

Evaluation of Ultra-Violet Photocatalytic Oxidation (UVPCO) for Indoor Air Applications: Conversion of Volatile Organic Compounds at Low Part-per-Billion Concentrations

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Abstract

Efficient removal of indoor generated airborne particles and volatile organic compounds (VOCs) in office buildings and other large buildings may allow for a reduction in outdoor air supply rates with concomitant energy savings while still maintaining acceptable indoor air quality in these buildings. Ultra-Violet Photocatalytic Oxidation (UVPCO) air cleaners have the potential to achieve the necessary reductions in indoor VOC concentrations at relatively low cost. In this study, laboratory experiments were conducted with a scaled, prototype UVPCO device designed for use in a duct system. The experimental UVPCO contained two 30 by 30-cm honeycomb monoliths coated with titanium dioxide and 3% by weight tungsten oxide. The monoliths were irradiated with 12 UVC lamps arranged in four banks.

The UVPCO was challenged with four mixtures of VOCs typical of mixtures encountered in indoor air. A synthetic office mixture contained 27 VOCs commonly measured in office buildings. A cleaning product mixture contained three cleaning products with high market shares. A building product mixture was created by combining sources including painted wallboard, composite wood products, carpet systems, and vinyl flooring. A fourth mixture contained formaldehyde and acetaldehyde. Steady-state concentrations were produced in a classroom laboratory or a 20-m³ environmental chamber. Air was drawn through the UVPCO, and single pass conversion efficiencies were measured from replicate air samples collected upstream and downstream of the reactor section. Concentrations of the mixtures were manipulated, with concentrations of individual VOCs mostly maintained below 10 ppb. Device

flow rates were varied between 165 and 580 m³/h. Production of formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid as reaction products was investigated.

Conversion efficiency data were generated for 48 individual VOCs or groups of closely related compounds. Alcohols and glycol ethers were the most reactive chemical classes with conversion efficiencies often near or above 70% at the low flow rate and near 40% at the high flow rate. Ketones and terpene hydrocarbons were somewhat less reactive. The relative VOC conversion rates are generally favorable for treatment of indoor air since many contemporary products used in buildings employ oxygenated solvents. A commercial UVPCO device likely would be installed in the supply air stream of a building and operated to treat both outdoor and recirculated air. Assuming a recirculation rate comparable to three times the normal outdoor air supply rate, simple mass-balance modeling suggests that a device with similar characteristics to the study unit has sufficient conversion efficiencies for most VOCs to compensate for a 50% reduction in outdoor air supply without substantially impacting indoor VOC concentrations.

Formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid were produced in these experiments as reaction byproducts. No other significant byproducts were observed. A coupled steady-state mass balance model is presented and applied to VOC data from a study of a single office building. For the operating assumptions described above, the model estimated a three-fold increase in indoor formaldehyde and acetaldehyde concentrations. The outcome of this limited assessment suggests that evaluation of the potential effects of the operation of a UVPCO device on indoor concentrations of these contaminants is warranted. Other suggested studies include determining VOC conversion efficiencies in actual buildings and evaluating changes in VOC conversion efficiency as monoliths age with long-term operation.

INTRODUCTION

Ultra-Violet Photocatalytic Oxidation (UVPCO) air cleaning technology has been in development over a number of years for the removal of gas-phase organic contaminants from air. This technology has generated interest with respect to indoor air applications as it has been shown in numerous laboratory studies to completely oxidize a wide range of organic compounds at room temperature. If UVPCO can be implemented successfully in buildings to reduce concentrations of volatile organic compounds (VOCs), a large class of air pollutants of concern,

it may be possible to reduce the supply of outdoor air without degrading indoor air quality. Such a reduction in ventilation requirements with concomitant energy savings and reductions in peak power consumption makes UVPCO a potentially attractive energy-conservation technology.

Ultra-violet (UV) photocatalysis was the subject of a recent comprehensive literature review (Zeltner and Tompkins, 2005; Tompkins et al., 2005a and 2005b) that includes descriptions of the photocatalytic process, reaction mechanisms, factors affecting reaction rates, and kinetic modeling, among other topics. In very simplified terms, UVPCO often utilizes a honeycomb configured, monolith reactor coated with titanium dioxide (TiO_2 or titania) as the photooxidative catalyst. This monolith design potentially can have high conversion rates with low pressure drop making it suitable for use in building heating, ventilating and air conditioning (HVAC) systems. The coated monolith is irradiated with UV light from fluorescent bulbs operating near either 254 nm (UVC) or 365 nm (UVA). Air containing organic pollutants flows through the monolith, where the VOCs adsorb on the catalyst. The UV light interacting with the catalyst in the presence of oxygen and water vapor, produces hydroxyl radicals. Hydroxyl radicals are highly chemically reactive and, in-turn, breakdown the adsorbed VOCs, ideally producing only carbon dioxide and water as products.

UVPCO appears to be particularly well suited for use in large commercial buildings, such as office and retail buildings where the major indoor-generated air pollutants of concern with respect to occupant health and comfort are believed to be gaseous VOCs and particles of various types including bioaerosols. Inorganic gases that are not destroyed by UVPCO, such as radon and nitrogen dioxide, can reach hazardous concentration levels in residences; but, in commercial buildings, high levels of these pollutants are rare. An analysis of data provided by Fisk et al. (2002 and 2005) and Mudarri et al., (1996) shows that use of high efficiency filters in commercial buildings likely is several times less expensive than the use of ventilation to reduce the concentrations of indoor generated particles (Appendix A). Thus, when improved particle filtration is combined with effective UVPCO removal of VOCs, it may be possible to reduce outdoor air supply rates by 50% or more while simultaneously maintaining indoor air quality and saving energy. The energy needed to dehumidify and thermally condition ventilation air will be reduced by a similar amount, and the additional energy needed to run the UV lamps and to overcome the pressure drop in the UVPCO system should be low relative to these savings. Additional savings may accrue with the physical downsizing of heating and cooling equipment

that is possible when outdoor air supply rates are diminished. As an example, energy savings were modeled for a prototype New York school assuming a 67% reduction in outside air (Lemcoff and Dobbs, 2003). This allowed the capacity of the HVAC equipment to be downsized 25%. The smaller equipment size produced an annual energy savings potential of about 30%, and the first cost of the smaller HVAC system with UVPCO was estimated not to exceed the cost of the larger system by itself.

UVPCO has been studied almost exclusively in laboratory settings. The large majority of these investigations have employed relatively high concentrations of a few VOCs often in an attempt to better understand the photocatalytic process and to improve various aspects of the technology. Although a variety of designs have been proposed and evaluated, the most current designs considered for use in building HVAC systems generally conform to the device description given above. One such device has been developed and refined over a number of years by the United Technologies Research Center (UTRC). This organization has performed many laboratory tests and has contributed substantially to the published literature on UVPCO (e.g., Obee and Brown, 1995; Obee, 1996; Obee and Hay, 1997; Obee and Hay, 1999). UTRC also has been moving toward the commercialization of the device for indoor air applications and has installed a prototype unit in a building on the UTRC campus in Hartford, CT (Lemcoff et al., 2003). However, comprehensive evaluations of the performance of this device, or of any other UVPCO device, under real or simulated indoor conditions have not been reported in the open literature. Such studies are needed to determine the feasibility of employing the technology as a means of reducing outdoor air ventilation requirements in large buildings.

In this current study, LBNL undertook an evaluation of a scaled, prototype UVPCO device designed for installation in a duct system. The device has a 1 x 1-ft (0.3 x 0.3-m) duct dimension and contains two catalyst coated monoliths and three banks of four lamps. Laboratory experiments were conducted in which the device was challenged with realistic mixtures of VOCs simulating mixtures often encountered in office buildings and other indoor environments. The primary objective of these experiments was to measure conversion efficiencies, reaction rates, and clean air delivery rates for the individual components of these mixtures, including determining the effects of inlet VOC concentrations and device air flow rates on these parameters. Secondly, we investigated the formation of gas-phase products of incomplete

conversion as these have the potential to adversely impact the application of the technology in occupied buildings.

METHODS

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. Degussa Titania P25 impregnated with 3% tungsten oxide by weight (TiO_2 / 3% WO_3) is used as the photocatalyst. The device contains two aluminum honeycomb monoliths with 64 cells per square inch. The honeycomb design offers the high surface to volume ratios needed for efficient operation with relatively low pressure drop. The monoliths are wash coated with the photocatalyst by a proprietary process. Each monolith has face dimensions of 12 by 12 in (30 by 30 cm) and is 1 in (2.5 cm) thick. The monoliths are mounted in series with their faces oriented transversely to the air flow path. They slide into tracts and are easily removable. Unused, newly prepared monoliths were installed at the beginning of the study and were used for the first seven experiments. These were replaced with another set of unused monoliths prior to the final four experiments.

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. Device power consumption with the lamps on is 220 watts. 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 distance between a lamp surface and the face of a monolith is about 2.5 cm. This lamp arrangement results in a reasonably uniform intensity distribution over the monolith faces. Since photocatalysis depends on approximately the square root of intensity, no significant performance differences accrue due to the small differences in light intensity over the various monolith cells. The lamps were reported to have approximately 1,000 h use prior to the study, so no significant change in lamp intensity was anticipated during the course of the study.

Compressed fiberglass duct board with an inner and outer aluminum foil facing, a standard material used in commercial building construction, forms the housing for the reactor and

supports the monoliths, the lamps and flow straightener elements positioned upstream and downstream of the monolith/lamp section. The aluminum foil inner lining reflects the UV light. The reactor housing is square in cross section and is approximately one meter long.

All joints, seams, and openings for the lamp wiring in the reactor housing were carefully sealed with aluminum tape to minimize potential air leaks. Sheet metal pieces were fabricated to fit the inlet and outlet of the device. These pieces provided transitions from the square reactor housing to 10-in (25-cm) diameter round sheet metal ducting. The upstream tapered transition (approximately 45-cm in length) was fitted with eight bored-through, 0.64-cm bulkhead unions (four each on two opposing sides of the transition) to provide ports for the collection of air samples. A temperature probe, a relative humidity (RH) probe, and a 0.32-cm OD tube for pressure monitoring additionally were installed in the center of the transition. Downstream, the transition went directly from the square reactor to a 60-cm long section of round ducting. This also was fitted with eight air-sampling ports arranged radially around the duct and with temperature and RH probes and pressure monitoring tubing.

A metal filter housing containing a pleated fabric air filter was installed at the inlet to the assembly. The filter element had a MERV 12 micro-particle performance rating and was built to a custom size of 36 by 42 by 4.4 cm (Nordic Pure Air Filters, McKinney, TX). For the experiments conducted in the laboratory classroom (described below), there was no upstream ducting, and room air directly entered the filter. For the experiments in the environmental chamber, air entered the filter assembly through an approximate 7-m section of 8-in (20-cm) round corrugated aluminum ducting.

The 30-cm duct at the outlet of the assembly made an 180° turn and entered a venturi flow meter (Model NZP1031-10"-1-CF, Themo Brandt Industries, Fuquay, NC) used for continuous monitoring of the air flow rate through the system. The outlet of the flow meter was connected to a duct blower (Model 207 INS, Delhi Industries, Inc., Delhi, Ontario, Canada) capable of providing 690 cfm (1,170 m³/h) air flow at 0.375-in of water (93 Pa) pressure drop. The duct blower exhausted through a rectangular mechanical damper used to establish the air flow rate through the system. The damper transitioned to a 10-in (30-cm) round corrugated aluminum ducting that exited directly to outdoors. All joints and seams throughout the entire system were carefully sealed with aluminum tape to minimize air leakage.

For these experiments, the UVPCO was operated at flow rate settings of approximately 100, 175, and 350 cfm (175, 300, and 600 m³/h). At these settings, the respective face velocities at the monoliths were 1.67, 2.9, and 5.8 ft/s (0.51, 0.89, and 1.78 m/s).

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 APTS and the sensors were calibrated by the manufacturer immediately prior initiating the study. The monitored experimental parameters were: venturi flow meter reading; differential pressure between the duct and the room at the upstream and downstream locations; upstream, downstream, and room temperature; upstream, downstream, and room RH; and the ozone instrument signal in some experiments. The pressure measurements have a resolution of 0.1 Pa. The temperature sensor has an accuracy of $\pm 0.25^{\circ}$ C, and the RH sensor has an accuracy of $\pm 5\%$ RH. Data were recorded electronically at 30-sec intervals.

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.

Air Sampling

Air samples for the analysis of VOCs, low molecular weight aldehydes and ketones, and low molecular weight carboxylic acids were collected upstream and downstream of the UVPCO reactor section in each experiment. For each analyte type, there were three replicate samples collected simultaneously at each location. The sampling media (described below) were connected to the bulkhead unions in the transition pieces. The VOC samplers were installed so the inlet ends extended approximately 4-cm into the air stream. Air flow rates through the three media types were regulated with electronic mass flow controllers (MFCs). There were six 0 – 500 standard cm³/min MFCs operated at approximately 100 cm³/min for the collection of VOC samples and six 0 – 2 standard L/min MFCs operated at approximately 1.5 L/min for the collection of aldehyde and acid samples. All MFCs were calibrated in the laboratory at standard conditions of 25^o C and 101.3 kPa prior to initiating the study. Sample volumes were established by controlling the length of the sampling interval. The sampling interval for the aldehyde and

acid samples was one hour. The sampling interval for the VOC samples was varied between 10 and 30 minutes depending upon the expected analyte concentrations. Most VOC samples were collected over 30 minutes.

Air sampling for an experiment was initiated after the device had operated for at least one hour at the established conditions. At this time, it was estimated that near steady state inlet VOC concentrations were achieved as the ventilation rate in the classroom laboratory was approximately 3.9 air changes per hour (h^{-1}), and in the environmental chamber, the ventilation rate was at least 7.8 h^{-1} . The sampling strategy was to first initiate the simultaneous collection of six VOC samples and six aldehyde samples. After the completion of aldehyde sampling, the simultaneous collection of six acid samples and a backup set of six VOC samples was initiated. Thus, the entire collection period extended over approximately two hours.

Air samples for the analysis 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). The sampling media for carboxylic acid samples were silica gel tubes treated with sodium hydroxide (P/N 22655, SKC-West, Inc., Fullerton, CA).

Chemical Analyses

VOC samples were analyzed by thermal desorption gas chromatography with mass selective detection and quantitation (TD-GC/MS) generally following U.S. EPA Method TO-1 (US EPA, 1984). 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.). Tube desorption temperature was 235° C for 6.5 min. The cryogenic trap was held at -100° C and then heated to 235° C for injection. Compounds were resolved on a Hewlett-Packard (HP) Model 6890-II GC with a DB-1701 column (P/N 122-0733, Agilent Technologies) using the following cycle: 1° C for 1.33 min, $5^\circ \text{ C}/\text{min}$ to 225° C and hold for 2 min. Compound mass was quantified with an HP Model 5973 MSD operated in electron ionization mode and scanned over m/z 30 – 350. Samples were analyzed on the day of collection or stored in a freezer for typically no more than one week before analysis. Most 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. A few analytes (related groups hydrocarbons) for which standards could not be obtained were identified using spectral libraries and quantified based on their total-ion-current (TIC) response, using the TIC current response of toluene as the reference. These measurements are less certain than analyses performed using pure compounds as standards.

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 C₁₈, 2.1- by 150-mm column (P/N WAT056975, Waters Corp.). Analytes were quantified from multi-point calibrations of external standard mixtures.

The carboxylic air samples were analyzed for formic and acetic acids by ion chromatography following the method described in the manufacturer's product manual for the analytical column (Dionex, 2002). Each sodium hydroxide coated cartridge was eluted with 18.2 MΩ deionized water into a 2-mL volumetric vial. These extracts were analyzed on a DX-120 ion chromatograph equipped with an AS40 automated sampler (Dionex Corp.). The compounds were resolved on an Ionpac® AS4A-SC analytical column, 4 by 250 mm (P/N 043174, Dionex Corp.) protected by a AG4A-SC guard column (P/N 043175, Dionex Corp.). The eluent was a water solution of 5 mM sodium tetraborate.

Additional Measurements

A recent study reported that hydrogen peroxide (H₂O₂) was generated by an experimental titania photocatalytic device (Kubo and Tatsuma, 2004). Thus, H₂O₂ in the exhaust of the study device was measured. The most sensitive analytical method involving chemical derivatization and analysis by HPLC with a fluorescence detector can achieve a detection limit of 1 ppb, or less. However, implementation of this method is difficult and was outside of the scope of the study. Instead, an instrument designed and used for industrial hygiene applications was selected. This instrument, the CMS Analyzer (P/N 6405300, Draeger Safety, Inc., Pittsburgh, PA), when equipped with a H₂O₂ specific chip (P/N 64006440, Draeger Safety, Inc.) achieves a sensitivity

of 0.2 ppm. Measurements were obtained by placing the CMS Analyzer with the H₂O₂ chip directly in the exhaust duct downstream of the UVPCO while the device was operating in the classroom laboratory at both 170 and 580 m³/h.

The potential production or destruction of ozone in the UVPCO was measured during one experiment in the classroom laboratory in which the device was operating at 580 m³/h. A calibrated ozone monitor (Model 1003AH, Dasibi Environmental Corp.) was alternately connected upstream and downstream of the reactor section. This instrument has a reported sensitivity of 1 ppb. Data were logged by the APTS.

Study Environments

The experiments with the UVPCO were conducted in two different environments. Experiments with the synthetic office VOC mixture and the cleaning product mixture (described below) were performed in relocatable school classroom sited at the LBNL campus and used as a laboratory for energy studies. This classroom laboratory was a doublewide manufactured structure with approximate interior dimensions of 23 by 39 ft (7 by 12 m) with an 8.5-ft (2.6-m) ceiling height. There were two exterior doors and no windows. The interior was bare with no partitions or built-in cabinetry. The floor was carpeted, the walls were vinyl-covered fiberboard, and the ceiling was coated fiberglass acoustical panels. At the time of the experiments, the classroom contained tables, and some instrumentation and supplies used for other studies. The building was equipped with a packaged compressor-based HVAC system mounted on one exterior wall. For the experiments, the outside air (OA) dampers were fixed in the fully open position and the supply fan was operated continuously to deliver approximately 500 cfm (850 m³/h) of OA. The temperature of the classroom was regulated to near 23 ± 2° C. Humidity was unregulated. Room temperature and humidity were recorded by the APTS. The UVPCO was sited directly in the space near one exterior doorway. The exhaust duct from the UVPCO was exited through a hole in a plywood panel fit to the doorway. The other door remained closed during an experiment.

