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New Air Cleaning Strategies for Reduced Commercial Building Ventilation Energy – FY11 Final Report

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Executive Summary

Introduction

Approximately ten percent of the energy consumed in U.S. commercial buildings is used by HVAC systems to condition outdoor ventilation air. Reducing ventilation rates would be a simple and broadly-applicable energy retrofit option, if practical countermeasures were available that maintained acceptable concentrations of indoor-generated air pollutants. The two general categories of countermeasures are: 1) indoor pollutant source control, and 2) air cleaning. Although pollutant source control should be used to the degree possible, source control is complicated by the large number and changing nature of indoor pollutant sources. Particle air cleaning is already routinely applied in commercial buildings. Previous calculations indicate that particle filtration consumes only 10% to 25% of the energy that would otherwise be required to achieve an equivalent amount of particle removal with ventilation. If cost-effective air cleaning technologies for volatile organic compounds (VOCs) were also available, outdoor air ventilation rates could be reduced substantially and broadly in the commercial building stock to save energy. The research carried out in this project focuses on developing novel VOC air cleaning technologies needed to enable energy-saving reductions in ventilation rates.

Effective and energy efficient VOC air cleaning, used together with existing particle filtration technologies, could enable outdoor air ventilation rates (VRs) to be reduced with indoor air quality maintained or improved. We envision two energy saving applications for VOC air cleaning in commercial buildings:

1. In a significant number of office buildings (and likely also in other buildings), VRs exceed the requirements specified in standards, yet indoor levels of formaldehyde (declared a human carcinogen by the World Health Organization and U.S. Department of Health and Human Services) are above guidelines, while concentrations of other pollutants are below guidelines. In these instances, reductions in VRs to the minimum levels specified in standards could pose

liabilities; however, formaldehyde specific air cleaning could enable VRs to be reduced with associated energy savings.

2. Through application of the indoor air quality (IAQ) procedure in the ASHRAE commercial ventilation standard, VRs can be reduced below the tabulated minimum values if other methods are employed to maintain IAQ. The indoor-generated pollutants of concern in most commercial buildings are various types of particles and VOCs. These buildings normally have negligible indoor sources of inorganic gaseous pollutants. The concentrations of indoor generated particles are readily controlled using existing particle filters. If effective and practical VOC air cleaning methods were available, widespread use of the IAQ procedure would be possible. In the longer term, ventilation standards might be changed to recommend less ventilation as a base case with VOC air cleaning required.

This study seeks to develop VOC air cleaning systems that address both of these applications. For application number 2, we targeted a VOC air cleaning system that could enable a 50% reduction in ventilation rates. In a typical commercial HVAC system that provides a mixture of recirculated and outdoor air, a VOC air cleaner in the supply airstream must have a 15% to 20% VOC removal efficiency to counteract a 50% reduction in outdoor air supply.

Progress achieved during FY10

This project started in FY10. During that first year, three air cleaning technologies were evaluated, and results summarized in our first report (Sidheswaran et al. 2010).

Activated Carbon Fiber Filters: In one technology, activated carbon fiber (ACF) cloths, which can be deployed in the same manner as particle filters, were used to adsorb a wide range of VOCs from the indoor air during the day. The ACF media can be

regenerated periodically, i.e., VOCs are driven off the media and vented outdoors. We evaluated regeneration with unheated outdoor air at a low flow rate. e.g., 10% - 20% of the flow during air cleaning and regeneration with even lower regeneration air flow rates (e.g., 1% of the flow during air cleaning) and a short period of heating of the carbon fiber media. In one condition using unheated outdoor air for regeneration, VOC removal efficiencies were in the 40% to 60% range for all VOCs except formaldehyde, which was removed with 15% efficiency. With heated regeneration air, VOC removal efficiencies were in the 60% to 85% range for all VOCs except formaldehyde, and 20% for formaldehyde. Calculations accounting for fan energy and regeneration heating energy (when employed), indicate that the cost of energy required to provide a unit of VOC-free air with the ACF system is only 2-15% of the cost of energy required to obtain the same amount of indoor VOC removal with ventilation. Mass balance modeling indicates that the combination of ACF air cleaning and 50% reductions in ventilation will substantially reduce concentrations of indoor VOCs (except formaldehyde) compared to today's conventional practices. The modeling predicts that indoor formaldehyde may decrease or increase moderately depending on the initial ventilation rate and the operational conditions of the ACF system.

Manganese Oxide-Based Catalyst: In another technology, a manganese oxide catalyst, produced by LBNL, irreversibly removed formaldehyde from the air that passes over the catalyst at room temperature. The materials used and synthesis process are low cost. The catalyst is being deployed as particles collected on a standard particle filter, but it may also be useful as an additive to common building materials or coatings. In initial tests performed under realistic HVAC operating conditions, the catalyst (3-4 g/m²) applied to a particle filter, maintained formaldehyde (concentration 30-40 ppb) removal efficiencies on the order of 80% for a period of up to one month. This system could be used for application 1 or, in conjunction with an ACF for application 2.

Zeolite-containing ceiling tile: The third technology evaluated in FY10 is a special zeolite-containing ceiling tile commercially available as a product for formaldehyde

control. Our preliminary evaluations indicated the product is largely ineffective for long-term formaldehyde control. Hence, we discontinued this line of research in FY11

Progress in FY11, Project Status and Outcomes

In FY11, we published two articles in peer-reviewed journals (Sidheswaran et al, 2011; Sidheswaran et al, 2012) based primarily on the FY10 research and one article in the journal of the Federation of European Heating and Air-Conditioning Associations (REHVA) (Fisk et al, 2011) that describes how VOC air cleaning could enable energy savings from reduced ventilation together with indoor air quality improvements.

During FY11, we also performed additional evaluations of the activated carbon filter and the manganese oxide technologies, since both are very promising.

Activated Carbon Fiber Filters: Heating air to regenerate the ACF media resulted in improved regeneration efficiency with respect to that achieved by directly heating the media, a finding that makes regeneration more practical using existing HVAC hardware; a double layer of ACF cloth showed improved performance for all VOCs, but most critically it doubled the removal efficiency of formaldehyde. To facilitate deployment of the air cleaning systems in existing buildings, including those with roof-top systems, we developed a conceptual design for an air cleaner that is connected to the ductwork of an existing HVAC system.

Manganese Oxide-Based Catalyst: We performed a successful field demonstration of significant formaldehyde removal under “real-world” conditions using a manganese oxide-coated HVAC filter. In laboratory experiments, we observed little inactivation after long-term continuous use (losing only ~18% of the initial performance after 65 days of continuous use). In addition, we observed that high humidity conditions do not significantly affect the performance of the manganese oxide catalysts. Additional analysis revealed that the catalyst is not only able to remove formaldehyde, but also a

suite of other volatile organic compounds (VOCs) including aromatic hydrocarbons (e.g., benzene, toluene) and carbonyls (e.g., acetaldehyde, hexanal), among others.

Summary of Technical Potential: Calculations indicate that application of ACF systems and simultaneous reductions in ventilation rates by 50% could decrease total ventilation energy costs by 35 to 48%, while also decreasing the indoor concentrations of a broad range of VOCs and reducing or maintaining unchanged formaldehyde concentrations. When necessary, the ACF system can be supplemented by the manganese oxide catalyst for formaldehyde, for which there are negligible energy costs. Total product costs have not yet been evaluated and will depend on system lifetimes. However, the manganese oxide nanocatalysts are expected to be inexpensive because the precursors are inexpensive and the synthesis process is simple.

IP Protection and Outreach to Industry: A US patent (application # 61/493,375) was filed on May 2011 to protect the intellectual property generated in this project. The LBNL Technology Transfer Office has been actively marketing the technology to industry since June 2011, to identify suitable licensees. In this relatively short period, several companies expressed interest in these technologies, including:

- a) Chemical companies
- b) Ventilation filter manufacturers
- c) HVAC companies
- d) Manufacturers of air cleaning technologies

Such strong expression of interest suggests that the technology can be licensed to one or more company for multiple potential applications. In addition, a manufacturer of the ACF media expressed an interest in partnering with us in the development of air cleaning technologies benefiting from the research developed in this project

1. Evaluations of Activated Carbon Air Cleaning with In-Situ Regeneration

If FY10, LBNL initiated studies of the use of activated carbon fiber (ACF) cloth media for VOC air cleaning. The ACF media was placed in an airstream and physically adsorbed a broad range of VOCs, yielding air with lower concentrations of VOCs that can be supplied to the occupied spaces of a building. Periodically, the flow of air delivered to occupied spaces was stopped, and the ACF media regenerated by passing unheated outdoor air through the ACF media, or by heating the ACF media while passing outdoor air through the media, in order to drive off the previously adsorbed VOCs, which are vented outdoors. The air cleaning process was then restarted. FY10 activities showed that this technique can be effective for a broad range of VOCs, but has a lower effectiveness for formaldehyde, a compound that is too volatile to be retained with high efficiency by sorbent media. With heating of the ACF media, the regeneration flows can be as low as 1% of the flow rate during air cleaning, with a regeneration period of 15 minutes each 12 hours. The energy required for regeneration is small relative to the energy needed to condition outdoor air that provides an equivalent amount of indoor VOC removal (Sidheswaran et al., 2012). In FY11 we expanded these studies to evaluate the effects of the following parameters on ACF media performance: higher face velocities, a double layer of the ACF media, alternative heating options for regeneration, the airflow direction during regeneration, and high relative humidity conditions. In addition, we developed a conceptual design of a system to facilitate easy deployment of air cleaning systems in existing buildings.

1.1 Sampling and Analytical Methods

Integrated volatile carbonyl samples were collected upstream and downstream of the ACF media using dinitrophenyl hydrazine (DNPH)-coated silica samplers (Waters) at a rate of $20 \text{ cm}^3 \text{ min}^{-1}$ for commercial catalyst or $100 \text{ cm}^3 \text{ min}^{-1}$ for LBNL-100 using

peristaltic pumps. Ambient ozone was removed with potassium iodide scrubbers preceding each DNPH sampler (Waters Sep-pak Ozone scrubber). The concentration value reported in each case corresponds to a time-integrated average over the sampled period, and is reported at the temporal center of each sampling period. The flow corresponding to each sample was measured using a primary air flow calibrator (Gilibrator ®) with a precision greater than 2%. DNPH cartridges were extracted with 2-mL aliquots of acetonitrile, and the extracts were analyzed by HPLC with UV detection at $\lambda_{\text{max}} = 360 \text{ nm}$ (Agilent 1200). A calibration curve for quantification was carried out using authentic standards of the formaldehyde-DNPH hydrazone.

Other VOCs were collected in multi-bed sorbent tubes with 70% bed of Tenax TA® sorbent backed with a section of Carbosieve ® (30%). Prior to use, the sorbent tubes were conditioned by helium purge (~10 cc/min) at 310 °C for 60 minutes and sealed in Teflon capped tubes. Sampling flow rates were monitored periodically and samples were collected at the rate of 70-80 cc/min for a period of 1 hour so that the net sample volume is ~ 5L. VOCs were qualitatively and quantitatively analyzed by thermal desorption-gas chromatography/mass spectrometry generally following U.S. EPA Methods TO-1 and TO-17. For quantitative and qualitative analysis of the target compounds, multi-point internal standard calibrations was created using pure compounds and 1-bromo-3-fluorobenzene as the reference compound. Sorbent tubes were thermally desorbed for analysis using a thermo-desorption auto-sampler, a thermo-desorption oven and a cooled injection system fitted with a Tenax-packed glass liner.

Desorption temperature was initially set at 25 °C with a 0.5 minute delay followed by a 60 °C/min ramp to 250 °C and a 4 minute hold time. The cryogenic trap was initially maintained at -10 °C and then heated within 0.2 minutes to 270 °C at a rate of 21 °C/s, and held for 3-minutes. Compounds were resolved on a GC equipped with a 30 meter DB-1701 14% Cyanopropyl Phenyl Methyl column at an initial temperature of 1 °C for 0.5 minutes then progressively ramped to 40 °C at 25 °C/min, subsequently to 115 °C at 3 °C/min and finally to 250 °C at 10 °C/min and held at 250 °C for 10 minutes. The

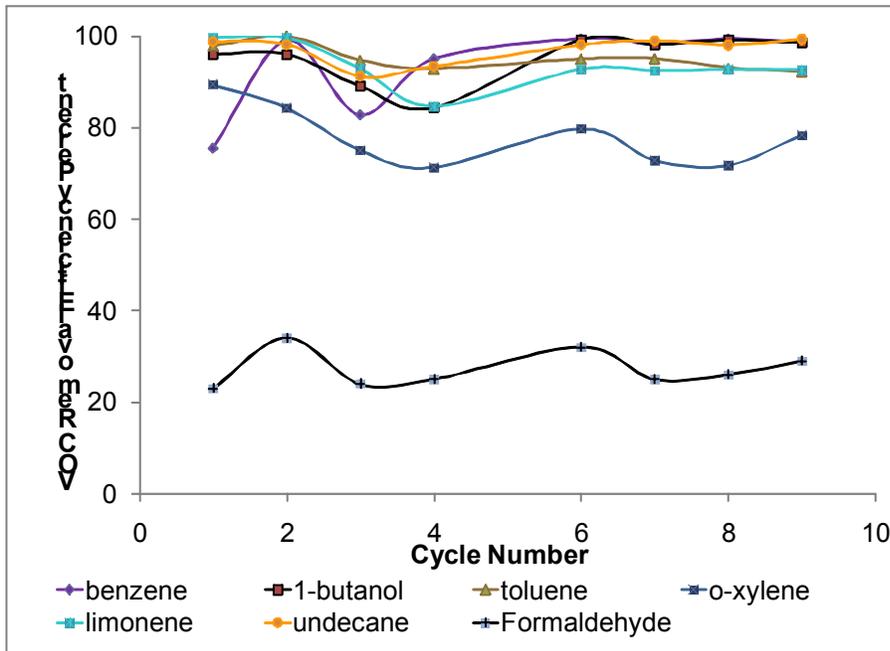
resolved analytes were detected using an electron impact MS system. The MS was operated in full scan mode (m/z range of 40 – 500). All pure standards and analytes were referenced to an internal standard (~ 120 ng) of 1-bromo-3-fluorobenzene.

