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Publication Date

2007-02-01

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Abstract

We previously reported that gas-phase byproducts of incomplete oxidation were generated when a prototype ultraviolet photocatalytic oxidation (UVPCO) air cleaner was operated in the laboratory with indoor-relevant mixtures of VOCs at realistic concentrations. Under these conditions, there was net production of formaldehyde and acetaldehyde, two important indoor air toxicants. Here, we further explore the issue of byproduct generation. Using the same UVPCO air cleaner, we conducted experiments to identify common VOCs that lead to the production of formaldehyde and acetaldehyde and to quantify their production rates. We sought to reduce the production of formaldehyde and acetaldehyde to acceptable levels by employing different chemisorbent scrubbers downstream of the UVPCO device. Additionally, we made preliminary measurements to estimate the capacity and expected lifetime of the chemisorbent media. For most experiments, the system was operated at $680 - 780$ m^3/h ($400 - 460$ cfm).

A set of experiments was conducted with common VOCs introduced into the UVPCO device individually and in mixture. Compound conversion efficiencies and the production of formaldehyde and acetaldehyde were determined by comparison of compound concentrations upstream and downstream of the reactor. There was general agreement between compound conversions efficiencies determined individually and in the mixture. This suggests that competition among compounds for active sites on the photocatalyst surface will not limit the performance of the UVPCO device when the total VOC concentration is low. A possible exception was the very volatile alcohols, for which there were some indications of competitive adsorption. The results also showed that formaldehyde was produced from many commonly

encountered VOCs, while acetaldehyde was generated by specific VOCs, particularly ethanol. The implication is that formaldehyde concentrations are likely to increase when an effective UVPCO air cleaner is used in buildings containing typical VOC sources. The magnitude of the expected increase will depend upon a number of interrelated factors.

Series of experiments were conducted to determine if the oxidizer, sodium permanganate ($NaMnO_4 \cdot H_2O$), has sufficient reaction rates and capacity to counteract formaldehyde and acetaldehyde production and enable a 50 % reduction in building ventilation rate without net increases in indoor aldehyde concentrations. A commercially produced filter element and two laboratory-fabricated media beds containing $NaMnO_4 \cdot H_2O$ chemisorbent media were evaluated. The effectiveness of a device for removal of formaldehyde, acetaldehyde and other VOCs was determined by measurement of concentrations immediately upstream and downstream of the device. In some experiments, conversion efficiencies and byproduct generation by the UVPCO device also were determined.

Six experiments were conducted with the commercial filter element installed downstream of the UVPCO reactor. Eleven experiments were conducted with a single panel media bed (30 cm by 61 cm by 2.5 cm deep) installed downstream of the UVPCO reactor; in these, the effects of temperature and air residence time on conversion efficiency were examined. Two experiments were conducted with a four-panel, folded, media bed (approximately four times the size of the single panel bed) installed downstream of the reactor.

Because the commercial unit contained activated carbon as an additional component, it was effective at removing lower volatility compounds that typically have low oxidation rates in the UVPCO reactor. The filter element also met the minimum efficiency objective for formaldehyde. However, the removal of acetaldehyde was less than required.

The air residence time in the single panel bed was not optimized as the removal efficiencies for both formaldehyde and acetaldehyde were strongly inversely related to the air flow rate through the device. In addition, the acetaldehyde removal efficiency decreased to less than 10 % with extended use of the device. The folded bed was considerably more effective; formaldehyde was removed with greater than 90 % efficiency, and acetaldehyde was removed at about 70 % efficiency. With the combined UVPCO/chemisorbent system, the net removal efficiencies for formaldehyde and acetaldehyde were 90 % and 40 %, respectively.

Two pairs of replicated experiments were conducted with the UVPCO system operating within a 50-m^3 environmental chamber in a simulated HVAC mode with recirculation of chamber air. For one pair, the UVPCO air cleaner was operated alone, and for the other, the combined system of UVPCO air cleaner plus a downstream chemisorbent was used. The results showed that the chemisorbent media contributed substantially to the removal of VOCs in this mode. Concentrations were pulled down within the first hour. Net reductions for formaldehyde and acetaldehyde at near steady-state conditions were in the range of 50 to 70 %.

From an analysis of $NaMnO_4 \cdot H_2O$ in new and used media and the conditions of the experiments with the single panel media bed, we estimated that, on average, about nine moles of $NaMnO_4 \cdot H_2O$ were needed to mineralize one mole of VOCs, and about three moles of the reactant were needed to mineralize one mole of carbon. These values were used to make estimates of the media consumption rate for the experimental conditions and for a hypothetical building application.

In summary, the use of a multi-panel, folded scrubber filled with $NaMnO_4 \cdot H_2O$ chemisorbent media downstream of the prototype UVPCO air cleaner effectively counteracted the generation of formaldehyde and acetaldehyde due to incomplete oxidation of VOCs in the UVPCO reactor. Thus, this combined UVPCO air cleaner and chemisorbent system appears to have sufficient VOC removal efficiency to enable a 50 % reduction in ventilation rate without increasing indoor aldehyde concentrations.

INTRODUCTION

The U.S. Department of Energy and other energy agencies seek to reduce the consumption of energy for thermally conditioning outdoor air used for ventilation in buildings. Ventilation air is provided to maintain acceptable indoor concentrations of indoor-generated air pollutants. In commercial buildings, the most important indoor generated air pollutants are particles and volatile organic compounds (VOCs). These buildings usually have weak indoor sources of inorganic gaseous pollutants such as carbon monoxide, nitrogen dioxide, ozone and radon. Consequently, implementation of air cleaning technologies for both particles and VOCs in commercial buildings may improve air quality and may enable indoor air quality levels to be maintained with reduced outdoor air supply and concomitant energy savings.

Practical air cleaning technologies for particles are widely available, typically consisting of fibrous filters installed in incoming outdoor air and recirculated air streams (i.e., supply air). Air cleaning technologies for VOCs are less advanced and surprisingly little has been published regarding their effectiveness and practicality when used in heating, ventilating and air conditioning (HVAC) systems of commercial buildings.

Activated carbon is the most commonly used physical adsorbent for removal of VOCs from air streams (Liu, 1993). The amount of carbon and the residence time for air are key determinants of sorbent system VOC removal performance (Muller, 1993; Liu, 1993). Systems with small amounts of carbon are effective for only short periods (Muller, 1993). VOC removal efficiency and capacity decrease with increased humidity and air temperature (e.g., Gong and Keener, 1993). When the inlet air contains multiple VOCs (which is always the case in buildings) and a significant fraction of carbon becomes saturated with VOCs, higher molecular weight VOCs can drive previously sorbed lower molecular weight VOCs back into the air stream (Liu, 1993). Also, activated carbon, without any additives or impregnants, has low retention of very volatile compounds such as formaldehyde (Muller and England, 1994; Tseng et al., 2005).

Ultraviolet photocatalytic oxidation (UVPCO) air cleaning is a promising air cleaning technology that may avoid some of the problems associated with activated carbon systems. UVPCO air cleaning has been under development for a number of years and appears to be generating increased interest for use in buildings (Zhao and Yang, 2003, Tompkins et al., 2005).

UVPCO devices often utilize a honeycomb configured monolith reactor coated with titanium dioxide (TiO_2 or Titania). The monolith is irradiated with fluorescent bulbs with peak irradiance near either 254 nm (UVC) or 365 nm (UVA). Air flows through the monolith, where the VOCs adsorb reversibly on the catalyst and react following described mechanisms (Hoffmann et al., 1995). For a prototype device we previously evaluated with realistic mixtures of VOCs, conversion efficiencies typically exceeded the minimum required to counteract predicted VOC concentration increases from a 50 % reduction in ventilation (Hodgson et al., 2005 and In press). However, several important issues were identified that need to be addressed before UVPCO air cleaning can be deployed practically and safely in buildings.

In particular, we found that gas-phase byproducts were generated when the prototype UVPCO device was operated with indoor relevant mixtures of VOCs at realistic concentrations (Hodgson et al., 2005 and In press). Under the experimental conditions, there was net production of formaldehyde, acetaldehyde, and 2-propanone (acetone). Formic acid and acetic acid also were produced in some experiments. Since formaldehyde and acetaldehyde are recognized as important inhalation toxicants and probable carcinogens by governmental agencies, their generation cannot be ignored for building applications.

Other experimental work supports our findings. Chen et al. (2005a) identified acetic acid as an oxidation byproduct when a UVPCO was operated with a challenge VOC mixture that contained seven classes of commonly encountered VOCs. Disdier et al. (2005) showed small increases in the concentrations of formaldehyde, acetaldehyde, and acetone due to operation of a UVPCO device in a room with the UVPCO lamps on versus with the lamps off. Ginestet et al. (2005) evaluated UVPCO configurations for aircraft cabin applications. When challenged with 10 ppm toluene, acetone, or ethanol, the device operated in single-pass mode produced about 40 – 60 ppb formaldehyde. Acetaldehyde was produced at lower concentrations except for ethanol, which resulted in a downstream concentration of 1.7 ppm. In recent study of UVPCO application in a simulated air craft cabin with occupants, Wisthaler et al. (2007) measured the generation of elevated concentrations of acetaldehyde and formaldehyde related to the use of wet wipes supplied with a meal. Ethanol concentrations in the cabin due to use of the wipes reached peak concentrations of 2,500 ppb, or more. Associated 95th percentile concentrations of acetaldehyde and formaldehyde were 230 – 670 ppb and 20 38 ppb, respectively.

The study reported here had two primary aims. Our first aim was to further explore the issue of byproduct generation. With the same prototype UVPCO device used previously, we conducted experiments to identify specific, commonly occurring, VOCs that lead to the production of formaldehyde and acetaldehyde and to quantify the production rates of these compounds. Our second aim was to reduce the production of formaldehyde and acetaldehyde to acceptable levels for buildings. Our approach, investigated here, was to employ additional air treatment downstream of the UVPCO device. For this, we utilized a chemisorbent media.

Common examples of chemisorbent media are activated carbon or zeolites impregnated with potassium or sodium permanganate, which reacts with formaldehyde and other compounds. The chemical reactions are irreversible; consequently, the reacted compound will not be released back into air. Such chemisorbent media are reported to remove a few to several percent of their weight in formaldehyde (Muller and England, 1994).

Chemisorbent media comes in several forms for installation in an air stream. The most traditional form consists of a tray, or packed bed, of granular media. Often, the sorbent grain size is several millimeters in diameter (Muller and Middlebrooks, 2001). Smaller grains can lead to better mass transfer of the VOC from the air to the media, but also result in higher air stream pressure drops. Manufacturers have started to offer devices with grains of media bonded onto a three-dimensional non-woven fiber matrix not intended for particle filtration. With this method of deployment, the packing of media grains is decoupled from media grain size and smaller grains may be used without encountering excessive air stream pressure drops. In non-woven media, a substantial quantity of media can be practically deployed in an air stream; but less media is deployed than in a packed bed of the same volume.

The major practical issues to be addressed with an air cleaner combining a UVPCO reactor with a chemisorbent scrubber, are the lifetimes of both the UVPCO monoliths and the chemisorbent when the combined system in deployed in commercial buildings. Thus, our secondary aim in conducting this study was to generate some preliminary information on the capacity and expected lifetime of the chemisorbent component. Further experiments will be needed to better characterize lifetime factors for the monoliths and the chemisorbent.

METHODS AND MATERIALS

UVPCO Reactor and Flow System

The UVPCO reactor used in this study is a prototype developed for the purpose of demonstrating air purification capabilities when installed in a HVAC duct system. It previously has been described in detail (Hodgson et al., 2005 and In press). Degussa Titania P25 impregnated with 3 % tungsten oxide by weight (TiO_2 / 3 % WO_3) is used as the photocatalyst. The reactor contains two treated, aluminum, honeycomb monoliths with face dimensions of 30 by 30 cm that are mounted in series with their faces oriented transversely to the air flow path.

A total of 12 UV lamps (Model G10T5L-S400, Voltarc Technologies, Inc., Waterbury, CT) are used. These are 18-Watt lamps with about 30 % efficiency. The total UV power is about 5 – 5.5 Watts, predominantly at 254 nm. The lamps are mounted transversely in three banks of four lamps each. The banks are centered between the monoliths as well as before the first and after the last monolith.

The reactor housing is constructed of compressed fiberglass duct board with an inner and outer aluminum foil facing. The housing is square in cross section and is approximately one meter long. Sheet metal pieces were fabricated to fit the inlet and outlet of the device. These pieces provided transitions from the square reactor housing to round sheet metal ducting. The upstream tapered transition was fitted with eight ports for the collection of air samples. Downstream, the transition went directly from the square reactor to a 60-cm section of 25-cm diameter round ducting. This ducting also was fitted with eight air-sampling ports. In previous experiments, similar and acceptable analytical precision for triplicate samples was recorded for both upstream and downstream sampling locations suggesting that the air in the reactor was reasonably mixed at these locations. Temperature probes, relative humidity (RH) probes, and ports with probes for pressure monitoring additionally were installed in the upstream and downstream transitions. A metal housing containing a pleated fabric air filter (MERV 12) was installed at the inlet to the assembly. For these experiments, air entered the filter assembly through an approximate 2-m section of 20-cm round corrugated aluminum ducting.

Provision was made to connect chemisorbent scrubbers downstream of the UVPCO reactor. The aluminum housing for these scrubbers was approximately 30 by 61 cm in cross

section and approximately 50 cm long. The 60-cm section of 25-cm diameter round ducting installed immediately downstream of the scrubber position contained a set of eight air sampling ports and a port for pressure monitoring. The scrubbers are described in detail below.

A variable-speed duct blower with provision for measuring duct pressures across the blower (Minneapolis Duct Blaster, The Energy Conservatory, Minneapolis, MN) was connected downstream of the scrubber section. Blower speed was adjusted to establish the air flow rate through the system. In experiments with the packed bed chemisorbent scrubbers, a secondary, fixed-speed, blower (Model DDF-12, Cincinnati Fan & Ventilator Company, Inc., Mason, OH) was mounted downstream of the variable-speed blower. In all single pass conversion experiments, the exhaust flow from the blower was ducted directly to outdoors. All joints and seams throughout the entire system were sealed with aluminum tape to minimize air leakage.

For most experiments, the system was operated at flow rate settings in the range of $680 – 780 \ m^3/h \ (400 – 460 \ cfm)$. At these settings, the face velocities at the monoliths were in a range of $2.0 – 2.3 \ m/s \ (6.8 – 7.7 \ ft/s)$.

Chemisorbent Scrubbers

Chemisorbent media impregnated with $NaMnO_4 \cdot H_2O$ is manufactured in several forms for air cleaning applications (Purafil, Inc.) The manufacturer has recently switched from potassium permanganate to the sodium form in order to achieve a higher loading of the reagent on the zeolite support (reportedly an increase from 8 % to 12 % by weight). A commercially produced filter element and two laboratory fabricated media beds containing the $NaMnO_4 \cdot H_2O$ media were individually evaluated.

Experiments first were conducted with the commercial filter element (Purafilter™, Purafil, Inc.) installed downstream of the UVPCO reactor. The filter element is contained in an aluminum housing and has face dimensions of 12 in by 24 in (30 cm by 61 cm), and a 12-in (30-cm) depth. In this particular device, the pleated non-woven fabric was loaded with CPS™ media (Purafil, Inc.) consisting of a fine-particle mixture of activated carbon and a zeolite impregnated with $NaMnO_4 \cdot H_2O$. This design results in low pressure drop.

Two packed beds with substantially more of the media were fabricated in the laboratory. One was a single panel design. This media bed, shown in Figure 1, was constructed with an

aluminum frame and course and fine wire mesh faces. It had face dimensions of 12 in by 24 in (30 cm by 61 cm) and was 1-in (2.5-cm) deep. It was filled with 4.2 kg of SP media (Purafil, Inc.). This form of the media consists of zeolite spheres, approximately 4-mm in diameter, impregnated with $NaMnO_4 \cdot H_2O$. We also fabricated a four-panel, folded, media bed with about four times the surface area and media mass as the single panel bed. The media bed, shown in Figure 2, was based on a commercial design (Vari-Pure, AirGuard, Louisville, KY). It was constructed from pieces of perforated steel sheet, 22 gauge, 0.079-in (2-mm) hole diameter; 0.109-in (2.8-mm) center-to-center hole spacing and 45 % open area (P/N 9255T471, McMaster-Carr). The "W" shape approximated that of a four-panel folded bed with each panel having dimensions of 12 in by 24 in (30 cm by 61 cm). The perforated sheets were spaced 2.5-cm apart. The bed was filled with 15.6 kg of Purafil SP media. Both beds were contained in a box housing fabricated of aluminum with open face dimensions of 12-in by 24-in (30-cm by 61-cm).

Environmental Chamber

The experimental apparatus was housed in a 50-m^3 environmental chamber. The chamber is intended to simulate a small room in a building. The walls and ceiling are finished in painted gypsum board, and the floor is covered with aluminum sheeting with approximately one-half finished with vinyl composition tile. The chamber is housed in a small building with a dedicated heat-pump HVAC system to control the temperature in the building. However, the system is not sufficiently sized to cool the building and maintain constant temperature during periods of high ambient temperature. Thus, there were excursions of the chamber temperature above the prescribed range during several experimental series.

For all single-pass experiments, conditioned building air was supplied to the chamber. Air entered a fabricated air cleaner containing a bed of granulated activated carbon (approximately 23 kg). The air cleaner was fitted with a blower and a downstream particle filter capable of supplying an air flow rate to the chamber in excess of the air flow rate exhausted from the chamber by the combined UVPCO/chemisorbent air cleaner system. A humidifier (Model 9940, Air King, Ontario, Canada) was operated in the chamber on days when chamber relative humidity was <45 %.

For the recirculation experiments, the environmental chamber was configured to maintain an approximate 180-m^3/h constant air flow rate. The UVPCO/chemisorbent system exhaust and

the high flow rate air supply system were removed. Outdoor air was supplied to the chamber by a separate system with flow control. Air exhausted the chamber through ports fitted with sliding valves to maintain a slight positive pressure in the chamber. The air flow rate into the chamber was measured by decay of injected carbon dioxide tracer gas prior to each pair of experiments.

VOC and Aldehyde Infusion

The experiments were conducted with VOCs that were contained in mixtures used in prior experiments with this UVPCO reactor (Hodgson et al., 2005 and In press). Here, we primarily focused on VOCs with relatively high UVPCO reaction rates as determined in the prior experiments as well as a few other VOCs of interest. In experiments to determine the predominant sources of formaldehyde and acetaldehyde generation, study VOCs were introduced into the UVPCO reactor both individually and in mixture. This mixture contained ten VOCs. A 15-component mixture (the original 10 compounds plus five additional compounds) subsequently was used in experiments to determine the effectiveness of chemisorbent scrubbers. Pure chemicals were added together to create the liquid mixtures. The relative amounts of the individual VOCs were selected to produce the desired concentration ratios when introduced into air.