The experiments with the building product mixture and the aldehyde mixture were conducted in a small laboratory containing a 20-m³ interior volume environmental chamber. The UVPCO was positioned outside the chamber. The chamber is constructed of low emitting materials and is lined with stainless steel. For these experiments, the air handling system

supplying conditioned air to the chamber was disconnected and the exhaust was sealed. The 20-cm diameter inlet tubing for the UVPCO was run through the 30-cm diameter inlet opening to approximately the center of the chamber near the ceiling. With the UVPCO duct blower operating, supply air for the chamber was, thus, drawn from the laboratory through the unsealed portion of this opening. Exhaust air from the UVPCO was directed to outdoors through an opening in the laboratory wall. Ventilation air consisting of 100% OA is supplied to the laboratory at about 1,200 cfm (2,000 m³/h). An electric heater located in the chamber and regulated by a proportional controller maintained the temperature of the chamber near 23 ± 2° C.

Preparation and Introduction of VOC Mixtures

A synthetic mixture of VOCs frequently detected in office buildings was formulated based on data summarized in a review of VOC concentrations measured in North America since 1990 (Hodgson and Levin, 2003a). The 27 compounds selected for the mixture represent broad ranges of functionality and vapor pressure. The components of the mixture are listed in Table 1. In this table and in subsequent tables, target compounds are ordered by chemical class with oxygenated compounds listed at the top; and within each class, the compounds are listed in order of decreasing volatility. In the data tables, some compounds are designated by the abbreviations shown in the second column of the mixture tables (Tables 1 – 3). The relative amounts of the individual compounds in the liquid mixture of office VOCs were based on their maximum reported mixing ratios or molar volume concentrations (parts per billion, ppb) in office buildings (ibid.). Three target levels were established at an approximate ratio of 1:3:10 (i.e., concentrations of the more abundant compounds were designed to be about one-half or one full order of magnitude higher than the concentrations of the least abundant compounds).

The liquid VOC mixture was introduced into the classroom laboratory at a controlled rate using a syringe pump (Model 975, Harvard Apparatus, Southnatic, MA). Either a 5-mL or a 10mL glass syringe was filled with the mixture. The syringe pump injection rate was set to produce the desired concentrations of VOCs in air. The syringe was connected to a tube that delivered the mixture to the surface of a heated glass dish in order to quickly evaporate the mixture. The air above the dish was locally ventilated with an oscillating fan operated on low setting.

The UVPCO duct blower and lamps, which were switched on about one hour before injection of the mixture, were operated for at least one hour after starting the injection and prior to sampling. As previously noted, the classroom laboratory was provided with almost four air changes of OA during this period.

A cleaning product mixture was formulated with three general-purpose cleaners that are widely used by residential consumers and are likely to be used for cleaning activities in commercial buildings. These were a pine-oil based cleaner, a cleaner utilizing 2-butoxyethanol as the solvent, and an orange-oil (i.e., d-limonene) based cleaner. The products were combined in a ratio of 2:1:1, respectively. The compounds in the cleaning product mixture selected for quantitative analysis are listed in Table 2. The pine-oil cleaner consists of a complex mixture of terpene hydrocarbons and terpene-derived alcohols and ethers, not all of which were quantified. d-Limonene was present in both the orange oil and pine oil cleaners. 2-Butoxyethanol was present in both the green and orange oil cleaners. The mixture was injected into the classroom laboratory by syringe pump as described above.

A realistic mixture of VOCs emitted by products widely used to finish building interiors was generated by placing a number of these products directly into the 20-m³ chamber. The products consisted of gypsum board panels recently painted on both sides with a flat interior latex paint (10.2 m²), residential rebounded urethane carpet cushion (13.4 m²), three types of residential broadloom carpet (15.5 m² total area), a single hard-backed commercial carpet (3.4 m²), two types of residential sheet vinyl flooring (4.7 m² total area), mixed particle board panels (19 m² all exposed surfaces), a plywood panel (5.9 m² all exposed surfaces), a decorative plywood panel (5.9 m² all exposed surfaces), and a hardboard panel (5.9 m² all exposed surfaces). These products emitted a complex mixture of VOCs. The compounds quantified in the exhaust of the chamber are listed in Table 3. In some cases, compounds were aggregated into related, unspeciated groups (e.g., C₁₁ alkyl substituted benzenes). The concentrations of these groups or mixtures were quantified using the summed total-ion current (TIC) responses of the individual chromatographic peaks calibrated using the TIC response of toluene as the standard. The combined masses of the listed compounds are estimated to account for 75 – 90% of the total mass of compounds emitted by the products. The chamber was continuously ventilated at a flow rate of about 175 m³ or higher while the products were in the chamber.

The fourth mixture consisted of an aqueous solution of formaldehyde and acetaldehyde. A preservative-free formalin solution was prepared by refluxing approximately 1 g of paraformaldehyde (CAS # 30525-89-4) in 200 mL water for 1 hour. The concentration of formaldehyde in the solution was determined by spiking 1 μ L of the resulting solution onto an aldehyde air sampling cartridge and analyzing it as described above. The measured concentration was 3.6 mg/mL. A 10-mL aliquot of this formalin solution was spiked with a measured micro-liter volume of pure acetaldehyde to produce a mixture of the two compounds. The mixture was injected into the 20-m³ chamber by syringe pump as described above.

Experimental Matrix

Eleven experiments were conducted using the four different mixtures of compounds (Table 4). Experiments 1 through 7 with the office and cleaning product mixtures were conducted in the classroom laboratory. The remaining experiments with the building product and aldehyde mixtures were conducted in the 20-m³ chamber. Average device air flow rate, inlet gas temperature, and inlet relative humidity were calculated from data recorded at 30-second intervals for three periods respectively corresponding to the collection of VOC, aldehyde and carboxylic acid samples. The relative standard deviation of the flow rate measurements consistently was less than 2%. The relative standard deviations for the temperature and humidity measurements consistently were less than 0.5%. Temperatures in the study spaces were regulated. These temperatures typically were near 23° C and within the range of 19.5 to 24° C. Humidities were unregulated and fell within the range of 42 to 65% RH.

Data Analysis

For each VOC, average concentrations in μ g/m³ were calculated from the individual sample masses and the respective sample volumes for all replicates (n = 3) collected at the upstream and downstream locations. These were converted to molar volume concentrations in ppb (i.e., mixing ratios) assuming standard conditions of 25 °C 101.3 kPa (i.e., the calibration conditions for the sampling MFCs). Single-pass conversion efficiency, which represents the fraction of a compound removed from the air stream flowing through the reactor (i.e., the fraction reacted), was calculated for each analyte. This value was determined as one minus the quotient of the average outlet concentration and the average inlet concentration. For reaction

products, the fraction of compound produced was similarly calculated. The standard deviations of all calculated quantities were determined by error propagation.

The reaction rate of a compound was calculated by first converting the concentration of the compound to units of $\mu\text{moles}/\text{m}^3$ by multiplying the ppb concentration by the standard molar volume (i.e., 24.45 L). This value was then multiplied by the air flow rate through the reactor in m^3/h to yield a rate in μmoles compound per hour. Reaction rates in μmoles carbon per hour were calculated by multiplying the compound reaction rates by the number of carbon atoms in the individual compounds. This quantity allows direct comparison among compounds on a standard per carbon basis.

A clean air delivery rate (CADR) in m^3/h was computed from the single-pass conversion efficiency as the fraction of a compound reacted times the air flow rate through the device in m^3/h .

RESULTS

Synthetic Office VOC Mixture

Experiments 1, 5, 6 and 7 were conducted with the synthetic office VOC mixture. The concentration of the mixture and the air flow rate through the UVPCO reactor were varied across these four experiments. The inlet VOC mixing ratio, or concentration, in ppb and the fraction of each compound reacted are shown for these experiments in Table 5. Each value is the mean plus or minus one standard deviation of the measurement. The fraction reacted is not shown if the downstream measurement was not significantly lower than the upstream measurement at the 95% confidence level as determined by a one-tailed Student's t test. The corresponding average reaction rates in μmole VOC per hour and μmole of carbon per hour are shown in Table 6. Area-specific reaction rates for comparison with literature values can be obtained by dividing the values in Table 6 by the combined monolith face area of $1,860 \text{ cm}^2$.

The summed inlet air concentrations of the 27 compounds were 100 ppb for Experiment 7, 250 ppb for Experiment 6, 350 ppb for Experiment 5, and 780 ppb for Experiment 1. The respective supply rates of total compounds to the reactor were 2,400, 6,000, 2,400, and 5,300 μmoles per hour.

Conversion efficiencies as shown by the fractions of compounds reacted were almost consistently higher at the low flow rate (Experiments 1 and 5) relative to the efficiencies at the high flow rate (Experiments 6 and 7). This is expected due to the longer residence time of the compounds within the reactor at about 170 m³/h versus 580 m³/h. Calculated clean air delivery rates (CADRs) for each compound by experiment are presented in Figure 1. The effects of the parameters of concentration and air flow rate on the efficiency of the reactions for the individual compounds are generally apparent. Experiments 1 and 5 conducted at the low flow rate resulted in very similar CADRs for most compounds, despite the two- to three-fold differences in inlet VOC concentrations between the two experiments. The uncertainties in these low flow rate measurements, as shown by the error bars representing two standard deviations of the measurement, generally were low. Experiments 6 and 7 conducted at the high flow rate produced similar CADRs for a number of compounds, again with two- to three-fold differences in inlet VOC concentrations between the two experiments. Some compounds had notably higher average efficiencies in Experiment 7 with the lower inlet VOC concentrations. In particular, the conversion efficiencies of ethanol, MTBE, isopropanol, 2-butanone, and carbon disulfide were higher than expected. However, the uncertainties of these measurements, as shown by the error bars, were high indicating that a number of the differences were not significant. Overall, these results show that the fraction of an inlet VOC that reacts (i.e., pollutant removal efficiency of the UVPCO) decreases approximately in direct proportion to increasing air flow rate and is less affected by the inlet VOC concentration. In consequence, the VOC reaction rate (i.e., destruction rate) is relatively unaffected by air flow rate and increases with inlet VOC concentration. As will be shown, this same general pattern is evident from results of the tests with the cleaning product mixture, but is less evident from results of tests with pollutants from a mixture of building materials.

The experiments with the synthetic office VOC mixture resulted in the net production of formaldehyde, acetaldehyde, formic acid, and acetic acid, which indicates incomplete decomposition of some of the VOCs in the inlet air stream. Additionally, there was no significant reduction in the acetone concentration in three experiments suggesting that acetone was another reaction product.

For Experiments 5 – 7, the formaldehyde concentration in the inlet air was about 3 ppb. In Experiment 1, the inlet formaldehyde concentration was about 11 ppb. The inlet acetaldehyde

concentrations ranged between 1.4 and about 4 ppb. The outlet concentrations of formaldehyde and acetaldehyde and the fractions of these compounds produced are shown in Table 7.

Formaldehyde was 7 – 10 ppb in the high flow rate Experiments 6 and 7. At the low flow rate, formaldehyde was 53 ppb with high VOC concentrations (Experiment 1) and 25 ppb with lower VOC concentrations (Experiment 5). The outlet concentrations of acetaldehyde ranged from 4 to 32 ppb and followed the same trend as observed for formaldehyde. The production rates of formaldehyde and acetaldehyde in μ mole compound and μ mole carbon per hour are shown in Table 8. The formaldehyde production rates appear to be related directly to the inlet VOC concentration.

The inlet formic acid concentrations were about 3 – 4 ppb in Experiments 5 – 7 and 9 ppb in Experiment 1. The inlet acetic acid concentration was with in the range of 5 to 8 ppb in Experiments 5 – 7. It was notably higher at 46 ppb in Experiment 1. The source of this discrepancy is unknown; however, the relative sizes of the acetic acid peaks in the GC/MS chromatograms confirm the result. The outlet concentrations of formic and acetic acids and the fractions of these compounds produced are shown in Table 7. A substantial amount of formic acid was produced in Experiment 1. The production rates of formic and acetic acid in μ mole compound and μ mole carbon per hour are shown in Table 8. The production rates of both compounds in Experiment 1 were approximately five times the values for Experiment 5 conducted at the same flow rate but with lower inlet VOC concentrations.

The TIC chromatograms of upstream and downstream VOC samples were compared in order to determine if intermediate reaction products within the volatile range were present downstream. Upstream and downstream chromatograms from Experiment 5 conducted at the low flow rate are shown in Figure 2. With the exception of acetic acid determined by separate analysis, no reaction products within the range of the VOC analysis were identified.

Cleaning Product Mixture

Experiments 2 – 4 were conducted with the cleaning product mixture. The concentration of the mixture and the air flow rate through the reactor were varied across these three experiments. The average inlet concentrations and the average fraction of each compound reacted are shown in Table 9. The corresponding average reaction rates in μ moles compound and μ moles carbon per hour are shown in Table 10. The summed inlet air concentrations of the target VOCs were

155 ppb for Experiment 3, 176 ppb for Experiment 4, and 54 ppb for Experiment 2. The supply rates of target compounds to the reactor were 3,700, 1,200, and 360 μ moles per hour, respectively.

Conversion efficiencies as shown by the fraction of compounds reacted were consistently higher at about 166 m^3/h relative to efficiencies at 580 m^3/h . CADRs for each target compound by experiment are shown in Figure 3. Experiments 2 and 4 conducted at the low flow rate resulted in nearly equivalent CADRs for all compounds, except for isopropanol with a non-significant upstream-downstream difference in Experiment 2. CADRs were higher in Experiment 3 conducted at the higher flow rate; but for a number of the target compounds, the improvements were small relative to the low flow rate experiments. Uncertainties in the measurements, as shown by the error bars representing two standard deviations of the mean, generally were low with the notable exceptions of the uncertainties for isopropanol, terpinolene, and γ -terpineol.

In these experiments, there also was net production of formaldehyde, acetaldehyde, and acetone presumably due to incomplete decomposition of some compounds in the inlet air stream. Data for formic and acetic acids are not available for these experiments due to problems encountered in the analysis of the samples. The formaldehyde inlet concentrations ranged between 4.5 and 10 ppb, and the acetaldehyde inlet concentration ranged between 1.8 and 3.5 ppb. The outlet concentrations of formaldehyde and acetaldehyde and the fractions of these compounds produced are shown in Table 11. Formaldehyde outlet concentrations ranged from about 17 to 27 ppb. Acetaldehyde outlet concentrations were low and within a range of about 5 to 6 ppb. Acetone outlet concentrations ranged from 23 to 44 ppb. For both formaldehyde and acetone, the highest outlet concentrations occurred in Experiment 4 conducted at low flow rate with higher VOC concentrations. The production rates of the three compounds in μ mole compound and μ mole carbon are shown in Table 12.

Upstream and downstream chromatograms from Experiment 4 are shown in Figure 4. An analysis of upstream and downstream VOC samples from these three experiments indicated that acetic acid, small amounts of butyl formate (CAS # 592-84-7), and two C₈ aliphatic alcohols (tentative identification) were formed.

Building Product Mixture

Experiments 13 and 14 were conducted with the building product mixture. The reactor was operated at air flow rates of 174 and 298 m³/h, respectively. Although VOC concentrations were anticipated to be about 40% lower in Experiment 14 due to the higher ventilation rate of the chamber, the inlet concentrations of the target VOCs for the two experiments were similar (Table 13). This might be explained by higher effective VOC emission rates at the higher ventilation rate due to the re-emission of sorbed mass on a short time scale, as only 3.5 hours elapsed between the change to the higher air flow rate and the initiation of sampling for Experiment 14.

The fractions of compounds reacted were generally indistinguishable between Experiments 13 and 14 as shown in Table 13. This was unanticipated as the previous experiments exhibited a reduction in compound conversion efficiencies when using a higher flow rate, consistent with the lower residence times of the compounds within the reactor. A possible contributing factor is the 1.2 – 1.4 °C lower temperature and the higher relative and absolute humidity during Experiment 13. The corresponding reaction rates in µmoles compound and µmoles carbon per hour are shown in Table 14. The summed inlet air concentrations of the target VOCs were 327 ppb for Experiment 14, and 246 ppb for Experiment 13. A substantial portion of this difference was due to the higher concentration of ethylene glycol in Experiment 14. However, it is notable that the analysis of ethylene glycol in Experiment 13 was highly uncertain. The respective supply rates of VOCs to the reactor were 4,000 and 1,750 µmoles per hour. CADRs for each target compound by experiment are shown in Figure 5. Experiment 14 conducted at the higher flow rate resulted in higher CADRs for all compounds. However, the differences for most compounds were probably insignificant due to the relatively high uncertainties of the measurements as shown by the error bars representing two standard deviations.

Net production of formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid was observed in these two experiments. It is noted that some carry over of the acids between experiments is possible due to relatively low vapor pressure of these compounds. The inlet concentrations of formaldehyde, acetaldehyde, formic acid, and acetic acid were similar between Experiments 13 and 14, at 26 – 27 ppb, 4 ppb, 8 – 9 ppb, and 35 – 36 ppb, respectively. The outlet concentrations of product compounds were also similar between the two experiments as shown in Table 15, with somewhat lower concentrations of formaldehyde, acetaldehyde, and

acetone in Experiment 14 conducted at the higher flow rate. The production rates of the five compounds in μ mole compound and μ mole carbon per hour are shown in Table 16. With the exception of acetic acid, the rates of reaction product formation in the two experiments were similar.

Upstream and downstream chromatograms from Experiment 13 are shown in Figure 6. An analysis of upstream and downstream VOC samples from these two experiments indicated that acetone, formic acid, and acetic acid were produced from incomplete decomposition of VOCs. This observation is consistent with the data presented in Table 15.

