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Publication Date

2023-02-01

DOI

10.1016/j.chemosphere.2022.137528

Peer reviewed



Published in final edited form as:

Chemosphere. 2023 February ; 313: 137528. doi:10.1016/j.chemosphere.2022.137528.

Controlled air exchange rate method to evaluate reduction of volatile organic compounds by indoor air cleaners

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Abstract

Air cleaning technologies are needed to reduce indoor concentrations and exposure to volatile organic compounds (VOCs). Currently, air cleaning technologies lack an accepted test standard to evaluate their VOC removal performance. A protocol to evaluate the VOC removal performance of air cleaning devices was developed and piloted with two devices. This method injects a VOC mixture and carbon dioxide into a test chamber, supplies outdoor air at a standard building ventilation rate, periodically measures the VOC concentrations in the chamber using solid phase microextraction-gas chromatography-mass spectrometry over a three-hour decay period, and compares the decay rate of VOCs to carbon dioxide to measure the VOC removal air cleaning performance. The method was demonstrated with both a hydroxyl radical generator and an activated carbon air cleaner. It was shown that the activated carbon air cleaner device tested had a clean air delivery rate an order of magnitude greater than the hydroxyl radical generator device (72.10 vs 6.32 m³/hour).

Keywords

Volatile organic compounds; air cleaning; indoor air quality; method of test; performance evaluation

1. Introduction

The concentration of gas-phase chemical contaminants is generally higher indoors compared to outdoors due to the small, enclosed volume of the indoor built environment with emission sources such as paint, personal hygiene products, air fresheners, building materials, furniture, and cooking related products that can emit volatile organic compounds (VOC).

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(Agency, 1987, Meier et al., 2015) Poor ventilation and lack of air cleaning methods that remove gas-phase contaminants compound these effects. Additionally, outdoor VOC sources can raise indoor VOC concentrations,(Tang et al., 2016) such as the extraordinary number of large wildfires in the US.(Xu et al., 2020) New VOC measurement technologies(Fung et al., 2019, Rajapakse et al., 2021, McCartney et al., 2017a) were used to sample outdoor VOCs during a major wildfire event, demonstrating a wide range of volatiles from different chemical families.(Simms et al., 2021) VOCs of greatest health concern are aromatic hydrocarbons, such as benzene family; benzene, toluene, ethyl benzene and xylenes (BTEX).(Fung et al., 2019) Health effects due to these chemical exposures range from minor to life-threatening depending on toxicant concentrations and duration of the exposure. (Fung et al., 2019, Jones, 1999) Therefore, it is necessary to take action to minimize VOC exposures either by monitoring air quality and avoiding hazardous environments or by improving indoor air quality using engineering tools such as air cleaning systems.

Hydroxyl (OH) radicals present in the troposphere are considered to be the most important oxidant and are sometimes referred to as the “detergent of the atmosphere” due to their ability to oxidize harmful carbon monoxide and methane to carbon dioxide (CO₂) and water. (Katja Riedel, 2008, Stone et al., 2012) In the past, OH radical generators have been used for air purification in certain environments as demonstrated by the National Aeronautics and Space Administration spacecrafts to keep the air safe for astronauts.(NASA, 2018, Graf, 1994) These devices rely on indoor humidity to generate OH radicals from water molecules in large numbers, although the radicals have a very short lifetime. The radicals are often spread by a fan in an indoor environment to reach the volatile contaminants, and these OH radicals may react and decompose such contaminants.(NASA, 2018, Graf, 1994) Manufacturers of hydroxyl generators sometimes claim the devices can remove or decompose hazardous VOCs from sources such as pet odor and cigarette smoke, in addition to destroying viruses, bacteria and molds. However, by-products from an OH radical generator may include oxygenated compounds and semi volatile organic compounds which can form secondary organic aerosol.(Collins and Farmer, 2021) Specifically, formation of secondary organic aerosol is considered to be one of the factors that increase mortality.(Pye et al., 2021)