An aqueous solution of formaldehyde and acetaldehyde also was created for the experiments with the chemisorbent scrubbers as previously described (Hodgson et al., 2005). A preservative-free formalin solution first was prepared by refluxing approximately 1 g of paraformaldehyde (CAS # 30525-89-4) in 200 mL water for 1 hour. After cooling, the solution was made up to 250 mL. The concentration of formaldehyde in the solution was determined by spiking 1 μL of the resulting solution onto an aldehyde air sampling cartridge and analyzing it as described below. The formalin solution then was spiked with a measured micro-liter volume of pure acetaldehyde to produce a mixture of the two compounds at the desired concentration ratio.

In all single-pass experiments, the individual VOCs and the VOC and aldehyde mixtures were infused directly into the section of 20-cm ducting attached to the inlet of the air cleaner system. Infusion rates were controlled using syringe pumps (Model NE-1000, New Era Pump Systems, Inc., Farmingdale, NY). VOC mixtures were loaded into a 250-μL glass syringe, and the aldehyde solution was loaded into a 10-mL polypropylene syringe. The typical infusion rates were 20 μL/min for the VOC mixture and 120 μL/min for the aldehyde mixture. The VOC

syringe was connected to 0.8-mm I.D. tubing that delivered the liquids into a small sleeve heater (6-mm I.D.) positioned in the center of the duct inlet. The aldehyde syringe was connected to a length of 1.6-mm I.D. copper tubing that was coiled on top of a hot plate with its outlet positioned in the duct inlet. The tubing was supplied with a flow of air at about 250 cm^3/min. The temperatures of the heating devices were adjusted to achieve rapid evaporation of the mixtures. For extended periods of operation, three-way, integral Luer lock, solenoid valves (Model CSAT031, Neptune Research & Development, Inc., West Caldwell, NJ) were fitted to the syringes. One leg of a valve was attached to the liquid delivery tubing and the other leg was attached to a raised, inverted reservoir containing the infusion mixture. A valve was controlled by its syringe pump to deliver the liquid at the controlled rate and then to rapidly refill the syringe in order to achieve nearly continuous infusion of the liquid.

For the recirculation experiments, the infusion system was moved directly outside of the 50-m^3 chamber. The system delivered the mixtures into a section of 1.6-mm I.D. copper tubing. This tubing was heated and supplied with a flow of air at about 250 cm^3/min. The tubing penetrated the wall of the chamber and delivered the vaporized compounds into a 2-m section of 20-cm ducting fitted with a fan at one end to achieve rapid mixing of VOCs in chamber air.

Monitoring Instrumentation

Temperatures, RH, and pressures were monitored continuously throughout each experiment with an Automated Performance Testing System (APTS) equipped with optional sensors and operating with data logging software (The Energy Conservatory, Minneapolis, MN). The monitored experimental parameters included system air flow rate; differential pressure between the duct and the room at the three sampling locations; differential pressure between the room and the building; temperature upstream and downstream of the UVPCO reactor; RH upstream and downstream of the reactor; and room temperature and RH. The pressure measurements have a resolution of 0.1 Pa. The temperature sensor has an accuracy of $\pm 0.25^o$ C, and the RH sensor has an accuracy of ± 5 % RH. Data were recorded electronically at 30-sec intervals. The uncertainties in the means of the measured parameters over the course of each experiment were determined from analysis of the recorded data.

The analog voltage outputs of the 12 mass flow controllers used for collection of air samples (described below) were recorded with four-channel data loggers (Model U12-006, Onset

Computer Corp., Bourne, MA). These data were recorded at 15-sec intervals. The measurement of air flow rate was highly precise with little recorded variation over the course of each experiment.

Air Sampling

Air samples for the analysis of VOCs and low molecular weight aldehydes and ketones were collected at two or three of the sampling locations in each experiment. For each analyte type, there were two or three replicate samples collected simultaneously at a location. The sampling media (described below) were connected to the bulkhead unions in the transition pieces. Air flow rates through the two media types were regulated with electronic mass flow controllers (MFCs). There were six $0 - 500$ standard cm^3/min MFCs operated at approximately 100 cm^3/min for the collection of VOC samples and six $0 - 2$ standard L/min MFCs used for the collection of aldehyde samples. Initially, aldehyde samples were collected at 1.5 L/min; this rate subsequently was reduced to about 1.0 L/min as it resulted in improved precision for duplicate measurements. All MFCs were calibrated in the laboratory at standard conditions of 25° C and 101.3 kPa. The sampling interval for the aldehyde samples was one hour. The sampling interval for the VOC samples was varied between 10 and 30 minutes depending upon the expected analyte concentrations.

Typically, air sampling for an experiment was initiated after the system had operated for one hour, or more, at the established conditions. The air sampling strategy varied with the experimental design. For single-pass experiments with just the UVPCO reactor, the strategy was to simultaneously collect replicate VOC and aldehyde samples at the sampling ports located upstream and downstream of the reactor. For single-pass experiments with the chemisorbent scrubber in place and the UVPCO reactor lamps off, samples were simultaneously collected at the sampling ports upstream and downstream of the scrubber. For single-pass experiments with both the UVPCO reactor and the chemisorbent scrubber active, samples first were simultaneously collected upstream and downstream of the reactor and then another set of samples was collected downstream of the scrubber; thus, in this case, the collection period extended over approximately two hours. For the recirculation experiments, VOC and aldehyde air samples were collected from the 50-m^3 chamber through sampling ports positioned in one wall of the chamber. Samples were collected initially with the chamber operating at near steady-

state conditions (i.e., following at least three changes of chamber air with constant source injection) and then every hour for a period of six hours after the air cleaner system was activated.

Air samples for the analysis of VOCs were collected onto sorbent tubes (P/N CP-16251, Varian Inc., Walnut Creek, CA) packed with Tenax-TA™ with a 15-mm section of Carbosieve™ S-III 60/80 mesh (P/N 10184, Supelco Inc., Bellefonte, PA) substituted for the Tenax at the outlet end. Air samples for aldehydes were collected onto XpoSure Aldehyde Samplers (P/N WAT047205, Waters Corp., Milford, MA).

Chemical Analyses

VOC samples were analyzed by thermal desorption gas chromatography with mass selective detection and quantitation (TD-GC/MS) as previously described (Hodgson et al., 2005). Briefly, sample tubes were thermally desorbed and concentrated on a cryogenic inletting system (Model CP-4020 TCT; Varian, Inc.) fitted with a Tenax-packed trap (P/N CP-16425; Varian, Inc.). Compounds were resolved on a Hewlett-Packard (HP) Model 6890-II GC with a DB-1701 column (P/N 122-0733, Agilent Technologies). Compound mass was quantified with an HP Model 5973 MSD operated in electron ionization, scan mode. Samples were analyzed on the day of collection or stored in a freezer for typically no more than one week prior to analysis. Analytes were quantified using multi-point calibration curves developed from pure compounds (Aldrich, Milwaukee, WI). Quantitation was referenced to an internal standard of 1-bromo-4-fluorobenzene.

Aldehyde air samples were analyzed for formaldehyde, acetaldehyde and 2-propanone (acetone) following ASTM Standard Method D 5197-97 (ASTM, 1997). Each sampling cartridge was extracted into 2 mL of acetonitrile. Extracts were analyzed by high-performance liquid chromatography (HPLC). The instrument was equipped with a diode array detector operated at a wavelength of 365 nm. Compounds were resolved on a Symmetry C_{18}, 2.1- by 150-mm column (P/N WAT056975, Waters Corp.). Analytes were quantified from multi-point calibrations of external standard mixtures.

Permanganate Analysis

The content of $NaMnO_4.H_2O$ in samples of Purafil SP chemisorbent media was determined by UV-visible spectrophotometry. For each media sample, 20 beads were crushed in a mortar to

generate a homogenized sample. A mass of 163 ± 1 mg was transferred to a beaker and extracted with deionized water. Used media was extracted in 100 mL of H_2O. New media was extracted in 250 mL of H_2O and was further diluted 1:10. Sodium permanganate concentration in the extracts was determined spectrophotometrically at $\lambda_{max} = 525$ nm, using pure (99 %) $NaMnO_4 \cdot H_2O$ (Aldrich) as a quantification standard in the range $5 - 45$ mg/L. The calibration curve was linear with $r^2 = 0.999$. The mass of $NaMnO_4 \cdot H_2O$ in each sample was calculated based on the extract concentrations.

RESULTS AND DISCUSSION

Individual VOCs – Reaction Rates and Aldehyde Production

Description of Experiments

Twelve experiments were conducted with 11 VOCs introduced individually into the UVPCO device (one VOC, 2-butoxyethanol, was repeated to evaluate the effect of inlet concentration). Another experiment was conduced with a mixture of ten VOCs (all 11 compounds less 2-propanone) introduced as a mixture into the UVPCO device. Compound conversion efficiencies (i.e., fractions reacted) and the production of formaldehyde, acetaldehyde and 2-propanone were determined by comparison of measurement results for air samples collected immediately upstream and downstream of the reactor.

The parameters for the 13 experiments are given in Table 1. The conditions were similar across the experiments. The inlet air flow rate was in the range of $740 - 780$ m^3/h; the temperature ranged from about 23 to 25 $^{\circ}$C; and the relative humidity varied over $45 - 49$ %. The selected VOCs and their inlet mixing ratios in the experiments with individual compounds are listed in Table 2. The selection primarily focused on compounds that were shown previously to have relatively high UVPCO reaction rates and that were likely to produce either formaldehyde or acetaldehyde as products of incomplete oxidation (Hodgson et al., 2005). These compounds included four low molecular weight alcohols, 2-butoxyethanol representative glycol ether), three low molecular weight ketones, hexanal, and d-limonene. Toluene also was included as it is a common air pollutant that often is used as a reference compound in UVPCO studies. 2-Butoxyethanol was introduced at two mixing ratios, 9.4 and 44 ppb. The mixing

ratios of the other compounds ranged between 25 and 154 ppb. Relatively high mixing ratios were used in order to increase our ability to detect and statistically discern production of formaldehyde, acetaldehyde and 2-propanone. Concentration ratios among the compounds were selected to roughly approximate their possible ratios in buildings; i.e., the most volatile compounds were introduced at the highest mixing ratios.

Results

The fractions reacted and the reaction rates for the 11 VOCs introduced individually into the UVPCO device are presented in Table 2. Ethanol and isopropanol had the highest fractions reacted of approximately 0.5 in a single pass through the device. The fraction reacted for 2-butoxyethanol was independent of the inlet concentration. Toluene had the lowest fraction reacted of approximately 0.2. Exclusive of toluene, the conversion efficiencies were in a range of 0.28 – 0.50. The calculated reaction rates of the individual VOCs are a function of the VOC inlet concentrations and the fractions reacted.

In Exp 19, ten of the 11 VOCs were introduced as a mixture into the UVPCO device (Table 3). 2-Propanone was excluded from the mixture, as it is a known reaction product. The inlet mixing ratios generally were lower but in a similar relationship as the ratios among compounds in the preceding experiments with the individual VOCs. In the mixture, isopropanol, 2-butoxyethanol, and hexanal had the highest fractions reacted and toluene had the lowest fraction reacted. Exclusive of toluene, the conversion efficiencies were in a relatively narrow range of 0.29 – 0.41.

The inlet and outlet mixing ratios of formaldehyde and the calculated UVPCO production rates of formaldehyde from incomplete oxidation of the 11 individual VOCs and of the 10-component mixture are presented in Table 4. The formaldehyde inlet mixing ratios were the background concentrations in the chamber on the days of the experiments. These values ranged from 2.5 – 5 ppb. Formaldehyde was generated as a reaction byproduct in all experiments. The formaldehyde production rates are all statistically significant with the exception of the value from Exp 5 with the low inlet concentration of 2-butoxyethanol.

The inlet and outlet mixing ratios of acetaldehyde and the UVPCO production rates of acetaldehyde in the 13 experiments are presented in Table 5. Significant production of acetaldehyde occurred due to incomplete oxidation of only four of the compounds. The

oxidation of ethanol resulted in the highest production rate. The other compounds leading to acetaldehyde generation were 1-butanol, 2-butanone and hexanal.

Table 6 presents the inlet and outlet mixing ratios of 2-propanone and the UVPCO production rates of this compound. Incomplete oxidation of six compounds resulted in significant production of 2-propanone. The oxidation of isopropanol and MIBK resulted in the highest production rates. The compounds not leading to production of 2-propanone were 2-butoxyethanol, hexanal and toluene.

Discussion

In Figure 3, the fractions of VOCs reacted when they were introduced individually into the UVPCO device (Table 2), are compared to the fractions reacted when they were introduced into the device as a mixture (Table 3). The two sets of values agree within the uncertainty of the measurements for most compounds. The two exceptions, ethanol and isopropanol, had higher reaction rates when introduced individually, which is indicative of relatively minor competitive adsorption on the catalyst. The general agreement between the individual compound and mixture results demonstrates that at relatively low concentrations, such as encountered in most non-industrial indoor environments, competition among compounds for active sites on the photocatalyst surface should not be a major factor limiting the performance of the UVPCO device. An assumption that the photocatalytic reaction efficiency for each analyte is not substantially affected by the presence of co-reacting VOCs, or by their oxidation products, is a reasonable first-order approximation when the total VOC concentration (and thus the total photocatalyst surface coverage) is low. However, if VOC concentrations are higher (e.g., in the ppm range), interference effects between co-reacting VOCs likely will be present, as has been reported by others (Chen et al. 2005a; Chen et al. 2005b; Yang et al. 2005).

Calculated ratios of the production rates of a carbonyl compound (formaldehyde, acetaldehyde and 2-propanone) to the reaction rates of the individual VOCs and of the 10-component mixture (μmole carbonyl production per hour / μmole VOC reacted per hour) are shown in Table 7. Incomplete oxidation of d-limonene, 2-butoxyethanol and MIBK resulted in the highest formaldehyde ratios of 0.23 – 0.4. Other VOCs with more than 0.1 μmole of formaldehyde produced per μmole of compound reacted were methanol, 2-butanone, hexanal and toluene. For acetaldehyde, oxidation of ethanol resulted in a ratio of 0.1; oxidation of

1-butanol, 2-butanone and hexanal resulted in lower ratios. Incomplete oxidation of both isopropanol and MIBK resulted in the production of approximately 0.4 μmole of 2-propanone per μmole of compound reacted. Incomplete oxidation of 2-butanone and d-limonene also resulted in 2-propanone production ratios in excess of 0.1.

Using the ratios for the production of carbonyl compounds generated from the experiments with the individual VOCs, we estimated the production rates of formaldehyde, acetaldehyde and 2-propanone for the 10-component mixture used in Exp 19 (Table 8). For formaldehyde, the predicted production rate calculated as the sum of the individually estimated rates was 320 μmole/h. This value was 127 % of the actual measured rate. The agreement for 2-propanone was closer; the predicted rate was 92 % of the measured rate. For acetaldehyde, the predicted rate, which was dominated by the incomplete oxidation of ethanol, was 53 % of the measured rate.

The generation of formaldehyde and, and to a lesser extent, 2-propanone via multiple reaction pathways involving different starting compounds indicates that some production of formaldehyde and 2-propanone can be expected for indoor air applications of an effective UVPCO air cleaner. On the other hand, the production of acetaldehyde was related to fewer starting compounds. This indicates that the production of acetaldehyde due to use of the UVPCO air cleaner indoors will be more related to the presence or absence of specific VOCs, such as ethanol, in the inlet air. Notably ethanol is present in human breath even in the absence of ethanol consumption (Fenske and Paulson, 1999). Thus, ethanol will be present at some level in any occupied building.

Detailed mechanisms of photo oxidation have been described for some of the studied VOCs, such as ethanol (Muggli et al., 1998) and toluene (d'Hennezel et al., 1998). In the case of ethanol, photo oxidation was shown to yield simultaneously acetaldehyde and formaldehyde in addition to the corresponding carboxylic acids. In the case of toluene, most oxidation products are significantly less volatile than the parent compound, and likely to remain adsorbed to the catalyst contributing to its inactivation. These reaction pathways involve several oxidation steps that can be affected differently by the presence of other VOCs.

Overall, the experiments with the individual VOCs lend confidence to our ability to predict the performance of the UVPCO air cleaner for an indoor environment application. The results

suggest that it is possible to predict with reasonable accuracy compound conversion efficiencies and the generation of unwanted aldehydes as byproducts based on data generated in the laboratory with individual compounds or simple mixtures.

Downstream Removal of Formaldehyde and Acetaldehyde

Description of Experiments

Experiments were conducted to determine if the oxidizer, sodium permanganate ($NaMnO_4 \cdot H_2O$), has sufficient reaction rates and capacity to counteract formaldehyde and acetaldehyde production due to incomplete oxidation of VOCs in the UVPCO device. A commercially produced filter element and two fabricated media beds containing the $NaMnO_4 \cdot H_2O$ media were individually evaluated. The effectiveness of a device for removal of formaldehyde, acetaldehyde and other VOCs was determined by comparison of measurement results for air samples collected immediately upstream and downstream of the device. In some experiments, VOC conversion efficiencies and byproduct generation by the UVPCO device also were determined from measurements made upstream and downstream (i.e., between the reactor and the media device) of the reactor section.

Six experiments were conducted with a mixed media filter element installed downstream of the UVPCO reactor. The conditions for the experiments are given in Table 9. Air flow rates through the system were 689 to 750 m^3/h. At 700 m^3/h, the measured pressure drop across the filter element was 32 Pa, consistent with the design of the device. Temperatures in the duct system downstream of the UVPCO were 24 – 28 ^{o}C. Relative humidity was in the range of 41 – 50 %. Exps 20 and 25 were conducted with the UVPCO lamps switched on; the lamps were off in the other experiments. Different infusion mixtures were used. A mixture of the ten VOCs from the UVPCO reaction rate experiments was used in Exp 20. A 15-component VOC mixture was used beginning with Exp 21. In addition to the ten original compounds, this mixture contained o-xylene, 1,2-dichlorobenzene (1,2-DCB), n-undecane, n-dodecane and decamethylcyclopentasiloxane (D5 siloxane). A VOC mixture containing only methanol, ethanol and isopropanol was used in Exp 24. An aqueous solution containing formaldehyde and acetaldehyde was injected in Exps 21 – 23 and 25.