Formaldehyde and Acetaldehyde Mixture

Experiments 23 and 24 were conducted with a mixture of formaldehyde and acetaldehyde volatilized into the chamber. An attempt was made to produce concentrations similar to those measured upstream in Experiments 13 and 14. Close correspondence was achieved between the concentrations for Experiments 24 and 14 conducted at the higher flow rate, while concentrations in Experiment 23 were somewhat higher than those in Experiment 13. As for the experiments with the building product mixture, ventilation air for the chamber was drawn from the laboratory. An analysis of VOCs upstream and downstream of the reactor in Experiments 23 and 24 showed that the inlet air contained a number of VOCs at low concentrations. The upstream and downstream concentrations of total VOCs quantified from the summed total-ion current (TIC) responses of the individual chromatographic peaks with toluene as the standard were 120 and 70 $\mu\text{g}/\text{m}^3$, respectively, for Experiment 23 and 90 and 60 $\mu\text{g}/\text{m}^3$, respectively, for Experiment 24. These values are roughly equivalent to outdoor air concentrations. Thus, the small reaction of these background compounds may have resulted in some undetermined production of formaldehyde and acetaldehyde. Formic acid was formed in Experiment 23 at 26 μ moles per hour. No significant production of acetic acid was observed. The results in Table 17 indicate a net conversion (i.e., destruction) of formaldehyde and acetaldehyde with higher fractions reacted at the lower flow rate as anticipated. The conversion rates of formaldehyde were 111 and 78 μ moles per hour at 167 and 280 m^3/h , respectively (Table 18). These compare to net production rates of 159 and 220 in corresponding Experiments 13 and 14 (Table 16).

Relative Conversion Efficiencies

The data from the 11 experiments were aggregated to evaluate the relative conversion efficiencies of all study compounds. Since conversion efficiencies generally were related to the device air flow rate, the low flow rate experiments (165 – 298 m³/h), which exhibited the highest efficiencies, were selected for this analysis. First, the VOC conversion efficiency data were averaged for the low flow rate experiments with each mixture. Experiments 1 and 5 were utilized for the synthetic office VOC mixture; Experiments 2 and 4 were utilized for the cleaning product mixture; and Experiments 13 and 14 were utilized for the building product mixture. These averages were then combined into a single list. In total, data were generated for 48 individual or closely related groups of VOCs, seven of which appeared in two mixtures. The compounds are listed in descending conversion efficiency order in Table 19. Acetone and dichloromethane, which did not react, are not listed. The uncertainties of the measurements are not indicated, so the precise order of the compounds is not highly relevant. In addition, the rankings of some of the VOCs that appeared in two mixtures are divergent. Hexanal had the most extreme difference with an indicated efficiency in the office VOC mixture of 65% versus 19% in the building product mixture. Other compounds (1,2,4-trimethylbenzene, phenol n-dodecane, and n-undecane) also exhibited a trend of higher conversion efficiency in the office VOC mixture versus the building product mixture. Notably, the inlet concentrations of hexanal, 1,2,4-TMB, and n-undecane in the building product mixture were all less than 1 ppb.

Despite the limitations of the analysis, some general trends are apparent. Alcohols and glycol ethers were the most efficiently converted chemical classes. At the top of the list were two terpene alcohols that contain unsaturated carbon–carbon bonds in addition to the alcohol functional group. Terpene hydrocarbons and ketones also had relatively high conversion efficiencies. At the other end of the spectrum, alkane hydrocarbons and many halogenated aliphatic hydrocarbons had relatively low conversion efficiencies. Aromatic hydrocarbons had intermediate values.

Pressure Drop and Additional Measurements

Duct pressure relative to the room was monitored upstream and downstream of the UVPCO reactor section during all experiments. Pressure drop across the reactor section was determined as the difference between the upstream and downstream measurements. In all

experiments conducted between 165 and 172 m³/h, the average pressure drop was 7 Pa. The pressure drop in Experiment 24 at 278 m³/h was 13 Pa, and the pressure drop in Experiment 14 at 298 m³/h was 16 Pa. In experiments conducted at near 580 m³/h, the pressure drop ranged between 33 and 35 Pa. Pressure drop (P) is plotted versus air velocity through the reactor in Figure 7. The data are best modeled by a power law function with an exponent of 1.3. This indicates that the flow characteristics of the system are closer to laminar flow than to turbulent flow, i.e., most of the pressure drop occurs in the small channels of the honeycomb reactor passages where the flow is likely to be laminar.

Measurements made with the UVPCO operating at 170 and 580 m³/h in the classroom laboratory without injection of VOCs did not detect hydrogen peroxide in the exhaust of the device above the 0.2 ppm sensitivity limit of the CMS Analyzer. Ozone was alternately monitored upstream and downstream of the reactor section in Experiment 6 with the UVPCO operating at 580 m³/h with the office VOC mixture. The upstream ozone concentration was 9 ± 1 ppb, and the downstream concentration was 6 ± 1 ppb indicating some ozone destruction in the UVPCO.

DISCUSSION

Relative VOC Conversion Efficiencies and Reaction Rates

The current study has addressed several key recommendations made by Tompkins et al. (2005a) at the conclusion of their evaluation of photocatalysis for gas-phase air cleaning. Specifically, they recommended that research be conducted to investigate: a) low-level concentrations of VOCs that are representative of indoor environments; b) the use of UVPCO in airstreams with typical mixtures of pollutants; and c) the potential formation of reaction by-products.

Our selection of the study compounds was based upon knowledge of VOCs frequently encountered in indoor air. These VOCs included compounds commonly present in North American office buildings, compounds used in the formulation of dominant consumer cleaning products, and compounds emitted by major indoor finish materials, including painted wallboard, composite wood products, resilient flooring, and carpet systems. The mixtures were comprised so that the individual VOCs were present at realistic relative abundances. The concentrations

used in the experiments also were selected to be representative of the concentrations encountered in office buildings and residences. As a result, the inlet concentrations of individual VOCs in many cases were less than 10 ppb, and in some cases the concentrations were less than 1 ppb. In total, conversion efficiency and rate coefficient data were generated under typical indoor conditions for 48 individual or closely related groups of VOCs spanning broad ranges of vapor pressure and chemical functionality.

Almost all of the previously reported experiments with UVPCO have utilized VOC concentrations in the part-per-million (ppm) range, with the lowest data points typically ending near 1 or 0.1 ppm. Much of the previous work also has focused on simple systems involving one or only several reactants. For the purpose of predicting the results for multi-component systems, Obee and Hay (1999) extended the theory of UVPCO by estimating photocatalytic rate constants based on molecular structure. They reported results for a series of experiments in which reaction rates were determined as a function of concentration for a group of four carbon chain molecules with different chemical functionality. Their study compounds were 1-butanol, an alcohol; 2-butanone, a ketone; 1-butene, an alkene hydrocarbon; and n-butane, an alkane hydrocarbon. UV intensity, water vapor concentration and oxygen concentration were held constant. The oxidation rates occurred in this order: 1-butanol > 2-butanone > 1-butene > n-butane. The order followed the strength of the expected type of attractive force between a compound and the hydrated titania surface, which was hydrogen bonding for 1-butanol, dipole-dipole interaction for 2-butanone, weak dipole-dipole interaction for 1-butene, and weak dispersive forces for n-butane. Obee and Hay (*ibid.*) also measured the reaction rates of a series of three normal alkane hydrocarbons consisting of n-butane, n-hexane, n-decane. These results showed that within a type of surface interaction energy, the oxidation rate increased with increasing molecular weight.

Our results obtained at low ppb concentrations generally support the theory regarding the relative reaction rates of different chemical classes. The oxidation rates of the represented chemical classes of compounds followed the approximate order: alcohols and glycol ethers > aldehydes, ketones, and terpene hydrocarbons > aromatic and alkane hydrocarbons > halogenated aliphatic hydrocarbons. A relationship between molecular weight and oxidation rate was less apparent in our data.

Sattler and Liljestrand (2003) attempted to correlate photocatalytic oxidation rate constants with other physical-chemical characteristics of the reactants. Although the applicability of their results to indoor air is questionable due to the near 100% relative humidity conditions, they found that the oxidation rate constants for alkene and alkane hydrocarbons varied directly with the gas-phase ionization potential (IP) and with the gas-phase hydroxyl radical reaction rate constant (k_{OH}). That is, the oxidation rate constants decreased with increasing IP and increased with increasing k_{OH} so that the highest molecular weight compounds in a series had the highest rate constants. For alcohols, the relationships were reversed with the lower molecular weight compounds having the highest oxidation rates. The authors speculated that this unexpected result was due to the high humidity level. As noted, relationships between molecular weight or correlated characteristics and oxidation rate were not easily discernable from our data.

The relative conversion rates of the various chemical classes within the UVPCO generally are favorable with respect to the use of the device for the treatment of indoor air in office buildings, schools, and residences. In a review of VOC concentrations measured in North American buildings since 1990, Hodgson and Levin (2003a) showed that the concentrations of chlorinated solvents such as 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene in residences have decreased relative to measurements made in the previous decade. This change likely was due to the phasing out of the use of these chemicals in products in response to the manufacturing regulations in the U.S. 1990 Clean Air Act Amendments. As a result, VOC measurements made in recent years in houses, schools, and office buildings rarely show these chemicals above low background levels (Hodgson et al., 2000, 2003, and 2004). Indoor air concentrations of aromatic hydrocarbon solvents likely are decreasing for the same reason. Contemporary products often use alcohols, glycol ethers, and terpene hydrocarbons as substitute solvents (Nazaroff and Weschler, 2004). Some of these oxygenated solvents that can occur at relatively high indoor concentrations have relatively low odor thresholds or chronic toxicity exposure guideline concentrations (Hodgson and Levin, 2003b). As a result, the high conversion efficiencies observed for alcohols, glycol ethers, and other oxygenated chemicals are well matched to the composition of chemicals of concern in indoor air. Conversely, the relatively poor performance observed for halogenated hydrocarbons is not viewed as a serious detriment.

UVPCO is being evaluated, in part, for its potential to enable a reduction in rates of outdoor air supply, with associated energy savings. In buildings such as offices, the sources of

inorganic pollutants are usually small, thus, a combination of efficient particle filtration and effective air cleaning for VOCs could substitute for a portion of OA supply. In a typical U.S. office building when minimum OA is being supplied, the supply air stream is often approximately 25% OA and 75% recirculated air. Consequently, from a mass balance calculation, we can show that a UVPCO system with a 33% destruction efficiency for an indoor-generated VOC in the recirculated air would provide as much VOC removal as the total OA supply. If the rate of OA supply were halved in the interest of energy savings, the UVPCO system would need a 14.3% destruction efficiency to prevent an increase in the indoor concentration of an indoor generated VOC. For the prototype UVPCO device evaluated here, the conversion efficiencies of the compounds listed in Table 19 all exceed 19%, and the conversion efficiencies for many compounds of concern are well above 19%. An examination of Tables 5, 9, and 13 indicates that conversion efficiencies for compounds with significantly lower downstream concentrations remained above, and generally substantially above, 16% with a single exception.

In the experiments conducted at the high air flow rates (approximately 580 m³/h), the face velocity through the catalyst coated monoliths was 1.8 m/s. This face velocity was selected to match the typical velocity expected in commercial HVAC applications, assuming that the velocity through the UVPCO device will correspond to the typical value for particle filters installed in these systems (i.e., 1.3 – 2.6 m/s). Thus, for most VOCs that are consumed, a UVPCO device with the same characteristics as the prototype unit has sufficient conversion efficiencies to compensate for at least a 50% reduction in OA supply.

Reaction Products

The production of gas-phase reaction products in UVPCOs has been sporadically evaluated. Tompkins et al. (2005a) reviewed photocatalytic oxidation studies of 43 organic chemicals. In some of these studies, they noted the production of reaction products or intermediates, including formaldehyde, acetaldehyde, formic acid, and acetic acid. However, these products apparently were not detected in the gas-phase of these experiments. Tompkins et al. (ibid.) also reviewed the formation of phosgene from the photocatalytic oxidation of trichloroethene. This issue was studied in detail by Jacoby et al. (1994). These researchers used a gas-phase Fourier transform infrared spectrometer to identify and quantify intermediates and

products and to provide carbon and chlorine mass balances for experiments with a small titania photocatalytic reactor. Dichloroacetyl chloride, phosgene, and hydrogen chloride were observed in the effluent stream. Alberici et al. (1998) utilized on-line mass spectrometry to identify gas-phase by products of the oxidation of trichloroethene, tetrachloroethene, choroform and dichloromethane. Phosgene, dichloroacetyl chloride, and trichloroacetyl chloride were detected as by-products in some of these experiments. Although the current study could not directly address this issue, the low indoor concentrations of trichloroethene and other chlorinated solvents in many indoor situations combined with their low oxidation rates generally suggests that phosgene production may not be a concern in indoor air applications of UVPCO.

Chen et al. (2005) identified acetic acid as an oxidation byproduct when a UVPCO was operated with a challenge mixture of 17 VOCs. Recently, Disdier et al. (2005) reported the results of experiments in which a UVPCO was operated in an ordinary indoor room over two-hour periods. They showed small increases in the concentrations of formaldehyde, acetaldehyde, and acetone due to the operation of the device with the lamps on versus with the lamps switched off. Also recently, Ginestet et al. (2005) evaluated various UVPCO configurations for potential 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.

The current study has generated substantially more data on the production of gas-phase byproducts when a UVPCO is operated with indoor relevant mixtures of VOCs at realistic indoor concentrations. Formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid were demonstrated to be produced in these experiments. No other significant byproducts were identified by the sampling and analytical methods employed in the study. Formaldehyde and acetaldehyde, and possibly the other byproducts, also were converted within the device. When formaldehyde and acetaldehyde were introduced in combination with only low-level concentrations of VOCs typical of outdoor air, they reacted at rates approaching 50% conversion efficiency at the low flow rate. Thus, the formaldehyde and acetaldehyde production rates observed in the other experiments are net values reflecting significant reaction within the device. The net formaldehyde production rates ranged between 60 and 290 μ moles per hour (median = 167 μ moles/h, n = 9). Relationships were examined between formaldehyde production and VOC

inlet concentrations in the nine experiments with the VOC mixtures. An approximate linear relationship was observed between the formaldehyde net production rate in μ moles per hour and the supply rate of total alcohols and glycol ethers in μ moles per hour as shown in Figure 8. Relationships between formaldehyde net production and supply rates of total summed VOCs or narrower categories of VOCs were less apparent. The observed relationship may evolve from the generally high reactivity of alcohols and glycol ethers relative to other VOCs. Other explanations related to surface interactions of compounds with an –OH group, may apply. Net acetaldehyde production rates ranged between 9 and 189 μ moles per hour (median = 69, n = 9) with inlet concentrations between 1.4 and 8.7 ppb. There was no apparent relationship between net acetaldehyde production and supply rates of total alcohols and glycol ethers. There was, however, an apparent linear relationship between net acetaldehyde production and the supply rates of total C₂ – C₃ alcohols and glycol ethers in seven of the nine experiments as shown in Figure 9; but, the values for Experiments 1 and 14 were strong outliers. Acetone production rates were higher than net production rates of formaldehyde and acetaldehyde.

Formaldehyde and acetaldehyde are recognized as important indoor air toxicants. They are categorized as carcinogens on the State of California Clean Water and Drinking Act of 1986 list of toxicants (OEHHA, 2005a). Recently, the International Agency for Research on Cancer has classified formaldehyde as a human carcinogen (IARC, 2004). The California Office of Environmental Health Hazard Assessment (OEHHA) has developed acute and chronic exposure guidelines for formaldehyde exposure among the general population including sensitive individuals. The one-hour acute Reference Exposure Level (REL) is 74 ppb (OEHHA, 2005b). The long-term (i.e., 10 years or more) chronic REL is 2.4 ppb (*ibid.*). The California Air Resources Board's recommended guideline for formaldehyde concentrations in occupied buildings is 27 ppb, a value derived from the acute REL assuming an eight-hour exposure period (CARB, 2004). The NIOSH guideline for formaldehyde in work environments including office buildings is 16 ppb (NIOSH, 2004). The OEHHA chronic REL for acetaldehyde is 5 ppb (OEHHA, 2005b). These governmental agency guidelines suggest that indoor concentrations of formaldehyde and acetaldehyde should be maintained at very low levels.

The other reaction products are of lesser concern. However, acetic acid has a low odor threshold. The 100% odor threshold detection level is 10 ppb (Cometto-Muñiz, 2001). The

formic acid odor threshold is several orders of magnitude higher (*ibid.*). There are no particular comfort or health concerns regarding acetone at indoor relevant concentrations below 1 ppm.

Estimating the Impact of UVPCO on Aldehyde Concentrations

Since a UVPCO device may exhibit a net production of formaldehyde and acetaldehyde as the result of incomplete decomposition of the reactants, the concentrations of these compounds in an office building utilizing a UVPCO on the supply air stream may be increased. The central question then is: “what is the magnitude of this potential increase?” From this study, we’ve generated information on the net production of these contaminants as functions of the VOC supply rate to a prototype reactor and on the decomposition rates of the contaminants under conditions with very low inlet VOC concentrations. We’ve also measured conversion efficiencies for a range of VOCs commonly found in indoor air in office buildings. In general, the results obtained with the studied UVPCO indicate that net production of formaldehyde and acetaldehyde may be low relative to the supply of reactants (Figures 8 and 9). The destruction rate of these two compounds also may be relatively low, particularly at higher air flow rates (Table 17). On the other hand, the conversion efficiencies of the most reactive alcohols and glycols ethers that may serve as sources of these compounds are higher, often approaching or exceeding 40% at a flow rate of 580 m³/h with this device (Tables 5 and 9).

Often, the OA supply rate in an office building is equivalent to one air change per hour (1 h⁻¹) and the recirculation rate is three times this value (3 h⁻¹). A UVPCO installation in an office building likely would position the device in the supply air stream so that a combination of outdoor and recirculated air are photocatalytically treated. To achieve energy savings, the OA supply rate would be cut by 50% and the recirculation rate would remain the same at 3 h⁻¹, or six times the OA supply in this case. Under this scenario, the indoor air concentrations of reactants would decrease over time due to the relatively high efficiency of the UVPCO for these compounds. This decrease likely would lower the net rate of formaldehyde and acetaldehyde production. Thus, the resulting impact of the UVPCO on the formaldehyde and acetaldehyde concentrations in the building would be less than if the reactants remained at higher concentration.

In Appendix B, we present a model with coupled steady-state, mass balance equations that accounts for ventilation and UVPCO as removal and generation sources for formaldehyde and

acetaldehyde and for ventilation and UVPCO as removal processes for reactants that lead to formaldehyde and acetaldehyde production. This model is applied to two building scenarios using geometric mean VOC concentration data from a call center (Hodgson et al, 2003). The first scenario is for a building without UVPCO. The second scenario is for the same building with a UVPCO functioning the same as the prototype unit and a 50% reduction in OA supply as described above. Under these assumptions, the model estimates an approximate three-fold increase in the formaldehyde and acetaldehyde concentrations for the UVPCO treated case versus untreated case.