To date, there is no accepted test standard to measure in-room air cleaning device performance for removal of specific hazardous VOCs from indoor air, such as BTEX, which is one of the most common indoor and outdoor air pollutants.(Esplugues et al., 2010, Jones, 1999, Ielpo et al., 2021) A 2011 literature review of 59 papers on the effectiveness of air cleaning techniques (inclusive of both particle and VOC removal performance) determined that “the existing data make it difficult to extract information such as clean air delivery rate” and that a standard approach to testing is needed.(Zhang et al., 2011) However, current residential air cleaning technologies still lack an accepted test standard for removal of gas-phase contaminants(Stephanie Licht et al., 2021, Zeng et al., 2021), in contrast to particle filtering performance validation methods that are now well developed.(AHAM, 2021, ASHRAE, 2017) Particle filtering technologies are widely accepted and can be compared by consumers using the clean air delivery rate (CADR) metric for portable air cleaners and the minimum efficiency reporting value (MERV) for central system filters. A laboratory test method is available to assess the single-pass gas-phase air-cleaning efficiency

of in-duct air cleaning devices, however the method is not suitable for in-room devices. (ASHRAE, 2016)

Several research approaches and devices have been recently applied to evaluate the VOC removal performance of air cleaning devices, including byproduct formation. Ye et al and Chen et al tested a variety of air cleaners in sealed chambers and calculated the CADR in response to a challenge VOC mixture.(Chen, 2005, Ye, 2018) Chen et al confirmed the sealed chamber had negligible air exchange rate (AER) of 0.001 to 0.004 h⁻¹. Fermo et al. analyzed VOC removal of a water-bath air cleaning device in an apartment with real-time measurement of total VOC content reduction with a photoionization based total VOC detector.(Fermo et al., 2021) While the study concluded that the air cleaner reduced VOCs by 50%, the methods lacked control or characterization of AER with the outdoors and chemical identification of specific VOCs. The removal rate of a VOC is a function of initial indoor concentration, outdoor concentration, AER between indoors and outdoors, atmospheric and surface losses, and air cleaner performance. AER in buildings varies as a function of window use, temperature, wind speed, and use of exhaust fans. It is important to characterize, and ideally control AER, when evaluating air cleaner performance so the results are not confounded by varying AER. (Yamamoto et al., 2010, Wallace et al., 2002) However, sealing a chamber completely to control AER (for an AER of effectively zero) does not account for the air exchange that naturally occurs in buildings due to natural and mechanical ventilation.

Electronic air cleaners such as plasma generators, ionizers and hydroxyl radical generators may claim hazardous volatile chemical modification to non-hazardous levels and such claims require testing and validation. Zeng et al. quantified real-time concentrations of 20 VOCs in response to a bipolar ionization device using both gas and liquid chromatography mass spectrometry as detection techniques and found that some VOCs decreased during the ionization process while others increased, although many comparisons were within the analytical uncertainty.(Yicheng Zeng 2022) The study was conducted in a chamber which, because of uncontrolled infiltration, had an AER of 1.8 – 2.0 h⁻¹ as generally measured at the end of each experiment. Additionally, Blondeau et al. tested the single-pass efficiency of six air cleaning devices, including VOC removal performance using ion molecule reaction mass spectrometry for five target VOCs and ASTM Method D5197 for formaldehyde measurements, and determined that only activated carbon was effective at VOC removal. (Blondeau et al., 2021) Joo et al. used a high-resolution time of flight chemical ionization mass spectrometer to characterize byproducts, including secondary organic aerosols, formed by operation of a hydroxy radical generator in a standard office (AER not reported) without additional VOCs added to the environment.(Joo, 2021) In summary, none of literature reviewed that used a chamber test method controlled AER with the outdoors to reflect standard building conditions (and some did not report AER). Controlling AER is important considering the impact that any variation in air exchange with the outdoors will have on VOC decay rates in an enclosed chamber.

In this current study, we build upon the wide variety of previous research to present a chamber measurement method for air cleaner VOC removal performance with two important features: 1) the control and continuous real-time characterization (using well established

tracer gas decay methods)(Cui, 2015) of AER with the outdoors and 2) periodic sampling of VOCs using solid phase micro extraction (SPME) fibers which were then analyzed off-site. CO₂ was used as the tracer gas for AER measurement because it is chemically inert, low-cost, easy to measure, and has low environmental impact.(Cui, 2015) Recognizing that electronic air cleaning devices are designed to be operated in buildings that exchange air with outdoors (and not sealed chambers), the test method operates the test chamber at an AER of 1.0 h⁻¹ to provide a realistic test condition.(Yamamoto et al., 2010, Wallace et al., 2002, Chan, 2005)