A series of 11 experiments were conducted with the single panel media bed installed downstream of the UVPCO reactor. The conditions for these experiments are given in Table 9. Air flow rates through the system were 677 to 693 m^3/h for Exps 26 through 34. The air residence time in the bed was approximately 0.025 s. At 680 m^3/h, the measured ΔP for the bed was 318 Pa. Temperatures in the duct system downstream of the UVPCO for Exps 26 through 30 ranged from 24 ^{o}C up to 32 ^{o}C in Exp 30. The high temperature recorded in Exp 30 occurred during a period of elevated ambient temperature. Exps 32 through 34 were conducted over a temperature range of 21 to 28 ^{o}C specifically to examine the effect of temperature on VOC removal efficiencies. Exps 35 through 37 were run at lower air flow rates to examine the effect of residence time on VOC removal efficiencies. Exp 30 was conducted with the UVPCO lamps switched on; the lamps were off in the other experiments.

Two experiments were conducted with the folded media bed installed downstream of the UVPCO reactor. The experimental conditions are shown in Table 9. Exp 38 was run with an air flow rate of 689 m^3/h, (nominal air residence time in the chemisorbent bed = 0.1 s; ΔP = 55 Pa) and Exp 39 was run at about one-half that flow rate (nominal air residence time = 0.05 s; ΔP = 16 Pa). Temperatures downstream of the UVPCO were 24 and 25 ^{o}C. Both experiments were run with the UVPCO lamps on.

Results

The VOC removal efficiencies for Exps 20 and 25 with the mixed media filter element are presented in Tables 10 and 11, respectively. These two experiments were conducted at the beginning and the end of the series with this device, approximately one month apart. As noted, a ten-component VOC mixture was used in Exp 20 and a 15-component mixture was used in Exp 25. In addition, the inlet mixing ratios were higher in Exp 25. Both UVPCO reaction efficiencies and filter element removal efficiencies for VOCs were determined in these experiments. For a number of compounds, there was general agreement between the UVPCO reaction efficiencies determined for both experiments. The largest discrepancies occurred for 1-butanol, 2-butoxyethanol and 2-butanone. On the other hand, the filter removal efficiencies were substantially lower in Exp 25 than in Exp 20 for all VOCs for which comparisons can be made.

The VOC removal efficiencies for Exps 21 and 22 are presented in Table 12. These two experiments were conducted four days apart with almost identical physical conditions. The UVPCO lamps were off, so VOC removal was due solely to the filter element. VOC concentrations measured at the inlet of the filter element were similar for the experiments. There was a general trend of lower VOC removal efficiencies in Exp 22. However, for many of the compounds, the differences in removal efficiencies between experiments are statistically insignificant.

The aldehyde and 2-propanone results for Exps 20 and 25 are presented in Tables 13 and 14, respectively. No aldehydes were injected in Exp 20 so the aldehyde concentrations measured at the inlet of the UVPCO were the background values. In both experiments, the formaldehyde mixing ratios at the inlet and outlet of the entire UVPCO/filter element system were about the same, i.e., filter element removal of formaldehyde was approximately the same as UVPCO generation. On the other hand, the concentrations of both acetaldehyde and 2-propanone significantly increased across the entire system as the result of higher production in the UVPCO than removal by the filter element.

The aldehyde and 2-propanone results for Exps 21 – 23 are compared in Table 15. The UVPCO lamps were off in all three experiments, and no VOCs were injected in Exp 23. Formaldehyde concentrations were reduced by the filter element with efficiencies ranging from 0.42 – 0.53. Concentrations of acetaldehyde were unchanged by the filter element except for a small, indicated reduction in Exp 23. Concentrations of 2-propanone increased with the largest increases occurring in the two experiments with injected VOCs.

Exp 24 was conducted with a mixture of methanol, ethanol and isopropyl alcohol to determine if any of these alcohols were oxidized by the media to produce aldehydes and/or 2-propanone. The results are presented in Table 16. The inlet concentrations of formaldehyde, acetaldehyde and 2-propanone were the background chamber concentrations on this day. The methanol concentration increased indicating production of this compound, and the 2-propanol concentration decreased indicating removal. Among the carbonyl compounds, the formaldehyde concentration decreased; the acetaldehyde concentration increased slightly; and there was a substantial increase in the concentration of 2-propanone.

The data suggest that the efficiency of the filter element for removal of formaldehyde may have decreased with time. Formaldehyde removal efficiencies for Exps 20 – 25 are plotted in chronological order in Figure 4. There is a general decrease in efficiency from 0.57 to 0.32 over this four-week period with nearly continuous operation of the device but only periodic infusion of VOCs and aldehydes. However, the significance of this trend cannot be established due to the relatively high uncertainties in the individual measurements. In addition, the trend may be impacted by differences in the formaldehyde inlet concentrations, the system temperature, the presence of other VOCs and the operational state of the UVPCO across the experiments.

The single panel media bed contained substantially more $NaMnO_4 \cdot H_2O$ media than the filter element and contained no activated carbon. The inlet concentrations of the 15 VOCs for the experiments with the single panel media bed are summarized in Table 17 (VOC measurements were not made in Exps 26 and 37). The concentrations of most, but not all, VOCs were highest in Exps 27 and 30 (data shown separately) and lower and similar in Exps 32 – 36 (data averaged across experiments). The fractions of VOCs removed in these seven experiments are shown in Table 18. The media was most effective at removing isopropanol, 2-butoxyethanol, 2-butanone, hexanal and d-limonene. Potential trends with elapsed time of exposure, temperature and residence time are not readily apparent or consistent among these five compounds. However, removal efficiencies for some compounds were relatively high in the first chronological experiment (Exp 27) and in the experiment conducted at the longest residence time (Exp 36).

Exp 29 was conducted with only a mixture of the three alcohols, methanol, ethanol and isopropanol. The results shown in Table 19 indicate low removal. Of the three compounds, isopropanol was removed with the highest efficiency. Due to an oversight, aldehyde data were not collected for this experiment.

The reaction efficiencies for formaldehyde removal by the single panel media bed are presented in Table 20 and are plotted in Figure 5. Exps 26 – 30 were run over a two-week interval in which the system was in nearly continuous operation with infused mixtures of VOCs and aldehydes (about 12 days total). The data show there was a decrease in formaldehyde removal efficiency over this interval from 0.66 to 0.37. As noted, Exp 30 at the end of this series was run at a relatively high temperature of nearly 32 $^{\circ}$C.

The results from Exps 32 – 34, which were run over a temperature range of 21 to 28 $^{\circ}$C, indicate that formaldehyde removal efficiency increases with increasing temperature (i.e., a small increase in efficiency from 0.33 to 0.40 was observed). Thus, the formaldehyde removal efficiency recorded in Exp 30 may have been elevated relative to the preceding experiments due to the higher temperature on this day.

Exps 34 – 37 were run over a decreasing air flow rate range of 677 – 132 m^3/h. The calculated residence times of air in the bed were in the range of 0.025 – 0.129 s over this range. Formaldehyde removal efficiencies increased as a function of residence time as shown in Figure 6, with the efficiency at 0.13 s approaching 0.90.

The reaction efficiencies for acetaldehyde removal by the single panel media bed are shown in Table 21. There appears to be about a four-fold decrease in the fraction of acetaldehyde removed from Exp 26 through Exp 34 (i.e., 0.32 to 0.07). There was no obvious effect of temperature (Exps 32 – 34). Efficiencies did increase with increasing residence time (Exps 34 – 37); however, the efficiency at the longest residence time did not return to the level recorded in the initial experiment.

2-Propanone was generated when the single panel media bed was challenged with mixtures of VOCs and aldehydes. The increases in 2-propanone concentrations across the media bed are shown in Table 22. The inlet concentrations of 2-propanone were the background concentrations measured on the days of the experiments. Since these concentrations ranged from 3 to 11 ppb, it is most informative to compare the 2-propanone production rates (μmole/h). These production rates declined over the first four experiments and then remained relatively constant over the final six experiments. This trend is generally consistent with the decline in formaldehyde and acetaldehyde reaction rates with time.

The four-panel, folded, media bed was designed to increase the air residence time, to reduce the pressure drop of the system and to add substantially more media relative to the single panel media bed.

The conditions for Exps 38 and 39 were similar except for the two-fold reduction of the air flow rate in Exp 39. The VOC results for Exp 38 are shown in Table 23. The folded media bed efficiently removed (i.e., >50 % removal efficiency) 2-butoxyethanol, hexanal, d-limonene and D5 siloxane. The highest combined (i.e., UVPCO plus chemisorbent media) removal

efficiencies occurred for 2-butoxyethanol, MIBK, hexanal, d-limonene and D5 siloxane, with complete or nearly complete removal of 2-butoxyethanol and d-limonene. The lowest combined removal efficiencies occurred for ethanol (not significant), toluene, 1,2-DCB, n-undecane and n-dodecane. Decreasing the flow rate (and increasing the residence time) in Exp 39 generally improved the combined VOC removal efficiencies (Table 24). At this condition, there was complete, or nearly complete, removal of 2-butoxyethanol, hexanal and d-limonene. Most of the improvement was due to the increased efficiency of the UVPCO reactor. The increases in the folded bed removal efficiencies were small.

The results for formaldehyde, acetaldehyde and 2-propanone in Exps 38 and 39 are presented in Tables 25 and 26, respectively. The UVPCO produced all three compounds; while the folded media bed removed formaldehyde and acetaldehyde and produced 2-propanone. At 690 m^3/h, the net removal of formaldehyde by the combined system was 0.9 and the net removal of acetaldehyde was 0.4. The concentration of 2-propanone increased about four fold to a final value of 30 ppb. At the lower 350 m^3/h flow rate, both devices were more efficient at producing or removing these compounds. The combined effect was a clear net increase in the removal of acetaldehyde and nearly a nine-fold increase in the outlet concentration of 2-propanone. Net formaldehyde removal was about the same as recorded for the higher flow rate.

No VOC products of incomplete oxidation other than formaldehyde, acetaldehyde and 2-propanone were detected in any of the experiments with downstream media scrubbing. The generation of acetic and formic acids, two additional products of incomplete oxidation identified previously using other methods (Hodgson et al., 2005), was not investigated here.

Discussion

In an assumed commercial building application of UVPCO air cleaning, the supply air flow rate in a building is often at least 25 % outdoor air and 75 % recirculated air. By mass balance, an air cleaner device with 33 % removal efficiency for an indoor-generated VOC would provide as much VOC removal as the total outdoor air supply. To counteract the predicted concentration increase from a 50 % reduction in ventilation, a VOC conversion efficiency of about 17 %, or greater, is required.

Because the commercial mixed media filter element contained activated carbon as one of its components, it was effective at removing compounds in the mixture that typically have low oxidation rates in the UVPCO reactor (i.e., the aromatic compounds, the alkane hydrocarbons and D5 siloxane). For example, in the one experiment in which the UVPCO reactor was operated with the full mixture of VOCs (Exp 25), the aromatics and alkanes were removed at or below the minimum required efficiency by oxidation in the UVPCO reactor. However, the downstream filter element was effective at removing these compounds, so that their net removal efficiencies were well in excess of the required value. The filter element had the additional benefit of very low pressure drop at the relatively high air flow rate used in the experiments.

The commercial mixed media filter element, either combined with or operated separately from the UVPCO reactor, also meet the minimum efficiency objective for formaldehyde. The filter element, however, did not have sufficient removal efficiency for acetaldehyde. Except for the first experiment, the removal of acetaldehyde was either non-significant or less than the required value.

Since the fabricated single panel media bed did not contain activated carbon, it had relatively low removal efficiencies for most VOCs, with the exceptions of isopropanol, 2-butoxyethanol, hexanal and d-limonene, which were most efficiently oxidized by the $NaMnO_4 \cdot H_2O$ media. In the initial three experiments with the single panel media bed, removal efficiencies for formaldehyde were about 0.5, or better, and removal efficiencies for acetaldehyde were 0.24 and higher. In subsequent experiments, the removal efficiencies for both compounds dropped with the values for acetaldehyde falling below the minimum required value. Although the cause of the decline in performance was not investigated, it is conceivable that it was related to a depletion of the $NaMnO_4 \cdot H_2O$ reagent in the zeolite spheres as discussed below.

The design of the single panel media bed resulted in a relatively high pressure drop of 318 Pa across the bed at the high flow rate used in most experiments (~680 m^3/h). In addition, it was clear that the residence time in the bed was not optimized for this application as the removal efficiencies for both formaldehyde and acetaldehyde increased at air flow rates that were a factor of three or more lower than the high rate. These results plus removal efficiencies for acetaldehyde that, in the later experiments, were below the minimum required value, led us to fabricate and evaluate the four-panel, folded, media bed.

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A comparison of the results for the single- and four-panel media beds shows the improvements in VOC removal efficiencies achieved with the increased mass of media and the longer residence time associated with the four-panel bed. In Figure 7, the median efficiencies in Exps 26 – 34 for six compounds including formaldehyde, acetaldehyde and four VOCs with high removal (2-butoxyethanol, hexanal, d-limonene and D5 siloxane) are compared to the corresponding efficiencies measured in Exp 38. With the exception of acetaldehyde, efficiencies improved by a factor of 2.3 – 5 with use of the four-panel media bed. There was almost a seven-fold improvement for acetaldehyde, since its removal efficiency by the single-panel bed declined rapidly to below 0.10 by the end of the series. Removal efficiencies in Exp 39 conducted with the four-panel bed at the reduced air flow rate showed only small improvements relative to the high flow rate condition. This indicated that the air residence time in the bed was nearly optimized for the high flow rate.

Performance of a Combined UVPCO/Chemisorbent Air Cleaner in Recirculation Mode

Description of Experiments

Four experiments were conducted with the UVPCO system operating in a recirculation mode. The experimental conditions are summarized in Table 27. Exps 45 and 46 were conducted with the four-panel, folded media bed installed downstream of the UVPCO reactor. Exps 47 and 48 were conducted without the media bed, but otherwise were identical. The recirculation rate of chamber air through the hybrid air cleaner system in all four experiments ($\sim$14 h^{-1}) was about four times the outdoor air supply rate ($\sim$3.5 h^{-1}) to the 50-m^3 chamber. Temperature and humidity conditions in the chamber were similar for all experiments. Also, approximately the same constant liquid injection rates were used for the VOC and aldehyde mixtures. As a result, the initial mixing ratios of the compounds in chamber air were nearly identical with a few exceptions. Air samples were collected prior to turning on the lamps and the blower for the UVPCO system and then at hourly intervals over a period of six hours after activating the lamps and blower.

Results

The results for Exps 45 and 46 are presented in Table 28. The initial concentrations of methanol and formaldehyde were highest in Exp 46, and the initial concentrations of d-limonene

and n-undecane were highest in Exp 45. In both experiments, the concentrations of VOCs and aldehydes were pulled down within the first hour and reached near steady-state concentrations within the first one to two hours. Concentrations over hours two through six (n = 5) were averaged. These near steady-state concentrations were the same for both experiments with several exceptions. The concentrations of formaldehyde decreased from 17 and 27 ppb initially to about 8 ppb. The concentrations of acetaldehyde decreased from 13 ppb initially to about 5 to 6 ppb. For many of the compounds, the concentrations decreased by a factor of two or more. Notably, higher fractions of MIBK, 1,2-dichlorobenzene, n-undecane, n-dodecane and D5 silxoane were removed in Exp 45 than in Exp 46. The concentration of 2-propanone increased substantially to about six to seven times the initial concentration. The near steady-state concentrations of 2-propanone during hours two through six of Exps 45 and 46 were 29 and 35 ppb, respectively.

The results for Exps 47 and 48 without the media bed are presented in Table 29. Good agreement was obtained between the two starting conditions with only isopropanol having a notably lower initial concentration at the beginning of Exp 48. Also, the near steady-state concentrations averaged over hours two through six with the UVPCO operating were in good agreement between the two experiments. Formaldehyde concentrations quickly increased from 25 and 21 ppb in Exps 47 and 48, respectively, to values in excess of 40 ppb. Acetaldehyde concentrations increased from about 13 ppb to about 30 ppb. 2-Propanone also was produced reaching concentrations of 26 and 29 ppb, similar to the concentrations obtained in Exps 45 and 46. With the partial exception of 1-butanol (see Exp 46), the fractions of compounds removed by the UVPCO alone were lower than in Exps 45 and 46, which also included the media bed.

Discussion

A comparison of the results for Exps 45 and 46 with the results for Exps 47 and 48 (Tables 28 and 29) shows that the Purafil SP media contributed substantially to the removal of VOCs when the hybrid air cleaner system was operated in recirculation mode. The presence of fresh media possibly was the cause of the relatively high removal rates for 1,2-dichlorobenzene, n-undecane and n-dodecane (three compounds with generally low reactivity) observed in Exp 46.

The net removal rates of individual compounds by the $NaMnO_4 \cdot H_2O$ media (μmoles compound per hour and μmoles carbon per hour) were calculated from the ppb concentrations at

near steady-state conditions in the recirculation experiments with and without the downstream media. By mass balance, the compound removal rates are equal to the difference between average steady-state concentrations in Exps 47 and 48 with UVPCO only and average steady-state concentrations in Exps 45 and 46 with UVPCO plus media bed times the outdoor air flow rate of 183 m^3/h, this quantity divided by the molar volume at standard indoor conditions (see Appendix A for the mass-balance derivation). Carbon removal rates were calculated by multiplying the compound removal rates by the numbers of carbon atoms. The results of this analysis are presented in Table 30. Compounds with the highest removal rates were formaldehyde, acetaldehyde and methanol. On a carbon basis, formaldehyde, acetaldehyde, d-limonene, n-undecane and n-dodecane had the highest removal rates. The media contribution to the total removal for each compound was calculated as the difference in steady-state concentration between UVPCO only and UVPCO with media bed experiments divided by the concentration with UVPCO only. The media contributed approximately one-half or more to the removal of methanol, 2-butoxyethanol, hexanal and d-limonene. Since the UVPCO produced formaldehyde and acetaldehyde, all of the removal of these compounds was due to the media. Both the UVPCO and the media produced 2-Propanone.

These results are generally consistent with the results from the single-pass experiments with the single panel media bed and the four-panel, folded, media bed, which also showed significant removal of a number of the target VOCs (Tables 18, 23 and 24). Low or undetectable removal by the $NaMnO_4 \cdot H_2O$ media in these single-pass experiments generally occurred for methanol, MIBK, toluene, o-xylene, 1,2-dichlorobenzene, n-undecane and n-dodecane. The ability to detect low removal apparently was enhanced by the relatively high recirculation of chamber air through the air cleaner system. The high removal rate for methanol in Exp 46 may have been an anomaly, possibly related to a sampling or analytical problem, since the single-pass experiments did not show significant removal of this compound. Sorption by the media probably played a minor role in removal since the compounds with the lowest vapor pressures, 1,2-dichlorobenzene and the alkane hydrocarbons, either were not significantly removed (single-pass experiments) or were removed at low rates (second recirculation experiment with media).