However, a wide range of outcomes is possible since building parameters can vary substantially, the UVPCO performance parameters are subject to considerable uncertainty, and a future commercialized UVPCO may perform differently.

RECOMMENDATIONS

The VOC conversion efficiencies achieved with the prototype device studied here suggest that a UVPCO air cleaner for gaseous contaminants may be beneficial for the large-scale treatment of air in occupied buildings and may ultimately allow for a 50% reduction of OA supply in offices and other buildings as an energy conservation measure. However, several issues remain to be investigated and addressed before proceeding with a plan for commercialization of a UVPCO device for indoor air applications. The following recommendations provide an outline for near-term research in support of this development.

- Further evaluate and model the likely effects of the prototype UVPCO on indoor air concentrations of formaldehyde and acetaldehyde for various scenarios simulating how such a device might be installed in a building's supply air stream. Consider non-steady state conditions such as morning HVAC startup and the response of the device to episodic use of cleaning solutions and other products that employ alcohols and glycol ethers as solvents. Evaluate the actual performance of the UVPCO under controlled conditions with recirculated air in a large-scale environmental chamber and compare the results to model predictions. Develop and evaluate various options for reducing the impact of a UVPCO device on indoor air concentrations of formaldehyde and acetaldehyde if these studies suggest potential adverse affects.

- Operate the prototype UVPCO in several types of buildings such as offices, retail stores, and schools with different sources and concentrations of VOCs. Some of these study environments should have relatively high concentrations of VOCs including formaldehyde, acetaldehyde and alcohols. Configure the installation of the device so the treated air exhausts directly to outdoors without any circulation. Measure single-pass conversion efficiencies and the production of reaction byproducts at building relevant device flow rates. Compare these results to the laboratory generated data.
- Operate the prototype UVPCO over extended periods of at least several months in a laboratory environment or in a building. Determine conversion efficiencies as a function of time and varying air humidity, possibly by periodically introducing a defined challenge mixture of VOCs. Since the long-term performance of UV lamps is well known, the focus should be on establishing the frequency at which the coated monoliths need to be cleaned or replaced. To this end, analyze the monolith surfaces for the accumulation of low volatility reaction byproducts.
- Refine models for estimating the costs of installing and operating a commercial UVPCO device for the treatment of air in office buildings, retail buildings, and schools. Estimate overall energy savings for different scenarios in which UVPCO and advanced particle filtration are substituted for 50% OA supply in these building types.

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Table 1. Components of synthetic office VOC mixture

| Compound | Abbreviation | CAS # | Chemical Class | Formula Weight |
|---------------------------------|--------------|-----------|----------------|----------------|
| Ethanol | | 6417-5 | Alcohol | 46.07 |
| 2-Propanol | Isopropanol | 67-63-0 | Alcohol | 60.10 |
| 1-Butanol | | 71-36-3 | Alcohol | 74.12 |
| 2-Ethyl-1-hexanol | Ethylhexanol | 104-76-7 | Alcohol | 130.23 |
| Phenol | | 108-95-2 | Alcohol | 94.11 |
| 2-Butoxyethanol | 2-BE | 111-76-2 | Glycol ether | 118.18 |
| <i>tert</i> -Butyl methyl ether | MTBE | 1634-04-4 | Ether | 88.15 |
| 2-Propanone | Acetone | 67-64-1 | Ketone | 58.08 |
| 2-Butanone | | 78-93-3 | Ketone | 72.11 |
| 4-Methyl-2-pentanone | MIBK | 108-10-1 | Ketone | 100.16 |
| Hexanal | | 66-25-1 | Aldehyde | 100.16 |
| d-Limonene | Limonene | 5989-27-5 | Terpene HC | 136.24 |
| Toluene | | 108-88-3 | Aromatic HC | 92.14 |
| m-Xylene | | 108-38-3 | Aromatic HC | 106.17 |
| 1,2,4-Trimethylbenzene | 1,2,4-TMB | 95-63-6 | Aromatic HC | 120.20 |
| n-Nonane | | 111-84-2 | Alkane HC | 128.26 |
| n-Decane | | 124-18-5 | Alkane HC | 142.29 |
| n-Undecane | | 1120-21-4 | Alkane HC | 156.31 |
| n-Dodecane | | 112-40-3 | Alkane HC | 170.34 |
| Trichlorofluoromethane | R-11 | 75-69-4 | Halo HC | 137.37 |
| Dichloromethane | DCM | 75-09-2 | Halo HC | 84.93 |
| 1,1,1-Trichloroethane | 1,1,1-TCA | 71-55-6 | Halo HC | 133.41 |
| Trichloroethene | | 79-01-6 | Halo HC | 131.39 |
| Tetrachloroethene | PCE | 127-18-4 | Halo HC | 165.83 |
| 1,2-Dichlorobenzene | 1,2-DCB | 95-50-1 | Halo HC | 147.00 |
| Carbon disulfide | CS2 | 75-15-0 | Sulfide | 76.14 |
| Decamethylcyclopenta-siloxane | D5 | 541-02-6 | Siloxane | 370.78 |

Table 2. Selected major VOC constituents of cleaning product mixture

| Compound | Abbreviation | CAS # | Chemical Class | Formula Weight |
|---------------------|--------------|-----------|----------------|----------------|
| 2-Propanol | Isopropanol | 67-63-0 | Alcohol | 60.10 |
| α -Terpineol | | 98-55-5 | Alcohol | 154.25 |
| γ -Terpineol | | 586-81-2 | Alcohol | 154.25 |
| 2-Butoxyethanol | 2-BE | 111-76-2 | Glycol ether | 118.18 |
| α -Pinene | | 80-56-8 | Terpene HC | 136.24 |
| Camphene | | 79-92-5 | Terpene HC | 136.24 |
| d-Limonene | Limonene | 5989-27-5 | Terpene HC | 136.24 |
| p-Cymene | | 99-87-6 | Terpene HC | 134.22 |
| γ -Terpinene | | 99-85-4 | Terpene HC | 136.24 |
| Terpinolene | | 586-62-9 | Terpene HC | 136.24 |

Table 3. VOCs quantified in air exhaust of 20-m³ chamber loaded with combination of building products

| Compound | Abbreviation | CAS # | Chemical Class | Formula Weight |
|---|--------------|------------|----------------|----------------|
| Phenol | | 108-95-2 | Alcohol | 94.11 |
| Butylated hydroxytoluene | BHT | 128-37-0 | Alcohol | 220.36 |
| Ethylene glycol | | 107-21-1 | Glycol ether | 62.07 |
| 2-(2-Butoxyethoxy) ethanol | DEGBE | 112-34-5 | Glycol ether | 162.23 |
| 2-Propanone | Acetone | 67-64-1 | Ketone | 58.08 |
| Formaldehyde | | 50-00-0 | Aldehyde | 30.03 |
| Acetaldehyde | | 75-07-0 | Aldehyde | 44.05 |
| Hexanal | | 66-25-1 | Aldehyde | 100.16 |
| 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (2 isomers) | TMPD-MIB | 25265-77-4 | Ester | 216.32 |
| 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate | TMPD-DIB | 6846-50-0 | Ester | 286.41 |
| Acetic acid | | 64-197 | Acid | 60.05 |
| Toluene | | 108-88-3 | Aromatic HC | 92.14 |
| 1,2,4-Trimethylbenzene | 1,2,4-TMB | 95-63-6 | Aromatic HC | 120.20 |
| C ₄ Alkylbenzenes* (mixture) | | | Aromatic HC | 134.22 |
| Naphthalene | | 91-20-3 | Aromatic HC | 128.17 |
| C ₁₀ Alkylbenzenes* (mixture) | | | Aromatic HC | 218.38 |
| C ₁₁ Alkylbenzenes* (mixture) | | | Aromatic HC | 232.41 |
| C ₁₂ Alkylbenzenes* (mixture) | | | Aromatic HC | 246.44 |
| C ₁₁ Alkane HCs* (mixture) | | | Alkane HC | 156.31 |
| n-Undecane | | 1120-21-4 | Alkane HC | 156.31 |
| n-Dodecane | | 112-40-3 | Alkane HC | 170.34 |
| n-Tridecane | | 629-50-5 | Alkane HC | 184.37 |
| n-Tetradecane | | 629-59-4 | Alkane HC | 198.40 |

*Quanitified using GC/MS total-ion-current response with toluene as standard

Table 4. Experimental conditions for 11 experiments conducted with UVPCO challenged with four VOC mixtures. Mean values are shown for three time periods corresponding to the collection of VOC, aldehyde, and carboxylic acid samples

| Exp No | Date | Mixture | Flow Rate (m ³ /h) | | | Temperature (°C) | | | Relative Humidity (%) | | |
|--------|---------|------------|-------------------------------|-----|------|------------------|------|------|-----------------------|-----|------|
| | | | VOC | Ald | Acid | VOC | Ald | Acid | VOC | Ald | Acid |
| 1 | 5/25/05 | Office | 165 | 165 | 165 | 23.2 | 22.9 | 22.8 | 58 | 57 | 57 |
| 2 | 5/26/05 | Cleaning | 165 | 166 | 165 | 23.4 | 22.9 | 22.9 | 54 | 56 | 56 |
| 3 | 6/1/05 | Cleaning | 580 | 582 | 581 | 22.8 | 22.8 | 22.9 | 50 | 50 | 48 |
| 4 | 6/3/05 | Cleaning | 167 | 167 | 167 | 23.5 | 23.5 | 23.4 | 50 | 50 | 50 |
| 5 | 6/6/05 | Office | 171 | 171 | 171 | 22.7 | 22.9 | 23.3 | 44 | 42 | 44 |
| 6 | 6/8/05 | Office | 579 | 579 | 580 | 24.0 | 24.0 | 24.0 | 55 | 55 | 56 |
| 7 | 6/10/05 | Office | 581 | 581 | 580 | 23.1 | 23.2 | 23.5 | 57 | 56 | 56 |
| 13 | 7/29/05 | Bldg. Prod | 174 | 173 | 172 | 19.5 | 19.5 | 19.9 | 65 | 65 | 64 |
| 14 | 8/01/05 | Bldg. Prod | 298 | 301 | 298 | 20.7 | 20.9 | 21.7 | 55 | 55 | 53 |
| 23 | 9/02/02 | Aldehydes | 167 | 167 | 166 | 23.8 | 23.7 | 23.8 | 48 | 48 | 48 |
| 24 | 9/06/05 | Aldehydes | 278 | 280 | 279 | 23.3 | 23.4 | 23.8 | 51 | 51 | 49 |

Table 5. Inlet VOC mixing ratios (ppb) and fractions of VOCs reacted (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with three inlet concentrations of synthetic office VOC mixture

| Compound | Exp 7 - Low Conc 581 m ³ /h | | Exp 6 - Mid Conc 579 m ³ /h | | Exp 5 - Mid Conc 171 m ³ /h | | Exp 1 - High Conc 165 m ³ /h | |
|--------------|---|---------------------|---|---------------------|---|---------------------|--|---------------------|
| | Mix Ratio (ppb) | Fraction Reacted | Mix Ratio (ppb) | Fraction Reacted | Mix Ratio (ppb) | Fraction Reacted | Mix Ratio (ppb) | Fraction Reacted |
| Ethanol | 15.9 \pm 0.8 | 0.69 \pm 0.07 | 36 \pm 3 | 0.34 \pm 0.11 | 80 \pm 2 | 0.71 \pm 0.03 | 134 \pm 1 | 0.80 \pm 0.05 |
| Isopropanol | 10.5 \pm 0.8 | 0.74 \pm 0.11 | 27 \pm 1 | 0.44 \pm 0.01 | 41 \pm 2 | 0.75 \pm 0.05 | 81 \pm 19 | 0.83 \pm 0.30 |
| 1-Butanol | 1.24 \pm 0.05 | 0.53 \pm 0.06 | 3.2 \pm 0.2 | 0.38 \pm 0.07 | 4.3 \pm 0.1 | 0.73 \pm 0.04 | 12.9 \pm 0.2 | 0.72 \pm 0.03 |
| Ethylhexanol | 1.84 \pm 0.03 | 0.40 \pm 0.02 | 4.5 \pm 0.1 | 0.39 \pm 0.01 | 5.4 \pm 0.1 | 0.71 \pm 0.01 | 12.0 \pm 0.1 | 0.70 \pm 0.02 |
| Phenol | 0.97 \pm 0.05 | 0.45 \pm 0.06 | 1.98 \pm 0.08 | 0.39 \pm 0.05 | 2.0 \pm 0.1 | 0.75 \pm 0.06 | 4.8 \pm 0.1 | 0.75 \pm 0.04 |
| 2-BE | 2.8 \pm 0.1 | 0.44 \pm 0.02 | 6.9 \pm 0.1 | 0.43 \pm 0.01 | 7.1 \pm 0.06 | 0.76 \pm 0.01 | 19.4 \pm 0.1 | 0.75 \pm 0.02 |
| MTBE | 2.8 \pm 0.3 | 0.58 \pm 0.12 | 8.4 \pm 0.2 | 0.28 \pm 0.08 | 9.5 \pm 0.4 | 0.52 \pm 0.07 | 26 | 0.68 |
| Acetone | 14.0 \pm 0.5 | 0.51 \pm 0.07 | 32 \pm 2 | Ns * | 45 \pm 4 | Ns | 103 \pm 6 | Ns |
| 2-Butanone | 0.95 \pm 0.09 | 0.63 \pm 0.13 | 3.0 \pm 0.1 | 0.23 \pm 0.06 | 3.7 \pm 0.1 | 0.52 \pm 0.05 | 9.7 \pm 0.1 | 0.59 \pm 0.05 |
| MIBK | 2.7 \pm 0.1 | 0.27 \pm 0.01 | 7.0 \pm 0.2 | 0.28 \pm 0.03 | 8.8 \pm 0.1 | 0.63 \pm 0.03 | 23 \pm 1 | 0.62 \pm 0.05 |
| Hexanal | 0.96 \pm 0.07 | 0.31 \pm 0.12 | 2.1 \pm 0.1 | 0.32 \pm 0.04 | 2.3 \pm 0.1 | 0.63 \pm 0.03 | 7.5 \pm 0.1 | 0.66 \pm 0.03 |
| Limonene | 1.65 \pm 0.04 | 0.32 \pm 0.03 | 4.1 \pm 0.1 | 0.28 \pm 0.03 | 3.7 \pm 0.2 | 0.57 \pm 0.06 | 12.4 \pm 0.3 | 0.62 \pm 0.05 |
| Toluene | 9.2 \pm 0.2 | 0.16 \pm 0.03 | 22 \pm 1 | 0.15 \pm 0.03 | 26 \pm 1 | 0.45 \pm 0.03 | 54 \pm 1 | 0.35 \pm 0.05 |
| m-Xylene | 3.0 \pm 0.1 | 0.23 \pm 0.01 | 7.1 \pm 0.1 | 0.22 \pm 0.02 | 8.3 \pm 0.1 | 0.57 \pm 0.03 | 20 \pm 1 | 0.54 \pm 0.06 |
| 1,2,4-TMB | 0.89 \pm 0.02 | 0.29 \pm 0.02 | 2.1 \pm 0.1 | 0.28 \pm 0.01 | 2.5 \pm 0.1 | 0.62 \pm 0.03 | 5.9 \pm 0.1 | 0.62 \pm 0.04 |
| n-Nonane | 1.92 \pm 0.01 | 0.13 \pm 0.01 | 4.9 \pm 0.1 | 0.13 \pm 0.02 | 6.0 \pm 0.1 | 0.43 \pm 0.03 | 15.5 \pm 0.2 | 0.38 \pm 0.05 |
| n-Decane | 1.77 \pm 0.03 | 0.17 \pm 0.02 | 4.4 \pm 0.1 | 0.16 \pm 0.02 | 5.4 \pm 0.1 | 0.46 \pm 0.03 | 12.8 \pm 0.1 | 0.43 \pm 0.05 |
| n-Undecane | 1.56 \pm 0.03 | 0.20 \pm 0.02 | 3.9 \pm 0.1 | 0.19 \pm 0.01 | 4.7 \pm 0.1 | 0.49 \pm 0.02 | 10.4 \pm 0.1 | 0.48 \pm 0.05 |
| n-Dodecane | 4.3 \pm 0.1 | 0.22 \pm 0.03 | 10.6 \pm 0.1 | 0.20 \pm 0.01 | 12.6 \pm 0.2 | 0.49 \pm 0.02 | 24 \pm 1 | 0.50 \pm 0.04 |

Table 5. Continued.

| Compound | Exp 7 - Low Conc 581 m ³ /h | | Exp 6 - Mid Conc 579 m ³ /h | | Exp 5 - Mid Conc 171 m ³ /h | | Exp 1 - High Conc 165 m ³ /h | |
|-----------------|---|-----------------------------|---|-----------------------------|---|-----------------------------|--|-----------------------------|
| | Mix Ratio (ppb) | <i>Fraction Reacted</i> | Mix Ratio (ppb) | <i>Fraction Reacted</i> | Mix Ratio (ppb) | <i>Fraction Reacted</i> | Mix Ratio (ppb) | <i>Fraction Reacted</i> |
| R-11 | 2.2±0.1 | 0.34±0.05 | 6.3±0.2 | Ns | 6.5±0.7 | Ns | 21 | 0.28 |
| DCM | 9.9±0.3 | 0.23±0.09 | 25±1 | Ns | 31±1 | Ns | 83±2 | Ns |
| 1,1,1-TCA | 4.6±1.0 | 0.51±0.24 | 16.7±0.6 | Ns | 17.2±2.0 | Ns | 52 | 0.45 |
| Trichloroethene | 0.69±0.02 | 0.30±0.07 | 1.88±0.11 | Ns | 2.3±0.1 | 0.25±0.03 | 6.6±0.1 | 0.21±0.04 |
| PCE | 1.77±0.02 | ≤0.05 | 4.5±0.1 | ≤0.05 | 5.4±0.1 | 0.23±0.03 | 14.2±0.1 | 0.19±0.04 |
| 1,2-DCB | 0.55±0.01 | 0.19±0.02 | 1.38±0.01 | 0.17±0.02 | 1.66±0.02 | 0.50±0.03 | 3.7±0.1 | 0.51±0.03 |
| CS2 | 0.94±0.14 | 0.52±0.18 | 2.5±0.5 | Ns | 3.7±0.1 | 0.16±0.07 | 10.1±0.4 | 0.32±0.12 |
| D5 | 0.64±0.01 | 0.22±0.02 | 1.62±0.01 | 0.24±0.01 | 1.95±0.01 | 0.52±0.02 | 4.7±0.1 | 0.50±0.02 |