Volatile concentrations were quantified in discrete timepoints over 3–5 h. The reduction in VOCs was converted to an equivalent AER, which includes VOC losses from outdoor air ventilation AER, atmospheric and surface losses, and air cleaning. The outdoor air ventilation AER, measured with CO₂ decay, was subtracted from the equivalent AER to determine removal from atmospheric and surface losses and air cleaning. Two air cleaners were selected for testing to serve as a case study for demonstrating the methodology. Results of air cleaner experiments were compared to a control case with no air cleaning to determine whether air cleaning devices significantly reduce indoor VOC concentrations relative to their removal through other mechanisms. The method was demonstrated with an activated carbon air cleaner and a hydroxyl radical generator.

2. Methods/Materials

2.1. Overview

We instrumented a test chamber to measure VOC removal performance without hazardous chemical exposure to occupants. This chamber (Figure 1) is located at the Western Cooling Efficiency Center at the University of California, Davis. It is a sealed and insulated stainless-steel walled enclosure with an inside volume of 12.68 m³ (length 2.44 m, width 2.13 m, height 2.44 m). The test chamber temperature and humidity were measured (Vaisala HMP110) and recorded every 10s. While the test chamber air was not conditioned during the experiments, the conditions were generally stable due to the surrounding laboratory environment.

The chamber and associated duct work were leak tested with a blower door (TEC Minneapolis Blower Door System) and leakage was below the limit of detection of 18.7 m³/hr at a pressurization of 50 Pa, whereas chamber pressure during normal operation is less than 10 Pa. The chamber has a highly controllable ventilation system that mixes outdoor air with return air, which is then supplied back to the chamber. The outdoor air flow rate is set at the beginning of the experiment by setting the position of the outdoor and return air damper assembly, and the speed of the supply air fan. Chamber air is exhausted into a laboratory exhaust system. For these experiments, the system was configured to provide a ventilation AER of 1 h⁻¹, which was estimated to be the 75th percentile for AER measurements made in 70,000 residential homes(Chan, 2005). A ceiling fan in the chamber was run at low speed for all tests to mix the chamber air.

Pure CO₂ was injected into the chamber to reach 1,500–2,000 ppm at the beginning of the experiment and the indoor CO₂ concentration was measured continuously. A factory-

calibrated high-accuracy (± 40 ppm) probe (Vaisala GMP 252, Finland) mounted on the chamber wall (Figure 1) was used to calculate the delivered outdoor air ventilation rate (inclusive of any minimal chamber infiltration) based on the CO₂ decay (see section “2.2 CO₂ decay”). Additionally, the chamber exhaust and return air were monitored with HVAC-grade accuracy (± 30 ppm +2% of reading) sensors (Vaisala GMW90) to confirm chamber air was well-mixed. These sensors were calibrated on-site using a three-point calibration with calibration gases of specified CO₂ concentration (425, 1100, 1700 ppm). (Frasier, 2021)

For the OH radical generator experiment, the device was set up on a rack and placed inside the chamber (Figure 1) along the left wall with air delivery toward the center of the chamber (as recommended by the manufacturer). While we are unable to provide specifics on the device, it was developed by a multinational consumer electronics company and is intended to improve indoor air quality in residential buildings as part of a cooling/heating air handling system. The system is designed to serve one room up to a floor area of 40 m². The test method was developed to evaluate the VOC removal performance of air cleaning technologies, although the OH radical generator tested is not marketed to remove VOCs. For activated carbon air cleaning experiments, a commercial device (IQAir Air Purifiers, Switzerland) was placed in the center of the chamber (drawing air from all sides) and operated per the manufacturer’s instructions with a self-reported airflow rate of 221 m³/hr. The results of this study should not be considered by the reader as an assessment of these air cleaning technologies, instead, these air cleaning devices were only used to demonstrate the VOC testing method described herein.