The reductions in the concentrations of formaldehyde and acetaldehyde in Exps 45 and 46 demonstrated that the $NaMnO_4 \cdot H_2O$ media is effective in controlling the concentrations of these two important indoor air pollutants when the combined UVPCO/chemisorbent air cleaner is

operated in a simulated HVAC mode with recirculation of air. Net fractional reductions for both compounds at near steady-state conditions were in the range of 0.5 to 0.7. The reasonably good fractional reduction of hexanal (76 %) also is worth noting. Although not measured, other higher molecular weight aldehydes, including nonanal, presumably would exhibit similar high removal rates.

Evaluation of Chemisorbent Performance and Lifetime

Measurements

The lifetime and performance of the chemisorbent media was preliminarily evaluated by comparing the amounts of $NaMnO_4 \cdot H_2O$ contained in new, unused media and in media collected from the single panel, media bed at the conclusion of Exps 26 – 37. The content of permanganate in chemisorbent media samples was determined by UV-visible spectrophotometry as described in Methods and Materials.

Results

Extract concentrations were used to evaluate the mass of $NaMnO_4 \cdot H_2O$ present in both samples and, by difference, the mass consumed due to reaction with VOCs and aldehydes when used in the single panel bed. The results of this analysis are presented in Table 31. In the case of the unused beads, the mass of $NaMnO_4 \cdot H_2O$ was 13.2 % of the total mass extracted, which is in good agreement with the 12 % composition informally reported by the manufacturer. In contrast, the media from the single panel only contained 0.88 % of reactant. The reduction of permanganate to form manganese dioxide (MnO_2) was observed clearly at the conclusion of the experiments with the single panel bed as the media spheres all had changed color from purple to black. In Table 31, we also calculate the moles of $NaMnO_4 \cdot H_2O$ reacted for the entire bed based on an estimated amount of reactant consumed and the mass of the media contained in the bed.

Discussion

Little information is available in the literature describing mechanisms and quantifying reaction rates of VOCs with permanganate in gas-solid heterogeneous reactions. Instead, most of the reported work on the reactivity of organics with permanganate was carried out in aqueous solution. Ladbury and Cullis (1958) reviewed early findings. More recent studies have focused on the characterization of acid and base catalysis of the reaction of permanganate with various

organic substrates. For example, Freeman et al. (1982) evaluated the kinetics and mechanism of the oxidation of pivalaldehyde (trimethylacetaldehyde) and other aliphatic aldehydes with permanganate in acidic media. Szammer and Jaky (1992) investigated the mechanism of methanol, ethanol, butanol and formaldehyde in a strong alkaline medium, suggesting a mechanism based on electron abstraction from the alkoxy anion and simultaneous nuclephilic attack by hydroxide ion (OH-).

Reactions of organics with permanganate in non-aqueous solvents also have been described. These were termed "heterogeneous" because the reaction takes place on the surface of solid permanganate. Permanganate can be present as a pure solid (Shaabani et al., 2005) or supported in polymeric materials (Chacko and Mathew, 2003). Jaky and Szammer (1997) showed that the addition of water to the organic solvents increased the reaction rates, indicating that the hydrate form of aldehydes is more reactive than the free form, and that acid catalyzed nucleophilic addition of permanganate is involved. Although not directly applicable to our study, this literature suggests that heterogeneous VOC-permanganate chemistry involves complex mechanisms, in which the presence of moisture likely plays a significant role.

Given the lack of published information, we attempted to use the experimental data to predict the useful lifetime of the chemisorbent media. Firstly, we estimated the molar ratio between $NaMnO_4 \cdot H_2O$ reacted and VOCs and aldehydes removed from air. For this exercise, we utilized the single panel media bed experiments as the relatively long period of operation was expected to produce more reliable data than the limited folded media bed experiments.

At the beginning of the experiments with the single panel media bed, the system was operated almost continuously over a period of about 12 days with constant infusion of the VOC and aldehyde mixtures. Exps 26 – 30 were conducted within this period. For the most part the UVPCO lamps were off. Subsequently in Exps 32 – 36, operation of the system was limited to an approximate four-hour period on each experimental day. We used the data from Exp 30 to estimate the reactive losses of VOCs and aldehydes due to oxidation by the media over the period of continuous operation. Data from the individual experiments were used to estimate the losses for these short intervals. The reaction rates for these intervals in μmole of total compounds per hour and μmole of total carbon per hour are given in Table 32. These reaction rates were determined from the flow rates through the media and the upstream and downstream

VOC mixing ratios. The products of the reaction rates and the interval operating times yield the μmoles of compounds consumed, or removed from air, over an interval. We multiplied these values by the numbers of carbon atoms to yield the μmoles of carbon consumed. In total, we estimate that about 0.35 and 1.11 moles of compounds and carbon, respectively, were removed from air by the single panel media bed. About 3.2 moles of $NaMnO_4 \cdot H_2O$ were consumed by reaction during this period (Table 31). Thus, on average, we estimate that about nine moles of $NaMnO_4 \cdot H_2O$ were needed to remove one mole of VOCs, and about three moles of the reactant were needed to remove one mole of carbon.

One kilogram of media with 13 % of the reactant by weight contains approximately 0.81 moles of $NaMnO_4 \cdot H_2O$. Our results suggest this amount is sufficient to oxidize about 0.27 moles of carbon, presumably to CO_2. In Exps 30 – 35 with the single panel media bed, an average of about 5,000 μmoles carbon were oxidized per hour considering both the reactive VOCs and aldehydes. Thus, 1 kg of media would be consumed in about 54 h of operation at these conditions (i.e., the media consumption rate is 0.019 kg/h).

For recirculation Exp 46, about 3,000 μmoles of carbon were oxidized by the media per hour considering both the reactive VOCs and aldehydes (Table 30). The reaction rate was lower than in single pass experiments due to ventilation of the chamber and the significant contribution of the UVPCO reactor in decreasing the concentrations of the VOCs in chamber air. Using the $NaMnO_4 \cdot H_2O$ consumption rate calculated above from the experiments with the single panel media bed, 1 kg of media would be consumed in about 90 h of system operation at these conditions (i.e., the media consumption rate is 0.011 kg/h).

The consumption rate can be normalized to a clean air delivery rate (CADR). The CADR for the recirculation experiments is calculated as follows. Assuming that ventilation and air cleaning are the dominant processes for removing indoor-generated VOCs from indoor air, then at steady state when there is no air cleaning

$$C = S/Q_V ,$$
(1)

where C is the indoor VOC concentration, S is the indoor pollutant source strength, and Q_v is the rate of outdoor air supply. With the addition of air cleaning

$$C_2 = \frac{S}{(Q_V + CADR)},\tag{2}$$

where *CADR* is the VOC removal rate by air cleaning. When Q_V and the ratio of *C* to C_2 are known, we can solve for *CADR* as follows

$$CADR = Q_V\left[(C/C_2) - 1\right].\tag{3}$$

In experiments 45 and 46, the average net concentration reduction for VOCs including formaldehyde and acetaldehyde, and neglecting 2-propanone, was 0.565 (i.e., C/C_2 equaled 2.3) and the outdoor air supply rate was 183 m³/h. From Equation 3, this yields a CADR of 238 m³/h. Thus to provide 100 m³/h of clean air, 1 kg of media would be consumed every 214 h of operation of the hybrid air cleaner with the same mixture, source strengths and concentrations of VOCs as used in the experiments (i.e., a total of 21,400 m³ of clean air would be delivered per 1 kg of media). Stated in conventional HVAC terms, provision of 100 cfm of clean air would consume 1 lb of media for about every 57 h of system operation (i.e., 343,000 ft³ of clean air per 1 lb of media).

The media consumption rate in most office buildings is expected to be lower. The VOC mixture and concentrations used in the experiments were realistic. Yet, the concentrations were highly skewed toward the upper ends of their distributions and, in some cases, were higher than maximum reported values for North American office buildings (Hodgson and Levin, 2003). Typical concentrations are likely to be substantially lower. For example, the sum of the central tendency values (median or mean) or maximum values in office buildings for 15 of the 18 compounds present in recirculation Exps 45 – 48 is 58 ppb (Hodgson and Levin, 2003; Table 8, no data for methanol, formaldehyde and acetaldehyde). Formaldehyde and acetaldehyde were measured in the U.S. EPA 100-building BASE study; their median concentrations were 13 and 2.6 ppb, respectively (M.G. Apte, LBNL; personal communication). Thus, a typical total concentration across office buildings of 17 of the 18 study VOCs is about 74 ppb. This compares to a total concentration of the same compounds in the recirculation experiments of about 290 ppb, a four-fold higher value. In addition, the data summarized by Hodgson and Levin (2003) are composites from a number of buildings. It is unlikely that all sources of these

compounds would be active simultaneously in one building. Plus, some of the compounds are believed to have highly intermittent sources, which would tend to result in partial temporal separation of VOCs within a building. For example, cleaning solutions and cleaning products, which are sources of volatile alcohols, 2-butoxyethanol and d-limonene likely have intermittent usage patterns. On average, it seems reasonable to assume that typical average concentrations of predominant VOCs in office buildings are about four to five fold lower than the concentrations used in the experiments. Such an assumption yields a media consumption rate of about 1 lb per 228 – 285 h of operation to provide 100 cfm of clean air. If the HVAC system operates 60 h per week, 52 weeks a year, about 11 – 14 lb of the chemisorbent media are required to provide 100 cfm of clean air over the course of a year (i.e., 0.11 – 0.14 lb per cfm year). Media consumption could be reduced, in many cases by at least a factor of two, through design of a HVAC system in which the supply air stream bypasses the air cleaner system during periods of economizer operation. In this manner, media consumption would be restricted to periods of minimum outdoor air supply.

Results from the experiments indicate that the performance of the chemisorbent media changes over the course of its lifetime. As reported above, VOC removal efficiency by the media appeared to drop with time over the course of an experimental series. This change was most evident at the beginning of a series starting with fresh media. One possible explanation for this observation is that an outer layer of MnO_2 forming on the media spheres may represent a diffusion barrier effectively slowing the reaction rates of VOCs in air with the remaining permanganate. Also, the mechanisms by which VOCs react with the media may be affected by the formation of MnO_2.

SUMMARY AND CONCLUSIONS

The conversion efficiencies for 11 commonly encountered VOCs in mixture were largely consistent with the results for the individual compounds and with the results from previous experiments with VOC mixtures (Hodgson et al., 2005 and In press). This consistency indicates that competition among compounds for active sites on the photocatalyst surface should not significantly limit the performance of the UVPCO device for its intended application in office buildings and other non-industrial buildings with relatively low concentrations of VOCs. This first order approximation also allows the performance of the UVPCO device in such settings to

be estimated by simple addition of the conversion efficiencies for individual compounds determined in laboratory experiments.

The generation of formaldehyde and acetaldehyde as byproducts of incomplete conversion of VOCs previously was identified as an issue that needed to be addressed before UVPCO air-cleaning technology could be recommended for use in occupied buildings (Hodgson et al., 2005 and In press). The experimental results presented here demonstrated that formaldehyde and, and, to a lesser extent, 2-propanone were produced from many of the commonly encountered VOCs. On the other hand, acetaldehyde was generated by specific starting compounds, particularly ethanol. The generation of these byproducts by the compounds in mixture was generally consistent with the summed results for the individual compounds; this consistency gives credibility to projections for buildings based on our laboratory results. The implication is that formaldehyde and 2-propanone concentrations are likely to increase when an effective UVPCO air cleaner is used in buildings that contain typical VOC sources. The impact of UVPCO air cleaning on acetaldehyde concentrations likely will be more dependent upon the presence of ethanol and sources of other specific VOCs in buildings. The magnitudes and temporal profiles of any potential increases will, of course, depend upon a number of interrelated factors encompassing VOC source parameters, building parameters, and UVPCO performance. As discussed elsewhere, the laboratory experiments were conducted under presumed worst-case conditions and the results likely are not representative of what may be expected to occur in typical buildings. We also note that other photocatalyst systems may have different yields of formaldehyde and acetaldehyde.

The health risks for acute and chronic inhalation exposures to formaldehyde are well established, and governmental agency guidelines exist for limiting these exposures in non-industrial indoor environments (CARB, 2004; OEHHA, 2005). Guidelines also exist for non-industrial exposures to acetaldehyde (OEEHA, 2005). Although we are not toxicologists, we consider the generation of 2-propanone (acetone) by the UVPCO air cleaner to be of less concern. There are no guidelines for non-industrial exposures to acetone. The 8-h time-weighted average TLV for occupational exposure to acetone is 500 ppm (ACGIH, 2001). This value is based on irritation as the primary health effect. For irritation, a 100-fold safety factor to protect the general population likely is conservative. An indoor guideline for acetone of approximately 5 ppm estimated from occupational experience would be about two orders of

magnitude above the maximum acetone concentrations (33 ppb) reported for office buildings (Hodgson and Levin, 2003). The laboratory experiments indicate that concentrations of acetone produced by a UVPCO device or by a hybrid air cleaner would be about the same magnitude (i.e., tens of parts per billion) under extreme conditions.

A major aim of this research was to evaluate a chemisorbent technique for removal of formaldehyde and acetaldehyde downstream of the UVPCO reactor. We selected sodium permanganate ($NaMnO_4 \cdot H_2O$) as the chemisorbent because it is a relatively strong oxidant and it is commercially available in a media form designed for the treatment of formaldehyde and other organic chemicals in air. Three different configurations of the $NaMnO_4 \cdot H_2O$ chemisorbent media were evaluated. The primary evaluation criterion for the media was its conversion efficiency for formaldehyde and acetaldehyde. The goal was to have sufficient conversion to allow a 50 % reduction in outdoor air ventilation when employed downstream of a UVPCO reactor.

The commercial, packaged, mixed media filter element with a mixture of activated carbon and $NaMnO_4 \cdot H_2O$ media on a pleated fabric support was effective at removing compounds in the mixture that typically have low oxidation rates in the UVPCO reactor such as higher molecular weight aromatic compounds and alkane hydrocarbons. The filter element also met the minimum efficiency objective for formaldehyde. However, it did not have sufficient removal efficiency for acetaldehyde.

The single panel bed contained 4.2 kg of zeolite spheres impregnated with $NaMnO_4 \cdot H_2O$. Initially, the removal efficiency for formaldehyde was about 50 %, or better, and the removal efficiency for acetaldehyde was 24 %, or better. The bed also oxidized isopropanol, 2-butoxyethanol, hexanal and d-limonene. However, these efficiencies declined in subsequent experiments with the values for acetaldehyde falling below the minimum required value. Experiments run at lower air flow rates produced higher removal efficiencies demonstrating that the air residence time in the bed was not optimized for this application.

The four-panel, folded bed contained 15.6 kg of the impregnated zeolite spheres. The design produced a four-fold increase in the nominal air residence time in the bed. The folded bed by itself removed 2-butoxyethanol, hexanal, d-limonene and D5 siloxane with greater than 50 % efficiency. The folded bed also was effective at removing formaldehyde and acetaldehyde.

Formaldehyde was removed with greater than 90 % efficiency and acetaldehyde was removed at about 70 % efficiency. At the 690-m^3/h air flow rate and with the UVPCO operating, the combined UVPCO/chemisorbent system removed formaldehyde and acetaldehyde with efficiencies of 90 % and 40 %, respectively. The experiment run at lower flow rate indicated that the air residence time in the folded bed was nearly optimized at the higher flow rate.

Having reasonably optimized the chemisorbent system, we conducted experiments in the 50-m^3 chamber in which room air was recirculated through the air cleaner system at about four times the outdoor air supply rate to the chamber. The total air flow rate through the device was 680 – 730 m^3/h and mixtures of VOCs and aldehydes were infused at constant rates into the chamber. Two replicate experiments were conducted with the four-panel folded chemisorbent bed installed downstream of the UVPCO reactor and two replicate experiments were conducted without the chemisorbent bed.

In all recirculation experiments, the chamber concentrations of VOCs and aldehydes were pulled down within the first one to two hours of system operation. Without the media bed, formaldehyde concentrations quickly increased from about 25 ppb to values in excess of 40 ppb and acetaldehyde concentrations increased from 13 ppb to about 30 ppb. Acetone concentrations approached 30 ppb. Addition of the downstream media bed contributed substantially to the removal of VOCs by the air cleaner system. Even the less volatile aromatic compounds and alkane hydrocarbons, which were not effectively removed by the UVPCO device, had removal efficiencies of about 20 %, or better. The net removal of formaldehyde and acetaldehyde by the combined UVPCO/chemisorbent system was in the range of 50 – 70 %. These results clearly demonstrated that the addition of the $NaMnO_4 \cdot H_2O$ chemisorbent scrubber is an effective way to control the concentrations of formaldehyde and acetaldehyde generated by incomplete oxidation of VOCs in the UVPCO device.

In order for a combined UVPCO/chemisorbent air cleaner system to be viable option for use in office buildings as a substitute for some amount of outdoor air ventilation, it must perform effectively over extended periods. Little useful information on the effective lifetimes of UVPCO monoliths or the $NaMnO_4 \cdot H_2O$ chemisorbent is available in the literature, and this study was not explicitly designed to investigate this issue. However, some preliminary data regarding the longevity of the chemisorbent were obtained from the experiments.

From the experiments with the single panel media bed, we were able to estimate that about nine moles of $NaMnO_4 \cdot H_2O$ were needed to mineralize one mole of VOCs, and about three moles of the reactant were needed to mineralize one mole of carbon. For the experiments with the single panel bed, we estimated that the media consumption rate was 0.019 kg/h; and, for the experiments with the four-panel folded bed, we estimated that the media consumption rate was 0.011 kg/h. Normalizing by clean air delivery rate achieved in the recirculation experiments, we estimated that to provide 100 m^3/h of clean air, 1 kg of media would be consumed every 214 h of operation of the combined UVPCO/chemisorbent air cleaner at the experimental conditions (i.e., 1 lb of media is needed per 57 h of operation to provide 100 cfm of clean air).

To make an estimate of chemisorbent lifetime for a typical office building, we allowed for four- or five-fold lower VOC concentrations relative to the concentrations used in the experiments. Such an assumption yielded a media consumption rate of about 1 lb per 228 – 285 h of operation to provide 100 cfm of clean air. If the HVAC system operates 60 h per week, 52 weeks a year, about 11 – 14 lb of the chemisorbent media would be required to provide 100 cfm of clean air over the course of a year, i.e., the estimated consumption rate is 0.11 – 0.14 lb per cfm year.