*Ns = Difference between upstream and downstream VOC concentration not significant at 95% confidence level by 1-tailed Student's t test

Table 6. VOC reaction rates in $\mu\text{mole VOC per hour}$ and $\mu\text{mole carbon per hour}$ (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with three inlet concentrations of synthetic office VOC mixture

| Compound | <i>Exp 7 - Low Conc 581 m³/h</i> | | <i>Exp 6 - Mid Conc 579 m³/h</i> | | <i>Exp 5 - Mid Conc 171 m³/h</i> | | <i>Exp 1 - High Conc 165 m³/h</i> | |
|--------------|---|---------------------|---|---------------------|---|---------------------|--|---------------------|
| | $\mu\text{mole/h}$ | $\mu\text{moleC/h}$ | $\mu\text{mole/h}$ | $\mu\text{moleC/h}$ | $\mu\text{mole/h}$ | $\mu\text{moleC/h}$ | $\mu\text{mole/h}$ | $\mu\text{moleC/h}$ |
| Ethanol | 260 \pm 20 | 520 \pm 40 | 290 \pm 90 | 580 \pm 180 | 400 \pm 10 | 800 \pm 30 | 720 \pm 40 | 1,440 \pm 80 |
| Isopropanol | 185 \pm 22 | 560 \pm 70 | 280 \pm 30 | 840 \pm 150 | 220 \pm 10 | 650 \pm 30 | 450 \pm 130 | 1,360 \pm 380 |
| 1-Butanol | 15.6 \pm 1.7 | 62 \pm 7 | 29 \pm 5 | 116 \pm 19 | 22 \pm 1 | 87 \pm 5 | 63 \pm 3 | 250 \pm 10 |
| Ethylhexanol | 17.7 \pm 0.8 | 142 \pm 6 | 42 \pm 1 | 340 \pm 10 | 27 \pm 1 | 210 \pm 10 | 57 \pm 2 | 460 \pm 10 |
| Phenol | 10.4 \pm 1.2 | 63 \pm 7 | 18.4 \pm 2.2 | 111 \pm 13 | 10.8 \pm 0.7 | 64 \pm 4 | 24 \pm 1 | 145 \pm 8 |
| 2-BE | 30 \pm 1 | 177 \pm 8 | 70 \pm 1 | 420 \pm 10 | 38 \pm 1 | 230 \pm 10 | 98 \pm 2 | 590 \pm 10 |
| MTBE | 38 \pm 7 | 192 \pm 34 | 56 \pm 16 | 280 \pm 80 | 35 \pm 5 | 174 \pm 23 | 122 | 610 |
| Acetone | 170 \pm 24 | 510 \pm 70 | * | | | | | |
| 2-Butanone | 14.4 \pm 2.6 | 57 \pm 10 | 16.5 \pm 4.4 | 66 \pm 18 | 13.4 \pm 1.2 | 53 \pm 5 | 38 \pm 3 | 154 \pm 12 |
| MIBK | 17.4 \pm 0.8 | 104 \pm 5 | 47 \pm 5 | 280 \pm 30 | 39 \pm 2 | 230 \pm 10 | 95 \pm 8 | 570 \pm 50 |
| Hexanal | 7.0 \pm 2.6 | 42 \pm 16 | 15.7 \pm 2.0 | 94 \pm 12 | 10.0 \pm 0.5 | 60 \pm 3 | 33 \pm 2 | 200 \pm 10 |
| Limonene | 12.4 \pm 1.0 | 124 \pm 10 | 27 \pm 3 | 270 \pm 30 | 14.6 \pm 1.4 | 150 \pm 10 | 52 \pm 4 | 520 \pm 40 |
| Toluene | 35 \pm 6 | 250 \pm 40 | 82 \pm 17 | 570 \pm 120 | 83 \pm 6 | 580 \pm 40 | 126 \pm 19 | 880 \pm 130 |
| m-Xylene | 16.2 \pm 0.8 | 130 \pm 6 | 38 \pm 3 | 300 \pm 30 | 33 \pm 2 | 260 \pm 10 | 74 \pm 8 | 590 \pm 60 |
| 1,2,4-TMB | 6.1 \pm 0.5 | 55 \pm 4 | 13.6 \pm 0.7 | 123 \pm 6 | 11.0 \pm 0.4 | 99 \pm 4 | 25 \pm 2 | 220 \pm 20 |
| n-Nonane | 5.9 \pm 0.5 | 53 \pm 4 | 15.5 \pm 2.6 | 139 \pm 24 | 17.9 \pm 1.3 | 161 \pm 11 | 40 \pm 5 | 360 \pm 50 |
| n-Decane | 7.1 \pm 0.7 | 71 \pm 7 | 16.7 \pm 1.6 | 167 \pm 17 | 17.3 \pm 1.0 | 173 \pm 10 | 37 \pm 4 | 370 \pm 40 |
| n-Undecane | 7.6 \pm 0.8 | 83 \pm 9 | 17.5 \pm 1.4 | 192 \pm 15 | 16.1 \pm 0.7 | 177 \pm 8 | 34 \pm 3 | 370 \pm 40 |
| n-Dodecane | 23 \pm 3 | 280 \pm 40 | 52 \pm 4 | 620 \pm 40 | 43 \pm 2 | 520 \pm 20 | 81 \pm 7 | 970 \pm 80 |

Table 6. Continued.

| Compound | <i>Exp 7 - Low Conc 581 m³/h</i> | | <i>Exp 6 - Mid Conc 579 m³/h</i> | | <i>Exp 5 - Mid Conc 171 m³/h</i> | | <i>Exp 1 - High Conc 165 m³/h</i> | |
|-----------------|---|----------|---|----------|---|----------|--|----------|
| | μmole/h | μmoleC/h | μmole/h | μmoleC/h | μmole/h | μmoleC/h | μmole/h | μmoleC/h |
| R-11 | 17.5±2.7 | 17.5±2.7 | | | | | 40 | 40 |
| DCM | 56±21 | 56±21 | | | | | | |
| 1,1,1-TCA | 56±23 | 111±47 | | | | | 159 | 320 |
| Trichloroethene | 5.0±1.2 | 10.0±2.4 | | | 4.1±0.5 | 8.3±0.9 | 9.4±1.7 | 18.8±3.4 |
| PCE | | | | | 8.8±1.2 | 17.6±2.5 | 18.2±3.9 | 36±8 |
| 1,2-DCB | 2.5±0.3 | 14.8±1.7 | 5.6±0.6 | 33±4 | 5.8±0.3 | 35±2 | 12.6±1.4 | 76±8 |
| CS2 | 11.5±3.6 | 11.5±3.6 | | | 4.3±1.9 | 1.3±1.9 | 22±8 | 22±8 |
| D5 | 3.4±0.2 | 34±2 | 9.3±0.5 | 92±5 | 7.1±0.3 | 71±3 | 16.0±0.6 | 160±6 |

*Value not shown if difference between upstream and downstream VOC concentration was not significant at 95% confidence level by 1-tailed Student's t test or was ≤5 %

Table 7. Outlet mixing ratios (ppb) of aldehydes and carboxylic acids and fractions produced (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with three inlet concentrations of synthetic office VOC mixture

| Compound | Exp 7 - Low Conc 581 m ³ /h | | Exp 6 - Mid Conc 579 m ³ /h | | Exp 5 - Mid Conc 171 m ³ /h | | Exp 1 - High Conc 165 m ³ /h | |
|--------------|---|------------------------------|---|------------------------------|---|------------------------------|--|------------------------------|
| | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> |
| Formaldehyde | 7.3 \pm 0.3 | 1.36 \pm 0.13 | 10.0 \pm 0.8 | 2.4 \pm 0.3 | 25 \pm 1 | 6.2 \pm 1.0 | 53 \pm 10 | 4.0 \pm 1.0 |
| Acetaldehyde | 3.8 \pm 0.3 | 1.29 \pm 0.27 | 6.4 \pm 0.7 | 3.6 \pm 0.5 | 13.2 \pm 2.2 | 5.0 \pm 1.0 | 32 \pm 5 | 7.6 \pm 1.6 |
| Formic acid | 7.0 \pm 0.6 | 1.20 \pm 0.78 | 12.6 \pm 1.5 | 2.4 \pm 0.3 | 19.6 \pm 5.6 | 4.5 \pm 1.9 | 98 \pm 7 | 10.2 \pm 3.9 |
| Acetic acid | 13.5 \pm 1.1 | 0.91 \pm 0.46 | 17.6 \pm 2.1 | 2.4 \pm 0.5 | 22 \pm 6 | 3.6 \pm 1.7 | 120 \pm 12 | 1.59 \pm 0.63 |

Table 8. Aldehyde and carboxylic acid production rates in μ mole VOC per hour and μ mole carbon per hour (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with three inlet concentrations of synthetic office VOC mixture

| Compound | Exp 7 - Low Conc 581 m ³ /h | | Exp 6 - Mid Conc 579 m ³ /h | | Exp 5 - Mid Conc 171 m ³ /h | | Exp 1 - High Conc 165 m ³ /h | |
|--------------|---|---------------|---|---------------|---|---------------|--|-----------------|
| | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h |
| Formaldehyde | 100 \pm 8 | 100 \pm 8 | 167 \pm 19 | 167 \pm 19 | 151 \pm 9 | 151 \pm 9 | 280 \pm 70 | 280 \pm 70 |
| Acetaldehyde | 51 \pm 8 | 102 \pm 17 | 119 \pm 17 | 240 \pm 30 | 77 \pm 16 | 154 \pm 31 | 189 \pm 33 | 380 \pm 70 |
| Formic acid | 91 \pm 39 | 91 \pm 39 | 210 \pm 40 | 210 \pm 40 | 112 \pm 39 | 112 \pm 39 | 600 \pm 50 | 600 \pm 50 |
| Acetic acid | 153 \pm 60 | 310 \pm 120 | 230 \pm 50 | 460 \pm 100 | 118 \pm 43 | 230 \pm 90 | 500 \pm 130 | 1,000 \pm 250 |

Table 9. Inlet VOC mixing ratios (ppb) and fractions of VOCs reacted (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with two inlet concentrations of cleaning product mixture

| Compound | Exp 3 - Mid Conc 580 m ³ /h | | Exp 4 - Mid Conc 167 m ³ /h | | Exp 2 - Low Conc 165 m ³ /h | |
|---------------------|---|---------------------|---|---------------------|---|---------------------|
| | Mix Ratio (ppb) | Fraction Reacted | Mix Ratio (ppb) | Fraction Reacted | Mix Ratio (ppb) | Fraction Reacted |
| Isopropanol | 63 \pm 10 | Ns* | 64 \pm 17 | 0.80 \pm 0.33 | 11.8 \pm 6.5 | Ns |
| α -Terpineol | 19.6 \pm 0.4 | 0.46 \pm 0.02 | 27 \pm 1 | 0.79 \pm 0.03 | 6.6 \pm 0.5 | 0.84 \pm 0.10 |
| γ -Terpineol | 1.14 \pm 0.08 | 0.49 \pm 0.10 | 2.3 \pm 0.2 | 0.84 \pm 0.09 | 0.50 \pm 0.02 | 0.87 \pm 0.06 |
| 2-Butoxyethanol | 32 \pm 1 | 0.41 \pm 0.02 | 40 \pm 1 | 0.72 \pm 0.02 | 16.3 \pm 0.7 | 0.77 \pm 0.06 |
| α -Pinene | 1.03 \pm 0.01 | 0.25 \pm 0.03 | 1.16 \pm 0.02 | 0.54 \pm 0.03 | 0.90 \pm 0.05 | 0.63 \pm 0.07 |
| Camphene | 0.63 \pm 0.01 | 0.22 \pm 0.02 | 0.75 \pm 0.01 | 0.49 \pm 0.03 | 0.38 \pm 0.03 | 0.61 \pm 0.11 |
| d-Limonene | 11.3 \pm 0.2 | 0.28 \pm 0.02 | 13.5 \pm 0.3 | 0.59 \pm 0.03 | 6.7 \pm 0.4 | 0.69 \pm 0.07 |
| p-Cymene | 5.3 \pm 0.2 | 0.28 \pm 0.06 | 6.4 \pm 0.1 | 0.55 \pm 0.03 | 2.9 \pm 0.2 | 0.59 \pm 0.09 |
| γ -Terpinene | 0.73 \pm 0.01 | 0.29 \pm 0.02 | 0.87 \pm 0.04 | 0.62 \pm 0.06 | 0.40 \pm 0.02 | 0.75 \pm 0.07 |
| Terpinolene | 3.6 \pm 0.5 | 0.31 \pm 0.23 | 6.2 \pm 0.8 | 0.68 \pm 0.18 | 2.7 \pm 0.5 | 0.79 \pm 0.22 |

*Ns = Difference between upstream and downstream VOC concentration not significant at 95% confidence level by 1-tailed Student's t test

Table 10. VOC reaction rates in μ mole VOC per hour and μ mole carbon per hour (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with two inlet concentrations of cleaning product mixture

| Compound | Exp 3 - Mid Conc 580 m^3/h | | Exp 4 - Mid Conc 167 m^3/h | | Exp 2 - Low Conc 165 m^3/h | |
|---------------------|---------------------------------|-----------------|---------------------------------|-----------------|---------------------------------|----------------|
| | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h |
| Isopropanol | * | | 350 \pm 110 | 1,050 \pm 340 | | |
| α -Terpineol | 210 \pm 10 | 2,100 \pm 100 | 145 \pm 5 | 1,450 \pm 50 | 37 \pm 3 | 370 \pm 30 |
| γ -Terpineol | 13.2 \pm 2.7 | 132 \pm 27 | 13.3 \pm 1.1 | 133 \pm 11 | 2.9 \pm 0.2 | 29 \pm 2 |
| 2-Butoxyethanol | 310 \pm 20 | 1,900 \pm 100 | 197 \pm 4 | 1,180 \pm 30 | 84 \pm 6 | 510 \pm 40 |
| α -Pinene | 6.1 \pm 0.7 | 61 \pm 6 | 4.2 \pm 0.2 | 42 \pm 2 | 3.9 \pm 0.4 | 39 \pm 4 |
| Camphene | 3.3 \pm 0.3 | 33 \pm 3 | 2.5 \pm 0.1 | 25 \pm 1 | 1.6 \pm 0.2 | 15.5 \pm 2.5 |
| d-Limonene | 74 \pm 6 | 740 \pm 60 | 54 \pm 3 | 540 \pm 30 | 32 \pm 3 | 320 \pm 30 |
| p-Cymene | 35 \pm 7 | 350 \pm 70 | 24 \pm 1 | 240 \pm 10 | 11.3 \pm 1.5 | 113 \pm 15 |
| γ -Terpinene | 5.1 \pm 0.3 | 51 \pm 3 | 3.7 \pm 0.3 | 37 \pm 3 | 2.0 \pm 0.2 | 20 \pm 2 |
| Terpinolene | 26 \pm 19 | 260 \pm 190 | 29 \pm 6 | 290 \pm 60 | 14.4 \pm 3.2 | 144 \pm 32 |

*Value not shown if difference between upstream and downstream VOC concentration was not significant at 95% confidence level by 1-tailed Student's t test

Table 11. Outlet mixing ratios (ppb) of aldehydes and carboxylic acids and fractions produced (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with two inlet concentrations of cleaning product mixture

| Compound | Exp 3 - Mid Conc 580 m ³ /h | | Exp 4 - Mid Conc 167 m ³ /h | | Exp 2 - Low Conc 165 m ³ /h | |
|--------------|---|------------------------------|---|------------------------------|---|------------------------------|
| | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> |
| Formaldehyde | 16.7 \pm 2.1 | 2.6 \pm 0.5 | 27 \pm 2 | 5.1 \pm 0.7 | 18.8 \pm 1.2 | 0.90 \pm 0.16 |
| Acetaldehyde | 6.4 \pm 0.9 | 1.56 \pm 0.39 | 6.3 \pm 1.2 | 2.4 \pm 0.8 | 4.8 \pm 0.6 | 0.39 \pm 0.22 |
| Acetone | 25 \pm 5 | 2.6 \pm 0.8 | 44 \pm 4 | 5.3 \pm 0.7 | 23 \pm 1 | 1.70 \pm 0.21 |
| Formic acid | Na* | | Na | | Na | |
| Acetic acid | Na | | Na | | Na | |

*Na = Data not available; problem with analysis

Table 12. Aldehyde and carboxylic acid production rates in μ mole VOC per hour and μ mole carbon per hour (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with two inlet concentrations of cleaning product mixture

| Compound | Exp 3 - Mid Conc 580 m ³ /h | | Exp 4 - Mid Conc 167 m ³ /h | | Exp 2 - Low Conc 165 m ³ /h | |
|--------------|---|-----------------|---|---------------|---|-----------------|
| | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h |
| Formaldehyde | 290 \pm 50 | 290 \pm 50 | 155 \pm 13 | 155 \pm 13 | 60 \pm 10 | 60 \pm 10 |
| Acetaldehyde | 92 \pm 22 | 185 \pm 43 | 30 \pm 8 | 60 \pm 17 | 9.2 \pm 5.1 | 18.5 \pm 10.2 |
| Acetone | 420 \pm 130 | 1,280 \pm 380 | 250 \pm 24 | 750 \pm 70 | 98 \pm 7 | 290 \pm 20 |
| Formic acid | Na* | Na | Na | Na | Na | Na |
| Acetic acid | Na | Na | Na | Na | Na | Na |