Prior to VOC experiments, the chamber was not used for any chemical related experiments for at least three days to avoid outside chemical interference, and the initial background VOC levels were measured just before experiments (see VOC introduction and sampling). We selected 10 VOCs (Sigma-Aldrich, Burlington, MA,) (Table 1) associated with wildfire smoke (Simms et al., 2021) due to an interest in evaluating air cleaner performance in reducing exposure to wildfire-related VOCs, however, the method is adaptable to other VOCs of interest. Notably, while BTEX is present in wildfire smoke, it is a common indoor and outdoor pollutant with a variety of sources. (Esplugues et al., 2010, Jones, 1999, Ielpo et al., 2021) The selected VOCs were evaporated as a mixture into the indoor chamber air at the beginning of their experiment. The decay rate of each VOC was compared for each air cleaner test in comparison to a control with no air cleaner operating. For all experiments, the outdoor air ventilation rate was held constant at an AER of 1 h⁻¹, which was confirmed with the CO₂ decay measurements. Our goal was to assess whether the OH radical device or the activated carbon device significantly reduced VOC concentrations relative to the removal provided by the ventilation system.

2.2. CO₂ Decay

The chamber CO₂ concentration was raised to 1,500 – 2000 ppm at the start of the experiment. The indoor chamber, exhaust, return, and outdoor CO₂ concentrations were measured and logged at 10 s intervals. The data was post-processed and the previous 5 min average outdoor CO₂ concentration (to reduce influence of noise from this signal) was subtracted from the indoor chamber CO₂ concentration to determine the CO₂ concentration

above the outdoors as a function of time. For a well-mixed chamber where CO₂ is inert, the AER of the chamber is calculated by fitting the data using a least-squares regression method to the equation:

$$C(t) = C_o e^{-AER_{vent} * t} \quad \text{Equation 1}$$

where C_o is the initial chamber CO₂ concentration above outdoors (determined from the regression), $C(t)$ is the chamber CO₂ concentration above outdoors as a function of time, t is time in hours, and AER_{vent} is the outdoor air changes per hour of outdoor air (determined from the regression).

To verify that the chamber air was well-mixed over the course of the test, the differences between 1) exhaust air and chamber air and 2) return air and chamber air were calculated at each time stamp and averaged over the test period. The result was checked to ensure that each average difference was less than 50 ppm. This method is consistent with Cui et al that concluded in-situ CO₂ measurements agree well with reference values and that a measurement taken at chamber exhaust provides an accurate measurement of air change rate (Cui, 2015).

2.3. VOC introduction and sampling

Volatiles were sampled by drawing a volume of chamber air into 5 L Tedlar bags (Restek Corporation, Bellefonte, PA) at discrete timepoints (Figure 2a). Then, VOCs were extracted from the Tedlar bags and analyzed using a solid phase microextraction-gas chromatography-mass spectrometry approach (SPME-GC-MS, Figure 2b). Polytetrafluoroethylene (PTFE) tubing with inner diameter 0.25 in was attached to the chamber with four inlets (named A, B, C, D) for sample air extraction from the chamber (Figure 1). The outlet tubing was passed through a sealed hole of the back wall of the chamber to a vacuum pump (MOA-P101-AA, GAST Manufacturing Inc., Benton Harbor, MI) placed outside the chamber. The total tubing length from each inlet to the pump was the same so that the flow sampled from each inlet is approximately equal.

Tedlar bags are made with a nonreactive polyvinyl fluoride polymer resin and are commonly used for air sampling of VOCs and ambient gases. During the sampling, the pump was run for 1–2 sec prior to connecting the bag to remove the dead air volume of the tubing and then the outlet of the vacuum pump was attached to the inlet port of an empty Tedlar bag. The pump was operated for 35 sec to fill the bag. Then, the port of the Tedlar bag was closed, and the sample line was disconnected.

Once the bag was filled with chamber air, divinylbenzene/carboxen/polydimethylsiloxane SPME fibers (57329-U, ThermoFisher Scientific Corporation, Waltham, MA) with a 1 cm needle was used to extract VOCs from the Tedlar bags. Three to four SPME fibers were inserted into the bag through a septum and remained in place for 30 min to extract VOCs. After extraction, SPMEs were immediately capped, stored in a –20 °C freezer and analyzed by GC-MS within 24 h.

