorinated compound	4.2359	82 m/z	C2HCl3	131
108-08-7	Pentane, 2,4-dimethyl-	indoor/outdoor		4.5738	85 m/z		
1122-60-7	Cyclohexane, nitro-	product of indoor air reaction?	nitrogenated compound	5.0416	55 m/z	C6H11NO2	
302-66-9	1-Pentyn-3-ol, 3-methyl-, carbamate	drug	nitrogenated compound	5.2278	81 m/z	C7H11NO2	
96-23-1	2-Propanol, 1,3-dichloro-	product of indoor air reaction (hydrolysis of tris(1,3-dichloro-2-propyl)phosphate (TDCPP)	chlorinated compound	5.3763	81 m/z		
111-87-5	1-Octanol	emission from electronic materials	alcohol	5.4597	71 m/z		
112-32-3	Formic acid, octyl ester	flavoring and perfume		5.5092	70 m/z (57)		
100-51-6	Benzyl Alcohol	emissions from carpets		5.5413	79 m/z		

112-25-4	Ethanol, 2-(hexyloxy)-	cleaning indoor/outdoors		5.7602	85 m/z		
100-52-7	Benzaldehyde	wood based products		5.9609	105 m/z (67)		
124-19-6	Nonanal	indoor/outdoor/perfume		6.2682	81 m/z		
123-19-3	4-Heptanone	indoor/outdoor and indicator of mold growth		6.6818	71 m/z		
934-32-7	1H-Benzimidazol-2-amine			7.4941	133 m/z		
112-05-0	Nonanoic acid	emissions from cooking		7.8251	73 m/z		
97-87-0	Propanoic acid, 2-methyl-, butyl ester	emissions from indoor plants		8.9004	89 m/z		
59-67-6	Niacin	vitamin, human effluent		9.3327	77 m/z		
532-27-4	Acetophenone, 2-chloro-			9.5904	77 m/z		
84-66-2	Diethyl Phthalate	PVC products, PVC flooring		10.7072	149 m/z		
13067-27-1	Pyrazine, 2,6-diethyl-	volatile constitutent of coffee		11.6969	135 m/z		
84-16-2	Phenol, 4,4'-(1,2-diethyl-1,2-ethanediyl)bis-, (R*,S*)-	synthetic estrogen!!		11.9305	135 m/z		
3622-84-2	Benzenesulfonamide, N-butyl-	plasticizer		12.2238	77 m/z		
127-35-5	Phenazocine	illicit drug?		13.7074	230 m/z (193)		
626-82-4	Hexanoic acid, butyl ester	polymer emissions		14.447	99 m/z		

57-11-4	Octadecanoic acid	personal care products - human emissions		14.5693	87 m/z (223)		
110-80-5	Ethanol, 2-ethoxy-	indoor/outdoor, emission from electronic materials		14.7178	59 m/z		
646-06-0	1,3-Dioxolane	human source		15.3917	73 m/z		
13674-87-8	Tris(1,3-dichloroisopropyl)phosphate	flame retardant		15.5814	75 m/z		
98-95-3	Benzene, nitro-	indoor/outdoor		15.7249	77 m/z		
75-83-2	Butane, 2,2-dimethyl-	emission from building matierals		15.9034	71 m/z		
791-28-6	Triphenylphosphine oxide	flame retardant		16.7484	277 m/z		

Table 2-S. Organic compounds extracted from filter cake in filters retrieved from a Port of Oakland building.

CAS	Name	Source	Chemical functionality	RT	m/z of Parent Ion	Formula	MW
65-85-0	Benzoic Acid	paints and building material	acid	6.8931	105	$C_7H_6O_2$	122
1783-84-2	8,11,14-Eicosatrienoic acid, (Z,Z,Z)-	plasticizer	acid	8.759	41	$C_{20}H_{34}O_2$	306
111-87-5	1-Octanol	emission from electronic materials	alcohol	2.5294	56	$C_8H_{18}O$	130
107-74-4	1,7-Octanediol, 3,7-dimethyl-	food flavoring/perfume	alcohol	5.683	59	$C_{10}H_{22}O_2$	174
35192-73-5	1-Nonen-4-ol	Soy bean volatiles	alcohol	5.893	55	$C_9H_{18}O$	142
13143-81-2	Bicyclo[2.2.1]hept-2-en-7-ol, 7-(4-methoxyphenyl)-, syn-	fragrance	alcohol	10.359	135	$C_{14}H_{16}O_2$	216
	Cholestan-3-ol, 2-methylene-, (3á,5à)-	esential oil	alcohol	11.45			
56554-77-9	13-Heptadecyn-1-ol	essential oil	alcohol	15.236	82	$C_{17}H_{32}O$	252