*Na = Data not available; problem with analysis

Table 13. Inlet VOC mixing ratios (ppb) and fractions of VOCs reacted (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with VOC mixture generated in 20-m³ chamber with combination of building products

| Compound | Exp 14 298 m ³ /h | | Exp 13 174 m ³ /h | |
|-------------------------------|---------------------------------|---------------------|---------------------------------|---------------------|
| | Mix Ratio (ppb) | Fraction Reacted | Mix Ratio (ppb) | Fraction Reacted |
| Phenol | 9.9 \pm 0.2 | 0.52 \pm 0.03 | 8.9 \pm 1.1 | 0.57 \pm 0.15 |
| BHT | 0.65 \pm 0.03 | 0.71 \pm 0.07 | 0.44 \pm 0.17 | 0.68 \pm 0.48 |
| Ethylene glycol | 155 \pm 9 | 0.80 \pm 0.08 | 83 \pm 24 | 0.45 \pm 0.39 |
| DEGBE | 48 \pm 2 | 0.54 \pm 0.05 | 33 \pm 4 | Ns* |
| Hexanal | 0.97 \pm 0.08 | 0.17 \pm 0.10 | 0.63 \pm 0.10 | 0.22 \pm 0.16 |
| TMPD-MIB | 26 \pm 1 | 0.43 \pm 0.05 | 31 \pm 1 | 0.35 \pm 0.05 |
| TMPD-DIB | 19.6 \pm 0.8 | 0.36 \pm 0.05 | 21 \pm 1 | 0.29 \pm 0.07 |
| Toluene | 0.66 \pm 0.26 | Ns | 0.58 \pm 0.01 | Ns |
| 1,2,4-TMB | 0.73 \pm 0.01 | 0.43 \pm 0.02 | 0.88 \pm 0.07 | 0.51 \pm 0.09 |
| C ₄ Alkylbenzenes | 3.4 \pm 0.2 | 0.40 \pm 0.05 | 3.9 \pm 0.2 | 0.49 \pm 0.06 |
| Naphthalene | 0.39 \pm 0.01 | 0.36 \pm 0.04 | 0.48 \pm 0.02 | 0.46 \pm 0.06 |
| C ₁₀ Alkylbenzenes | 5.5 \pm 0.2 | 0.41 \pm 0.05 | 4.6 \pm 0.8 | 0.29 \pm 0.20 |
| C ₁₁ Alkylbenzenes | 8.1 \pm 0.03 | 0.43 \pm 0.05 | 8.5 \pm 1.2 | 0.41 \pm 0.16 |
| C ₁₂ Alkylbenzenes | 2.6 \pm 0.2 | 0.42 \pm 0.08 | 2.7 \pm 0.3 | 0.35 \pm 0.15 |
| C ₁₁ Alkane HCs | 19.4 \pm 0.1 | 0.28 \pm 0.02 | 18.9 \pm 4.4 | Ns |
| n-Undecane | 0.65 \pm 0.14 | 0.38 \pm 0.25 | 0.64 \pm 0.06 | 0.29 \pm 0.11 |
| n-Dodecane | 3.5 \pm 0.1 | 0.32 \pm 0.03 | 3.8 \pm 0.3 | 0.38 \pm 0.10 |
| n-Tridecane | 12.7 \pm 0.4 | 0.32 \pm 0.03 | 14.0 \pm 1.0 | 0.38 \pm 0.09 |
| n-Tetradecane | 8.6 \pm 0.3 | 0.34 \pm 0.04 | 9.6 \pm 0.5 | 0.41 \pm 0.07 |

*Ns = Difference between upstream and downstream VOC concentration not significant at 95% confidence level by 1-tailed Student's t test

Table 14. VOC reaction rates in μmole VOC per hour and μmole carbon per hour (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with VOC mixture generated in 20-m³ chamber with combination of building products

| Compound | <i>Exp 14</i> 298 m ³ /h | | <i>Exp 13</i> 174 m ³ /h | |
|--|--|----------------------------|--|----------------------------|
| | $\mu\text{mole}/\text{h}$ | $\mu\text{moleC}/\text{h}$ | $\mu\text{mole}/\text{h}$ | $\mu\text{moleC}/\text{h}$ |
| Phenol | 63 \pm 3 | 380 \pm 20 | 36 \pm 8 | 220 \pm 50 |
| BHT | 5.6 \pm 0.5 | 85 \pm 7 | 2.1 \pm 1.2 | 32 \pm 19 |
| Ethylene glycol | 1510 \pm 120 | 3000 \pm 200 | 270 \pm 210 | 530 \pm 430 |
| DEGBE | 320 \pm 30 | 2500 \pm 200 | * | |
| Hexanal | 2.1 \pm 1.2 | 12.3 \pm 6.9 | 1.0 \pm 0.7 | 5.8 \pm 4.2 |
| TMPD-MIB | 140 \pm 16 | 1680 \pm 190 | 78 \pm 10 | 940 \pm 120 |
| TMPD-DIB | 87 \pm 11 | 1390 \pm 170 | 43 \pm 10 | 680 \pm 160 |
| Toluene | | | | |
| 1,2,4-TMB | 3.8 \pm 0.1 | 34 \pm 1 | 3.2 \pm 0.5 | 29 \pm 4 |
| C ₄ Alkylbenzenes | 16.3 \pm 2.1 | 163 \pm 21 | 13.5 \pm 1.6 | 135 \pm 16 |
| Naphthalene | 1.7 \pm 0.2 | 17.0 \pm 1.9 | 1.6 \pm 0.2 | 15.7 \pm 2.1 |
| C ₁₀ Alkylbenzenes | 28 \pm 3 | 440 \pm 50 | 9.4 \pm 6.2 | 150 \pm 98 |
| C ₁₁ Alkylbenzenes | 42 \pm 4 | 720 \pm 70 | 25 \pm 9 | 420 \pm 150 |
| C ₁₂ Alkylbenzenes | 13.5 \pm 2.3 | 240 \pm 40 | 6.7 \pm 2.9 | 121 \pm 51 |
| C ₁₁ Alkane HC _s | 66 \pm 4 | 730 \pm 40 | | |
| n-Undecane | 3.0 \pm 1.9 | 33 \pm 20 | 1.3 \pm 0.5 | 14.3 \pm 5.4 |
| n-Dodecane | 14.0 \pm 1.2 | 167 \pm 14 | 10.2 \pm 2.5 | 122 \pm 30 |
| n-Tridecane | 50 \pm 5 | 650 \pm 60 | 38 \pm 8 | 490 \pm 110 |
| n-Tetradecane | 36 \pm 4 | 500 \pm 50 | 28 \pm 4 | 390 \pm 60 |

*Value not shown if difference between upstream and downstream VOC concentration was not significant at 95% confidence level by 1-tailed Student's t test

Table 15. Outlet mixing ratios (ppb) of aldehydes and carboxylic acids and fractions produced (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with VOC mixture generated in 20-m³ chamber with combination of building products

| Compound | <i>Exp 14</i> 298 m ³ /h | | <i>Exp 13</i> 174 m ³ /h | |
|--------------|--|------------------------------|--|------------------------------|
| | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> | Outlet Mix Ratio (ppb) | <i>Fraction Produced</i> |
| Formaldehyde | 44 \pm 1 | 0.69 \pm 0.04 | 50 \pm 3 | 0.82 \pm 0.11 |
| Acetaldehyde | 9.6 \pm 0.2 | 1.37 \pm 0.06 | 11.6 \pm 0.8 | 2.2 \pm 0.2 |
| Acetone | 38 \pm 1 | 2.0 \pm 0.1 | 47 \pm 2 | 3.2 \pm 0.1 |
| Formic acid | 40 \pm 2 | 3.4 \pm 0.6 | 44 \pm 12 | 4.4 \pm 1.7 |
| Acetic acid | 50 \pm 1 | 0.45 \pm 0.04 | 50 \pm 9 | 0.38 \pm 0.26 |

Table 16. Aldehyde and carboxylic acid production rates in μ mole VOC per hour and μ mole carbon per hour (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with VOC mixture generated in 20-m³ chamber with combination of building products

| Compound | <i>Exp 14</i> 298 m ³ /h | | <i>Exp 13</i> 174 m ³ /h | |
|--------------|--|---------------|--|---------------|
| | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h |
| Formaldehyde | 220 \pm 10 | 220 \pm 10 | 159 \pm 21 | 159 \pm 21 |
| Acetaldehyde | 69 \pm 3 | 137 \pm 6 | 56 \pm 6 | 112 \pm 12 |
| Acetone | 310 \pm 10 | 940 \pm 20 | 260 \pm 10 | 770 \pm 30 |
| Formic acid | 380 \pm 30 | 380 \pm 30 | 260 \pm 90 | 260 \pm 90 |
| Acetic acid | 192 \pm 18 | 380 \pm 40 | 98 \pm 66 | 196 \pm 131 |

Table 17. Inlet VOC mixing ratios (ppb) of aldehydes and carboxylic acids and fractions reacted (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with aldehyde mixture generated in 20-m³ chamber

| Compound | Exp 24 280 m ³ /h | | Exp 23 167 m ³ /h | |
|--------------|---------------------------------|-----------------------------|---------------------------------|-----------------------------|
| | Inlet Mix Ratio (ppb) | <i>Fraction Reacted</i> | Inlet Mix Ratio (ppb) | <i>Fraction Reacted</i> |
| Formaldehyde | 25 \pm 3 | 0.28 \pm 0.12 | 33 \pm 2 | 0.49 \pm 0.06 |
| Acetaldehyde | 5.3 \pm 0.6 | 0.18 \pm 0.11 | 8.7 \pm 0.7 | 0.44 \pm 0.09 |

Table 18. Aldehyde and carboxylic acid reaction rates in μ mole VOC per hour and μ mole carbon per hour (mean \pm 1 std. deviation) in UVPCO operated at two flow rate settings and challenged with aldehyde mixture generated in 20-m³ chamber

| Compound | Exp 24 280 m ³ /h | | Exp 23 167 m ³ /h | |
|--------------|---------------------------------|---------------|---------------------------------|---------------|
| | μ mole/h | μ moleC/h | μ mole/h | μ moleC/h |
| Formaldehyde | 78 \pm 33 | 78 \pm 33 | 111 \pm 11 | 111 \pm 11 |
| Acetaldehyde | 10.9 \pm 6.4 | 22 \pm 13 | 26 \pm 5 | 52 \pm 10 |

Table 19. Target VOCs ordered by decreasing percent conversion efficiency (% Eff) in low flow rate experiments (165 – 298 m³/h) with synthetic office VOC, cleaning product and building product mixtures. Six VOCs occurred in two mixtures

| Compound | Chem Class | % Eff | Compound | Chem Class | % Eff |
|------------------------|--------------|-------|-------------------------------|-------------|-------|
| γ-Terpineol | Alcohol | 85 | D5 | Siloxane | 51 |
| α-Terpineol | Alcohol | 82 | 1,2-DCB | Halo HC | 50 |
| Isopropanol | Alcohol | 79 | n-Dodecane ^a | Alkane HC | 49 |
| 2-BE ^a | Glycol ether | 76 | n-Undecane ^a | Alkane HC | 48 |
| Ethanol | Alcohol | 75 | 1,2,4-TMB ^c | Aromatic HC | 47 |
| Phenol ^a | Alcohol | 75 | 1,1,1-TCA | Halo HC | 45 |
| 2-BE ^b | Glycol ether | 74 | n-Decane | Alkane HC | 44 |
| Terpinolene | Terpene HC | 74 | C ₄ Alkylbenzenes | Aromatic HC | 44 |
| 1-Butanol | Alcohol | 72 | C ₁₁ Alkylbenzenes | Aromatic HC | 42 |
| Ethylhexanol | Alcohol | 71 | Naphthalene | Aromatic HC | 41 |
| BHT | Alcohol | 70 | n-Nonane | Alkane HC | 40 |
| γ-Terpinene | Terpene HC | 68 | Toluene | Aromatic HC | 40 |
| Hexanal ^a | Aldehyde | 65 | TMPD-MIB | Ester | 39 |
| Limonene ^b | Terpene HC | 64 | C ₁₂ Alkylbenzenes | Aromatic HC | 39 |
| Ethylene glycol | Glycol ether | 62 | n-Tetradecane | Alkane HC | 38 |
| MIBK | Ketone | 62 | C ₁₀ Alkylbenzenes | Aromatic HC | 35 |
| 1,2,4-TMB ^a | Aromatic HC | 62 | n-Tridecane | Alkane HC | 35 |
| MTBE | Ether | 60 | n-Dodecane ^c | Alkane HC | 35 |
| Limonene ^a | Terpene HC | 59 | n-Undecane ^c | Alkane HC | 33 |
| α-Pinene | Terpene HC | 58 | TMPD-DIB | Ester | 32 |
| p-Cymene | Terpene HC | 57 | R-11 | Halo HC | 28 |
| m-Xylene | Aromatic HC | 55 | C ₁₁ Alkane HCs | Alkane HC | 28 |
| 2-Butanone | Ketone | 55 | CS2 | Sulfide | 24 |
| Camphene | Terpene HC | 55 | Trichloroethene | Halo HC | 23 |
| Phenol ^c | Alcohol | 55 | PCE | Halo HC | 21 |
| DEGBE | Glycol ether | 54 | Hexanal ^c | Aldehyde | 19 |

a. Synthetic office VOC mixture

b. Cleaning product mixture

c. Building product mixture

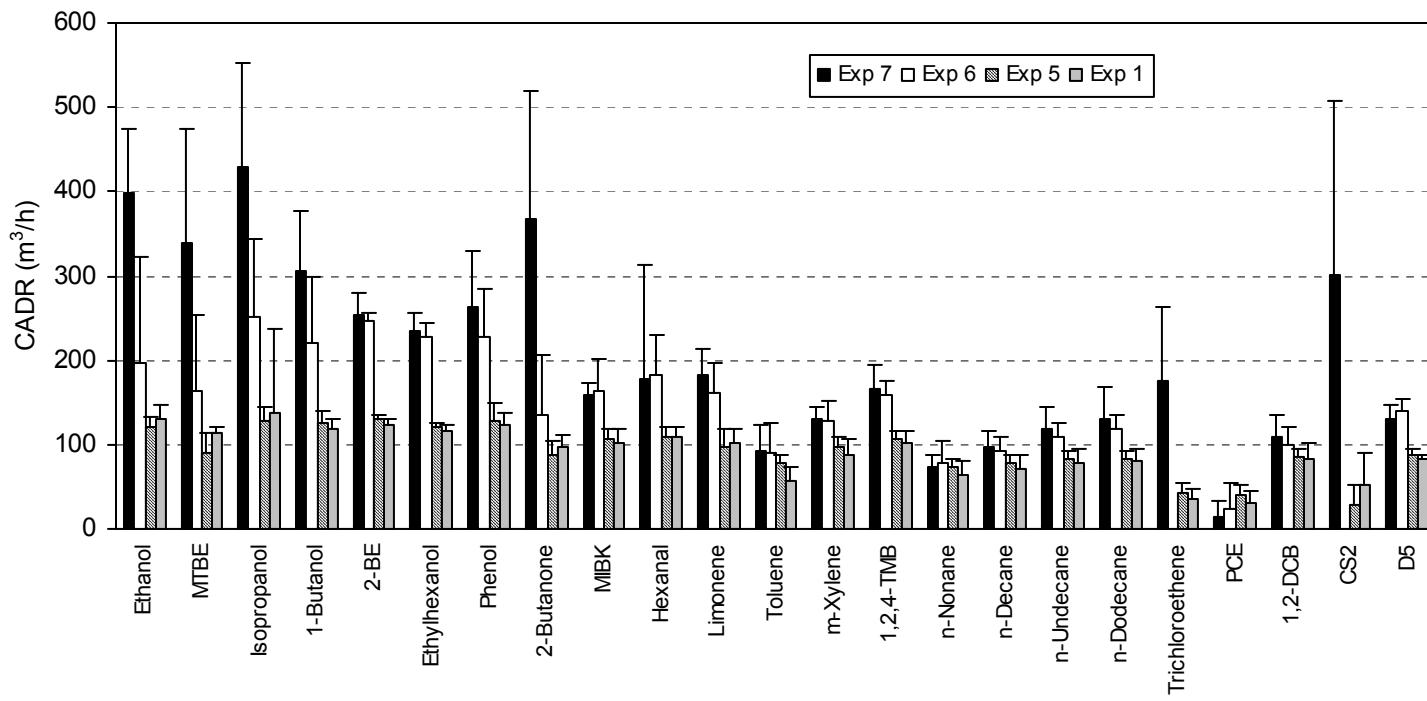


Figure 1. Clean air delivery rates (CADRs) of VOCs in four experiments conducted with synthetic office VOC mixture. Four compounds (acetone, R11, DCM, and 1,1,1-TCA) with mostly insignificant differences between upstream and downstream concentrations were omitted from the plot. In Experiments 7 and 6, UVPCO was operated at $\sim 580 \text{ m}^3/\text{h}$; in Experiments 5 and 1, UVPCO was operated at $165 - 171 \text{ m}^3/\text{h}$. Inlet VOC concentrations were lowest in Experiment 7 and highest in Experiment 1. Inlet concentrations were intermediate and similar in Experiments 6 and 5.