First, a sample of the chamber air prior to VOC introduction was collected to ensure the system was free of contamination (Figure 2(a) timeline). Then, 10 μL of the standard VOC mixture in liquid phase was added to the center of the chamber. VOC concentrations in the liquid mixture were calculated such that their evaporated volume would yield a specific concentration (concentration range of 120–177 ppb for 10 chemicals) based on the chamber volume. The mixture equilibrated for 15 min with the chamber ventilation system off and the ceiling fan on to ensure the VOCs evaporated and dispersed throughout the chamber air. At time t_0 , which was set at the end of 15 min evaporation period, an initial chamber air sample was collected and then the air cleaning device, if used, was turned on. Subsequent chamber air samples were taken relative to the end of the 15 min evaporation period (Figure 2a). More frequent time points, time t_1 , t_2 and t_3 were used within the first hour of the sampling when the chemical concentration decay rate was high and then sampling frequency was reduced to one hour time intervals from time t_4 and onwards as the concentration decay rate was considerably low. The VOC decay with no air cleaning device was measured for five hours. Analysis confirmed that a three-hour experiment provided sufficient data to calculate decay coefficients and thus the other experiments were shortened to three hours.

Tedlar bags were reused for subsequent tests. They were checked for damage and cleaned overnight in a vacuum oven. The cleaning process was validated by sampling cleaned bags for contamination; no contamination was detected.

2.4. GC-MS analysis of VOCs

VOCs from SPME fibers were analyzed using a thermal desorption GC-MS method. An SPME fiber was injected into a Cooled Injection System (“CIS”, Gerstel US) inside an Agilent 6890N gas chromatograph coupled with a 5795C mass spectrometer (Agilent Technologies Inc., Santa Clara, CA). When the SPME was introduced, the CIS temperature was initially 250 $^{\circ}\text{C}$ then ramped at 10 $^{\circ}\text{C}/\text{min}$ to 270 $^{\circ}\text{C}$, which was held for 5 min. Desorbed VOCs were injected in splitless mode onto the HP-5 ms GC column (30 m \times 0.25 mm \times 0.25 μm , Agilent Technologies Inc., Santa Clara, CA). Helium was used as carrier gas at a constant 1.5 mL/min. The oven was set using a temperature gradient at initial 40 $^{\circ}\text{C}$ for 4 min, raised to 65 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$, held for 1 min, and then ramped to 250 $^{\circ}\text{C}$ at 40 $^{\circ}\text{C}/\text{min}$. The transfer line to the MS was set at 260 $^{\circ}\text{C}$ and the mass spectrometer operated in scan and selected ion monitoring (SIM) mode, simultaneously. A mass range was measured between 35 and 550 amu, and SIM mode was defined with specific ions corresponding to the targeted VOCs in a retention time range (Table 2). Because p- and m-xylene do not separate on the HP-5ms column, their concentrations are combined in all experimental data.

2.5. VOC Calibration Curves

Seven Tedlar bags were filled with ultrahigh purity nitrogen and each bag was spiked with a known concentration of the VOC mixture. Ideal gas law was used to calculate the required chemical volume from the original vial and the stock concentration of 1000 ppm was prepared using purified air filled Tedlar bags. Serial dilutions were made using additional Tedlar bags to achieve the desired concentrations in the calibration range. The seven calibration concentrations were selected to cover the range of concentrations expected in the chamber over the course of the three-hour decay. Triplicates of SPME fibers per bag

were exposed for 30 min and measured by the same thermal desorption GC-MS method previously described. The known concentration (Please refer Table S2, column “conc range” for the concentrations) in each of the seven Tedlar bags along with the measured abundance data from the SPME-GC-MS analysis was used to build calibration curves to convert the SPME-GC-MS data from the chamber experiments to chemical concentrations.

2.6. VOC Decay Calculations

Since the chamber is ventilated with outdoor air, it is expected that VOC concentrations will decrease during experiments even without active air cleaning due to dilution by outdoor air and through atmospheric and surface reactions. VOC concentrations were used to calculate the equivalent AER, which includes the impacts of both outdoor air ventilation (also measured by the CO₂ decay), atmospheric and surface losses, and any VOC removal from air cleaning devices. The equivalent AER was calculated by fitting the concentration data for each VOC using a least-squares regression method to the equation:

$$VOC(t) = VOC_{bg} + (VOC_o - VOC_{bg}) e^{-AER_{eq}t} \quad \text{Equation 2}$$

where VOC_o is the initial chamber VOC concentration above background (determined from the regression), VOC_{bg} is the background VOC concentration in the environment (determined from the regression, with a minimum of zero), $VOC(t)$ is the chamber VOC concentration above background as a function of time, t is time in hours, and AER_{eq} is the equivalent AER which includes both outdoor air exchange, atmospheric and surface losses, and air cleaning. While the background concentration was also measured prior to each experiment, predicting the background concentration from the multiple SPME samples over the course of the test produces better decay fit results due to high relative uncertainties with measuring low background concentrations, which were near or below the SPME-GC-MS limits of detection.