5989-33-3	2-Furanmethanol, 5-ethenyltetrahydro-à,à,5-trimethyl-, cis-	vapor constituent of roasted coffee	alcohol		59	$C_{10}H_{18}O_2$	170
88-40-4	Benzene, 1-(1,1-dimethylethyl)-2-methoxy-4-methyl-	flavoring agent	aromatic	18.491	163	$C_{12}H_{18}O$	178
3788-32-7	Cyclopentane, (2-methylpropyl)-	polymer emission - plasticizer	cyclo alkane	2.537	41	C_9H_{18}	126
930-89-2	Cyclopentane, 1-ethyl-2-methyl-, cis-	polymer emission - plasticizer	cyclo alkane	2.627	55	C_8H_{16}	112
101-97-3	Benzeneacetic acid, ethyl ester	flavoring agent	ester	6.2641	91	$C_{10}H_{12}O_2$	164
2566-89-4	5,8,11,14-Eicosatetraenoic acid, methyl ester, (all-Z)-	plasticizer	ester	8.892	79	$C_{21}H_{34}O_2$	318
2566-90-7	4,7,10,13,16,19-Docosahexaenoic acid, methyl ester, (all-Z)-	plant oil extract	ester	8.927	79	$C_{23}H_{34}O_2$	342
56847-03-1	6,9-Octadecadiynoic acid, methyl ester	pyrolysis of meat and bone, bio oil	ester	9.219	91	$C_{19}H_{30}O_2$	290
42175-41-7	Decanoic acid, phenylmethyl ester	fragrance	ester	9.5702	91	$C_{17}H_{26}O_2$	262

55268-58-1	Nonanoic acid, 9-(3-hexenylidenecyclopropylidene)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester, (Z,Z,Z)-	pepper plant extract/mould inhibitor	ester	12.356	79	$C_{21}H_{36}O_4$	352
100-44-7	Benzyl chloride	plasticizer and precursor to perfumes and flavorants	halogenated compound	5.3274	91	C_7H_7Cl	126
532-27-4	Acetophenone, 2-chloro-	pharmaceutical intermediate	halogenated compound	6.8931	105	C_8H_7ClO	154
51-71-8	Hydrazine, (2-phenylethyl)-	drug - indoor source	nitrogenated compound	3.6084	45	$C_8H_{12}N_2$	136
84-66-2	Diethyl Phthalate	plasticizer	phthalate	10.716	149	$C_{12}H_{14}O_4$	222
131-11-3	Dimethyl phthalate	plasticizer	phthalate	16.37	163	$C_{10}H_{10}O_4$	194
141-79-7	3-Penten-2-one, 4-methyl-	aldol condensation of acetone/Used in paint removers, as a solvent for plastics, and as an insect repellent.	ketone	2.921	83	$C_6H_{10}O$	98
1122-60-7	Cyclohexane, nitro-	product of indoor air reaction	nitrogenated compound	3.8889	55	$C_6H_{11}NO_2$	129
122-78-1	Benzeneacetaldehyde	volatiles from mould/filter surface growth	aldehyde	6.2641	91	C_8H_8O	120
85-44-9	Phthalic anhydride	oxidation of naphthalene, also produced from plasticizer emissions	phthalate	8.4391	104	$C_8H_4O_3$	148
82304-66-3	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	Secondary organic aerosols and oxidation product	ketone	13.037	57	$C_{17}H_{24}O_3$	276

23024-54-6	cis-2,3-Epoxyoctane	chemical intermediate/ reaction product	epoxide	14.783	56	C8H16O	128
28180-70-3	trans-2,3-Epoxyoctane	chemical intermediate/ reaction product	epoxide	19.364	56	C8H16O	128
123-42-2	2-Pentanone, 4-hydroxy-4-methyl-	solvent	ketone	3.2621	43	C6H12O2	116
79-34-5	Ethane, 1,1,2,2-tetrachloro-	refrigirant and solvent	halogenated compound	4.2365	83	C2H2Cl4	166
105-58-8	Carbonic acid, diethyl ester	solvent	ester	5.3274	45	C5H10O3	118
624-20-4	Hexane, 1,2-dibromo-	solvent	halogenated compound	5.492	83	C6H12Br2	242
24774-58-1	Hexane, 2,5-dibromo-	solvent	halogenated compound	5.618	83	C6H12Br2	242
565-59-3	Pentane, 2,3-dimethyl-	solvent	alkane	5.765	56	C7H16	100
2040-96-2	Cyclopentane, propyl-	unkown	cyclo alkane	2.892	69	C8H16	112
7423-69-0	1-Hexene, 3,5-dimethyl-	unkown	alkane	2.935	41	C8H16	112
108-85-0	Cyclohexane, bromo-	unknown	halogenated compound	5.942	83	C6H11Br	162
69511-49-5	2-Butynoic acid, 4-[(tetrahydro-2H-pyran-2-yl)oxy]-, methyl ester	unkown	acid	6.107	83	C10H14O4	198
	Phosphorous acid, dicyclohexyl ester	unknown	acid	6.193			
63843-03-8	2,6-Octadiene, 2,4-dimethyl-	unknown	alkane	6.218	83	C10H18	138
74752-93-5	Cyclopropane, 1,1,2,3-tetramethyl-	unknown	cyclo alkane	6.251	55	C7H14	98