1.2 Impact of High Face Velocity

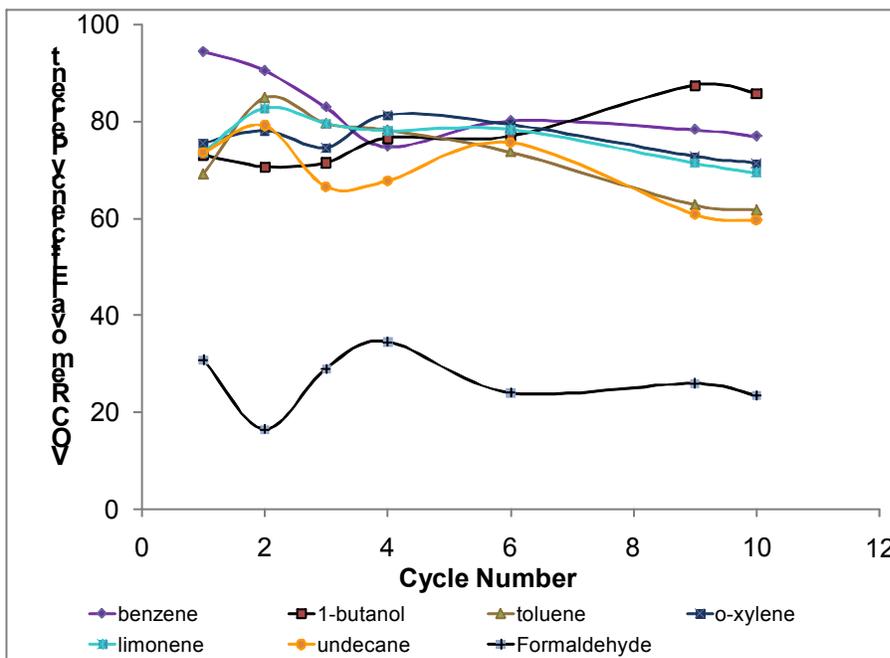
Details of the experimental setup and electrothermal regeneration methods can be found elsewhere (Sidheswaran et al., 2010; Sidheswaran et al, 2012). In electrothermal regeneration, the activated carbon is heated by passing an electrical current through the ACF media. With the ACF deployed as a pleated filter 10 cm deep, the air velocity through the media will typically be about 0.5 m s^{-1} and most prior tests were performed using this air velocity. However, in some applications higher air velocities may be more practical. Two different face velocities, 0.75 m s^{-1} and 1.0 m s^{-1} have been studied to evaluate the performance of ACF at elevated face velocities. The pressure drop across the ACF cloth was periodically monitored during these runs. Before we subjected the cloth to periodic adsorption and regeneration, the cloth was conditioned at $150 \text{ }^\circ\text{C}$ for 15 hours. The ACF filters were saturated with a mixture of model VOCs for a period of 105 hours.

The physical properties of the VOCs used in this study can be found in other previous reports (Sidheswaran et al., 2010; Sidheswaran et al, 2012). In the results reported here, one cycle refers to a 12 hour adsorption period followed by a 15 minute electrothermal regeneration period at $150 \text{ }^\circ\text{C}$ at 1/100th face velocity used during air cleaning.

Figure 1.1 (a) and (b) show the VOC percent removal for different organics at a face velocity of 0.75 m s^{-1} and 1.0 m s^{-1} respectively. The pressure drop across the ACF was measured to be $\sim 78 \text{ Pa}$ and 98 Pa for each of those conditions. These pressure drop values are comparable to those of relatively low efficiency unused particulate filters, hence making these cloths suitable for operation under high face velocity regimes.



(a)



(b)

Figure 1.1. VOC removal efficiency of ACF at (a) face velocity of 0.75 m s⁻¹, (b) face velocity of 1.0 m s⁻¹.

For both face velocities of $0.75 \text{ m}\cdot\text{s}^{-1}$ and $1.0 \text{ m}\cdot\text{s}^{-1}$ an average formaldehyde removal efficiency of $\sim 25\%$ was achieved which is comparable to what was found earlier (Sidheswaran et al., 2010) for lower face velocities. The o-xylene removal efficiency of the carbon cloth for the face velocity of $0.75 \text{ m}\cdot\text{s}^{-1}$ was found to be between 70 and 80% while that of other compounds such as benzene, toluene, limonene and 1-butanol were found to be consistently above 90%. At the higher face velocity of $1 \text{ m}\cdot\text{s}^{-1}$ the VOCs other than formaldehyde had average removal efficiencies ranging between 70-80% with very high initial removal rates. From the previous study at $0.5 \text{ m}\cdot\text{s}^{-1}$ face velocity (Sidheswaran et al., 2010) it was inferred that prolonged operation of the cloth at such conditions may lead to a marginal decrease in performance.

1.3 Use of a Double Layer of ACF Cloth System

In these tests, we evaluated the use of two layers of ACF cloth, with a second layer placed immediately downstream of the first layer. We hypothesized that a double layer system would have a sufficiently high VOC removal efficiency, including for formaldehyde, with high air velocities to make it possible to deploy ACF filters with limited pleating that are 5 cm deep or less. The experimental methods are the same as those described earlier (Sidheswaran et al., 2010). Two layers of ACF cloth were fitted in a filter holder system and subjected to continuous adsorption and regeneration cycles. An adsorption – regeneration cycle in this experimental section refers to a 12 hour VOC adsorption (air-cleaning) period at a face velocity of $0.5 \text{ m}\cdot\text{s}^{-1}$ followed by a 12 hour room temperature ACF regeneration period at a face velocity of $0.005 \text{ m}\cdot\text{s}^{-1}$. We used ambient unheated air regeneration methods to regenerate the ACF cloth pieces.

Figure 1.2 shows the VOC removal efficiency performance of double-layered ACF cloth. We monitored the pressure drop across the ACF cloth and it was found to be 94 Pa. Although the pressure drop is higher than usual pressure drops across single ACF cloth systems, the multi layered ACF shows consistent good performance even with

room temperature regeneration using outdoor air. Also, the pressure drop value compares to those observed through unused low-efficiency particle filters. Formaldehyde removal was consistently higher than 40%. This removal rate was twice as much as that observed with the single layered cloth. As observed in our previous study (Sidheswaran et al., 2010), the efficiency of formaldehyde removal may increase when regenerated by heating. VOC removal efficiency of greater than 95% was observed for all other VOCs. This is a 20 – 30% improvement over the removal efficiency observed for the single layer cloth. These results are encouraging and suggest that the ACF can be used in multiple layers successfully. The air velocity in these tests is typical of the velocity through media in a 5 cm thick pleated particle filter, thus the results indicate that a the system would be effective, even for formaldehyde, with such a filter which requires little space in HVAC system.

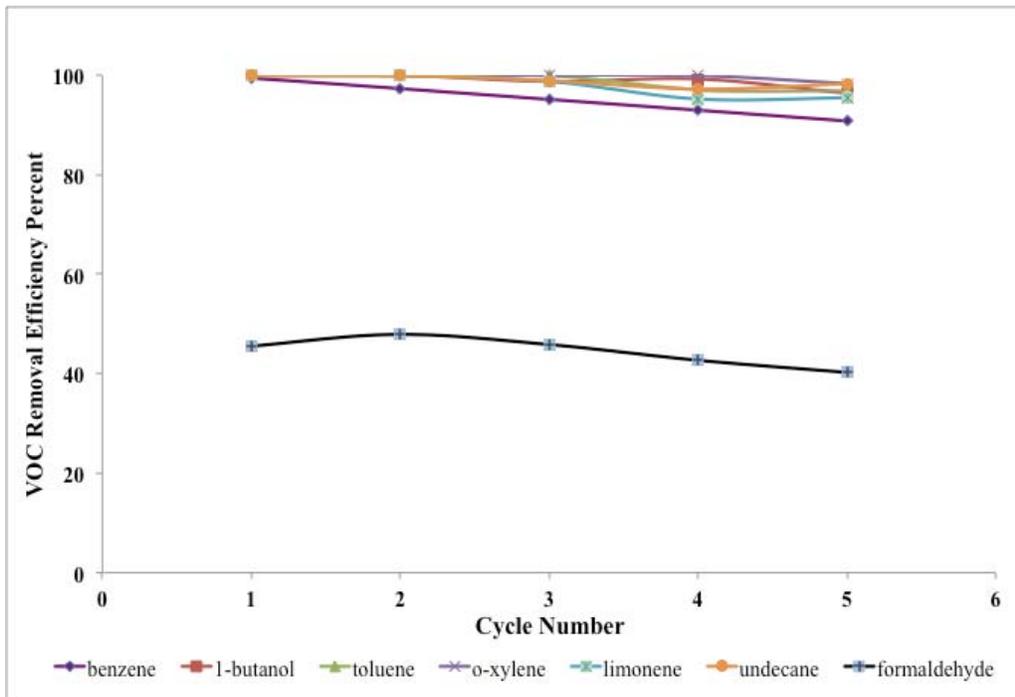


Figure 1.2. VOC removal efficiency of double-layered ACF.

1.4 Evaluation of Regeneration Heating Options

In all of our previous experiments, periodic regeneration was achieved by passing an electrical current through the ACF media to reach the desired heating level. However, in large HVAC systems, implementation of the technology by heating the ACF media may not be practical. In these tests, we explored the possibility of instead heating the regeneration air.

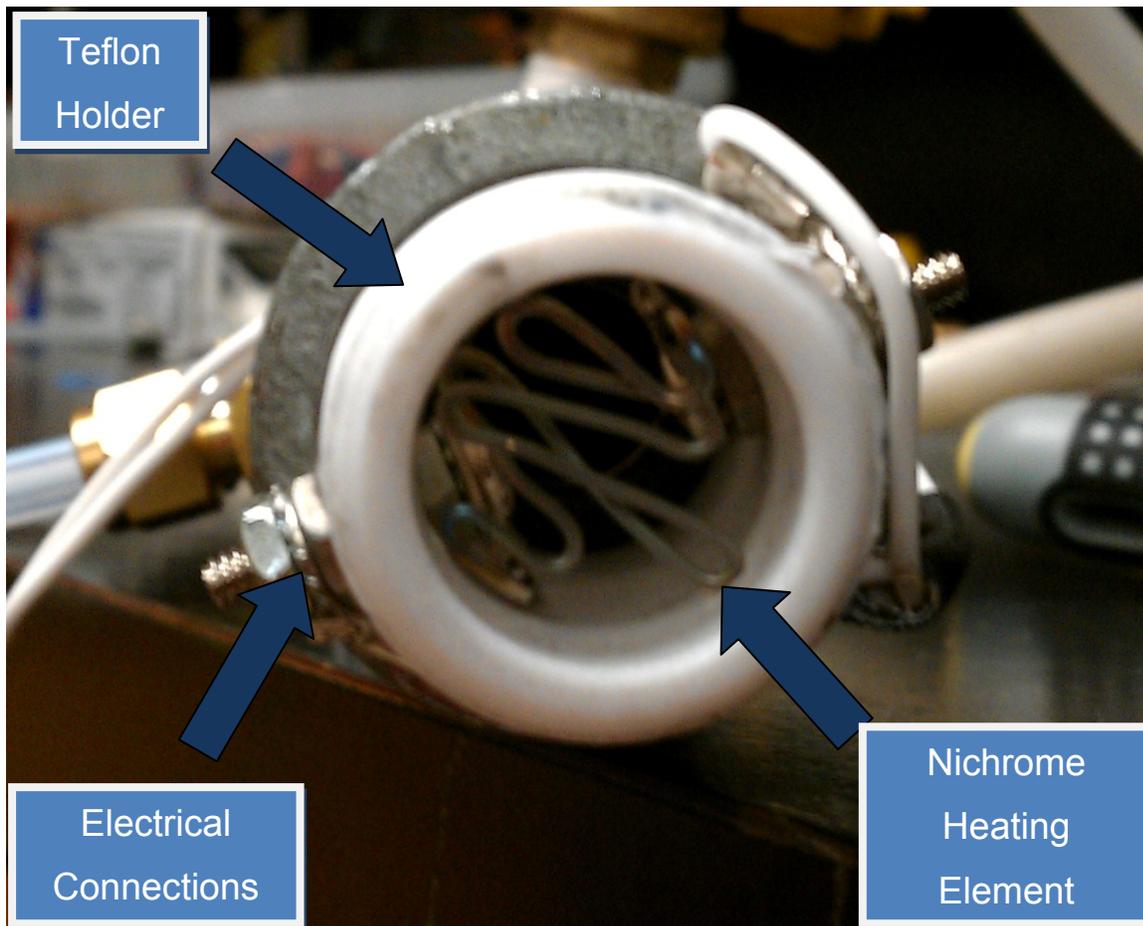


Figure 1.3. Air heating element for regenerating the ACF.

A heating element was made using Nichrome wire (diameter 0.04 m , length 0.09 m and resistance 0.8 Ω /ft). The wire was weaved inside a Teflon holder and a differential voltage of $\sim 2V$ was applied across the ends. The heating element is shown in Figure

1.3. The temperature downstream of the ACF media was monitored and recorded using a thermocouple data logger (Extech Easy View 15). The voltage was measured with a multimeter (Keithley 177 Microvolt DMM) and the current was measured with an ampmeter. The temperature of the air downstream of the cloth was maintained at 120 °C. This yielded a cloth surface temperature of ~ 150 °C, which we measured during initial setup of the heating element.