In conclusion, the prototype air cleaner system with the UVPCO reactor and a downstream, multi-panel, folded scrubber filled with $NaMnO_4 \cdot H_2O$ chemisorbent media removed a broad range of commonly encountered VOCs. The conversion efficiencies for these VOCs often were well in excess of the minimum required value for the intended application. Most importantly, the use of the chemisorbent media in this configuration effectively counteracted the generation of formaldehyde and acetaldehyde due to incomplete oxidation of VOCs in the UVPCO reactor.

RECOMMENDATIONS

Several issues remain to be investigated and addressed before proceeding with a plan for commercialization of a combined UVPCO/chemisorbent air cleaner for indoor air applications. The following recommendations provide an outline for near-term research needed to support this development.

- Data are needed on the performance of the combined UVPCO/chemisorbent air cleaner when installed in real buildings. Deployment of the system in at least one building would

allow performance data to be generated under realistic conditions over an extended time period. Indoor air pollutant measurements during periods with and without air cleaner operation can be made to assess how the system quantitatively impacts the composition and concentrations of VOCs including formaldehyde and acetaldehyde. A questionnaire-based survey administered to occupants during periods in which the system is switched on and off without their knowledge can be used to assess occupant responses, for example, to changes in odor and the general acceptability of indoor air quality and in irritation symptoms. Measurement of VOC conversion efficiencies of both the photocatalyst and the chemisorbent over time can generate data on the effective lifetimes of these components.

- Data are needed on the effective lifetimes of the photocatalyst and the chemisorbent in a variety of indoor environments. Since the environmental conditions and air pollutant composition and concentrations can vary substantially among office buildings, deployment of small-scale versions of the UVPCO/chemisorbent air cleaner in a number of different buildings can be used to assess the impacts of these variables under different realistic conditions. At periodic intervals, VOC conversion efficiencies of the photocatalyst and the chemisorbent can be measured either in the field or in the laboratory. For the chemisorbent, the residual content of the reactant also can be measured as a function of time.

- The total costs of advanced air cleaning using the combined UVPCO/chemisorbent device need to be determined with reasonable accuracy. The data on photocatalyst and chemisorbent lifetimes are essential components of this economic analysis. Current costs for a number of other parameters also are needed. All of these inputs can be combined to predict the costs per unit of clean air supplied in buildings of various types in different climatic zones. A concurrent updated assessment of the energy and total costs of ventilation in different buildings and climatic zones can serve as a basis for determining the economic viability of the UVPCO/chemisorbent air cleaning technology.

ACKNOWLEDGEMENTS

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Table 1. Summary of experiments conducted to measure UVPCO reaction rates of 11 VOCs introduced individually and in a mixture containing 10 of the 11 VOCs. In this and subsequent tables, uncertainties are ± 1 standard deviation of the means.

Exp No	Date	Compound	Flow Rate (m^3/h)	Temp (^{o}C)	Rel Humd (%)
2	4/11/06	Isopropanol	777	23.0 ± 0.2	46.1 ± 0.5
4	4/13/06	1-Butanol	773	24.3 ± 0.2	49.8 ± 0.5
5	4/13/06	2-Butoxyethanol	771	24.7 ± 0.1	49.5 ± 0.8
8	4/19/06	2-Butanone	762	23.5 ± 0.3	49.6 ± 0.4
9	4/19/06	MIBK	757	24.9 ± 0.1	46.4 ± 0.5
10	4/25/06	Hexanal	765	22.7 ± 0.1	45.3 ± 0.3
11	4/25/06	d-Limonene	763	22.9 ± 0.1	46.0 ± 0.1
13	5/5/06	Methanol	756	23.5 ± 0.1	49.3 ± 0.2
14	5/16/06	Ethanol	769	23.0 ± 0.2	46.5 ± 2.1
16	5/18/06	2-Butoxyethanol	776	24.5 ± 0.6	47.5 ± 3.0
17	5/19/06	2-Propanone	761	23.0 ± 0.1	49.4 ± 0.2
18	5/22/06	Toluene	752	23.2 ± 0.3	46.7 ± 1.9
19	5/25/06	10 VOC Mixture	736	24.0 ± 0.5	45.3 ± 1.2

Table 2. Inlet mixing ratios, fractions reacted and reaction rates for 11 VOCs introduced individually into UVPCO.

Compound	Exp No	In Mix Ratio (ppb)	Fraction Reacted	Reaction Rate (μmole/h)	Reaction Rate (μmole C/h)
Methanol	13	154 ± 5	0.28 ± 0.04	1,370 ± 180	1,370 ± 180
Ethanol	14	140 ± 7	0.51 ± 0.07	2,200 ± 300	4,400 ± 600
Isopropanol	2	77 ± 6	0.49 ± 0.11	1,190 ± 240	3,600 ± 730
1-Butanol	4	26 ± 1	0.40 ± 0.05	330 ± 40	1,330 ± 140
2-Butoxyethanol	5	9.4 ± 0.4	0.40 ± 0.06	118 ± 18	710 ± 110
2-Butoxyethanol	16	44 ± 1	0.39 ± 0.01	540 ± 20	3,200 ± 100
2-Propanone	17	106 ± 15	0.25 ± 0.15	850 ± 490	2,500 ± 1,500
2-Butanone	8	54 ± 4	0.30 ± 0.10	510 ± 160	2,000 ± 650
MIBK	9	38 ± 1	0.31 ± 0.07	380 ± 80	2,200 ± 500
Hexanal	10	25 ± 1	0.43 ± 0.02	330 ± 10	2,000 ± 100
d-Limonene	11	27 ± 1	0.31 ± 0.03	260 ± 30	2,600 ± 300
Toluene	18	28 ± 1	0.19 ± 0.03	172 ± 28	1,210 ± 190

Table 3. Experiment 19: Inlet mixing ratios, fractions reacted and reaction rates for 10 VOCs introduced as a mixture into UVPCO.

Compound	In Mix Ratio (ppb)	Fraction Reacted	Reaction Rate (µmole/h)	Reaction Rate (µmole C/h)
Methanol	56 ± 3	0.29 ± 0.07	510 ± 130	510 ± 130
Ethanol	70 ± 3	0.30 ± 0.05	650 ± 100	1,300 ± 200
Isopropanol	53 ± 3	0.35 ± 0.04	580 ± 60	1,740 ± 170
1-Butanol	22 ± 1	0.31 ± 0.03	210 ± 20	860 ± 77
2-Butoxyethanol	13.6 ± 0.1	0.41 ± 0.02	176 ± 8	1,050 ± 50
2-Butanone	17.9 ± 0.6	0.21 ± 0.07	119 ± 38	480 ± 150
MIBK	16.0 ± 0.1	0.31 ± 0.03	157 ± 15	950 ± 90
Hexanal	14.6 ± 0.2	0.38 ± 0.03	174 ± 14	1,050 ± 80
d-Limonene	12.0 ± 0.2	0.33 ± 0.03	124 ± 13	1,240 ± 130
Toluene	18.3 ± 0.1	0.17 ± 0.02	98 ± 9	690 ± 60

Table 4. Inlet and outlet mixing ratios and UVPCO production rates of formaldehyde from reactions of 11 individual VOCs and of a 10-component mixture.

Compound	Exp No	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Formaldehyde Production Rate (µmole/h)
Methanol	13	3.3 ± 0.3	8.7 ± 2.6	107 ± 81
Ethanol	14	4.2 ± 0.3	8.6 ± 1.3	135 ± 42
Isopropanol	2	3.2 ± 0.1	4.5 ± 0.4	43 ± 11
1-Butanol	4	4.1 ± 0.1	4.9 ± 0.4	25 ± 14
2-Butoxyethanol	5	4.9 ± 0.1	5.4 ± 0.5	Ns*
2-Butoxyethanol	16	5.0 ± 0.5	9.4 ± 1.3	137 ± 45
2-Propanone	17	4.1 ± 0.4	5.9 ± 1.2	57 ± 40
2-Butanone	8	3.6 ± 0.3	6.2 ± 0.6	81 ± 21
MIBK	9	4.0 ± 0.1	6.7 ± 1.0	85 ± 33
Hexanal	10	2.8 ± 0.1	3.9 ± 0.3	39 ± 9
d-Limonene	11	2.5 ± 0.0	5.9 ± 0.6	107 ± 18
Toluene	18	4.0 ± 0.1	4.9 ± 0.4	28 ± 13
10 VOC Mixture	19	3.9 ± 0.5	12.1 ± 0.5	260 ± 20

*Ns = Not significant, p = 0.05

Table 5. Inlet and outlet mixing ratios and UVPCO production rates of acetaldehyde from reactions of 11 individual VOCs and of a 10 component mixture.

Compound	Exp No	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Acetaldehyde Production Rate	
				(μmole/h)	(μmole C/h)
Methanol	13	1.7 ± 0.5	2.2 ± 0.6	Ns*	Ns
Ethanol	14	2.3 ± 0.4	9.6 ± 1.8	230 ± 60	450 ± 120
Isopropanol	2	2.0 ± 0.2	2.0 ± 0.4	Ns	Ns
1-Butanol	4	1.8 ± 0.1	2.5 ± 0.4	22 ± 14	44 ± 27
2-Butoxyethanol	5	2.2 ± 0.1	2.1 ± 0.1	Ns	Ns
2-Butoxyethanol	16	2.3 ± 0.6	2.8 ± 0.5	Ns	Ns
2-Propanone	17	2.1 ± 0.2	2.0 ± 0.4	Ns	Ns
2-Butanone	8	1.7 ± 0.2	3.0 ± 0.2	40 ± 9	81 ± 17
MIBK	9	2.6 ± 0.2	2.2 ± 0.3	Ns	Ns
Hexanal	10	1.7 ± 0.2	2.2 ± 0.2	15.8 ± 7.9	32 ± 16
d-Limonene	11	1.6 ± 0.1	1.8 ±0.3	Ns	Ns
Toluene	18	2.0 ± 0.2	1.8 ± 0.3	Ns	Ns
10 VOC Mixture	19	1.9 ± 0.2	8.2 ± 0.3	197 ±11	390 ± 20

*Ns = Not significant, p = 0.05

Table 6. Inlet and outlet mixing ratios and UVPCO production rates of 2-propanone from reactions of ten individual VOCs and of a 10-component mixture.

Compound	Exp No	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	2-Propanone Production Rate	
				(μmole/h)	(μmole C/h)
Methanol	13	1.8 ± 0.4	2.9 ± 0.7	35 ± 26	105 ± 79
Ethanol	14	2.6 ± 0.3	3.5 ± 0.5	27 ± 19	80 ± 56
Isopropanol	2	2.3 ± 0.3	16.3 ± 1.2	440 ± 40	1,320 ± 110
1-Butanol	4	2.3 ± 0.2	2.8 ± 0.2	17.7 ± 10.2	53 ± 31
2-Butoxyethanol	5	2.3 ± 0.0	2.5 ± 0.2	Ns*	Ns
2-Butoxyethanol	16	2.6 ± 0.3	2.7 ± 0.6	Ns	Ns
2-Butanone	8	2.6 ± 0.3	4.4 ± 0.4	56 ± 15	169 ± 45
MIBK	9	3.2 ± 0.4	8.1 ± 1.3	151 ± 43	450 ± 130
Hexanal	10	3.0 ± 0.4	3.2 ± 0.1	Ns	Ns
d-Limonene	11	2.6 ± 0.3	4.0 ± 0.4	42 ± 17	126 ± 50
Toluene	18	2.5 ± 0.1	2.5 ± 0.2	Ns	Ns
10 VOC Mixture	19	3.7 ± 0.6	15.6 ± 1.0	370 ± 40	1,120 ± 110

*Ns = Not significant, p = 0.05

Table 7. Ratio of production rate of carbonyl compound (formaldehyde, acetaldehyde and 2-propanone) to reaction rate of individual VOC and a 10-component mixture (μmole per hour / μmole per hour).

Compound	Exp No	Production Rate / Reaction Rate		
		Formaldehyde	Acetaldehyde	2-Propanone
Methanol	13	0.124	--	0.026
Ethanol	14	0.061	0.103	0.012
Isopropanol	2	0.036	--	0.37
1-Butanol	4	0.074	0.066	0.054
2-Butoxyethanol	16	0.25	--	--
2-Propanone	17	0.067	--	--
2-Butanone	8	0.161	0.080	0.111
MIBK	9	0.23	--	0.40
Hexanal	10	0.103	0.047	--
d-Limonene	11	0.41	--	0.163
Toluene	18	0.161	--	--
10 VOC Mixture	19	0.091	0.070	0.133

Table 8. Experiment 19 with 10-component mixture: Comparison of predicted production rate of carbonyl compound (formaldehyde, acetaldehyde and 2-propanone) derived from experiments with individual VOCs to measured rate for mixture.

Compound	Predicted Production Rate (μmole/h)		
	Formaldehyde	Acetaldehyde	2-Propanone
Methanol	63	6.0	13.0
Ethanol	40	67	7.8
Isopropanol	21	--	210
1-Butanol	15.9	14.2	11.5
2-Butoxyethanol	45	--	--
2-Butanone	19.1	9.5	13.3
MIBK	36	--	64
Hexanal	17.9	8.3	--
d-Limonene	51	--	20
Toluene	15.8	--	--
Sum Predicted rate	320	105	340
Measured rate	260	200	370
Predicted/Measured (%)	127	53	92

Table 9. Summary of experiments conducted to measure efficiency of a mixed media filter element and two configurations of a packed media bed for removal of VOCs and carbonyl compounds (formaldehyde, acetaldehyde and 2-propanone).

Exp No	Date	Downstream Treatment Device	Flow Rate (m^3/h)	Temp (^oC)	Rel Humd (%0	UVPCO On Y/N?	Infusion Mixtures*
20	5/31/06	Mixed media filter	750	24.4 ± 0.3	50.5 ± 2.0	Y	VOC
21	6/16/06	Mixed media filter	706	26.9 ± 0.2	40.7 ± 1.6	N	VOC & Ald
22	6/20/06	Mixed media filter	706	26.7 ± 0.2	42.8 ± 0.7	N	VOC & Ald
23	6/21/06	Mixed media filter	701	26.0 ± 0.4	44.8 ± 0.4	N	Ald
24	6/22/06	Mixed media filter	704	25.5 ± 0.2	41.6 ± 1.1	N	Alcohols
25	6/28/06	Mixed media filter	689	27.8 ± 0.3	44.0 ± 1.1	Y	VOC & Ald
26	7/11/06	Single panel bed	681	24.3 ± 0.3	44.3 ± 0.3	N	VOC & Ald
27	7/13/06	Single panel bed	693	27.6 ± 0.1	39.1 ± 0.5	N	VOC & Ald
28	7/14/06	Single panel bed	680	27.2 ± 0.1	41.5 ± 0.9	N	Ald
29	7/19/05	Single panel bed	678	26.2 ± 0.1	39.3 ± 1.3	N	Alcohols
30	7/24/06	Single panel bed	678	31.8 ± 0.4	38.8 ± 3.6	Y	VOC & Ald
32	8/23/06	Single panel bed	686	21.3 ± 0.3	49.8 ± 1.1	N	VOC & Ald
33	8/29/03	Single panel bed	682	23.4 ± 0.1	45.8 ± 0.1	N	VOC & Ald
34	9/1/06	Single panel bed	677	28.2 ± 0.1	40.2 ± 1.0	N	VOC & Ald
35	9/8/06	Single panel bed	402	23.3 ± 0.1	44.1 ± 0.1	N	VOC & Ald
36	9/12/06	Single panel bed	201	24.0 ± 0.2	43.4 ± 1.5	N	VOC & Ald
37	9/20/06	Single panel bed	132	27.9 ± 0.4	33.8 ± 1.0	N	VOC & Ald
38	9/25/06	4-Panel folded bed	689	24.4 ± 0.3	42.8 ± 1.7	Y	VOC & Ald
39	9/27/06	4-Panel folded bed	346	24.9 ± 0.4	43.3 ± 0.6	Y	VOC & Ald

*VOC = 10 or 15-component VOC mixture; Ald = mixture of formaldehyde and acetaldehyde; Alcohols = mixture of methanol, ethanol and isopropanol

Table 10. Experiment 20 with UVPCO and mixed media filter element positioned downstream of UVPCO: VOC mixing ratios at inlet, between UVPCO and filter element, and at outlet of combined system and VOC fractions reacted and removed by UVPCO, filter element, and system.

Compound	In Mix Ratio (ppb)	Btw Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Removed		
				UVPCO	Filter	System
Methanol	43 ± 4	39 ± 6	30 ± 2	Ns*	0.23 ± 0.17	0.30 ± 0.11
Ethanol	56 ± 4	44 ± 7	34 ± 1	0.21 ± 0.14	0.22 ± 0.16	0.39 ± 0.07
Isopropanol	37 ± 4	21 ± 7	10.6 ± 0.4	0.41 ± 0.21	0.51 ± 0.34	0.71 ± 0.12
1-Butanol	22 ± 1	10.9 ± 2.2	7.0 ± 0.3	0.49 ± 0.11	0.36 ±0.22	0.68 ± 0.05
2-Butoxyethanol	14.8 ± 0.8	10.9 ± 0.2	1.6 ± 0.3	0.26 ± 0.06	0.85 ± 0.04	0.89 ± 0.08
2-Butanone	16.2 ± 1.7	5.7 ± 1.5	Nd**	0.65 ± 0.15	1.00 ± 0.38	1.00 ± 0.15
MIBK	14.6 ± 0.7	11.1 ± 0.2	2.4 ± 0.3	0.24 ± 0.05	0.78 ± 0.04	0.84 ± 0.07
Hexanal	10.1 ± 0.4	6.9 ± 0.3	1.6 ± 0.2	0.32 ± 0.05	0.77 ± 0.06	0.85 ± 0.05
d-Limonene	13.3 ± 0.6	9.3 ± 0.4	1.0 ± 0.2	0.30 ± 0.06	0.89 ± 0.06	0.92 ± 0.06
Toluene	17.3 ± 0.9	15.7 ± 0.3	5.0 ± 0.5	0.09 ± 0.05	0.68 ± 0.04	0.71 ± 0.07

*Ns = Not significant, p = 0.05
**Nd = Not detected

Table 11. Experiment 25 with UVPCO and mixed media filter element positioned downstream of UVPCO: VOC mixing ratios at inlet, between UVPCO and filter element, and at outlet of combined system and VOC fractions removed by UVPCO, filter element, and system.