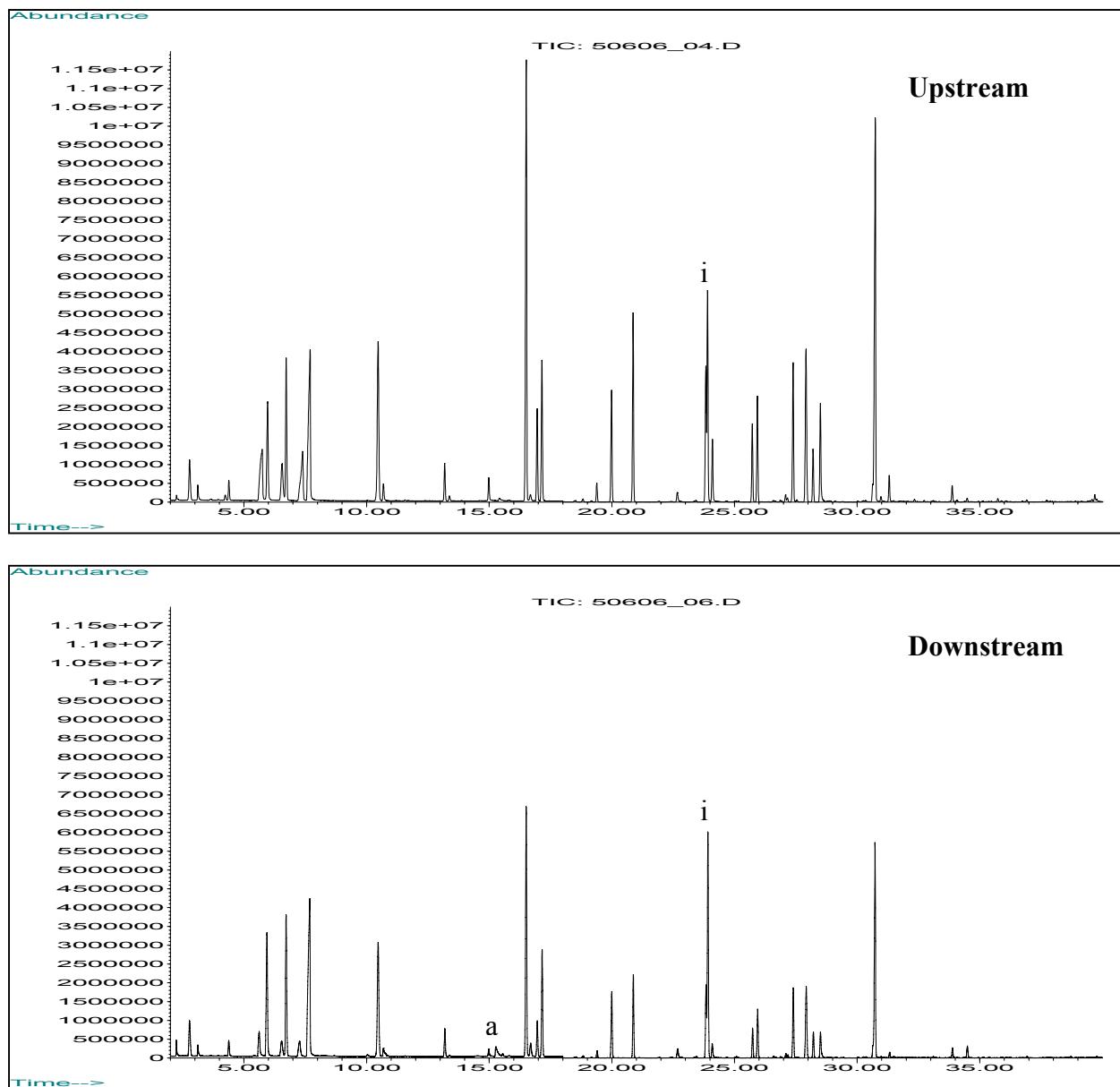


Figure 2. Comparision of total-ion-current chromatograms obtained by TD-GC/MS analysis of air samples collected upstream and downstream of UVPCO reactor in Experiment 5 with synthetic office VOC mixture. Production of acetic acid is indicated in downstream sample. a = Acetic acid, i = Internal standard.

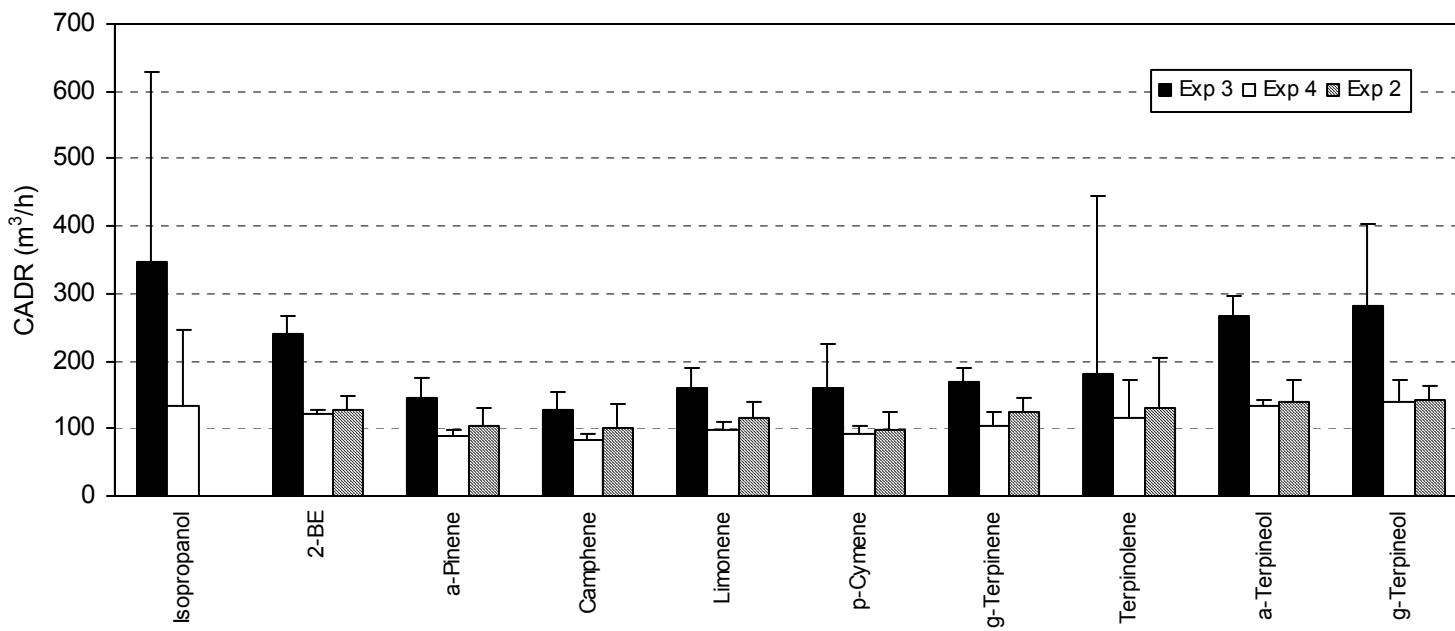


Figure 3. Clean air delivery rates (CADRs) of VOCs in three experiments conducted with cleaning product mixture. In Experiment 3, UVPCO was operated at $580 \text{ m}^3/\text{h}$; in Experiments 4 and 2, UVPCO was operated at $\sim 165 \text{ m}^3/\text{h}$. Inlet VOC concentrations were lowest in Experiment 2. Inlet concentrations were higher and similar in Experiments 3 and 4.

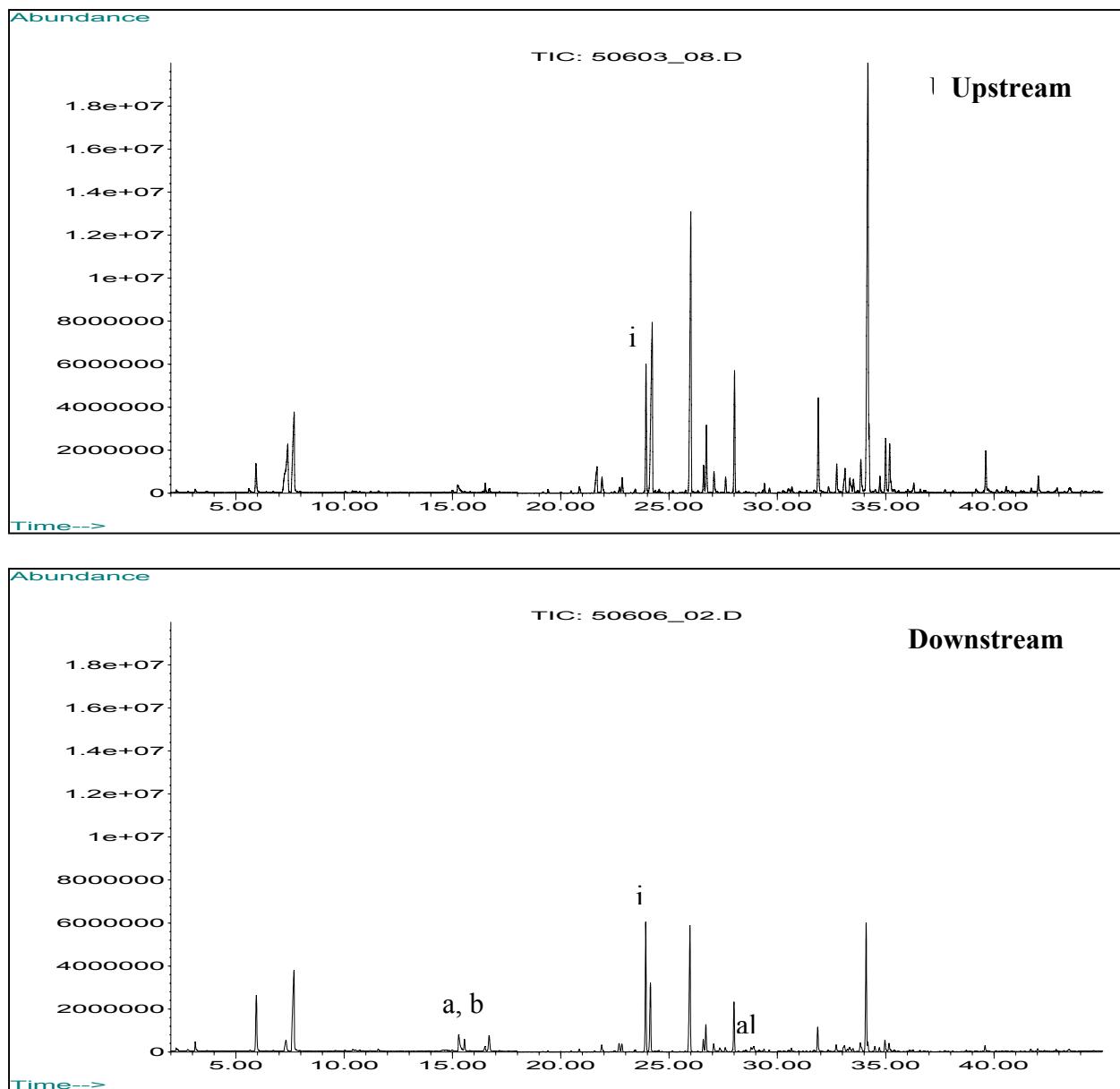


Figure 4. Comparision of total-ion-current chromatograms obtained by TD-GC/MS analysis of air samples collected upstream and downstream of UVPCO reactor in Experiment 4 with cleaning product mixture. Production of acetic acid, butyl formate, and two C₈ aliphatic alcohols is indicated in downstream sample. a = acetic acid, b = Butyl formate, al = Alcohols, i = Internal standard.

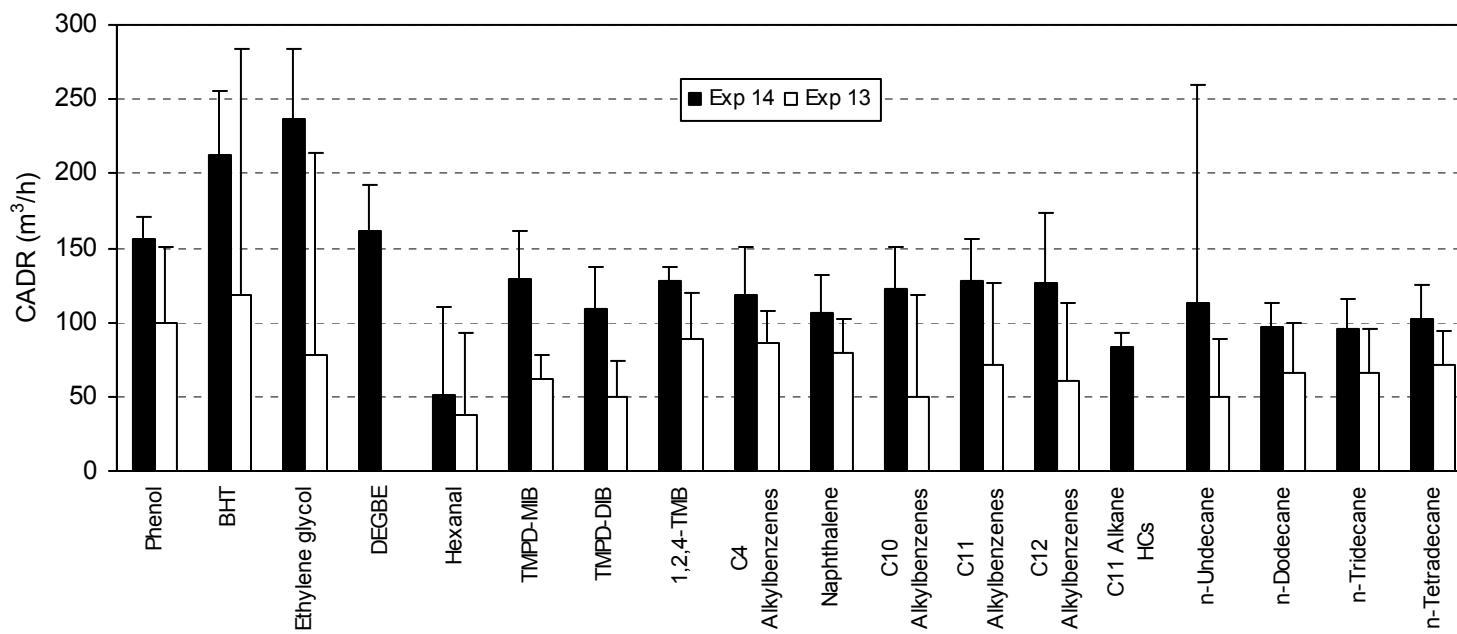


Figure 5. Clean air delivery rates (CADRs) of VOCs in two experiments conducted with building product mixture. Toluene with insignificant differences between upstream and downstream concentrations was omitted from the plot. In Experiment 14, UVPCO was operated at 298 m³/h; in Experiment 13, UVPCO was operated at 174 m³/h. Inlet VOC concentrations were similar in both experiments.

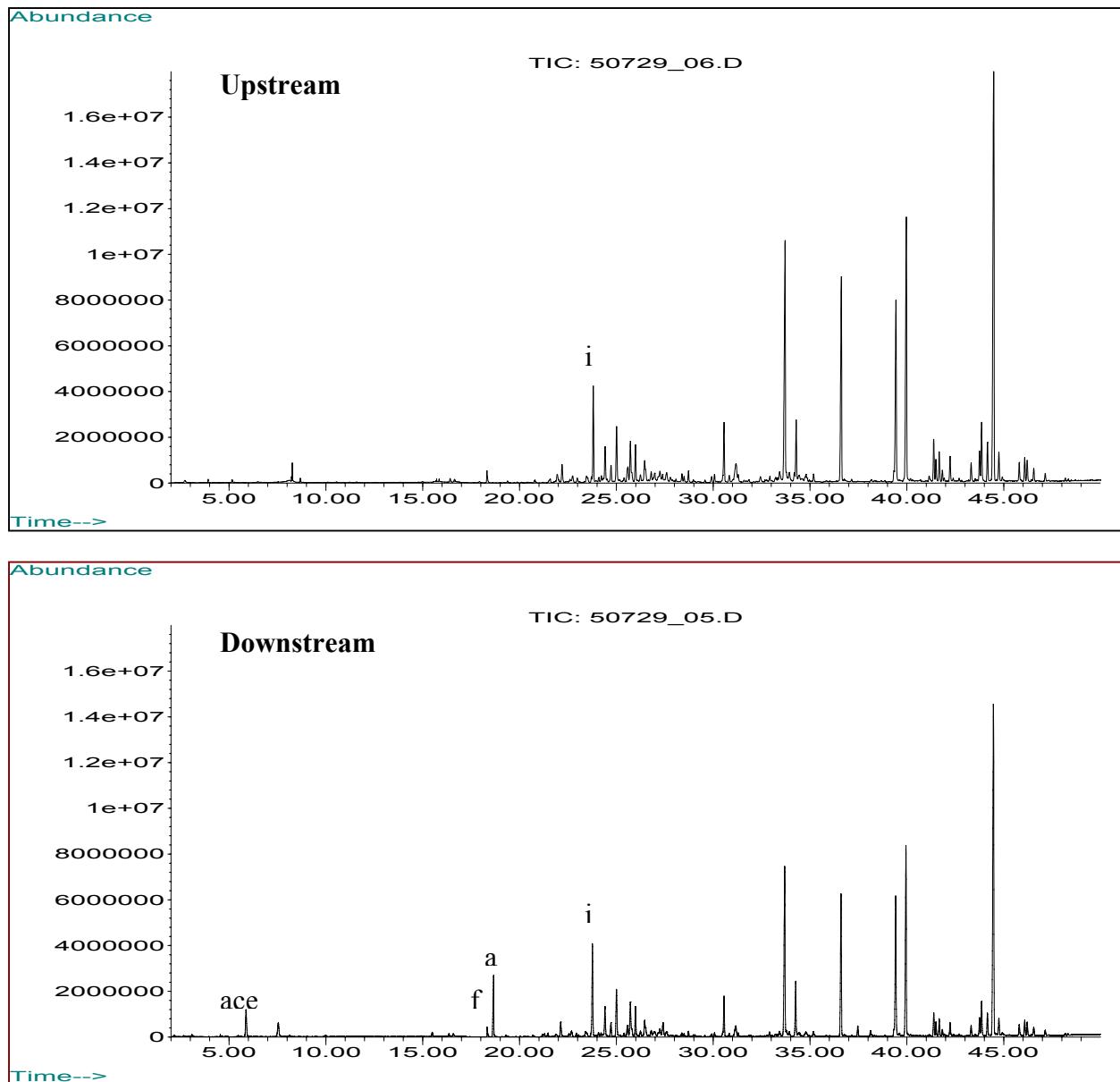


Figure 6. Comparision of total-ion-current chromatograms obtained by TD-GC/MS analysis of air samples collected upstream and downstream of UVPCO reactor in Experiment 13 with building product mixture. Production of acetone, formic acid, and acetic acid is indicated in downstream sample. a = Acetic acid, f = Formic acid, ace = Acetone, i = Internal standard.