The heating element was placed upstream of the ACF media during regeneration. Hot air was passed through the ACF filter at 1/100th of the adsorption face velocity. The media was regenerated for a period of 15 minutes. The face velocity during adsorption (air cleaning) was maintained at 0.5 m s⁻¹. The experimental setup to determine the adsorption efficiency of ACF with heated air regeneration is similar to the procedure employed in previous studies (Sidheswaran et al., 2010; Sidheswaran, 2012). In these experiments, similar to the experiments described on heating the ACF for regeneration, an adsorption-regeneration cycle refers to a 12 hour adsorption period followed by a 15 minute regeneration period with 1/100th the air face velocity of adsorption. Before the ACF was subject to periodic adsorption and regeneration cycles, the material was saturated based on the results from the isotherm for a period of 105 hours, as determined in our FY10 tests.

Figure 1.4 shows the comparison between VOC removal efficiency of ACF at the end of 6th cycle when it was regenerated by heating the ACF with an electrical current and by heating the regeneration air. The ACF that was regenerated by heating the air performed better than the electrically-heated ACF media by about 20 - 40% for most VOCs except formaldehyde. Both cases show consistent performance. Regeneration by heating the air could prevent damaging the carbon fiber cloth structure and prolong the life of the media unlike when the ACF itself is heated. Also, the method of heating the regenerating air proves advantageous since it is easier to implement in large HVAC systems. It is also possible to successfully recover heat from the exhaust air to minimize energy usage.

The findings of this study were surprising. We expected a similar VOC removal performance when heated air was used for regeneration of the ACF media as opposed to heating the ACF with an electrical current. While we cannot explain the findings, we offer two possibilities. First, we note the difficulties in measuring the temperature of the ACF media during regeneration. To measure the temperature during regeneration, we embedded a small temperature sensor in the ACF cloth, but given the porous nature of the cloth this measurement may not accurately indicate the average temperature of the cloth. Possibly, the average regeneration temperature was higher in the system that regenerated with heated air. Second, we hypothesize that imperfect electrical connections to the ACF cloth when it is regenerated with an electrical current may potentially have led to uneven heating of the ACF media reducing the effectiveness of regeneration.

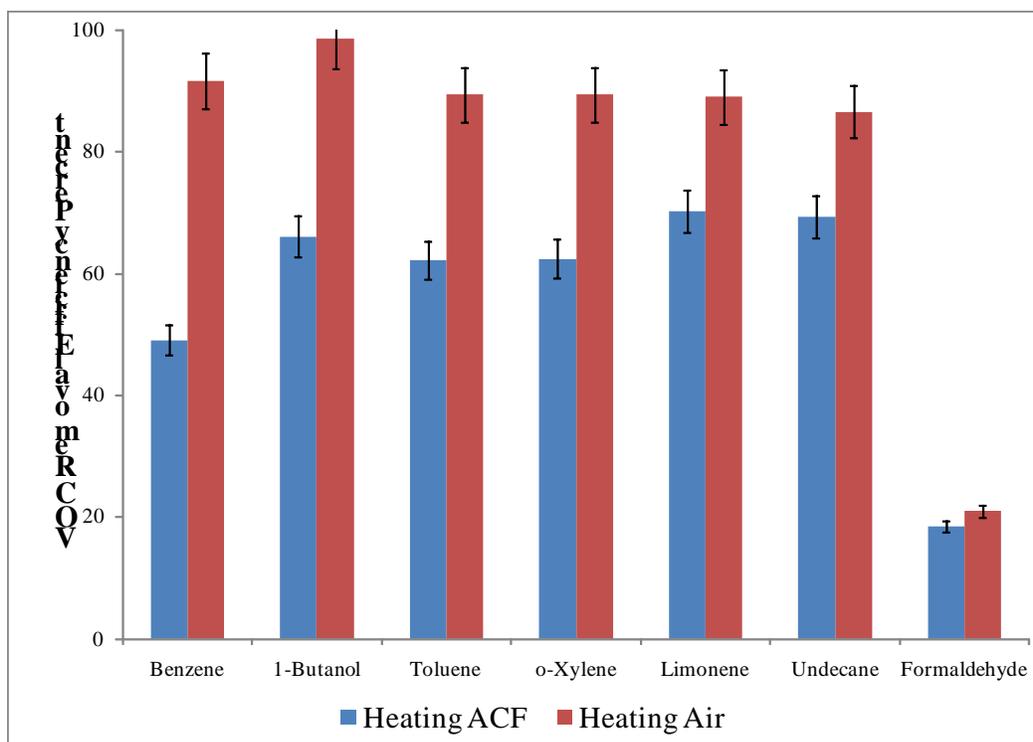


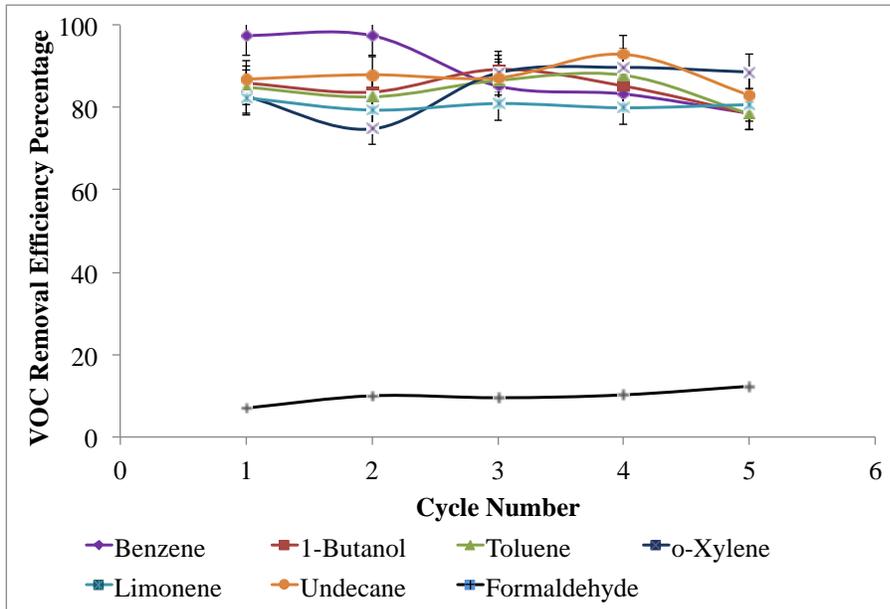
Figure 1.4. Comparison of different regeneration techniques.

1.5 Evaluation of Direction of Airflow During Regeneration of the ACF Media

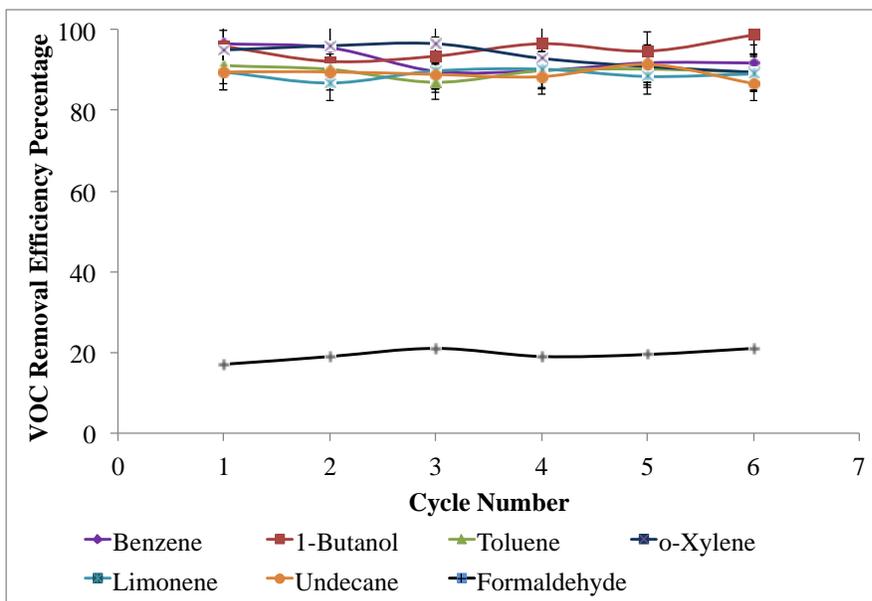
Small-scale tests were performed to determine how ACF regeneration performance compares when the direction of airflow through the ACF media is changed. In theory, regeneration with air flowing opposite of the direction during air cleaning is optimal, but the benefits may be modest. In prior research, the regeneration airflow direction was reverse of the airflow direction during air cleaning. If both airflow directions lead to good ACF performance, deployment options will be increased.

The ACF cloths were loaded with VOCs as described in the earlier sections at a face velocity of 0.5 m s^{-1} . Heated air was used to regenerate the ACF media at $150 \text{ }^{\circ}\text{C}$ with a face velocity of 0.005 m s^{-1} for a period of 15 minutes. The method of regeneration is described in the previous section. In one test system, the airflow direction was the same as that during air cleaning and in a second test system the air flow direction was reversed during regeneration.

Figure 1.5 (a) and (b) show the VOC removal efficiency of the ACF cloths for two different regeneration air flow directions. Better VOC removal performance was obtained when the direction of airflow was reversed during regeneration (Figure 1.5b) compared to not reversing the airflow direction (Figure 1.5a). However, the variability is less than 15% for most VOCs suggesting that the direction of airflow during regeneration can be in the same direction of air cleaning for practical purposes.



(a)



(b)

Figure 1.5. VOC removal efficiency percentage for (a) same direction of air flow during air cleaning and regeneration and (b) opposite direction of air flow during air cleaning and regeneration.

1.6 Evaluation of Effect of High Relative Humidity on Adsorption Characteristics of ACF Media

Humidity is another challenge that needs to be addressed when the ACF media is deployed in HVAC systems. Additional experiments were carried out at 75% relative humidity to evaluate the effect of humidity on adsorption of the VOCs by the ACF media. The tests with 75% humidity, as compared to the previous experimental scenarios where the humidity was maintained at ~30-40%, were conducted for a period of 12 hours with a face velocity of 0.5 m s^{-1} during air cleaning followed by hot air regeneration for 15 minutes at 0.005 m s^{-1} face velocity and a temperature of $150 \text{ }^{\circ}\text{C}$. Upstream and downstream VOC samples were collected at the end of 12 hours to evaluate the effect of humidity on adsorption capabilities of the carbon fiber in the presence of humidity.

The results of the adsorption (air cleaning) experiments with 75% RH and regeneration at $150 \text{ }^{\circ}\text{C}$ are presented in Figure 1.6. The percent removal of non-polar compounds by the ACF such as benzene decreased by 20% while that of compounds soluble in water such as formaldehyde increased by about 10%. The heated regeneration of the activated carbon was effective in restoring the adsorption properties of the ACF.

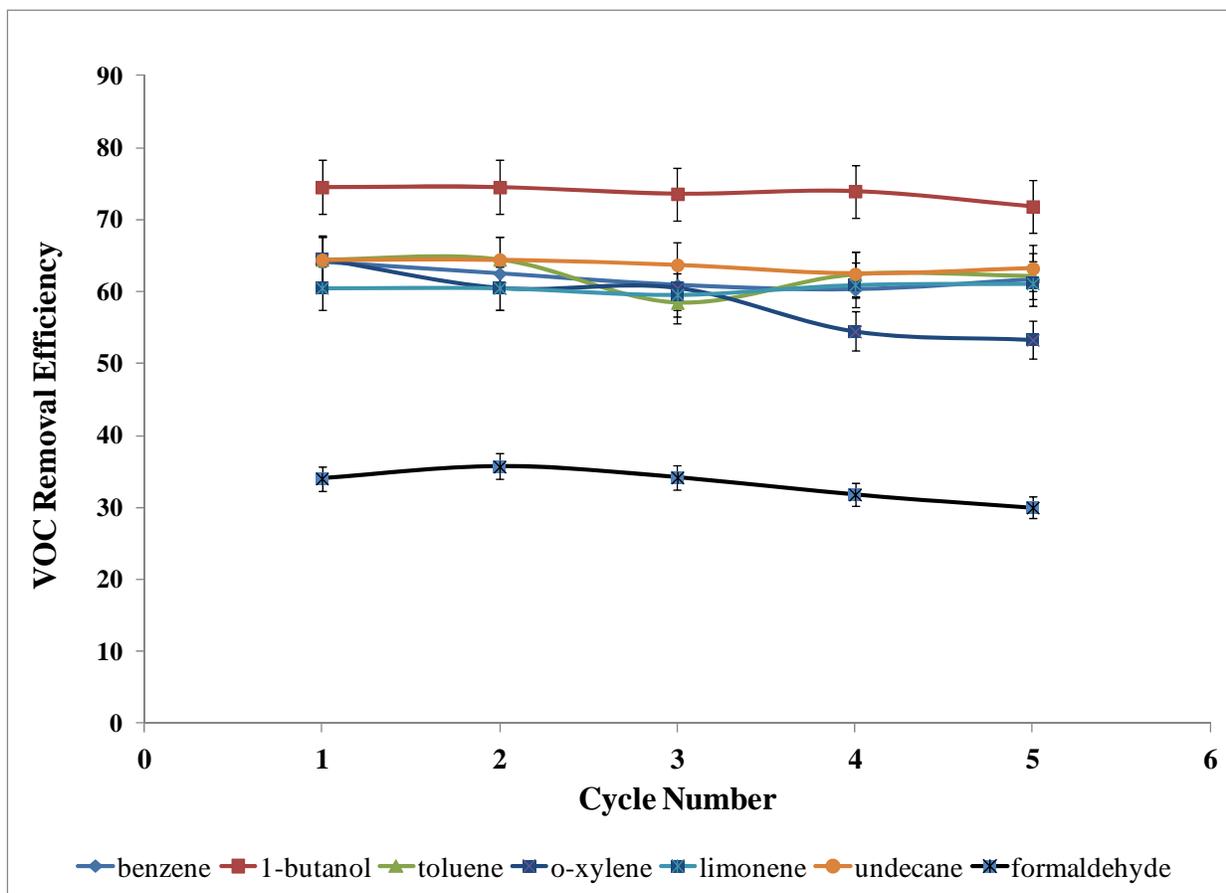


Figure 1.6. VOC removal efficiency of ACF for 12 hour adsorption cycle at face velocity of -0.5 m s^{-1} with 75% RH and 15 min. regeneration period at $150 \text{ }^{\circ}\text{C}$ at a face velocity of 0.005 m s^{-1} .