103-81-1	Benzeneacetamide	unknown	nitrogenated compound	6.2641	91	C8H9NO	135
98-88-4	Benzoyl chloride	unknown	halogenated compound	6.8931	105	C7H5ClO	140
	2-(1,1-Dimethylethyl)-5-oxohexanal	unknown	acid	11.436	58	C10H18O2	170
65646-68-6	Fenretinide	unknown	nitrogenated compound	12.314	109	C26H33NO2	391
55622-44-1	Cyclopropanedecanoic acid, à-(acetyloxy)-2-hexyl-, methyl ester	unknown	ester	12.987	55	C22H40O4	368
	Tricyclo[5.4.3.0(1,7)]tetradecane-3,6-diol, 4-formyl-2,4,7,14-tetramethyl-, diacetate	unknown	alcohol	13.346	149	C23H36O5	392
56053-11-3	Androstane, 17,18-diiodo-, (5à,17á)-	unknown	halogenated compound	13.925	95	C19H30I2	512
116-31-4	Vitamin A aldehyde	unknown	aldehyde	14.607	91	C20H28O	284
58422-90-5	1,3-Dioxolane-2-heptanenitrile, α-methyl-δ-oxo-2-phenyl-	unknown	nitrogenated compound	16.496	149	C17H21NO3	287
	3-Methoxymethoxy-3,7,16,20-tetramethyl-heneicosa-1,7,11,15,19-pentaene	unknown	ether	18.237	45	C27H46O2	402
56877-40-8	1,1,3-Propanetricarboxylic acid, 3-[[(phenylmethoxy)carbonyl]amino]-, 1,1-bis(1,1-dimethylethyl) 3-methyl ester, (.+-.)-	unknown	ester	19.152	91	C23H33NO8	451
	1-(2,2-Dimethyl[1,3]dioxan-4-yl)ethanol	unknown	alcohol	22.473	43	C8H16O3	160
10178-59-3	2-Ethylthiolane, S,S-dioxide	emissions from o-rings (moving parts of machines)	sulfur compound	2.791	56	C6H12O2S	148

106-93-4	Ethane, 1,2-dibromo	fumigant	halogenated compound	2.915	107	C2H4Br2	186
108-90-7	Benzene, chloro-	herbicide/dyes/pesticides/intermediate in the production of such compounds	halogenated compound	3.3345	112	C6H5Cl	112
20296-29-1	3-Octanol	urban	alcohol	5.699	59	C8H18O	130
	Oxalic acid, isobutyl nonyl ester	Volatiles from imported rice	ester	6.184	83	C17H30O4	298
79-19-6	Hydrazinecarbothioamide	pesticide	nitrogenated compound	6.2632	91	CH5N3S	91
25217-18-9	Carbanilic acid, p-chloro-, 2-chloroethyl ester	pesticide	nitrogenated compound	9.9918	233	C9H9Cl2NO2	233
124-18-5	decane	fuel	alkane	12.785			
2676-41-7	6,9,12-Octadecatrienoic acid, methyl ester	volatile products from rice	ester	14.935	41	C19H32O2	292
111-84-2	nonane		alkane	15.236			128
821-55-6	2-Nonanone	urban pollution	ketone	21.289	43	C9H18O	142
630-01-3	Hexacosane	fuel emissions	alkane	23.617			366
879-12-9	trimethylnaphthalene	fuel emissions	PAH	24.153			170
545-47-1	Lupeol	fuel emissions	alcohol	25.348	43	C30H50O	426
630-02-4	Octacosane	fuel emissions	alkane	25.394			394
	Cyclopentanol, 2,2-dichloro-1,4-dimethyl-	fuel emissions	halogenated compound	26.519	85	C7H12Cl2O	182

7194-86-7	Nonatriacontane	fuel emissions	alkane	28.476			548
218-01-9	Chrysene	fuel emissions	alkane	30.179			228
481-21-0	Cholestane	fuel emissions	alkane	31.37		C27H48	
53584-60-4	C27 20S 5α(H),14α(H),17α(H)-cholestane	fuel emissions	alkane	34.28		C29H50	
53584-62-6	17α(H),21 β(H)-30-Norhopane	fuel emissions	alkane	35.095			
	22S-17α(H),21 β(H)-30,31 -Bishomohopane	fuel emissions	alkane	38.218			
	C29 Hopane	fuel emissions	alkane	40.278		C29H50	
	C30 Hopane	fuel emissions	alkane	42.235		C30H52	
92397	10H-Phenothiazine, 2-chloro-	fumigant	halogenated compound		233	C12H8ClNS	233
30390-60-4	2,2-Dimethyl-4-octenal	vegetation	aldehyde	5.526	83	C10H18O	154
546-49-6	1,5-Heptadien-4-one, 3,3,6-trimethyl-	vegitation/ essential oil	ketone	5.816	83	C10H16O	152

546-97-4	Columbin	plant root extract	ester	13.426	44	$C_{20}H_{22}O_6$	358
1808-26-0	5,8,11,14-Eicosatetraenoic acid, ethyl ester, (all-Z)-	marine life	ester	16.295	79	$C_{22}H_{36}O_2$	332
593-08-8	2-Tridecanone	naturally occuring insectiside	ketone	18.634	58	$C_{13}H_{26}O$	198