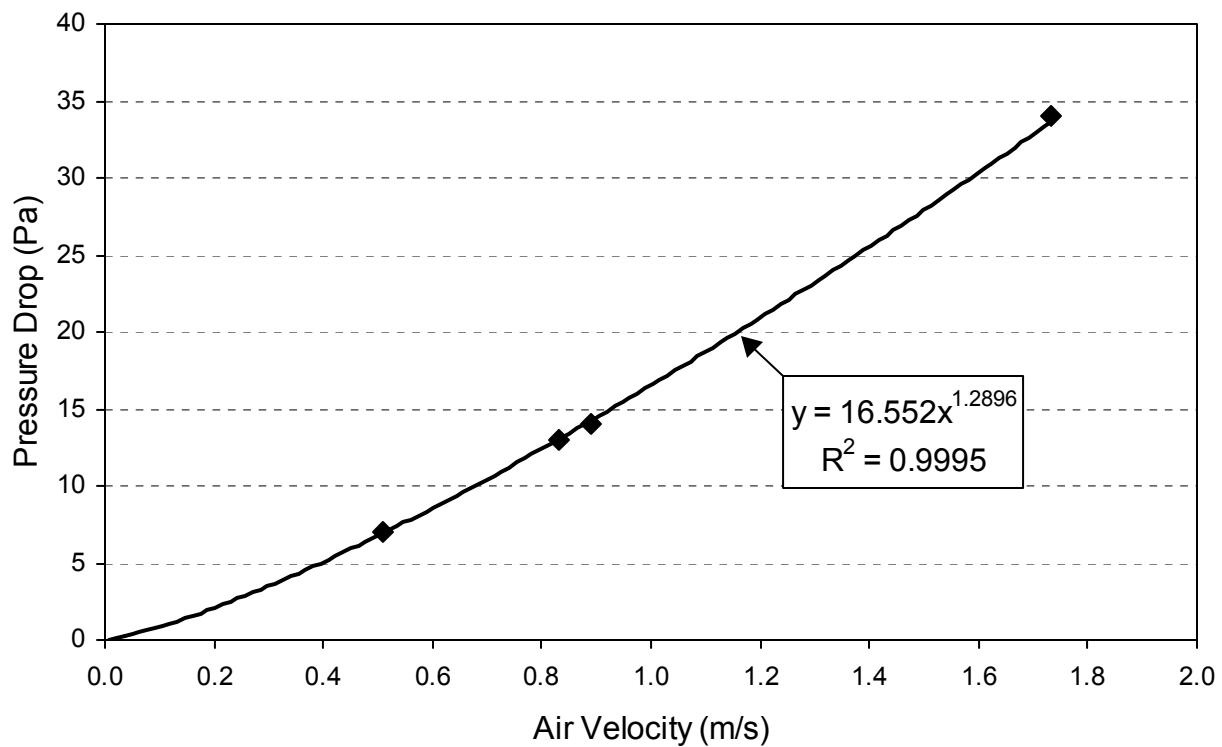


Figure 7. Pressure Drop (ΔP) across the UVPCO reactor section versus air velocity through the reactor.

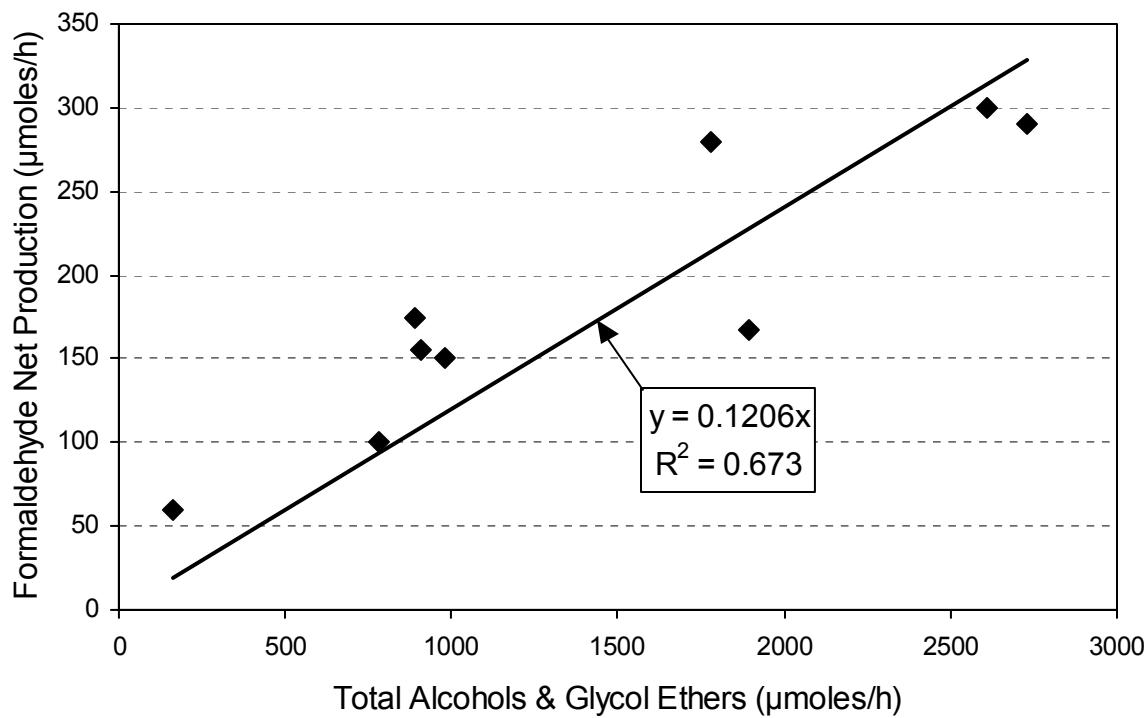


Figure 8. Formaldehyde net production rate in nine experiments versus the supply rate of total alcohols and glycol ethers to the UVPCO.

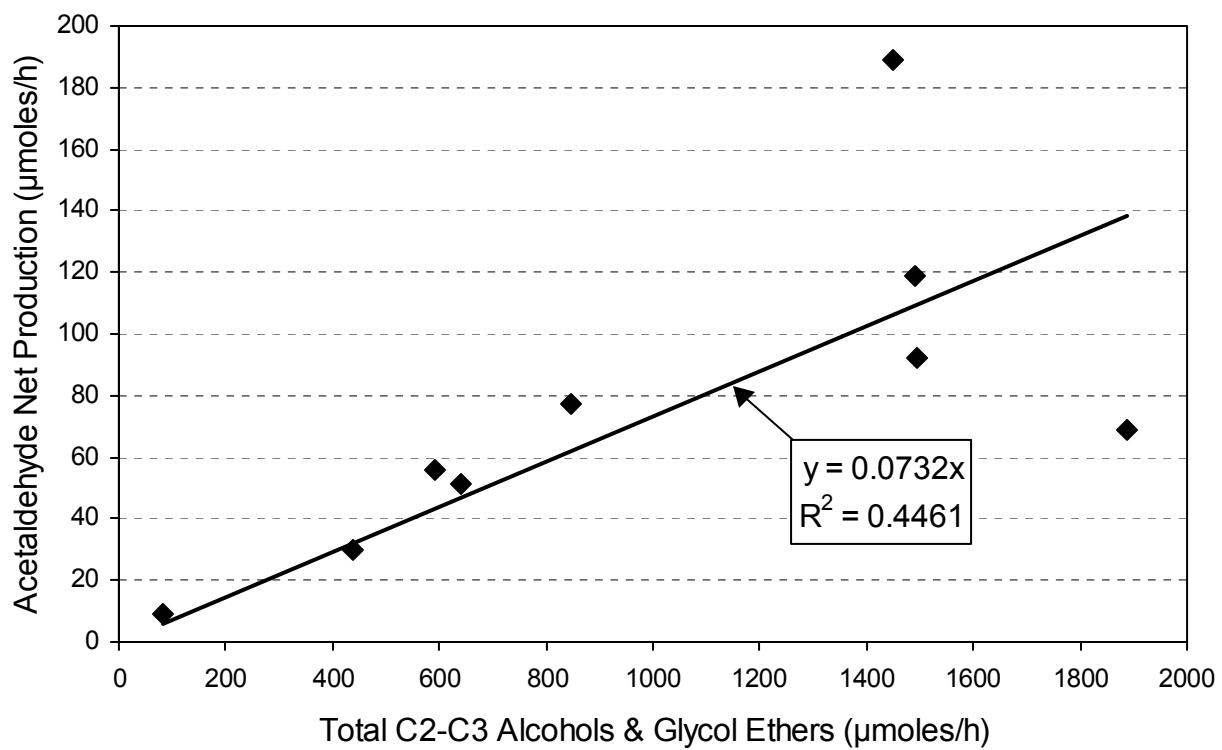


Figure 9. Acetaldehyde net production rate in nine experiments versus the supply rate of C₂ – C₃ alcohols and glycol ethers to the UVPCO.

APPENDIX A

Controlling Indoor Generated Particles: A Comparison of the Costs of Filtration and Ventilation

Options for reducing indoor concentrations of indoor generated particles include using high efficiency filters in a building's HVAC system and increasing the rate of outdoor air supply. While no formal comparison of the relative costs of these two options has been published; this appendix provides several examples indicating that filtration is the much less expensive option.

An analysis of energy costs of using a high efficiency filter is outlined in Table A1, drawing upon data in Figure 7 from Fisk et al. (2002).

Table A1. Example filter performance and cost estimates

| Filter Efficiency Rating Dust Spot (MERV) | Particle Removal Efficiency at particle size 0.2 μm 0.5 μm 1 μm | Clean Air Delivery Rate ^a - $\text{m}^3/\text{hr}\text{-person}$ at particle size 0.2 μm 0.5 μm 1 μm | Annual Filtration Energy Cost ^b \$/person - year | Annual Filtration Energy Cost ^c \$ per m^3/hr clean air at particle size 0.2 μm 0.5 μm 1 μm |
|--|--|--|--|--|
| 90 (13 – 14) | 0.50 0.70 0.93 | 150 210 280 | \$8.4 - \$12.6 | \$0.07 \$0.05 \$0.04 |

- a. Assumes air flow through filter of $300 \text{ m}^3/\text{hr}$ per person, the clean air delivery rate is the product of the air flow rate and the particle removal efficiency
- b. Assumes 7 persons per 1000 ft^2 (93 m^2) of floor area
- c. Uses average of costs from previous column

For comparison, we have analyzed estimates of the energy costs of ventilation for office buildings and compiled the results in Table A2. The paper by Mudarri et al., (1996) did not provide sufficient information to allow updating of their cost estimates for energy price inflation; however, their annual costs should be increased by at least 50% for direct comparison to the more recent estimate of Fisk et al. (2005).

Table A2. Estimates of energy costs of providing 1 m³/hr of outdoor air to an office building

| Reference | Annual Energy Cost per m ³ /hr of Outdoor Air | | |
|----------------------|--|-------------|--------|
| | Washington D.C. | Minneapolis | Miami |
| Mudarri et al. 1996* | \$0.28 | \$0.22 | \$0.45 |
| Fisk et al. 2005** | \$0.42 | --- | --- |

- a. Uses 1994 national average energy prices of \$0.50 per kWh and \$0.50 per therm of natural gas
- b. Uses 2001 energy prices in Washington D.C. of \$0.76 per kWh and \$1.15 per therm of natural gas

From a comparison of the cost estimates in the last column of Table A1 with the estimates in Table A2, it is clear that the use of ventilation to control indoor-generated particles is several times more expensive than using a high-efficiency particle filter in the HVAC system. The particle filter has the additional advantage of removing particles from the incoming outdoor air, while outdoor air ventilation is itself a source of particles to the building.

References

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APPENDIX B

Estimating Indoor Concentrations of Reaction Products with UVPCO Operation

The prototype UVPCO device produced significant quantities of formaldehyde and acetaldehyde, apparently from incomplete decomposition of reactants (possibly alcohols and glycol ethers) in the inlet air stream. At the same time, a portion of the formaldehyde and acetaldehyde is destroyed as air containing these compounds passes through the device. We have developed a simple steady-state mass balance model to estimate the net impact of UVPCO operation on the indoor concentrations of formaldehyde and acetaldehyde. This model assumes that the UVPCO system is installed in the supply air stream of the HVAC system and, therefore, treats the mixture of outdoor and recirculated indoor air. The model and model inputs are described below.

With no UVPCO system operating, the indoor concentration of reactants is calculated from the simple expression:

$$C_r = \frac{S_r}{\lambda} \quad (1)$$

where subscript r refers to reactants; C_r is the total indoor concentration of all reactants; S_r is the indoor source strength of reactants per unit indoor volume; and λ is the rate of outdoor air supply divided by the indoor volume. The concentration of a reaction product is calculated identically, because in this case no product is produced by the UVPCO system.

$$C_p = \frac{S_p}{\lambda} \quad (2)$$

where subscript p refers to a reaction product (e.g., formaldehyde or acetaldehyde).

With a UVPCO system operating, the mass balance calculation must account for the destruction of compounds by the UVPCO system and also for the production of products due to incomplete decomposition of reactants. For reactants, the mass balance yields:

$$C_r' = \frac{S_r}{\lambda' + R' \lambda' \varepsilon_r} \quad (3)$$

where the superscript ' denotes with UVPCO operation; R' is the ratio of recirculation air flow to outdoor airflow through the UVPCO system; and ε is the pollutant conversion efficiency of the UVPCO device. For a reaction product, the indoor concentration is estimated from the equation:

$$C_p' = \frac{S_p + R' \lambda' C_r' F}{\lambda' + R' \lambda' \varepsilon_p} \quad (4)$$

where the right-hand term in the numerator accounts for the fact that the UVPCO system is an additional indoor source of products. In this term, F is the ratio of mass (or moles) of product produced per unit time by the UVPCO system to the total UVPCO inlet mass (or moles) flow of reactants, estimated from our experimental data. This expression assumes that the quantity of reactants in the outdoor air passing through the UVPCO is negligible relative to the quantity of reactants in recirculated air.

The equations above were used with appropriate model inputs to estimate how concentrations of indoor formaldehyde and acetaldehyde will compare in two scenarios. Scenario 1 is normal building operation with an outdoor air ventilation rate of one air change per hour ($\lambda = 1 \text{ h}^{-1}$) and no UVPCO operation. In Scenario 2, the outdoor air ventilation rate is reduced to 0.5 air changes per hour ($\lambda' = 0.5 \text{ h}^{-1}$) and a UVPCO system is operated in the supply air stream with a recirculation air flow rate equal to six times the outdoor air flow rate, or 3 h^{-1} ($R' = 6$).

To utilize the equations, we must have estimates of typical indoor emission rates of reactants (S_r) and products (S_p) in office buildings. We estimate S_r and S_p from the equations:

$$S_r = \sum C_i^{typ} \lambda^{typ} \quad (5)$$

$$S_p = C_p^{typ} \lambda^{typ} \quad (6)$$

where C_i^{typ} is a typical concentration of reactant i (e.g., one of multiple alcohols and glycol ethers) from prior measurements in office buildings; C_p^{typ} is a typical concentration of a product (i.e., formaldehyde or acetaldehyde); and the typical ventilation rate (λ^{typ}) is assumed to be 1 h^{-1} .

Values of C_i^{typ} and C_p^{typ} were obtained from a recent study of indoor VOCs in a call center (Hodgson et al., 2003). The other model parameters were taken or derived from the results of this study assuming a commercial device would have similar performance characteristics. We've assumed first order reactions, i.e., no change in conversion efficiency with concentration. The input parameters and model results for formaldehyde and acetaldehyde are presented in Table B1. For formaldehyde, $\sum C_i^{\text{typ}}$ was taken to be the sum of the geometric mean concentrations of alcohols and glycol ethers in the call center. These compounds are ethanol, isopropanol, 1-butanol, 2-ethyl-1-hexanol, and 2-butoxyethanol. For acetaldehyde, we simply used the geometric mean ethanol concentration, as ethanol is likely the primary reactant leading to acetaldehyde formation. The reactant source strength for Scenario 2 was taken from Scenario 1. The reactant conversion efficiencies are taken from experiments conducted at $580 \text{ m}^3/\text{h}$. Many alcohols and glycol ethers had efficiencies near 40%. The average efficiency for acetaldehyde was 36%. The experiments did not generate conversion efficiencies for formaldehyde and acetaldehyde at the $580 \text{ m}^3/\text{h}$ flow rate. Instead, we took the efficiencies at $280 \text{ m}^3/\text{h}$ and halved them to account for the shorter residence time. The product production rates as functions of the reactant supply rates were taken as the slopes of the relationships shown in Figures 8 and 9. There is considerable scatter in the data, particularly for acetaldehyde. For this one limited example, the estimated formaldehyde concentration for Scenario 2 was 33 ppb versus 12 ppb in Scenario 1. The acetaldehyde concentration increased to 10.5 ppb Scenario 2 from 3 ppb in Scenario 1.

Reference

Hodgson AT, Faulkner D, Sullivan DP, DiBartolomeo DL, Russell ML, and Fisk WJ (2003)
Effect of outside air ventilation rate on volatile organic compound concentrations in a call center. *Atmospheric Environment* 37(39-40):5517-5527.

Table B1. Estimation of the impact of UVPCO operation in a building with reduced ventilation rate on indoor formaldehyde and acetaldehyde concentrations (Scenario 2) compared to a building with normal ventilation and no UVPCO (Scenario 1). See text for an explanation of the sources of the parameters for reactant and product concentrations for Scenario 1 and reactant and product conversion efficiencies and product production rates for Scenario 2

| Model Parameter | Symbol | Units | Parameter Value | |
|---------------------------------------|-----------------|---|-----------------|--------------|
| | | | Formaldehyde | Acetaldehyde |
| Scenario 1 – No UVPCO | | | | |
| Air change rate | λ | h^{-1} | 1.0 | 1.0 |
| Reactant concentration | C_r | ppb | 87 | 38 |
| Reactant concentration | C_r | $\mu\text{moles}/\text{m}^3$ | 3.6 | 1.6 |
| Product concentration | C_p | ppb | 11.9 | 3.0 |
| Product concentration | C_p | $\mu\text{moles}/\text{m}^3$ | 0.49 | 0.12 |
| Scenario 2 – With UVPCO | | | | |
| Air change rate | λ | h^{-1} | 0.5 | 0.5 |
| Recirculation ratio | R' | | 6 | 6 |
| Reactant source strength | S_r | $\mu\text{mole}/\text{m}^3\text{-h}$ | 3.6 | 1.6 |
| Product source strength | S_p | $\mu\text{mole}/\text{m}^3\text{-h}$ | 0.49 | 0.12 |
| Reactant conversion efficiency | ε_r | | 0.40 | 0.36 |
| Product conversion efficiency | ε_p | | 0.14 | 0.09 |
| Product production vs reactant supply | F | $\mu\text{moles}/\text{h per }\mu\text{moles}/\text{h}$ | 0.12 | 0.07 |
| Estimated product conc. | C'_p | $\mu\text{moles}/\text{m}^3$ | 1.35 | 0.43 |
| Estimated product conc. | C'_p | ppb | 33 | 10.5 |
| Conc. Scenario 2 vs. conc. Scenario 1 | | ppb/ppb | 2.8 | 3.5 |