1.7 Evaluation of Thermal Regeneration of ACF Media with Polluted Indoor Air

We evaluated the possibility of using in-situ thermal regeneration of ACF with polluted indoor air. The performance of regenerating ACF with polluted indoor air will simplify the design and power conception of an additional fan required to regenerate the ACF using outdoor air. Figure 1.7 shows the effect of regeneration using the chamber air at $150 \text{ }^{\circ}\text{C}$ for a period of 15 minutes of a single layer ACF FM100. The ACF was subject to a 12-hour adsorption cycle at a face velocity of 0.5 m s^{-1} and regenerated with the same chamber air at $150 \text{ }^{\circ}\text{C}$ at a face velocity of 0.005 m s^{-1} . It can be inferred from figure 1.7

that the VOC removal efficiency decreases with the number of adsorption-regeneration cycles. The VOC removal efficiency using polluted air regeneration was found to be ineffective and the adsorption capacity of the carbon fiber decreased substantially after 60 hours. Formaldehyde removal constantly decreased from 12%, with net desorption toward the end of the experiment.

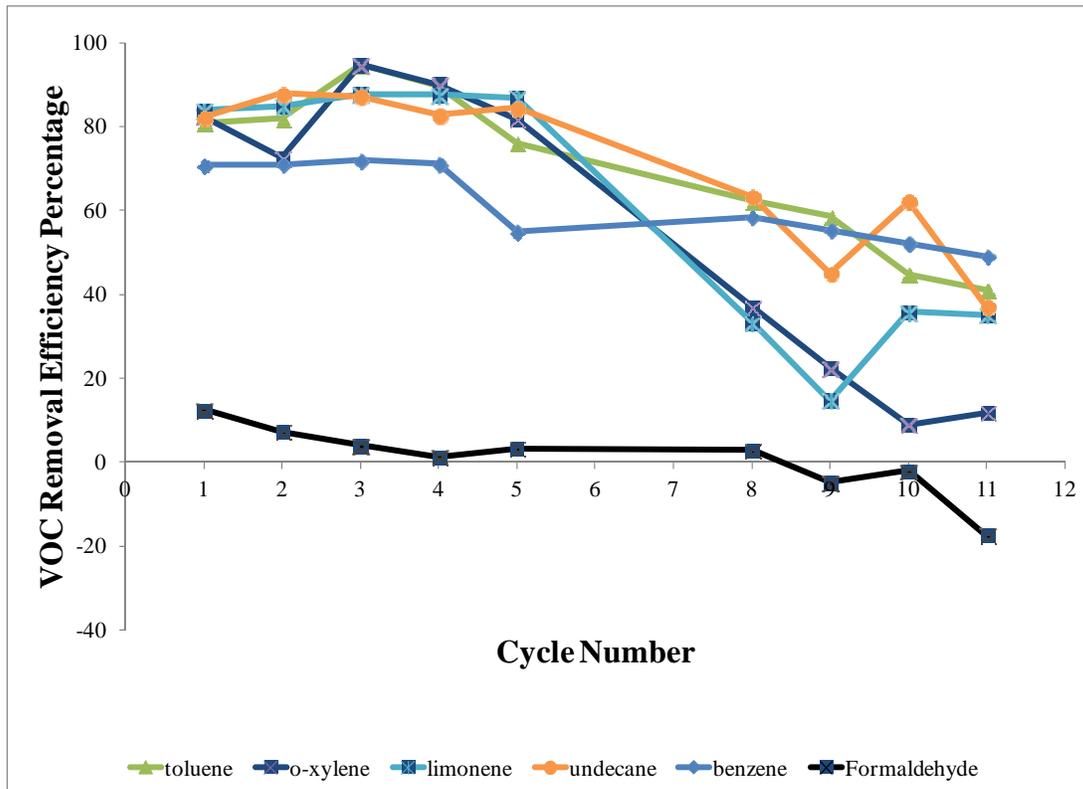


Figure. 1.7. VOC removal efficiency of ACF for 12 hour adsorption cycle at face velocity of 0.5 m s^{-1} and 15 min regeneration period at $150 \text{ }^\circ\text{C}$ at a face velocity of 0.005 m s^{-1} using polluted chamber air.

1.8 Conceptual Design of a System to Facilitate Easy Deployment of Air Cleaning Systems in Existing Buildings

One deployment option for the ACF system is installation of the ACF media and regeneration equipment in the supply airstream of an HVAC system. Addition of the

required components by HVAC system manufacturers will be straightforward. However, in some already-installed HVAC systems, particularly roof-top HVAC systems, retrofits will be difficult because of poor access or inadequate space. To address this need, we developed a conceptual design for an air cleaner with integral fan that is connected via ducts to the ductwork of existing HVAC systems. This air cleaner, shown schematically in Figure 1.8, can contain the ACF system, or the ACF system used in conjunction with the MnOx catalyst and could potentially be a product bolted on to the cabinet of an existing roof-top HVAC system. To minimize fan power, this air cleaner is designed to have low air velocities and high VOC removal efficiencies. Consequently, the amount of air that must be cleaned to compensate for a 50% reduction in minimum outdoor air ventilation could be as low as 10% to 15% of the supply air flow rate.

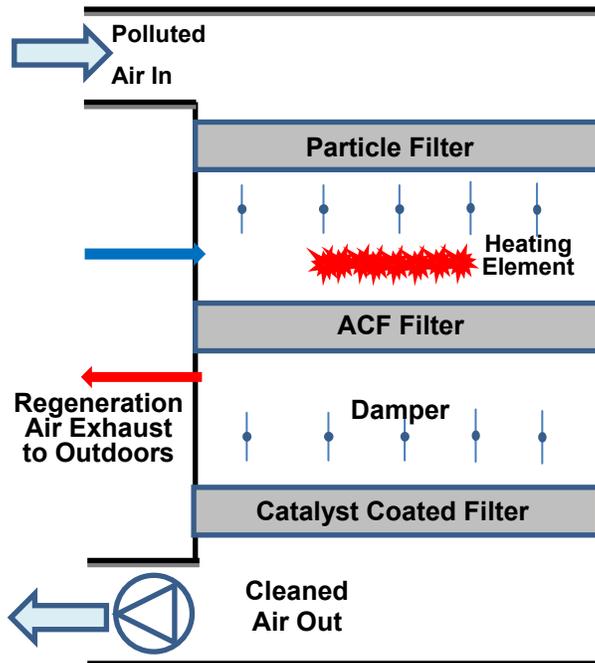


Figure 1.8. Schematic of a standalone air cleaner that can be connected via ducts to an existing HVAC system.

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2. Manganese Oxide Catalyst System

In FY10, LBNL initiated research on this catalyst. FY 10 activities included developing the methods to produce the catalyst in small quantities, characterizing the catalyst, and conducting pilot studies of the performance of the catalyst in breaking down formaldehyde leading to quantitative conversion into carbon dioxide and water vapor (i.e., mineralization) (Sidheswaran et al, 2010; Sidheswaran et al, 2011). This section summarizes progress in the evaluation of a manganese oxide catalyst applied to particle filters to break down formaldehyde and other VOCs under room temperature conditions during FY11. We have improved catalyst coating techniques, evaluated the mechanical stability of coatings, the effect of tackifiers on catalyst performance and the effect of high relative humidity. In addition, we performed long-term studies to evaluate catalyst performance over an extended period of up to 95 days, we carried out a limited field study to evaluate the performance of the catalyst under “real world” conditions and investigated the implementation of this catalyst as an additive in paint formulations for passive formaldehyde removal.

2.1. *Catalyst Coating Technique*

Manganese oxide based material (LBNL-100) was synthesized according to methods described in a previous study (Sidheswaran et al., 2011). A spray coating technique for applying the LBNL-developed catalyst with highest efficiency (called “LBNL-100”) to typical fibrous particle filters was developed and tested. For application of the catalyst to particle filters, a powder-coating gun with a powder reserve (69-207 kPa, powder coating system, Chicago Pneumatic) was procured. The reserve tank of the powder coating system was filled with the LBNL-100 catalyst and fitted to the laboratory air-handling unit. The inlet air to the reservoir was pressurized to 100 kPa to obtain uniform particle size during spraying. The particulate filter to be coated with the catalyst material was fitted in a duct system enabled with a fan/blower. This allowed for

the air to be pulled through the filter when the catalyst was sprayed onto the filter. A series of HEPA filters were fitted downstream of the particulate filter media and before the fan, to trap and recover excess catalyst. After each coating, the direction of airflow through the filter was reversed to remove any weakly-attached catalyst from the surface. Each filter media was weighed before and after the coating to obtain the total mass of catalyst deposited on the filter surface, which was typically in the range 3-4 g-m⁻² of filter media. The spray application process could easily be automated so that minimal labor is required.

2.2 Test of Mechanical Stability of Catalyst on Fiber Filter Surface

Manganese oxides are a common constituent of the earth's crust minerals and urban dust, and exposure of humans to manganese oxides present in the environment is a common occurrence. Reports of long-term occupational exposure to high levels of manganese oxide particles resulting from welding suggest a possible association with health effects. Based on those exposures, the California Office of Environmental Health Hazard Assessment (OEHHA) established a reference level for inhalation exposure of manganese-containing compounds of 0.2 µg-m⁻³. The particulate filter coated with manganese oxide catalyst used for tests in the commercial office building was subject to catalyst particle elutriation test at different face velocities (0.5 m-s⁻¹, 1.5 m-s⁻¹ and 2.0 m-s⁻¹) in a duct system. Particles upstream and downstream of the catalyst coated fiber filter were captured using 0.2 µm Teflon filter (Pall Corp) and analyzed using a Perkin Elmer DRCII Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). Gallium was used as the internal standard and the instrument was operated in Dynamic Reaction Cell (DRC) mode using ammonia as reaction gas to estimate concentrations in trace quantities.

The ICP-MS results for upstream and downstream concentration of particles analyzed after subjecting the catalyst coated filter to different air velocities for a period of 24 hours show that the catalyst was retained by the filter. Table 2.1 shows the results

of Mn concentration obtained for upstream and downstream of the catalyst-coated filter. It was observed that the upstream Mn concentration was higher than the downstream Mn concentration, showing that the filter removed naturally occurring particles containing manganese. The limit of detection for Mn was 0.02 ng-m^{-3} , several orders of magnitude below the OEHHA inhalation exposure levels.

| Type of Filter | Face Velocity, m-s^{-1} | Upstream Concentration, $\mu\text{g-m}^{-3}$ | Downstream Concentration, $\mu\text{g-m}^{-3}$ |
|------------------------|-------------------------------------|--|--|
| Non-catalyst filter | 1.0 | 1.8 | 0.03 |
| Catalyst-coated Filter | 0.5 | 1.4 | 0.01 |
| Catalyst-coated Filter | 1.0 | 1.4 | 0.01 |
| Catalyst-coated Filter | 2.0 | 0.8 | 0.02 |

Table 2.1. Manganese concentration upstream and downstream of the filter in air

These preliminary results indicate that there is no or minimal catalyst entrainment from the filter. The other test performed was a gravimetric determination of catalyst loss from the substrate after it had been used to remove formaldehyde for more than 40 days at a face velocity of 50 cm-s^{-1} . The difference in filter weight before and after reaction was below the detection limit ($<0.1 \text{ mg}$), showing undetectable loss of the catalyst. Both preliminary tests suggest that catalyst particles do not significantly enter the airstream that passes through the filter.

We have also scaled up this test for catalyst coated filters to be deployed in the field. The air velocity through a catalyst-coated filter was maintained at 1 m-s^{-1} . Upstream and downstream particle samples were collected for a period of 24 hours using $0.2 \mu\text{m}$ (pore-size) Teflon filter at a sampling rate of 1 L-m^{-1} . The particles were analyzed using ICP-MS. The net Mn concentration downstream was lower than that observed upstream

indicating that the catalyst was not released from the filter into the airstream, and that, instead, the filter removed naturally-occurring particles containing Mn.

2.3 Sampling and Analytical Methods

Integrated volatile carbonyl samples were collected upstream and downstream of the catalyst using dinitrophenyl hydrazine (DNPH)-coated silica samplers (Waters) at a rate of $20 \text{ cm}^3 \text{ min}^{-1}$ for commercial catalyst or $100 \text{ cm}^3 \text{ min}^{-1}$ for LBNL-100 using peristaltic pumps. Ambient ozone was removed with potassium iodide scrubbers preceding each DNPH sampler (Waters Sep-pak Ozone scrubber). The concentration value reported in each case corresponds to a time-integrated average over the sampled period, and is reported at the temporal center of each sampling period. The flow corresponding to each sample was measured using a primary air flow calibrator (Gilibator®) with a precision greater than 2%. DNPH cartridges were extracted with 2-mL aliquots of acetonitrile, and the extracts were analyzed by HPLC with UV detection at $\lambda_{\text{max}} = 360 \text{ nm}$ (Agilent 1200). A calibration curve for quantification was carried out using authentic standards of the formaldehyde-DNPH hydrazone.

Other VOCs were collected in multi-bed sorbent tubes with 70% bed of Tenax TA® sorbent backed with a section of Carbosieve® (30%). Prior to use, the sorbent tubes were conditioned by helium purge ($\sim 10 \text{ cm}^3 \text{ min}^{-1}$) at $310 \text{ }^\circ\text{C}$ for 60 minutes and sealed in Teflon capped tubes. Sampling flow rate were monitored periodically and collected at the rate of 70-80 cc/min for a period of 1 hour so that the net sample volume is $\sim 5\text{L}$. VOCs were qualitatively and quantitatively analyzed by thermal desorption-gas chromatography/mass spectrometry generally following U.S. EPA Methods TO-1 and TO-17. For quantitative and qualitative analysis of the target compounds, multi-point internal standard calibrations was created using pure compounds and 1-bromo-3-fluorobenzene as the reference compound. Sorbent tubes were thermally desorbed for analysis using a thermo-desorption auto-sampler, a thermo-desorption oven and a cooled injection system fitted with a Tenax-packed glass liner.