Compound	In Mix Ratio (ppb)	Btw Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Removed		
				UVPCO	Filter	System
Methanol	125 ± 5	117 ± 10	109 ± 4	Ns	Ns	Ns
Ethanol	118 ± 7	92 ± 7	81 ± 7	0.22 ± 0.09	Ns	Ns
Isopropanol	69 ± 5	39 ± 5	35 ± 7	0.44 ± 0.10	Ns	Ns
1-Butanol	35 ± 1	28 ± 1	27 ± 0.4	0.22 ± 0.04	Ns	Ns
2-Butoxyethanol	20 ± 1	11.8 ± 0.5	5.8 ± 0.7	0.41 ± 0.07	0.51 ± 0.08	0.71 ± 0.08
2-Butanone	56 ± 3	39 ± 5	36 ± 7	0.30 ± 0.12	Ns	Ns
MIBK	22 ± 1	17.2 ± 0.9	14.7 ± 0.7	0.21 ± 0.07	0.15 ± 0.07	0.33 ± 0.07
Hexanal	16.8 ± 2.4	11.7 ± 0.9	7.0 ± 0.7	0.30 ± 0.17	0.40 ± 0.07	0.58 ± 0.17
d-Limonene	21 ± 1	15.5 ± 0.8	5.9 ± 0.7	0.28 ± 0.06	0.62 ± 0.07	0.72 ± 0.07
Toluene	26 ± 1	24 ± 1	19.8 ± 0.8	Ns	0.17 ± 0.06	0.22 ± 0.06
o-Xylene	23 ± 1	19.5 ± 0.8	12.4 ± 0.9	0.14 ± 0.06	0.36 ± 0.07	0.45 ± 0.06
1,2-DCB	13.3 ± 0.6	11.8 ± 0.5	5.8 ± 0.5	0.11 ± 0.06	0.51 ± 0.06	0.56 ± 0.06
n-Undecane	22 ± 1	19.0 ± 0.8	7.0 ± 0.5	0.12 ± 0.06	0.63 ± 0.06	0.68 ± 0.06
n-Dodecane	18.2	16.2 ± 0.6	6.1 ± 0.6	0.11 ± 0.04	0.62 ± 0.06	0.66 ± 0.03
D5 Siloxane	5.2 ± 0.2	4.1 ± 0.2	1.7 ± 0.1	0.20 ± 0.06	0.58 ± 0.05	0.66 ± 0.06

*Ns = Not significant, p = 0.05
**Nd = Not detected

Table 12. Experiments 21 and 22 with mixed media filter element: VOC mixing ratios at inlet and outlet of filter element and fractions of compounds removed. UVPCO lamps off.

Compound	Experiment 21			Experiment 22		
	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Filter Fraction Removed	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Filter Fraction Removed
Methanol	120 ± 13	110 ± 11	Ns*	108 ± 5	108 ± 32	Ns
Ethanol	108 ± 8	96 ± 6	Ns	94 ± 10	92 ± 15	Ns
Isopropanol	67 ± 12	51 ± 4	0.23 ± 0.19	59 ± 16	60 ± 17	Ns
1-Butanol	34 ± 1	21 ± 1	0.37 ± 0.03	33 ± 1	25 ± 1	0.23 ± 0.03
2-Butoxyethanol	22 ± 1	3.5 ± 0.5	0.84 ± 0.02	19.6 ± 1.3	4.5 ± 0.5	0.77 ± 0.09
2-Butanone	42 ± 7	26 ± 5	0.40 ± 0.21	46	37 ± 5	0.20
MIBK	20 ± 1	5.8 ± 0.8	0.71 ± 0.04	19.2 ± 1.0	8.7 ± 0.8	0.55 ± 0.07
Hexanal	14.5 ± 0.1	4.1 ± 0.6	0.71 ± 0.04	13.2 ± 0.8	4.6 ± 0.4	0.65 ± 0.08
d-Limonene	20 ± 1	3.5 ± 0.6	0.83 ± 0.04	19.2 ± 1.4	4.6 ± 0.5	0.76 ± 0.09
Toluene	24 ± 1	9.2 ± 0.9	0.62 ± 0.04	23 ± 1	12.5 ± 0.9	0.46 ± 0.06
o-Xylene	21 ± 1	6.2 ± 0.6	0.71 ± 0.03	20 ± 1	7.6 ± 0.6	0.63 ± 0.07
1,2-DCB	12.7 ± 0.1	3.5 ± 0.4	0.72 ± 0.03	11.7 ± 0.8	4.0 ± 0.4	0.66 ± 0.08
n-Decane	19.5 ± 0.2	6.2 ± 0.6	0.68 ± 0.03	18.3 ± 1.1	6.8 ± 0.4	0.63 ± 0.07
n-Undecane	21 ± 1	6.6 ± 0.6	0.68 ± 0.03	19.6 ± 1.1	7.7 ± 0.4	0.63 ± 0.07
D5 Siloxane	5.0 ± 0.1	1.9 ± 0.2	0.62 ± 0.04	4.7 ± 0.3	2.0 ± 0.1	0.57 ± 0.07

*Ns = Not significant, p = 0.05

Table 13. Experiment 20 with UVPCO and mixed media filter element positioned downstream of UVPCO: Carbonyl compound mixing ratios at inlet, between UVPCO and filter element, and at outlet of combined system and fractions of compounds produced or removed by UVPCO, filter element, and system.

Compound	Experiment 20					
	In Mix Ratio (ppb)	Btw Mix Ratio (ppb)	Out Mix Ratio (ppb)	Produced UVPCO	Removed Filter	Produced System
Formaldehyde	5.9 ± 0.3	12.8 ± 1.2	5.5 ± 0.7	1.16 ± 0.21	0.57 ± 0.12	Ns*
Acetaldehyde	2.5 ± 0.3	8.1 ± 0.9	6.4 ± 0.8	2.2 ± 0.04	0.21 ± 0.15	1.52 ± 0.38
2-Propanone	5.1 ± 0.3	15.0 ± 1.8	11.9 ± 1.4	1.94 ± 0.38	0.21 ± 0.16	1.32 ± 0.29

*Ns = Not significant, p = 0.05

Table 14. Experiment 25 with UVPCO and mixed media filter element positioned downstream of UVPCO: Carbonyl compound mixing ratios at inlet, between UVPCO and filter element, and at outlet of combined system and fractions of compounds produced or removed by UVPCO, filter element, and system.

Compound	Experiment 25					
	In Mix Ratio (ppb)	Btw Mix Ratio (ppb)	Out Mix Ratio (ppb)	Produced UVPCO	Removed Filter	Produced System
Formaldehyde	21 ± 1	35 ± 5	24 ± 1	0.65 ± 0.23	0.32 ± 0.15	0.13 ± 0.05
Acetaldehyde	7.1 ± 0.1	17.5 ± 3.3	16.1 ± 0.4	1.47 ± 0.47	Ns*	1.27 ± 0.06
2-Propanone	3.7 ± 0.1	14.1 ± 3.2	14.8 ± 0.3	2.8 ± 0.9	Ns	3.0 ± 0.2

*Ns = Not significant, p = 0.05

Table 15. Three experiments with mixed media filter element: Carbonyl compound (formaldehyde, acetaldehyde and 2-propanone) mixing ratios at inlet and outlet of filter element and fractions of compounds removed. Negative value for 2-propanone indicates fraction produced. UVPCO lamps off.

Compound	Experiment 21			Experiment 22			Experiment 23		
	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Filter Fraction Removed	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Filter Fraction Removed	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Filter Fraction Removed
Formaldehyde	22 ± 1	10.1 ± 1.8	0.53 ± 0.11	35 ± 1	18.0 ± 3.0	0.49 ± 0.09	39 ± 1	23 ± 1	0.42 ± 0.04
Acetaldehyde	9.0 ± 0.6	7.7 ± 1.5	Ns*	11.4 ± 0.5	10.5 ± 1.0	Ns	12.4 ± 0.9	11.2 ± 0.4	0.10 ± 0.08
2-Propanone	4.9 ± 0.2	8.3 ± 1.7	-0.69 ± 0.35	4.8 ± 0.3	8.3 ± 0.4	-0.74 ± 0.10	5.5 ± 0.9	6.7 ± 0.2	-0.23 ± 0.17

*Ns = Not significant, $p = 0.05$

Table 16. Experiment 24: Mixing ratios of alcohols (methanol, ethanol and isopropanol) and carbonyl compounds (formaldehyde, acetaldehyde and 2-propanone) at inlet and outlet of filter element and fractions of compounds removed. Negative values indicate fractions produced.

Compound	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Removed
Methanol	93 ± 4	133 ± 12	-0.44 ± 0.14
Ethanol	113 ± 5	112 ± 3	Ns*
Isopropanol	74 ± 4	52 ± 3	0.29 ± 0.07
Formaldehyde	8.6 ± 0.2	5.3 ± 0.3	0.38 ± 0.04
Acetaldehyde	5.0 ± 0.1	5.3 ± 0.1	-0.06 ± 0.02
2-Propanone	6.9 ± 0.2	10.7 ± 0.3	-0.56 ± 0.06

*Ns = Not significant, p = 0.05

Table 17. Summary of inlet mixing ratios of 15 VOCs for seven experiments with single panel media bed. Inlet mixing ratios for Experiments 32 – 36 were similar and were averaged.

Compound	Inlet Mixing Ratio (ppb)		
	Exp 27	Exp 30	Exps 32 – 36
Methanol	133	121	67 ± 9
Ethanol	136	116	69 ± 9
Isopropanol	86	52	51 ± 8
1-Butanol	33	31	26 ± 2
2-Butoxyethanol	19.4	13.6	11.5 ± 4.8
2-Butanone	55	23	31 ± 4
MIBK	21	19.2	11.9 ± 2.1
Hexanal	14.1	19.6	11.8 ± 1.9
d-Limonene	19.6	18.7	14.2 ± 5.8
Toluene	25	26	22 ± 2
o-Xylene	20	23	18.5 ± 2.9
1,2-Dichlorobenzene	11.3	13.6	12.7 ± 4.4
n-Undecane	21	21	12.4 ± 5.1
n-Dodecane	19.7	17.0	8.6 ± 3.7
D5 Siloxane	5.4	4.1	3.3 ± 1.6

Table 18. Fractions of VOCs removed for experiments with single panel media bed.

Compound	Fraction Removed						
	Exp 27	Exp 30*	Exp 32	Exp 33	Exp 34	Exp 35**	Exp 36**
Methanol	Ns[+]	Ns	0.17 ± 0.07	Ns	Ns	Ns	Ns
Ethanol	0.20 ± 0.02	0.11 ± 0.08	Ns	0.13 ± 0.04	0.12 ± 0.03	0.17 ± 0.04	0.21 ± 0.03
Isopropanol	0.45 ± 0.05	Ns	Ns	0.36 ± 0.03	0.37 ± 0.07	0.41 ± 0.02	0.42 ± 0.03
1-Butanol	0.04 ± 0.01	Ns	Ns	Ns	0.05 ± 0.02	0.06 ± 0.02	0.17 ± 0.02
2-Butoxyethanol	0.51 ± 0.04	0.26 ± 0.09	0.46 ± 0.00	0.38 ± 0.01	0.36 ± 0.02	0.50 ± 0.02	0.68 ± 0.04
2-Butanone	0.31 ± 0.14	Ns	Ns	0.15 ± 0.04	0.23 ± 0.01	0.17 ± 0.03	0.34 ± 0.07
MIBK	Ns	Ns	0.11 ± 0.01	Ns	0.07 ± 0.02	0.09 ± 0.03	0.21 ± 0.04
Hexanal	0.41 ± 0.02	0.22 ± 0.12	0.26 ± 0.03	0.19 ± 0.04	0.21 ± 0.01	0.25 ± 0.02	0.42 ± 0.03
d-Limonene	0.43 ± 0.03	0.20 ± 0.12	0.35 ± 0.01	0.23 ± 0.03	0.21 ± 0.01	0.28 ± 0.03	0.70 ± 0.04
Toluene	Ns	Ns	0.06 ± 0.01	Ns	0.04 ± 0.01	Ns	Ns
o-Xylene	Ns	Ns	0.05 ± 0.01	Ns	0.05 ± 0.02	Ns	Ns
1,2-Dichlorobenzene	Ns	Ns	0.04 ± 0.01	Ns	Ns	Ns	Ns
n-Undecane	Ns	Ns	0.06 ± 0.01	Ns	0.05 ± 0.01	Ns	0.11 ± 0.04
n-Dodecane	Ns	Ns	0.07 ± 0.02	Ns	0.06 ± 0.01	Ns	0.13 ± 0.02
D5 Siloxane	0.10 ± 0.02	Ns	0.15 ± 0.01	0.11 ± 0.04	0.12 ± 0.01	0.16 ± 0.03	0.26 ± 0.01

*UVPCO lamps off
**Reduced air flow rate; Exp 36 = 201 m^3/h; Exp 37 = 132 m^3/h
[+]Ns = Not significant, p = 0.05

Table 19. Experiment 29: Mixing ratios of alcohols (methanol, ethanol and isopropanol) at inlet and outlet of single panel media bed and fractions of compounds removed.

Compound	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Removed
Methanol	156 ± 4	140 ± 5	0.10 ± 0.04
Ethanol	139 ± 2	119 ± 2	0.14 ± 0.02
Isopropanol	86 ± 2	66 ± 6	0.23 ± 0.07

Table 20. Formaldehyde: Inlet and outlet mixing ratios, fractions removed and reaction rates for experiments with single panel media bed.

| Exp No | Formaldehyde | | | |
	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Removed	Reaction Rate (μmole/h)
26	21 ± 2	7.2 ± 1.2	0.66 ± 0.12	390 ± 60
27	39 ± 1	18 ± 1	0.53 ± 0.01	580 ± 10
28	38 ± 1	19.3 ± 0.9	0.49 ± 0.03	510 ± 30
30	40 ± 1	25 ± 1	0.37 ± 0.01	410 ± 10
32	36 ± 1	24 ± 1	0.33 ± 0.01	340 ± 10
33	38 ± 1	24 ± 1	0.38 ± 0.04	410 ± 40
34	39 ± 1	23 ± 1	0.40 ± 0.01	430 ± 10
35	40 ± 1	20 ± 2	0.49 ± 0.05	320 ± 30
36	42 ± 1	11.2 ± 0.1	0.73 ± 0.02	250 ± 10
37	43 ± 1	6.0 ± 0.3	0.86 ± 0.02	200 ± 10

Table 21. Acetaldehyde: Inlet and outlet mixing ratios, fractions removed and reaction rates for experiments with single panel media bed.

Exp No	Acetaldehyde				
	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Removed	Reaction Rate	
				(µmole/h)	(µmole C/h)
26	7.6 ± 1.0	5.1 ± 0.8	0.32 ± 0.18	68± 36	136 ± 73
27	13.5 ± 0.2	10.2 ± 0.1	0.24 ± 0.01	91 ± 6	182 ± 11
28	12.8 ± 0.1	9.7 ± 0.4	0.24 ± 0.03	86 ± 10	173 ± 20
30	15.6 ± 0.4	14.0 ± 0.1	0.10 ± 0.03	44 ± 12	88 ± 24
32	12.5 ± 0.1	11.7 ± 0.1	0.06 ± 0.01	23 ± 3	46 ± 6
33	11.5 ± 0.2	10.7 ± 0.1	0.08 ± 0.02	24 ± 6	49 ± 11
34	11.9 ± 0.5	11.1 ± 0.2	0.07 ± 0.04	24 ± 14	47 ± 27
35	12.0 ± 0.1	10.8 ± 0.1	0.10 ± 0.01	20 ± 2	41 ± 5
36	16.0 ± 0.2	13.4 ± 0.1	0.16 ± 0.02	21 ± 2	42 ± 4
37	15.3 ± 0.3	12.5 ± 0.2	0.19 ± 0.02	15.6 ± 1.7	31 ± 3

Table 22. 2-Propanone: Inlet and outlet mixing ratios, fractions produced and production rates for experiments with single panel media bed challenged with 17-component mixture of VOCs and aldehydes (formaldehyde and acetaldehyde).

Exp No	2-Propanone				
	In Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Produced	Production Rate	
				(µmole/h)	(µmole C/h)
26	3.6 ± 0.3	7.6 ± 1.5	1.07 ± 0.43	109 ± 43	330 ± 130
27	4.4 ± 0.0	9.7 ± 0.3	1.22 ± 0.08	151 ± 10	450 ± 30
30	11.1 ± 0.4	14.1 ± 0.3	0.26 ± 0.04	81 ± 13	240 ± 40
32	6.0 ± 0.3	7.6 ± 0.2	0.27 ± 0.06	45 ± 10	135 ± 29
33	3.3 ± 0.0	5.1 ± 0.2	0.53 ± 0.07	49 ± 6	147 ± 19
34	3.8 ± 0.1	5.8 ± 0.2	0.50 ± 0.06	53 ± 6	160 ± 19
35	3.2 ± 0.1	5.9 ± 0.2	0.82 ± 0.08	43 ± 4	130 ± 11
36	6.8 ± 0.6	11.2 ± 0.3	0.64 ± 0.11	36 ± 5	108 ± 16
37	6.1 ± 0.2	14.5 ± 0.4	1.38 ± 0.08	46 ± 2	137 ± 7

Table 23. Experiment 38 with UVPCO and four-panel, folded, media bed positioned downstream of UVPCO, 689 m^3/h: VOC mixing ratios at inlet, between UVPCO and media bed, and at outlet of combined system and VOC fractions removed by UVPCO, media bed and system.