Desorption temperature was initially 25 °C with a 0.5 minute delay followed by a 60 °C/min ramp to 250 °C and a 4 minute hold time. The cryogenic trap was initially maintained at -10 °C and then heated within 0.2 minutes to 270 °C at a rate of 21 °C/s, and held for 3-minutes. Compounds were resolved on a GC equipped with a 30 meter DB-1701 14% Cyanopropyl Phenyl Methyl column at an initial temperature of 1 °C for 0.5 minutes then progressively ramped to 40 °C at 25 °C/min, subsequently to 115 °C at 3 °C/min and finally to 250 °C at 10 °C/min and held at 250 °C for 10 minutes. The resolved analytes were detected using an electron impact MS system. The MS was operated in full scan mode (m/z range of 40 – 500). All pure standards and analytes were referenced to an internal standard (~120 ng) of 1-bromo-3-fluorobenzene.

2.4 Effect of Humidity on Catalyst Performance

Studies of the effect of humidity on the manganese oxide catalyst synthesized in the laboratory showed promising results. The filter loaded with manganese oxide was tested using an airstream saturated with water for a period of 100 hours at a face velocity of 0.5 m·s⁻¹. The details of the experimental setup can be found in our previous reports (Sidheswaran et al., 2010; Sidheswaran et al, 2011).

Figure 2.1 shows the results obtained for the experiments conducted at near saturation humidity conditions. The formaldehyde removal efficiencies at near-saturation humidity were slightly lower than the formaldehyde conversion at 25-30% RH reported previously (Sidheswaran et al., 2010) where efficiencies were as high as 85 – 90%. When the humidity in the system was reduced back to 29% RH, the removal efficiency of formaldehyde increased from 80% to 85%, showing the ability of the catalyst to recover at a lower humidity. The slight decrease in formaldehyde removal efficiency at higher humidity conditions might be attributed to the competitive adsorption of water on the surface of the catalyst.

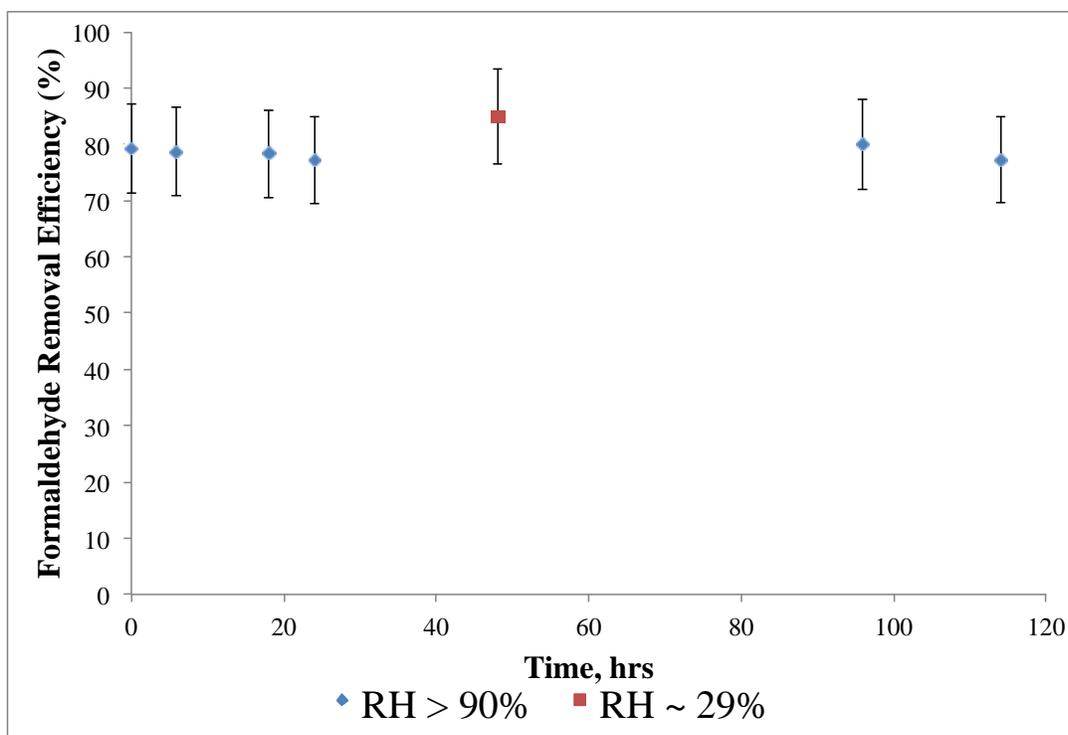


Figure 2.1. Formaldehyde removal performance of laboratory synthesized manganese oxide catalyst for different RH conditions.

2.5 Effect of Filter Tackifier on Catalyst Performance

We also studied whether the performance of the catalyst was affected by the adhesives or tackifiers that are present on some commercially available filters. Previous studies by Destailats et al. (2011) have reported that some filters coated with tackifiers can be a source of formaldehyde in the presence of humidity. These oily coatings are applied on filter surfaces to improve the performance of the filter in trapping particulate matter. We tested three different catalyst-coated filters with heavy, medium and mild applications of tackifier. Approximately 3 mg of the same manganese oxide catalyst material was coated on 10 cm² filter surfaces on all three types of filters. The filters were fitted in the experimental setup used in our FY10 studies (Sidheswaran et al., 2010). The formaldehyde inlet concentration was maintained at ~ 70 ppb and the face velocity was ~ 0.75 m s⁻¹.

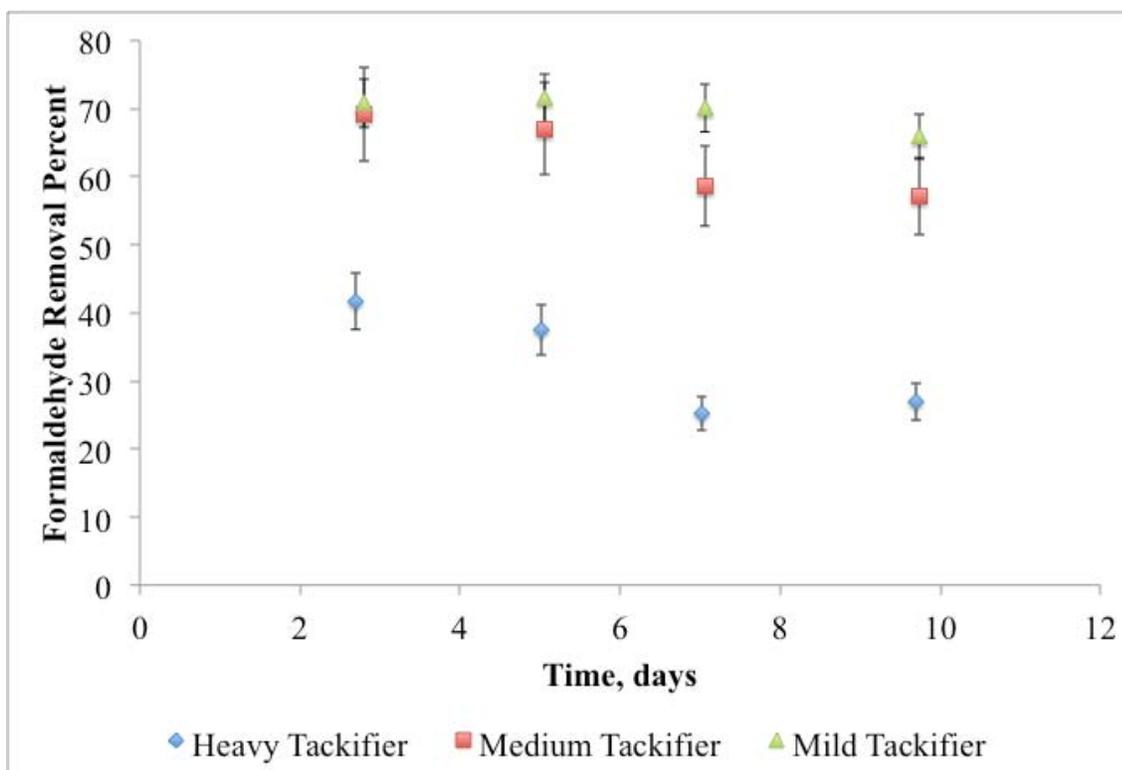


Figure 2.2. Performance of manganese oxide coated filters with different tackifier loading.

Figure 2.2 shows the plot of formaldehyde removal vs. time for manganese oxide coated filters with different tackifier loadings. It was found that tackifier loading on the filter surface has an important effect on formaldehyde removal efficiency. The catalyst-coated filter with lower or medium tackifier loading performed significantly better than the catalyst coated filter with heavy tackifier loading. It should be noted that although the performance of the filter with heavy tackifier coating was not as impressive as the other filters, it is still far better than a similar filter without any catalyst coating.

2.6 Long Term-performance of the Catalyst in the Removal of Formaldehyde and Other VOCs

Following the successful experiments reported in FY10, we performed long term MnO_x tests of the catalyst under the same flow conditions and formaldehyde concentration. The catalyst was applied to a filter coated with a mild tackifier loading. Room air was drawn at a flow rate of 30 L min^{-1} through a 4-L stainless steel source chamber containing a 25 cm by 10 cm cabinetry specimen, which served a strong formaldehyde source. Characterization of this diffusive source was performed in a previous study at our laboratory (Maddalena et al, 2009). The 10 cm^2 filter sample loaded with 3 mg of LBNL-100 MnO_x catalyst was placed downstream of the stainless steel chamber. VOC and formaldehyde samples upstream and downstream were periodically collected using DNPH and Tenax sorbent tubes.

Figure 2.3 shows the removal efficiency of formaldehyde, other volatile aldehydes and other VOCs using the LBNL-100 catalyst for a period of 95 days. We also observed that the catalyst was effective in removing various VOCs present in upstream air. Figure 2.4 shows the VOC upstream and downstream concentrations, as well as the percent removal, for representative VOCs: nonanal, 3-carene and limonene. The formaldehyde removal efficiency of the catalyst decreased from $\sim 80\%$ to about 50% while the TVOC removal efficiency decreased from 70% to 50% . There may be several factors leading to the decrease in efficiency. The HVAC filter has a mild loading of tackifier oils that may degrade catalyst performance with time. Also, over time, airborne particles are accumulating on the filter surfaces and these particles may limit access to the catalyst's active sites. We also measured particle number concentration upstream and downstream the filter in our experimental setup to estimate particle accumulation on the surface of the filter. We found that the number concentration decreased from $\sim 4000 \text{ particles cm}^{-3}$ to $1500 \text{ particles cm}^{-3}$ showing accumulation on the surface of the filter. This may be a reason for decreased performance of the LBNL-100 coated filter operating continuously over a period of 95 days. A continuous operation for 95 days in our experimental setup is equivalent to 190 days of filter deployment in a commercial building with 12 hours per day of HVAC operation. Since most filters are replaced within

or before 190 days of deployment, our test validates the performance of the catalyst over the lifetime of the filter used as support. The use of throw-away pre-filters is a common practice to extend the lifetime of HVAC filters, which may also help preserve the high activity of MnOx catalysts for an extended period. Finally, it should be pointed out that, even though performance decreased in the studied period, the final removal efficiency (50%) was still remarkably high.

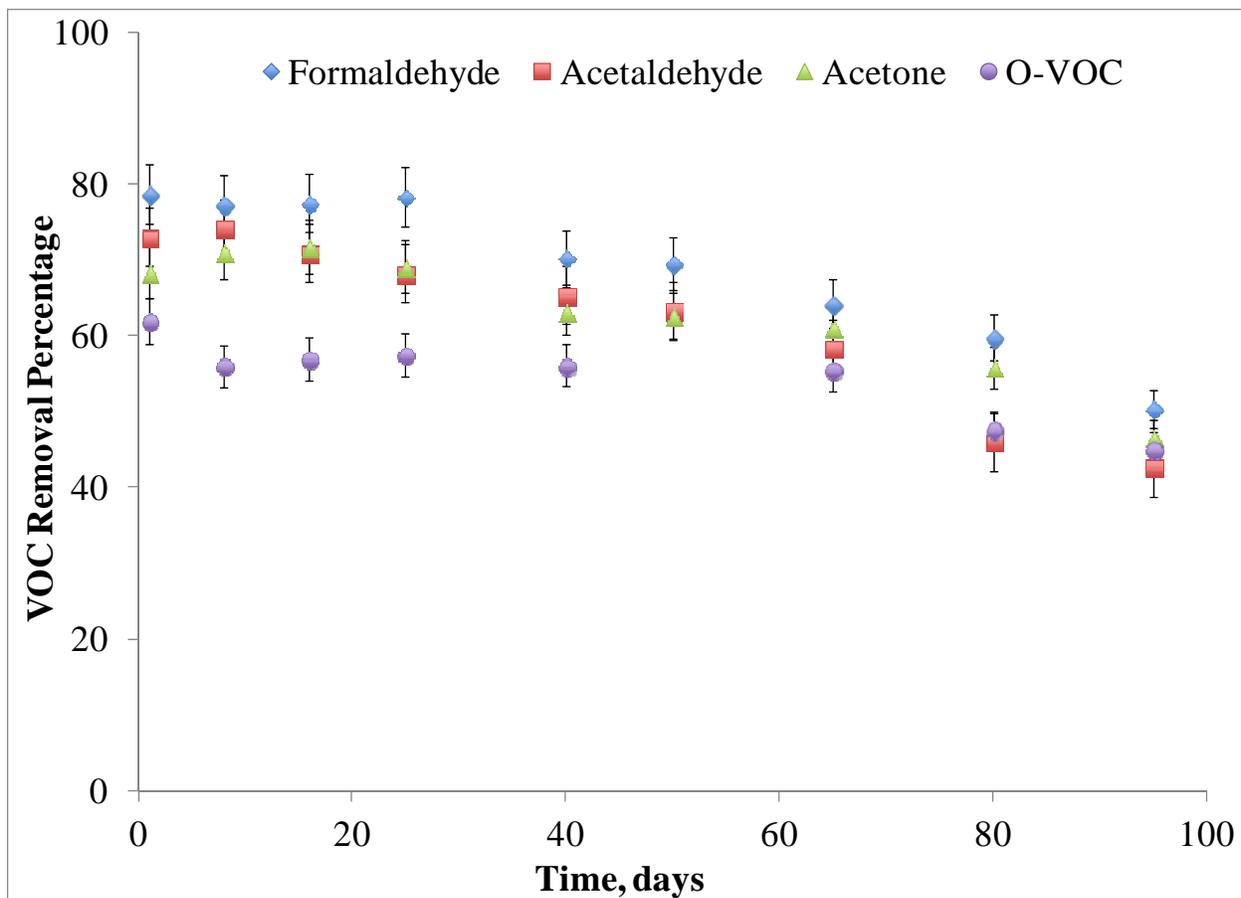


Figure 2.3. Long term removal of formaldehyde, acetaldehyde, acetone and other VOCs

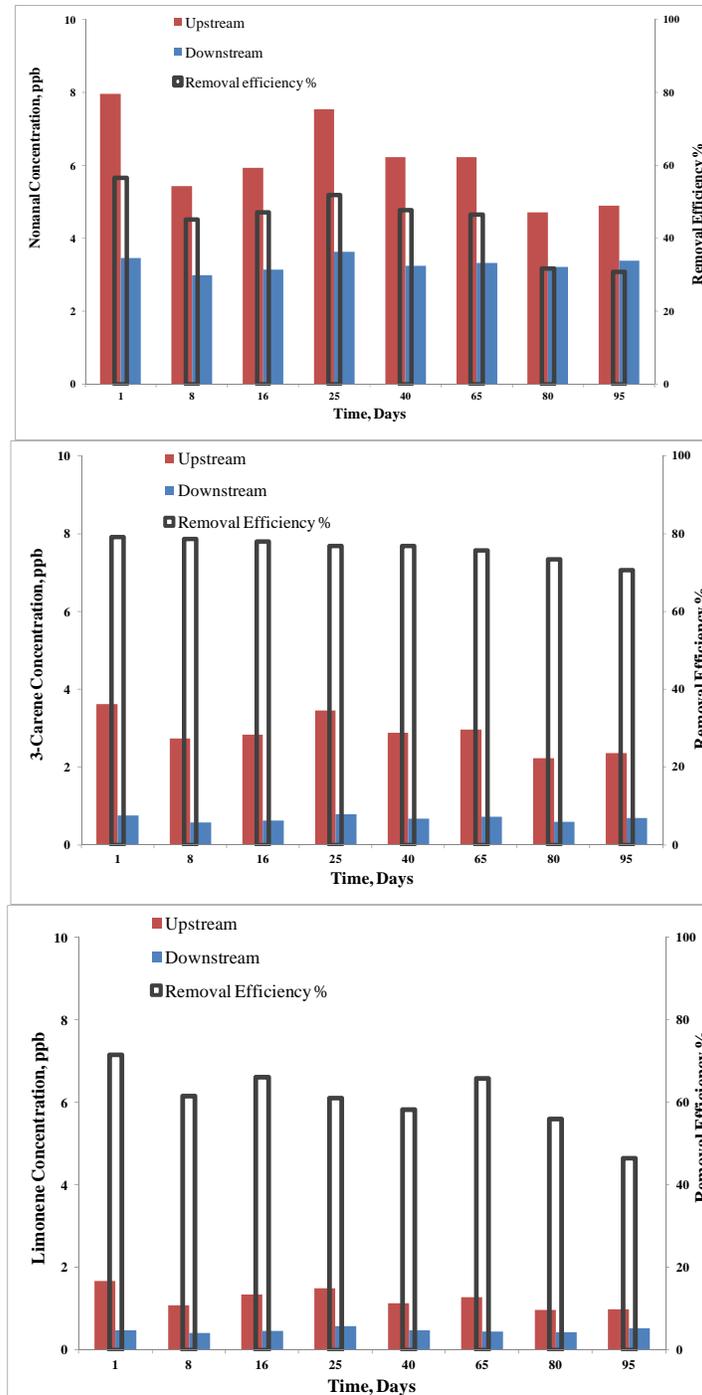
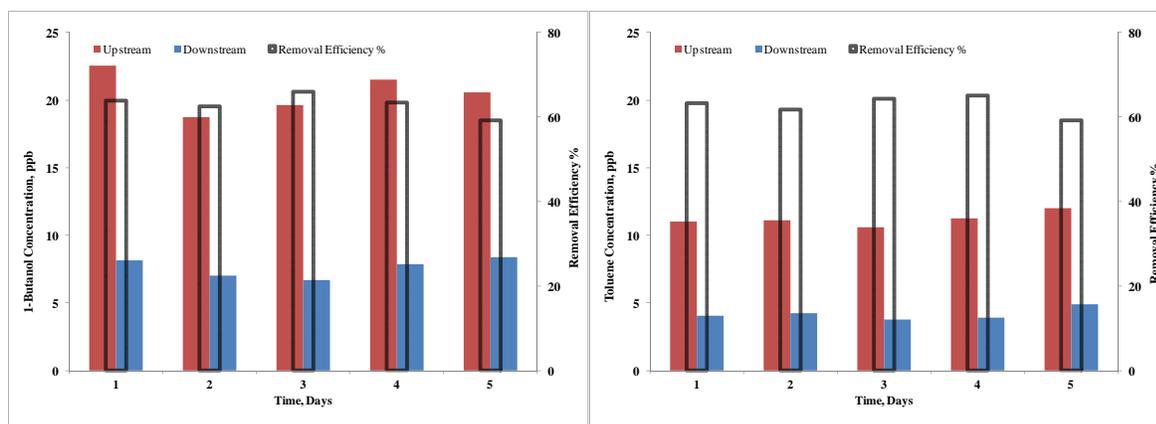


Figure 2.4. Long-term experiments: Upstream and downstream concentration and removal efficiency of representative VOCs.

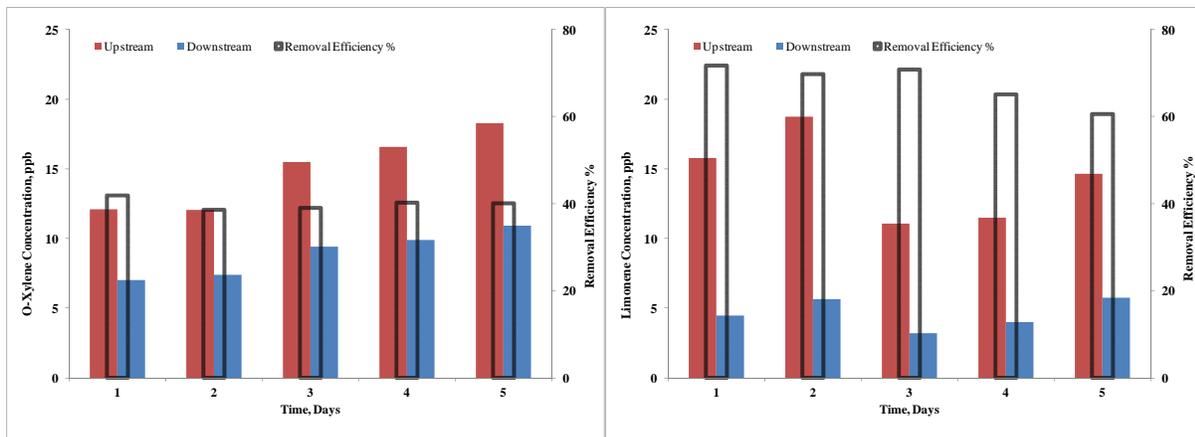
Manganese oxide catalyst was evaluated in a separate study with a standard mix of VOCs with known concentrations using the experimental setup described in section 1.1

and a total concentration of ~106 ppb. A VOC mixture comprising benzene, 1-butanol, toluene, o-xylene, limonene and undecane was injected at a constant rate, with the concentration of individual VOCs maintained between 15 and 25 ppb. Formaldehyde was injected using a separate injection pump and evaporated using a tube heater and mixed in the chamber. The formaldehyde concentration in the chamber was maintained at 20 ppb. Air was pulled through a filter coated with the MnO_x catalyst at a face velocity of 0.5 m s^{-1} . The experiment was carried out for a period of 5 days. Tenax and DNPH samples were taken periodically every day. The results of the experiment are presented in Figure 2.5 (a)-(g). It should be noted that the initial VOC concentrations for these experiments were one order of magnitude higher than those in the long-term experiments discussed above. The experiment did not evaluate the by-product formation from the oxidation of the VOCs. We observed a net reduction in the concentration of the target VOCs. An average VOC reduction of ~58% was obtained.



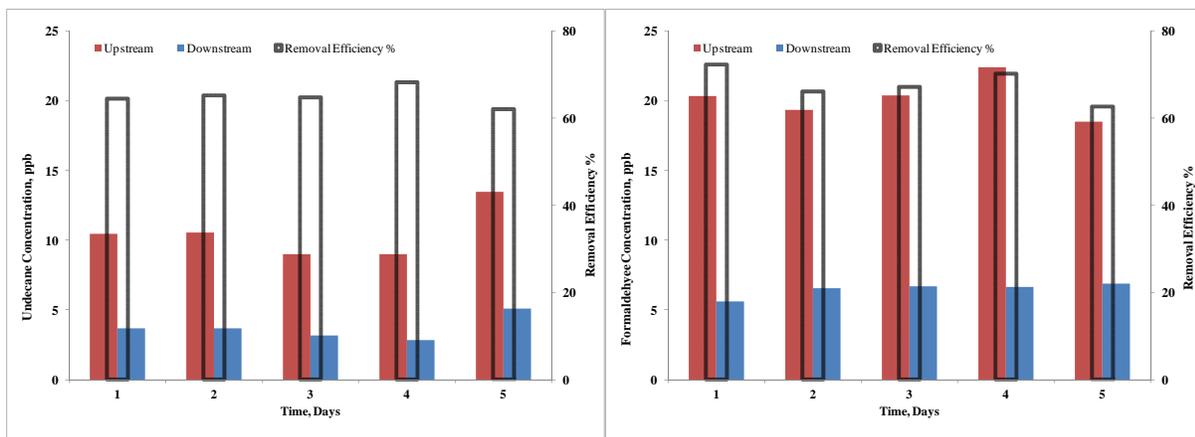
(a)

(b)



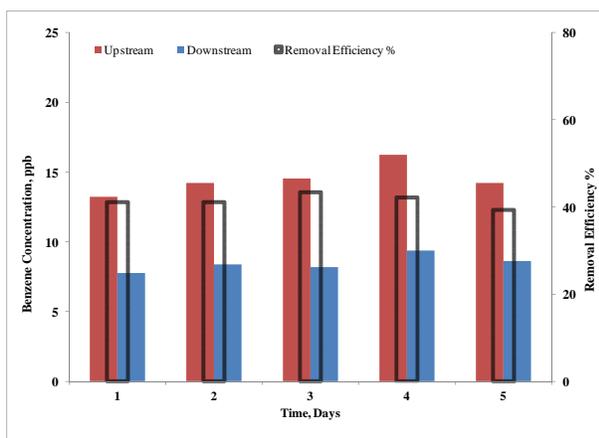
(c)

(d)



(e)

(f)



(g)

Figure 2.5. Short-term experiments: Upstream and downstream concentration and removal efficiency of representative VOCs: (a) 1-Butanol, (b) Toluene, (c) Limonene, (d) O-Xylene, (e) Undecane, (f) Formaldehyde, (g) Benzene.

2.7 Field Study of MnO_x-coated HVAC Filters in a Small Commercial Building

A brief field study was performed to assess the potential benefits of MnO_x-coated HVAC filters under “real world” conditions. A small commercial office building that had been characterized in a previous study at our group was selected to conduct this task, because it combined two key features: relatively high formaldehyde levels and a single-filter HVAC unit. The small commercial office building was located in Sonoma County, CA, was approximately 850 sq. ft and was constructed in 2006. The office space flooring was a mix of ceramic tiles and carpet and was equipped with a single air handling system with three returns and six supplies. The office space was served by a single roof top unit with no visible outside air intake. The ventilation to the office space was predominantly through building leakage. The front door was kept shut most time and the re-circulated air through the AHU and building leakage were used as the main factors to obtain the right thermal comfort. The return and supply velocities were measured using a Balometer. The office space consisted of a reception area, a side office and a main office. The air handler was set to auto during the day and since the outdoor temperature during the day was in the thermal comfort zone, the fan was switched off most of the time. The indoor formaldehyde concentration in that office building was determined in the previous study to be ~ 35 ppb.