Compound	In Mix Ratio (ppb)	Btw Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Removed		
				UVPCO	Media Bed	System
Methanol	73 ± 17	65 ± 5	55 ± 1	Ns*	Ns	Ns
Ethanol	73 ± 6	56 ± 6	46 ± 1	Ns	Ns	0.38 ± 0.09
Isopropanol	53 ± 11	33 ± 11	22 ± 1	Ns	Ns	0.58 ± 0.23
1-Butanol	28 ± 1	20 ± 1	17.2 ± 0.1	0.26 ± 0.02	0.16 ± 0.01	0.38 ± 0.01
2-Butoxyethanol	15.2 ± 0.2	7.6 ± 0.2	1.0 ± 0.1	0.50 ± 0.02	0.87 ± 0.04	0.94 ± 0.02
2-Butanone	32 ± 1	19.3 ± 6.1	19.2 ± 0.4	Ns	Ns	0.39 ± 0.03
MIBK	13.1 ± 0.1	7.7 ± 0.2	6.3 ± 0.2	0.41 ± 0.01	0.19 ± 0.04	0.52 ± 0.01
Hexanal	12.7 ± 0.9	7.4 ± 0.3	1.7 ± 0.5	0.41 ± 0.08	0.77 ± 0.09	0.86 ± 0.10
d-Limonene	17.5 ± 0.3	11.1 ± 0.2	Nd**	0.37 ± 0.02	1.00 ± 0.03	1.00 ± 0.02
Toluene	24 ± 1	18.5 ± 0.1	18.6 ± 0.1	0.23 ± 0.01	Ns	0.22 ± 0.01
o-Xylene	21 ± 1	15.2 ± 0.1	15.0 ± 0.2	0.29 ± 0.01	Ns	0.29 ± 0.01
1,2-DCB	14.1 ± 0.2	11.2 ± 0.1	11.3 ± 0.2	0.21 ± 0.02	Ns	0.20 ± 0.02
n-Undecane	14.6 ± 0.1	13.5 ± 0.2	13.2 ± 0.3	0.08 ± 0.01	Ns	0.10 ± 0.02
n-Dodecane	11.8 ± 0.1	10.6 ± 0.2	9.6 ± 0.1	0.11 ± 0.02	0.09 ± 0.02	0.19 ± 0.01
D5 Siloxane	3.5 ± 0.1	3.1 ± 0.1	1.3 ± 0.1	0.11 ± 0.02	0.58 ± 0.02	0.62 ± 0.01

*Ns = Not significant, p = 0.05
**Nd = Not detected

Table 24. Experiment 39 with UVPCO and four-panel, folded, media bed positioned downstream of UVPCO, 346 m^3/h: VOC mixing ratios at inlet, between UVPCO and media bed, and at outlet of combined system and VOC fractions removed by UVPCO and media bed, respectively.

Compound	In Mix Ratio (ppb)	Btw Mix Ratio (ppb)	Out Mix Ratio (ppb)	Fraction Removed		
				UVPCO	Media Bed	System
Methanol	91 ± 8	67 ± 4	55 ± 13	0.26 ± 0.10	Ns*	0.39 ± 0.16
Ethanol	84 ± 10	45 ± 2	34 ± 1	0.47 ± 0.13	0.23 ± 0.04	0.59 ± 0.14
Isopropanol	61 ± 14	23 ± 2	15.3 ± 1.6	0.63 ± 0.27	0.33 ± 0.13	0.75 ± 0.28
1-Butanol	33 ± 1	19.0 ± 0.2	15.4 ± 0.5	0.42 ± 0.01	0.19 ± 0.03	0.53 ± 0.02
2-Butoxyethanol	15.8 ± 0.2	6.7 ± 0.4	0.6 ± 0.1	0.58 ± 0.03	0.91 ± 0.08	0.96 ± 0.02
2-Butanone	41 ± 1	17.1 ± 1.9	17.8 ± 0.6	0.59 ± 0.06	Ns	0.57 ± 0.04
MIBK	17.2 ± 0.1	6.2 ± 0.4	5.6 ± 0.3	0.64 ± 0.02	Ns	0.67 ± 0.02
Hexanal	17.5 ± 0.1	7.6 ± 0.3	1.0 ± 0.1	0.56 ± 0.02	0.86 ± 0.06	0.94 ± 0.01
d-Limonene	18.5 ± 0.1	10.3 ± 0.5	Nd**	0.44 ± 0.03	1.00 ± 0.07	1.00 ± 0.01
Toluene	29 ± 1	17.3 ± 0.5	17.2 ± 0.7	0.40 ± 0.02	Ns	0.40 ± 0.02
o-Xylene	23 ± 1	14.5 ± 0.5	14.2 ± 0.5	0.38 ± 0.02	Ns	0.39 ± 0.02
1,2-DCB	14.3 ± 0.3	11.9 ± 0.04	11.9 ± 0.5	0.17 ± 0.04	Ns	0.17 ± 0.04
n-Undecane	16.6 ± 0.2	12.4 ± 0.5	11.6 ± 0.07	0.25 ± 0.03	Ns	0.30 ± 0.03
n-Dodecane	11.7 ± 0.1	8.8 ± 0.4	7.7 ± 0.3	0.25 ± 0.04	0.13 ± 0.06	0.35 ± 0.03
D5 Siloxane	3.8 ± 0.1	2.6 ± 0.1	1.1 ± 0.1	0.32 ± 0.03	0.56 ± 0.05	0.71 ± 0.02

*Ns = Not significant, p = 0.05
**Nd = Not detected

Table 25. Experiment 38 with UVPCO and four-panel, folded, media bed positioned downstream of UVPCO, 689 m³/h: Carbonyl compound (formaldehyde, acetaldehyde and 2-propanone) mixing ratios at inlet, between UVPCO and media bed, and at outlet of combined system and fractions of compounds produced or removed by UVPCO, media bed and system. For 2-propanone, negative values indicate fractions produced.

| Compound | Experiment 38 | | | | | |
	In Mix Ratio (ppb)	Between Mix Ratio (ppb)	Out Mix Ratio (ppb)	UVPCO Fraction Produced	Media Bed Fraction Removed	System Fraction Removed
Formaldehyde	40 ± 1	50 ± 3	4.1 ± 0.3	0.25 ± 0.07	0.92 ± 0.07	0.90 ± 0.01
Acetaldehyde	13.4 ± 0.1	25 ± 3	7.9 ± 0.3	0.83 ± 0.21	0.68 ± 0.14	0.41 ± 0.02
2-Propanone	6.5 ± 0.1	20 ± 3	30 ± 1	2.2 ± 0.5	-0.49 ± 0.17	-3.7 ± 0.1

Table 26. Experiment 39 with UVPCO and four-panel, folded, media bed positioned downstream of UVPCO, 346 m³/h: Carbonyl compound (formaldehyde, acetaldehyde and 2-propanone) mixing ratios at inlet, between UVPCO and media bed, and at outlet of combined system and fractions of compounds produced or removed by UVPCO, media bed and system. For 2-propanone, negative values indicate fractions produced.

| Compound | Experiment 39 | | | | | |
	In Mix Ratio (ppb)	Between Mix Ratio (ppb)	Out Mix Ratio (ppb)	UVPCO Fraction Produced	Media Bed Fraction Removed	System Fraction Removed
Formaldehyde	40 ± 1	58 ± 1	2.2 ± 0.1	0.46 ± 0.04	0.96 ± 0.03	0.94 ± 0.03
Acetaldehyde	12.6 ± 0.4	28 ± 1	4.6 ± 0.3	1.25 ± 0.11	0.84 ± 0.05	0.63 ± 0.05
2-Propanone	3.9 ± 0.1	25 ± 2	37 ± 1	5.3 ± 0.5	-0.52 ± 0.09	-8.6 ± 0.2

Table 27. Summary of experiments conducted in 50-m^3 chamber to measure efficiency of UVPCO and four-panel, folded, media bed system for removal of VOCs and carbonyl compounds (formaldehyde and acetaldehyde) when operated in recirculation mode with constant VOC emission rates.

Exp No	Date	OA Supply Rate (m^3/h)	System Flow Rate (m^3/h)	System Temp (°C)	System Rel Humd (%)	Infusion Mixtures	System Configuration
45	10/18/06	183	729	25.8 ± 2.1	33.1 ± 2.2	VOC & Ald	UVPCO + Media
46	10/19/06	183	729	26.2 ± 1.8	35.1 ± 2.9	VOC & Ald	UVPCO + Media
47	10/23/06	169	683	25.5 ± 1.2	37.5 ± 1.4	VOC & Ald	UVPCO alone
48	10/24/06	169	688	25.2 ± 1.2	40.5 ± 0.9	VOC & Ald	UVPCO alone

Table 28. Two recirculation experiments with UVPCO and four-panel, folded, media bed positioned downstream of UVPCO: VOC mixing ratios initially prior to turning on system, at approximately 1-hour elapsed time, and averaged over hours 2 – 6 (n = 5). Fractions of VOCs removed were determined by dividing the differences between the initial mixing ratios and the corresponding averages for hours 2 – 6 by the initial mixing ratios. Negative values indicate fractions produced.

Compound	Experiment 45				Experiment 46			
	Initial Mix Ratio (ppb)	Hour 1 Mix Ratio (ppb)	Hour 2-6 Mix Ratio (ppb)	System Fraction Removed	Initial Mix Ratio (ppb)	Hour 1 Mix Ratio (ppb)	Hour 2-6 Mix Ratio (ppb)	System Fraction Removed
Methanol	56	30	24 ± 6	0.57	100	25	19.3 ± 3.1	0.81
Ethanol	55	31	25 ± 4	0.55	53	28	22 ± 3	0.58
Isopropanol	43	18.3	14.3 ± 2.6	0.67	43	14.1	12.1 ± 3.6	0.72
1-Butanol	22	14.1	11.6 ± 2.9	0.47	22	9.4	8.6 ± 0.7	0.61
2-Butoxyethanol	9.8	2.3	2.1 ± 0.3	0.79	8.3	2.8	2.4 ± 0.2	0.71
2-Propanone	3.7	24	29 ± 2	-6.8	5.1	33	35 ± 4	-5.9
2-Butanone	21	9.9	9.7 ± 1.6	0.54	21	12.8	10.4 ± 3.0	0.50
MIBK	8.0	1.6	2.2 ± 0.8	0.73	8.0	4.1	3.4 ± 0.4	0.52
Formaldehyde	16.6	8.3	8.1 ± 0.2	0.51	27.2	8.5	8.2 ± 1.3	0.70
Acetaldehyde	13.4	5.4	4.7 ± 0.2	0.65	13.1	6.0	5.6 ± 1.0	0.58
Hexanal	9.3	2.6	2.3 ± 0.2	0.76	9.2	2.3	2.2 ± 0.2	0.76
d-Limonene	16.7	1.1	1.1 ± 0.8	0.93	10.6	2.5	2.1 ± 0.2	0.80
Toluene	17.2	11.3	10.6 ± 0.9	0.38	17.3	15.3	13.0 ± 0.9	0.25
o-Xylene	14.7	8.1	7.4 ± 0.7	0.50	14.6	10.7	9.0 ± 0.7	0.39
1,2-DCB	10.1	6.3	6.1 ± 0.7	0.40	8.5	8.6	7.5 ± 0.7	0.11
n-Undecane	14.4	6.3	5.7 ± 0.7	0.61	9.0	8.6	7.3 ± 0.7	0.19
n-Dodecane	9.0	5.1	4.1 ± 0.3	0.54	6.6	6.3	5.4 ± 0.5	0.18
D5 Siloxane	2.8	1.0	0.8 ± 0.1	0.71	2.2	1.2	1.1 ± 0.1	0.51

Table 29. Two recirculation experiments with UVPCO only: VOC mixing ratios initially prior to turning on system, at approximately 1-hour elapsed time, and averaged over hours 2 – 6 (n = 5). Fractions of VOCs removed were determined by dividing the differences between the initial mixing ratios and the corresponding averages for hours 2 – 6 by the initial mixing ratios. Negative values indicate fractions produced.

	Experiment 47				Experiment 48			
Compound	Initial Mix Ratio (ppb)	Hour 1 Mix Ratio (ppb)	Hour 2-6 Mix Ratio (ppb)	System Fraction Removed	Initial Mix Ratio (ppb)	Hour 1 Mix Ratio (ppb)	Hour 2-6 Mix Ratio (ppb)	System Fraction Removed
Methanol	61	60	44 ± 6	0.28	58	46	48 ± 7	0.17
Ethanol	59	38	36 ± 4	0.39	52	36	35 ± 4	0.33
Isopropanol	45	24	21 ± 1	0.52	27	23	19.5 ± 5.4	0.28
1-Butanol	22	12.2	11.5 ± 0.4	0.49	23	11.9	11.8 ± 0.4	0.48
2-Butoxyethanol	9.0	5.5	4.6 ± 0.3	0.50	8.5	5.3	4.8 ± 0.1	0.44
2-Propanone	6.3	28	29 ± 2	-3.7	5.0	27	26 ± 2	-4.3
2-Butanone	23	20	15.2 ± 1.4	0.33	19.5	19.5	15.4 ± 3.8	0.21
MIBK	8.7	6.0	5.4 ± 0.7	0.37	9.0	5.8	5.8 ± 0.4	0.36
Formaldehyde	25	40	44 ± 3	-0.77	21	42	41 ± 4	-0.92
Acetaldehyde	13.8	30	32 ± 2	-1.28	13.0	30.8	30 ± 2	-1.28
Hexanal	9.7	4.5	4.6 ± 0.9	0.53	9.3	4.5	4.8 ± 0.7	0.49
d-Limonene	11.4	7.3	6.2 ± 0.7	0.46	10.6	7.1	6.7 ± 0.3	0.37
Toluene	18.0	16.3	14.8 ± 1.0	0.17	18.1	15.8	15.5 ± 0.6	0.15
o-Xylene	14.9	12.1	10.8 ± 0.8	0.27	15.0	11.8	11.5 ± 0.4	0.23
1,2-DCB	8.4	8.8	8.0 ± 0.5	0.04	8.0	8.6	8.6 ± 0.2	-0.07
n-Undecane	10.2	9.9	8.8 ± 0.7	0.14	9.6	9.7	9.5 ± 0.3	0.01
n-Dodecane	7.2	7.2	6.8 ± 0.5	0.05	7.2	7.0	7.3 ± 0.3	-0.02
D5 Siloxane	2.4	2.0	1.8 ± 0.1	0.27	2.4	1.9	1.9 ± 0.1	0.22

Table 30. VOC removal rates (μmole compound/h and μmole carbon/h) attributable to use of four-panel, folded, media bed downstream of UVPCO. Compound removal rates were calculated as difference between average steady-state concentrations in Exps 47 and 48 with UVPCO only and average steady-state concentrations in Exps 45 and 46 with UVPCO plus media bed times the outdoor air flow rate of 183 m^3/h, this quantity divided by the molar volume at standard indoor conditions. Carbon removal rates were calculated by multiplying the compound removal rates by the numbers of carbon atoms. Fractions of media contribution to total removal were calculated as difference in steady-state concentration between UVPCO only and UVPCO with media bed experiments divided by concentration with UVPCO only.

Compound	Steady-state Conc (ppb)		Removal Rate		Media Contribution
	Avg Exp 47 & 48	Avg Exps 45 & 46	μMole Compound/h	μMole Carbon/h	
Methanol	46	22	181	181	0.53
Ethanol	35	24	88	176	0.33
Isopropanol	20	13.2	53	107	0.35
1-Butanol	11.7	10.1	11.9	48	0.14
2-Butoxyethanol	4.7	2.2	18.2	109	0.52
2-Propanone	28	32	-31	-92	-0.15
2-Butanone	15.3	10.0	39	157	0.34
MIBK	5.6	3.0	19.2	115	0.46
Formaldehyde	42	8.2	260	260	1.0*
Acetaldehyde	31	5.1	190	380	1.0*
Hexanal	4.7	2.2	18.3	110	0.52
d-Limonene	6.5	1.6	36	360	0.75
Toluene	15.2	11.8	25	175	0.22
o-Xylene	11.1	8.2	22	177	0.27
1,2-DCB	8.3	6.8	11.3	68	0.18
n-Undecane	9.1	6.5	19.7	220	0.29
n-Dodecane	7.1	4.8	17.1	205	0.32
D5 Siloxane	1.8	0.9	6.6	66	0.48
Total**			1,010	2,900	

*Since formaldehyde and acetaldehyde were produced by the UVPCO, all of the observed removal was due to the media

**Total excludes 2-propanone, which was produced by UVPCO and media bed

Table 31. Analysis of NaMnO$_4$·H$_2$O reactant contained in Purafil SP media and consumed in experiments with the single panel, media bed. Measurements were made at the conclusion of experiments with the bed.

Parameter	Units	New media	Single bed media
Mass fraction of reactant in media	%	13.2	0.88
Mass fraction of reactant consumed	%	--	12.3
Mass of media in bed	kg	--	4.2
Mass of reactant consumed	kg	--	0.52
Mole of reactant consumed	mole	--	3.2

Table 32. Estimated moles of compounds (VOCs and aldehydes) and carbon consumed during use of single panel, media bed in Exps 26 – 37. Also shown are estimated ratios of the moles of NaMnO$_4$·H$_2$O reacted to the moles of total compounds and carbon reacted over the course of these experiments.

Period	Time (h)	Reaction Rate, µMole/h Compound	Reaction Rate, µMole/h Carbon	Amount Reacted, Mole Compound	Amount Reacted, Mole Carbon
Exps 26 – 30*	288	1,130	3,500	0.32	1.00
Exp 32	4	1,180	4,600	0.0047	0.0183
Exp 33	4	1,640	5,400	0.0066	0.021
Exp 34	4	1,890	6,800	0.0075	0.027
Exp 35	4	1,430	4,900	0.0057	0.0196
Exp 36	4	830	2,500	0.0033	0.0099
Exp 37	4	370	1,180	0.00149	0.0047
Total				0.35	1.11
NaMnO$_4$·H$_2$O Reacted				3.2	3.2
Molar Ratio**				9.1	2.9

*Data from Exp 30 used to represent period of continuous operation
**Ratio of moles NaMnO$_4$·H$_2$O reacted to moles compound or carbon reacted, unitless
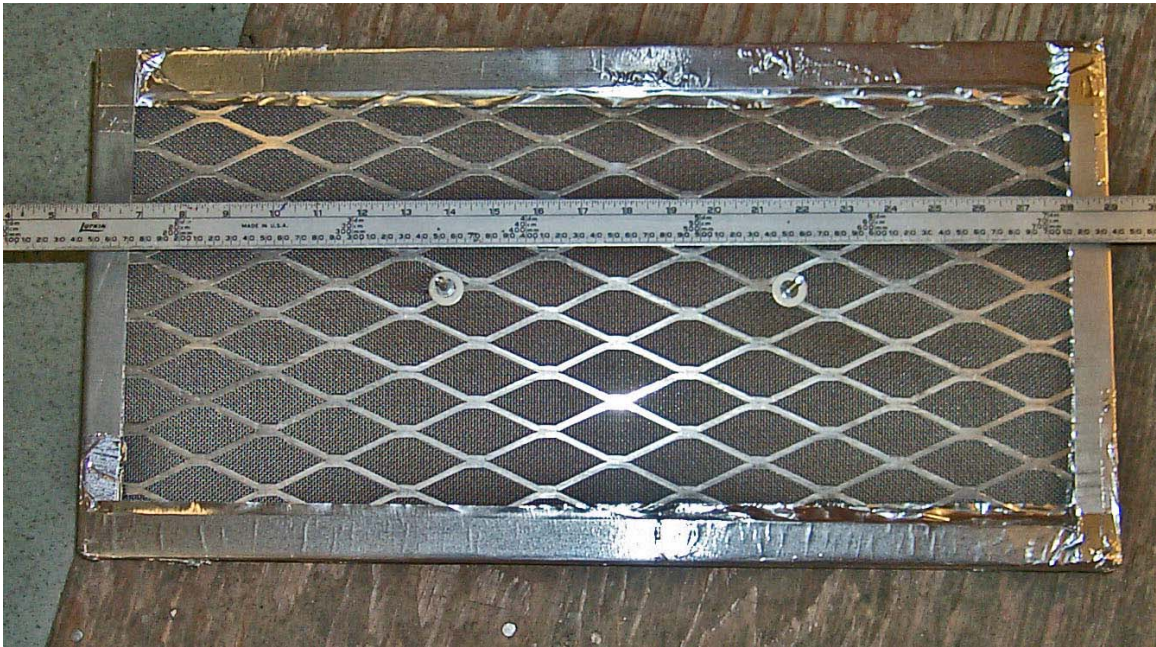
Figure 1. Single panel, packed bed, chemisorbent scrubber fabricated in laboratory. Face dimensions are 12 in by 24 in (30 cm by 61 cm); depth is 1-in (2.5-cm) deep. Bed was filled with 4.2 kg of zeolite spheres impregnated with $NaMnO_4 \cdot H_2O$ (SP media, Purafil, Inc.).

Figure 2. Four-panel, packed bed, chemisorbent scrubber fabricated in laboratory. "W" shape approximates that of a four-panel folded bed with each panel having dimensions of 12 in by 24 in (30 cm by 61 cm). The perforated sheets are spaced 1-in (2.5-cm) apart. Bed was filled with 15.6 kg of zeolite spheres impregnated with $NaMnO_4 \cdot H_2O$ (SP media, Purafil, Inc.). Loaded bed was contained in a box housing fabricated of aluminum with open face dimensions of 12-in by 24-in (30-cm by 61-cm).
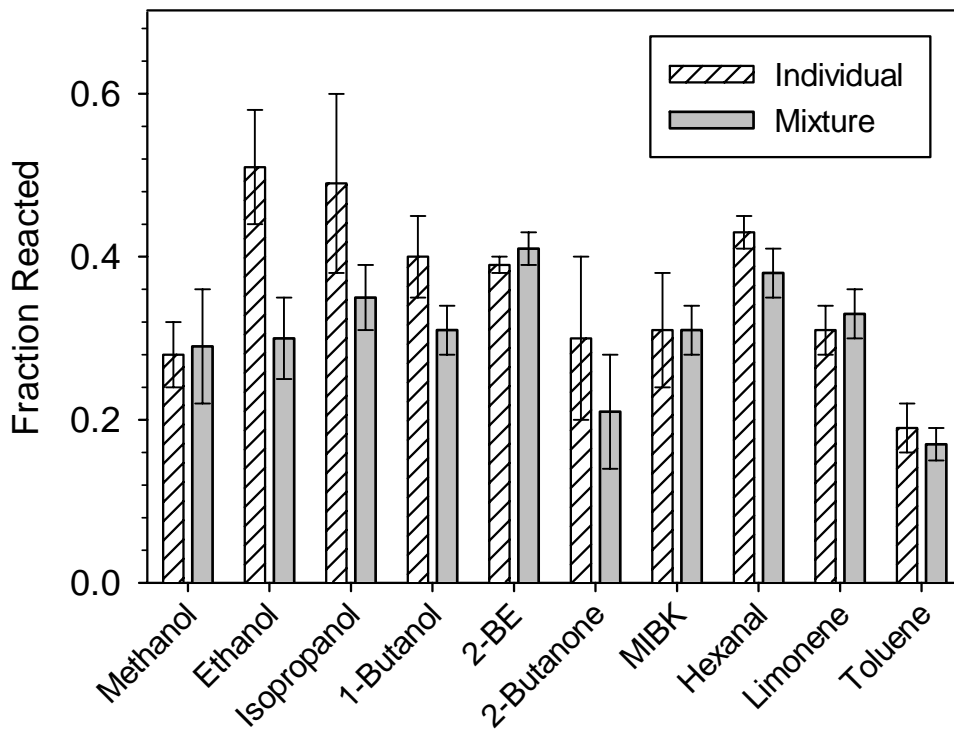
Figure 3. Fractions of VOCs reacted when they were introduced individually into the UVPCO device compared to fractions reacted when they were introduced into the device as a mixture. Error bars represent ±1 standard deviation of the means.
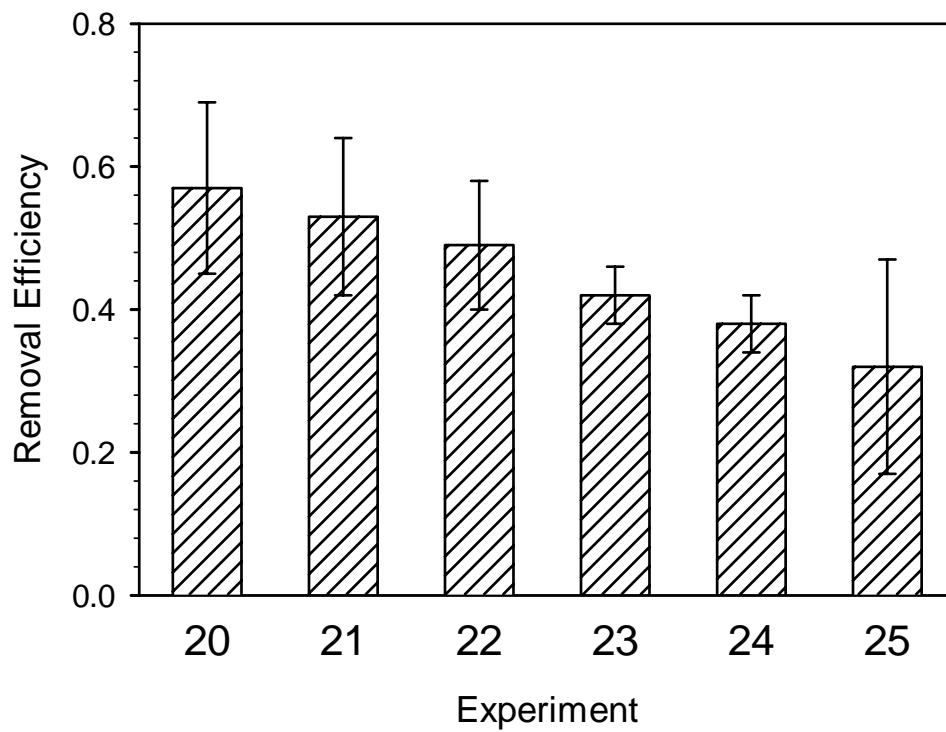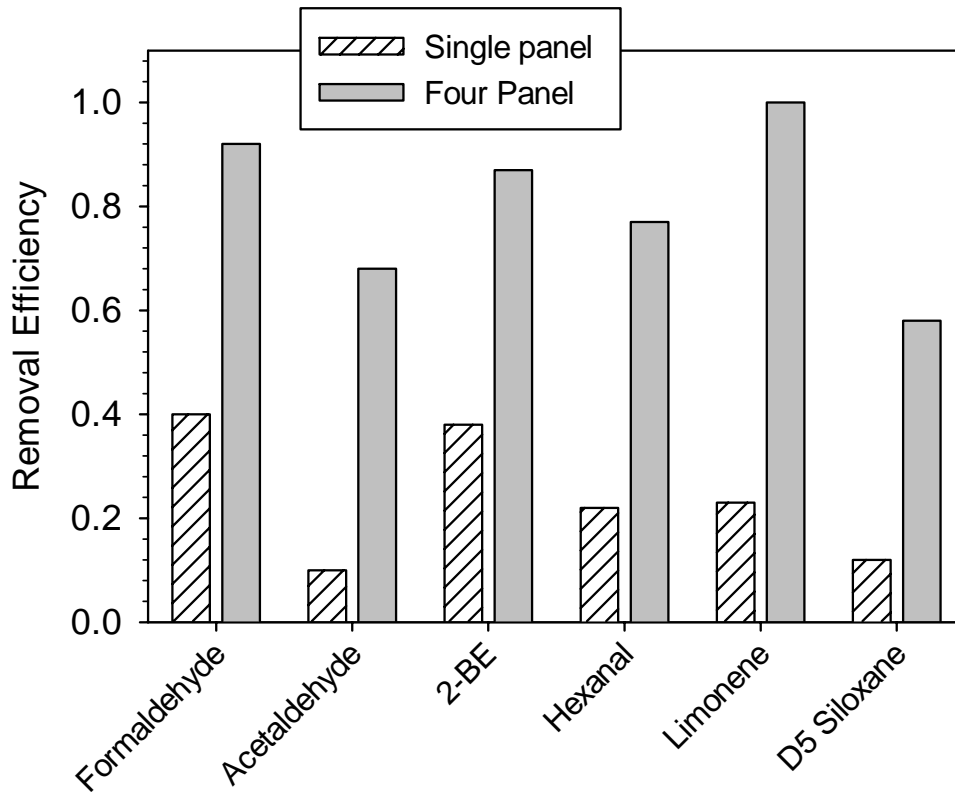
Figure 4. Formaldehyde removal efficiencies by commercial, mixed media, filter element used in Exps 20 – 25. Experiments were conducted in chronological order over a period of approximately four weeks. Error bars represent ±1 standard deviation of the means.
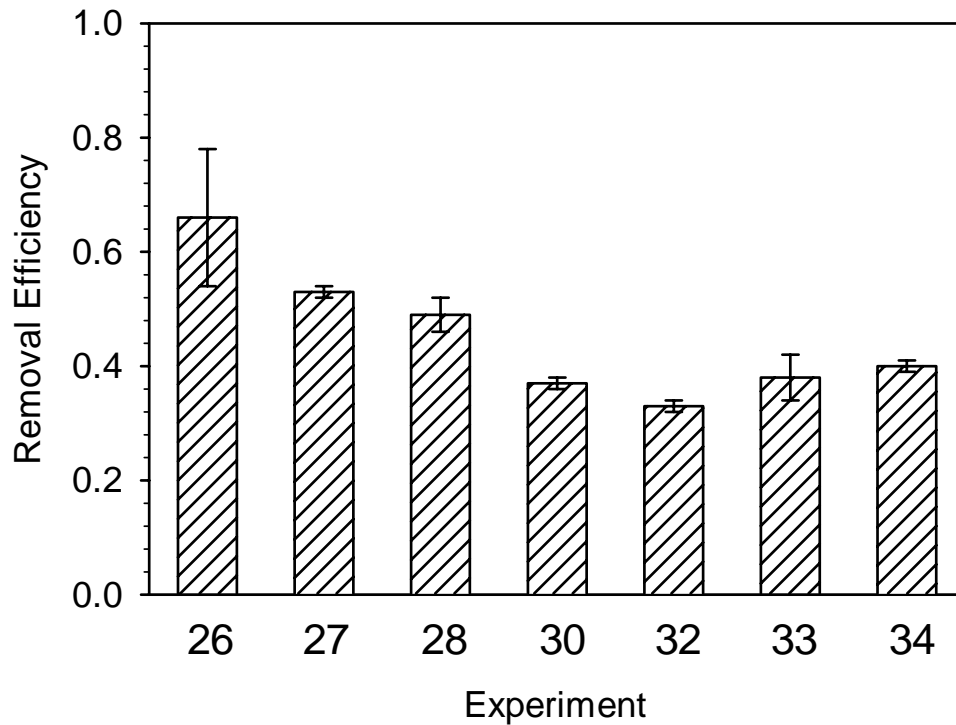
Figure 5. Formaldehyde removal efficiencies by the fabricated single panel media bed used in Exps 26 – 34. Exps 26 – 30 were run over two-week interval of nearly continuous operation with infused mixtures of VOCs and aldehydes. Exps 32 – 34 were run at 21, 23 and 28 ^{o}C, respectively, to examine effect of temperature on removal efficiency. Error bars represent ±1 standard deviation of the means.
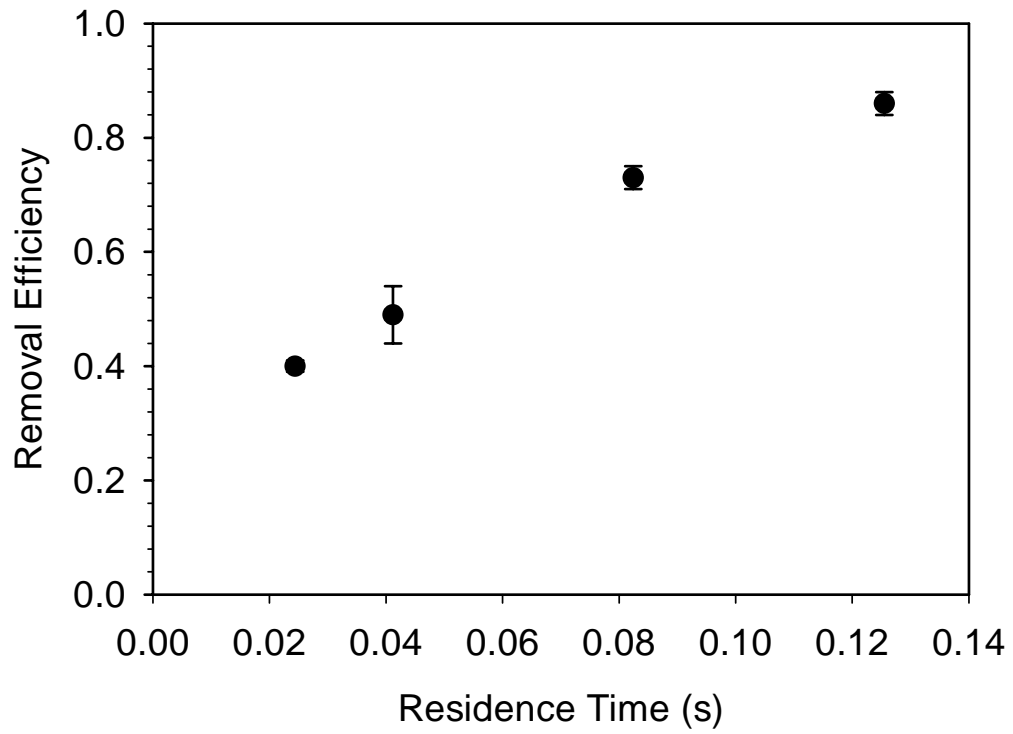
Figure 6. Formaldehyde removal efficiency versus nominal residence time of air in single panel media bed. Error bars represent ±1 standard deviation of the means.

Figure 7. Median removal efficiencies by the single panel media bed in Exps 26 – 34 for six
compounds including formaldehyde, acetaldehyde and four VOCs with high removal
(2-butoxyethanol, hexanal, d-limonene and D5 siloxane) compared to the corresponding
efficiencies by the four-panel, folded, media bed in Exp 38 at approximately the same air
flow rate

APPENDIX A

Estimation of VOC Removal by the Chemisorbent System

This appendix describes the method used to estimate the rate of VOC removal by the chemisorbent system located downstream of a UVPCO air cleaner. We employ equations, based on steady state mass balances assuming insignificant steady state losses of VOCs by sorption on surfaces or chemical reactions in room air.

The context for our calculations is the experimental conditions employed in Exps 45 – 48. Air cleaning was employed to reduce VOC concentrations in a chamber ventilated with outdoor air. In each experiment, VOCs were injected into the chamber air at approximately the same rate. Exps 45 and 46 were conducted with the four-panel, folded media chemisorbent bed installed downstream of the operating UVPCO reactor. Exps 47 and 48 were conducted without the media bed, but conditions otherwise were identical.

We consider three different cases. In case 1, neither a UVPCO system nor a chemsorbent bed is utilized, but the chamber is ventilated with outdoor air at a rate Q_{OA}. The steady state chamber VOC concentration is denoted C_1. At steady state from a mass balance, the VOC injection rate S must equal the VOC removal rate by ventilation, which equals the product of the ventilation flow rate and the steady state VOC concentration. Consequently

$$S = Q_{OA} C_1 \qquad\qquad A1$$

In case 2, there is VOC removal by a UVPCO air cleaning system and by ventilation, but no downstream chemisorbent. The *total* VOC removal rate by ventilation plus air cleaning (still equal to the VOC injection rate) can be characterized by the product of an effective removal flow rate, denoted Q_{EFF2} and the steady state chamber VOC concentration demoted by C_2. In equation form,

$$S = Q_{EFF2} C_2 \qquad\qquad A2$$

The VOC removal rate by ventilation in case 2 equals the product of Q_{OA} and C_2.

In case 3, we add a chemisorbent air cleaner downstream of the UVPCO system. The total VOC removal rate by ventilation plus both forms of air cleaning (still equal to the VOC injection rate) can be characterized by the product of an another effective removal flow rate, denoted Q_{EFF3} and the steady state chamber VOC concentration demoted by C_3. Thus,

$$S = Q_{EFF3} C_3 \qquad \text{A3}$$

The VOC removal rate by ventilation in case 2 equals the product of Q_{OA} and C_3.

If S is the same for all three cases

$$Q_{OA} C_1 = Q_{EFF2} C_2 = Q_{EFF3} C_3 \qquad \text{A4}$$

With algebraic manipulations, we obtain

$$Q_{EFF2} = Q_{OA} \frac{C_1}{C_2} \qquad \text{A5}$$

and

$$Q_{EFF3} = Q_{OA} \frac{C_1}{C_3} \qquad \text{A6}$$

The rate of VOC removal by the UVPCO system in case 2, demoted R_{UVPCO2} ,equals the total VOC removal rate minus that by ventilation, i.e.,

$$R_{UVPCO2} = Q_{EFF2} C_2 - Q_{OA} C_2 = Q_{OA}(C_1 - C_2) \qquad \text{A7}$$

Similarly, the rate of VOC removal by both the UVPCO system and chemisorbent media in case 3, demoted $R_{AIRCLEAN3}$, equals the total VOC removal rate minus that by ventilation, i.e.,

$$R_{AIRCLEAN3} = Q_{EFF3} C_3 - Q_{OA} C_3 = Q_{OA}(C_1 - C_3) \qquad \text{A8}$$

Finally, we estimate the net VOC removal by the chemisorbent media in case 3, demoted $R_{SORBENT3}$, from the difference between $R_{AIRCLEAN3}$ and R_{UVPCO2}. Because the VOC removal by

ventilation in cases 2 and 3 are not exactly the same, due to the different steady state chamber VOC concentrations, this estimate approximates the rate of VOC removal by the chemisorbent. The resulting expression is

$$R_{SORBENT3} \cong Q_{OA}(C_2 - C_3) \qquad \text{A9}$$