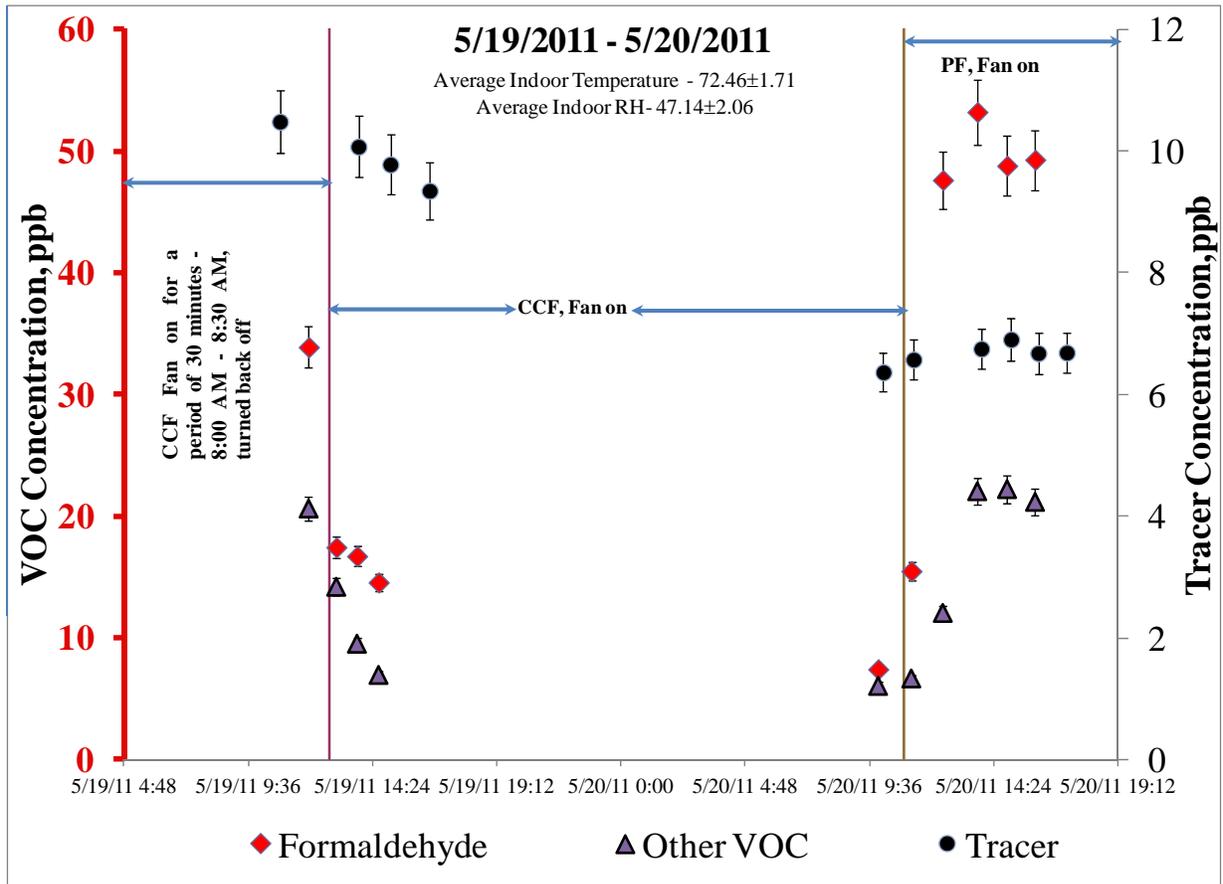
The field test was conducted over a period of several consecutive weeks during which we alternated between a plain filter without catalyst (PF) and a catalyst-coated filter (CCF) placed in the HVAC system. Concentrations of formaldehyde and other VOCs in the indoor air, return and supply duct and outdoor air were monitored. The formaldehyde concentration indoors was observed to be ~ 45 – 50 ppb. The outdoor formaldehyde levels were less than 3 ppb. The formaldehyde concentration in the office space was thus due to significant indoor sources. Temperature and humidity were logged. Dodecapolyfluorocyclobutane (PDCB) tracers were used in the field to measure ventilation rates. Emission rates of 3 glass vials (Kimble Glass, 28X57 mm) containing 20 ml of PDBC were obtained for a period of 14 days prior to deployment in the field. Each of these vials was deployed in different locations in the office space to obtain

uniform concentration. A 51 cm by 63.5 cm by 2.54 cm deep pleated air filter (ACE 4045134) was spray coated with LBNL-100 MnO_x catalyst with a loading of 4 g m^{-2} of filter media for catalyst evaluation purposes. An identical non-catalyst coated filter was alternatively replaced with the catalyst-coated filter to establish formaldehyde reduction and buildup with and without the catalyst coated filter. The test conditions and time-line of test is listed in Table 2.2.

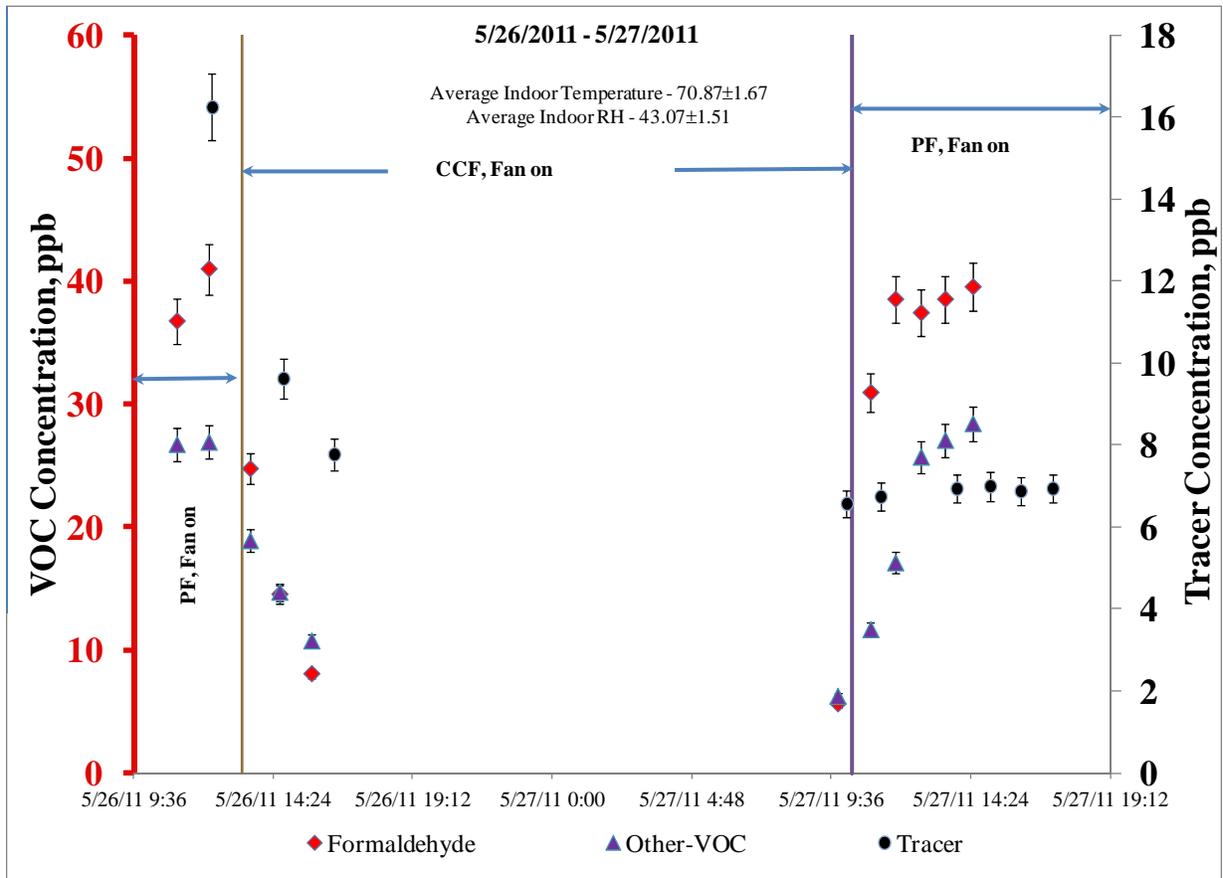
Figure 2.6 (a) and (b) show the transient concentration reduction of formaldehyde and other VOCs in the office space from when CCF is switched with PF. Figure 2.6(a) shows the transient reduction of formaldehyde and other VOCs for the period of May 19 to May 20, 2011. The catalyst-coated filter was installed on May 13, 2011 and left in the air handler prior to this test. Similarly after the catalyst-coated filter was tested, it was replaced with the plain filter to study the pollutant buildup in the office space. Due to long periods during which the AHU fan was turned off, it was difficult to assess the functionality of CCF during the week. The VOC and formaldehyde concentrations were determined during periods in which the fan was switched off. Tenax, DNPH, and tracer bag samples were collected in one-hour period intervals. When results from Figure 2.6(a) and (b) are compared it can be realized that the initial concentration when the fan is turned off for the catalyst-coated filter (Figure 2.6 (a)) is lower than the initial concentration for the plain filter. This can be explained as a result of brief periods of fan operation during both cases for plain and catalyst-coated filter prior to our tests. It was observed that the concentration of acetone decreased when CCF was placed in the HVAC unit. However when CCF was replaced with PF, the concentration of acetone was observed to increase without reaching steady state. The increase in acetone levels can be attributed to emissions by building occupants and researchers, since human breath is a significant indoor source of that compound. Table 2.3 reports VOC concentrations (in ppb) in periods with PF and CCF installed in the AHU and the AHU fan operating. The concentrations of a broad range of VOCs are substantially reduced with the CCF installed, relative to when the PF was installed. These results suggest that the catalyst is effective in removing not only formaldehyde, but also a wide range of VOCs.

| Date | Type of Filter, Initial | Type of Filter, Final | Initial AHU fan status | Activity |
|----------------|--|---------------------------|------------------------|---|
| April 21, 2011 | PF - Glassfloss Z-line (ZL) 20"x25"x1" | Plain Filter - ACE 404531 | Auto - off | Replaced the existing filter with a new plain filter ACE 4045134. Turned the fan on and took background samples. Deployed PFT vials in different locations in the office space. SF ₆ tracer decay was also obtained to estimate ventilation rate. |
| April 29, 2011 | PF - ACE 4045134 | CCF | Auto - off | Replaced PF with CCF, turned on the AHU fan and took samples to observe decay of VOC concentrations. |
| May 5, 2011 | CCF | CCF | Auto - off | Obtained an initial sample with the fan off and turned on the fan and collected samples to observe decay of VOC concentrations. The fan was left on overnight. |
| May 6, 2011 | CCF | PF - ACE 4045134 | On | Obtained two initial samples to determine the stabilized VOC concentration with the CCF and fan on. Switched the CCF with PF and collected samples to observe the concentration buildup. The AHU setting was switched back to auto control once the test was completed. |
| May 13, 2011 | PF - ACE 4045134 | CCF | Auto - off | Obtained an initial sample with the fan turned off. Turned the fan on and obtained two more samples with PF in place. The filter was switched with CCF and VOC concentration decay profile was obtained. The AHU setting was switched back to auto control once the test was completed. |
| May 19, 2011 | CCF | CCF | Auto - off | Obtained an initial sample with the fan off and turned on the fan and collected samples to observe decay of VOC concentrations. The fan was left on overnight. |
| May 20, 2011 | CCF | PF | On | Obtained two initial samples to determine the stabilized VOC concentration with the CCF and fan on. Switched the CCF with PF and collected samples to observe the concentration. The AHU setting was reverted to auto control. |
| May 26, 2011 | PF | CCF | Auto-off | Obtained an initial sample with the fan turned off. Turned the fan on and obtained two more samples with PF in place. The filter was switched with CCF and VOC concentration decay profile was obtained. The fan was left on overnight. |
| May 27, 2011 | CCF | PF | On | Obtained two initial samples to determine the stabilized VOC concentration with the CCF and fan on. Switched the CCF with PF and collected samples to observe the concentration. The AHU was set to auto at the end of the test. |

Table 2.2. Field Study test conditions and activities



(a)



(b)

Figure 2.6. Evaluation of formaldehyde and other VOCs reduction by manganese oxide catalyst coated filter for the period between (a) May 19 – May 20, 2011 and (b) May 26 – May 27, 2011.

| Filter Type with the AHU turned on: | | CCF | PF | PF | CCF | Average % decrease with CCF |
|-------------------------------------|-------------------------|--------------------|----------------------|---------------------|--------------------|-----------------------------|
| CAS Number | Compound | 5/20/11 9:56 AM | 5/20/2011 4:00 PM | 5/26/11 12:11 PM | 5/27/11 9:49 AM | |
| 106-46-7 | 1,4-dichlorobenzene | 0.01 | 0.15 | 0.14 | 0.04 | 86 |
| 6846-50-0 | (TXIB) | 0.20 | 0.24 | 0.23 | 0.18 | 20 |
| 111-76-2 | 2-butoxyethanol | n.d. | 0.12 | 0.08 | 0.01 | 95 |
| 75-07-0 | acetaldehyde | 1.28 | 14.0 | 7.9 | 1.66 | 87 |
| 67-64-1 | acetone | 1.40 | 40 | 19.4 | 2.19 | 94 |
| 80-56-8 | a-pinene | 1.66 | 4.53 | 4.23 | 0.90 | 71 |
| 99-85-4 | a-terpenene | 0.58 | 1.08 | 1.06 | 0.35 | 57 |
| 100-52-7 | Benzaldehyde | 0.22 | 0.94 | 0.94 | 0.07 | 85 |
| 71-43-2 | Benzene | 0.03 | 0.18 | 0.18 | 0.04 | 79 |
| 56-23-5 | Carbon tetrachloride | 0.01 | 0.15 | 0.16 | 0.05 | 81 |
| 67-66-3 | Chloroform | 0.01 | 0.16 | 0.14 | 0.03 | 88 |
| 541-02-6 | D5-siloxane | 1.98 | 2.38 | 2.03 | 1.79 | 14 |
| 112-31-2 | Decanal | 0.02 | 0.23 | 0.26 | 0.04 | 87 |
| 84-66-2 | Diethyl phthalate (DHP) | 0.03 | 0.25 | 0.33 | 0.05 | 87 |
| 5989-27-5 | d-Limonene | 0.46 | 1.16 | 1.12 | 0.22 | 71 |
| 100-41-4 | Ethylbenzene | 0.01 | 0.09 | 0.10 | 0.02 | 84 |
| 50-00-0 | Formaldehyde | 7.4 | 42 | 41 | 5.6 | 84 |
| 66-25-1 | Hexanal | 0.19 | 1.76 | 2.17 | 0.06 | 94 |
| 108-38-3 | m/p-Xylene | 0.02 | 0.08 | 0.18 | 0.03 | 80 |
| 91-20-3 | Naphthalene | 0.09 | 0.27 | 0.30 | 0.06 | 74 |
| 110-54-3 | n-Hexane | n.d. | 0.17 | 0.13 | 0.03 | 91 |
| 124-19-6 | Nonanal | 0.04 | 1.07 | 0.98 | 0.21 | 88 |
| 124-13-0 | Octanal | 0.11 | 0.82 | 0.93 | 0.11 | 87 |
| 106-42-3 | o-Xylene | 0.03 | 0.22 | 0.28 | 0.04 | 85 |
| 87-66-1 | Phenol | 0.16 | 1.54 | 1.43 | 0.03 | 94 |
| 100-42-5 | Styrene | 0.05 | 0.33 | 0.39 | 0.05 | 85 |
| 127-18-4 | Tetrachloroethylene | 0.01 | 0.14 | 0.11 | 0.02 | 87 |
| 108-88-3 | Toluene | 0.12 | 0.43 | 0.93 | 0.10 | 84 |
| 79-01-6 | Trichloroethylene | 0.01 | 0.11 | 0.13 | 0.04 | 81 |

Table 2.3. Concentration (ppb) of VOCs for experiments performed on two different weeks – The concentrations given are the initial concentrations for each test and the concentration after the catalyst-coated filter was used for a period of 20-24 hours.

2.8 Deployment of the Catalyst as Paint Additive for Passive Air Cleaning Applications

We explored the possibility of using manganese oxide catalyst in paint or primer as a passive technology to remove formaldehyde from indoor air. We mixed ~ 10 mg of manganese oxide LBNL-100 in 250 ml of primer (VOC free, Mythic tint base) and 500 ml of paint (VOC free Mythic semi-gloss enamel) and prepared four different painted surfaces with the catalyst added to the paint and/or primer. Case 1 used MnOx in primer plus normal paint, Case 2 used MnOx in both primer and paint, Case 3 used normal primer and MnOx added to paint, and Case 4 used normal paint and normal primer. Paint testing charts (Leneta Form1B Penopac Chart) were used as substrates for testing the paint samples. The testing charts were weighed before and periodically after painting to obtain a steady mass of painted sample. This was performed for all samples to account for the volatile losses from the paint. One unpainted chart was also tested as an experimental blank. The details of the paint samples and the weights are listed in Table 2.4. The samples were then introduced in five different experimental test cells to evaluate the formaldehyde removal capabilities of manganese oxide paint and primer samples. The experimental setup is shown in Figure 2.7. A 2 ml amber vial containing 5% formalin solution was used as the formaldehyde source and placed inside a 200 L chamber. After the experiment was run for 10 days, we decided to implement a step change in formaldehyde concentration to saturate the paint samples and the substrate (Leneta chart). The 5% formalin solution was replaced with 37% formalin solution to achieve this step change. The formaldehyde concentration was restored in the system after a period of 5 days to the original value of 20 – 30 ppb. House air was connected to the chamber inlet and pulled through the test cells at the rate of 0.2 L·min⁻¹ resulting in a residence time for air comparable to that in a room (20 min). Dinitrophenylhydrazine (DNPH) cartridges were used to collect upstream and downstream air samples to measure formaldehyde concentration in the flow cells. DNPH cartridges were extracted with 2-mL aliquots of acetonitrile, and the extracts were analyzed by HPLC with UV detection at $\lambda_{\max} = 360$ nm (Agilent 1200). A calibration curve for quantification was carried out using authentic standards of the formaldehyde-DNPH hydrazone.

| Sample ID | Sample Type | Mass of Paint and primer applied (g) |
|-----------|---|--------------------------------------|
| Case 1 | Paint on Primer | 7.2 |
| Case 2 | Paint on MnO _x Primer | 7.6 |
| Case 3 | MnO _x Paint on Primer | 10.3 |
| Case 4 | MnO _x Paint on MnO _x Primer | 10.4 |
| Case 5 | No Paint | - |

Table 2.4. Mass of paint and primer applied to substrate.

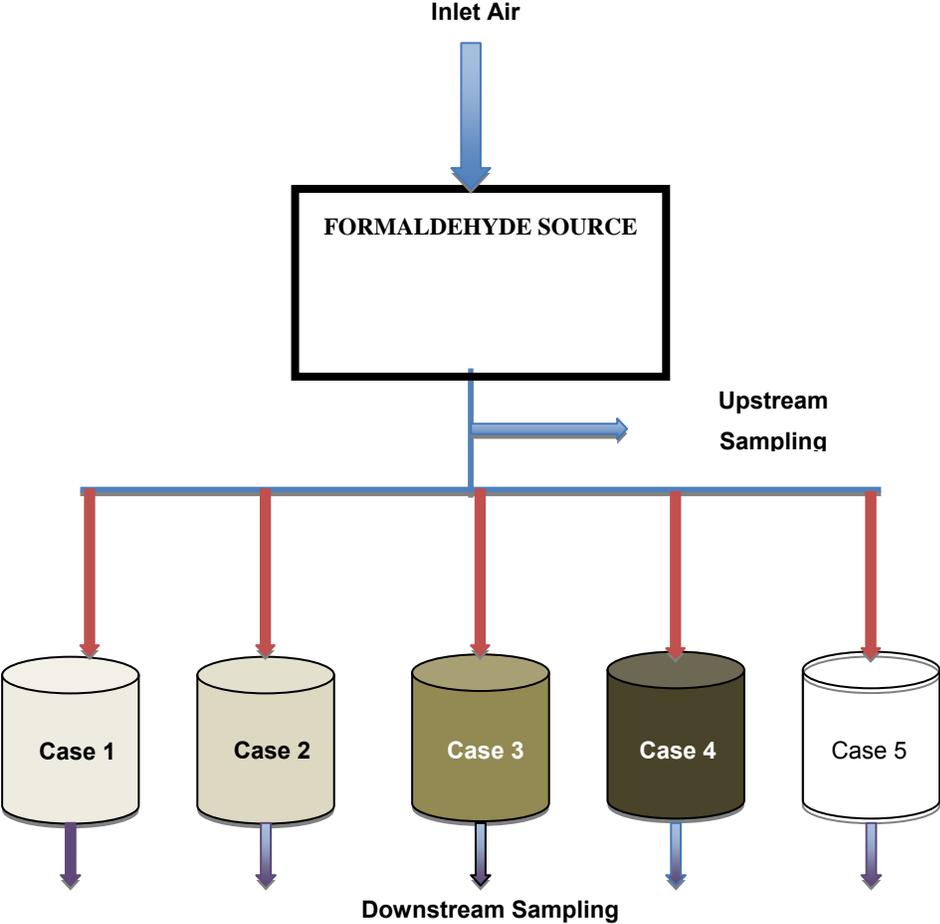


Figure 2.7. Experimental system for evaluation of formaldehyde removal by paints mixed with manganese oxide catalyst.

The initial experimental results obtained from these experiments are shown in Figure 2.8. The inlet concentration to all of the flow cells was monitored and the concentration was maintained at ~20 ppb. The Laneta chart substrate and the paint show initial formaldehyde removal, possibly by simple adsorption. When the inlet concentration was increased 40-fold, the formaldehyde removal efficiency of the samples increased to ~50%. The samples Case 2, Case 3, and Case 4 showed improvement in their performance with time. An average of removal of 25 – 30% was seen for all samples. Sample Case 2, which is paint on manganese oxide coated primer performs moderately compared to the other manganese oxide coated samples. The comparatively low performance of manganese oxide catalyst in paint could be attributed to multiple factors. The pore structure and the surface area of the catalyst may be altered when mixed in paint or primer. At present this system does not appear highly promising.

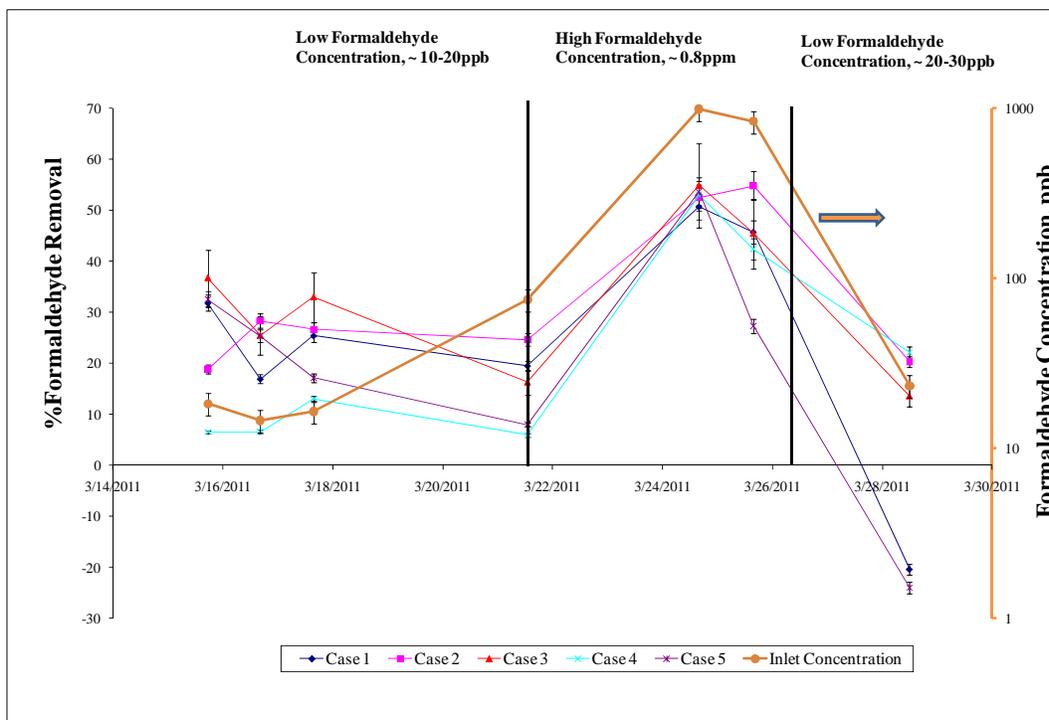


Figure 2.8. Formaldehyde removal efficiency of painted samples with and without catalyst.

2.9 Cost Analysis of Catalyst System

We performed a simple calculation to estimate the costs of materials needed to produce the catalyst. Using prices for research-grade chemicals needed to produce the LBNL-100 catalyst (totaling \$0.23/g of catalyst), the required quantity of catalyst (~ 3 g per square meter of filter media), and assuming a typical air velocity through filter media (0.35 m/s), we projected a materials cost of \$0.7 per each square meter of filter media and \$2 for each $1 \text{ m}^3 \text{ s}^{-1}$ of filtered air. Using commercial grade, as opposed to research grade, chemicals to produce the catalyst, the expected materials cost would be lower, perhaps dramatically lower. For comparison, the retail cost of particle filters was estimated from sample data as \$5 to \$20 per square meter of filter media. Also, the total monthly cost for particle filtration, considering the cost of filters, labor, and energy, has been estimated to be \$9 to \$17 per each cubic meter of air (Fisk et al. 2002). Assuming a typical four-month filter period between replacements of the catalyst-coated filter, the monthly cost of the catalyst applied to the filter is \$0.5 per each cubic meter of filtered air. Thus, the cost of the catalyst is small relative to the existing costs of particle filtration.

2.10 Summary

A manganese oxide catalyst was synthesized using inexpensive precursors and a simple process, and can help preserve or improve indoor air quality at reduced ventilation rates that may enable significant energy savings. Relative to the commercial product, the synthesized manganese oxide has a much higher surface area and different crystal size and chemical composition, consistent with superior catalytic performance. We have optimized catalyst coating techniques, evaluated the mechanical stability of coatings, the effect of tackifiers on catalyst performance, the effect of high relative humidity. In addition, we performed long-term studies to evaluate catalyst performance over an extended period of up to 95 days, we carried out a limited field study to evaluate the performance of the catalyst under “real world” conditions and

investigated the implementation of this catalyst as an additive in paint formulations for passive formaldehyde removal. The synthesized catalyst, applied to a typical particle filter, removed formaldehyde with a stable ~80% efficiency at room temperature in initial conditions, and preserved a significant activity (~60% removal efficiency) after more than 3 months of continuous operation.

2.11 References

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Conclusions

The results of FY11 research performed to date are very promising. The main accomplishments and findings are as follows:

1. The ACF system retained VOC removal efficiencies above the required levels for all VOCs other than formaldehyde, with air velocities increased by 50% and 100% of the velocity employed in FY10 studies.
2. Using heated air to regenerate the ACF media resulted in higher VOC removal efficiencies than regeneration by heating the ACF media with an electrical current. This finding will make regeneration very practical with standard hardware.
3. VOC removal efficiencies were improved, as expected, with a double layer of ACF cloth. Most importantly, the VOC removal efficiency for formaldehyde approximately doubled, resulting in a system that clearly exceeds targets for all tested VOCs.
4. Only modest reductions in VOC removal efficiency occurred when the direction of airflow during regeneration was not reversed relative to the airflow direction during air cleaning. This finding expands the options for ACF system design.
5. To facilitate deployment of the air cleaning systems in existing buildings, including those with roof-top systems, we developed the conceptual design for an air cleaner that is connected by ducts to the ductwork of an existing HVAC system.
6. Systems for producing manganese oxide catalyst were scaled up by a factor of one hundred.
7. A convenient spray process was developed for applying catalyst to particle filters. Tests indicate that the catalyst remains attached to the particle filter during subsequent filter deployment

8. A test indicates that high humidity does not substantially degrade catalyst performance.
9. Experiments determined that heavy layers of tackifier (adhesive) applied to some particle filters can degrade catalyst effectiveness.
10. Experiments to date indicate that the performance of manganese oxide catalyst has diminished by only ~ 30% after 95 days of continuous use in a typical building, corresponding to 190 days of use in a building with 12-hours per day of HVAC operation.
11. The initial results of a field study of the catalyst system are very encouraging, with approximately 80% reductions in indoor formaldehyde concentrations obtained simply by replacing existing particle filters with catalyst-treated filters. The catalyst showed also similarly high removal efficiencies for a broad range of VOCs as well.
12. Initial tests results indicate that application of the catalyst in paint for passive formaldehyde removal is not highly promising.