Finally, the CADR for VOC removal produced by the air cleaner was calculated from the equation:

$$CADR = (\overline{AER_{eq}} - AER_{vent}) * V \quad \text{Equation 3}$$

where AER_{vent} is determined from equation 1, $\overline{AER_{eq}}$ is the average result of AER_{eq} for all VOC decays calculated using equation 2, and V is the chamber volume. The CADR method allows results to be compared for tests conducted in chambers of different volumes, as long as the chamber size is appropriate for the air cleaning device.

2.7. Experiments Conducted

The OH radical device contained two components: a fan, which could operate with and without OH radical generation, and the OH radical generator, which could only operate with the fan on. To ensure any VOC degradation with the OH radicals were not resulting from the device fan, two experiments were run with the device (fan ON, OH radicals off; and fan ON, OH radicals ON).

In total, four experiments were performed, all of which were done with the chamber ventilation operating and the ceiling fan set to low speed: (1) control (no device), (2) OH radical device, fan ON and OH radical generation OFF (no air cleaning), (3) OH radical device, fan ON and OH radical generator ON, and (4) activated carbon device ON.

3. Results and Discussion

Environmental conditions in the chamber were consistent between tests, with average chamber air temperature ranging from 21.4 to 22.2 °C and average relative humidity between 46.3 to 52.6% (Table S1). Outdoor air CO₂ concentration was relatively stable and averaged between 450 to 490 ppm across tests (Table S1). Average difference between the chamber exhaust air and indoor air CO₂ concentration was less than 40 ppm and average difference between the chamber return air and indoor air CO₂ concentration was less than 20 ppm (Table S1), indicating that the chamber was well-mixed and that mixing was consistent between experiments.

The results of the calibration curves of the 10 experimental VOCs are shown in Figure S1 and Table S2, where MW is the molecular weight of each chemical, RT is gas chromatograph retention time in minutes for each of the chemicals, ion is the detected m/z value (experimental) from the mass spectrometer reading, and LOQ is limit of quantification. The SPME-GC-MS method resulted in LOQ for all VOCs down to 2–5 ppb, and all compounds had appropriate linear fits. The lowest experimentally detectable concentration level from the “concentration range” column in Table S2 was taken as the LOQ, the last column of the same table.

An example of raw GC-MS data plots (prior to integration of raw counts to obtain peak area and conversion to concentration using calibration curves) is shown in Figure 3, which plots counts on same Y scale to visualize the natural reduction of VOC concentration (i.e. reduction of GC peak height and area) without air cleaning device operation. The processed measured VOC concentrations were then used to calculate resulting exponential decay curve fits.

As an example, the decay curve fits for benzene are shown for each test in Figure 4. The dispersion of VOC concentrations at higher concentrations in contrast to the lower concentrations may be associated with the considerable GC peak shape variations associated with larger GC peak areas resulted by larger concentrations. The results illustrate the importance of SPME replicates for each concentration. Although the initial concentration of each VOC in the chamber varied between tests, the calculation of AER_{eq} can be made at a range of initial concentrations as long as the decay signal measurement is above the instrument’s LOQ. The complete set of nine VOC curve fits for each test are included in supplementary material (Figures S2 through S5). Results for the least-squares regression solutions to Equation 2 for each test for each VOC and are included in Table S3. The background concentration measurement made prior to each experiment to check for contamination is also reported. As expected, background concentrations were much lower than the VOC concentrations introduced into the chamber.

The calculated AER_{eq} for decay of each VOC, average \overline{AER}_{eq} for all VOCs, AER_{vent} measured from CO_2 decay, and CADR for the OH radical generator and activated carbon air cleaner are tabulated in Table 3 for all four experiments. The comparison of AER_{vent} and \overline{AER}_{eq} , which compares the VOC decay resulting from ventilation to the total VOC decay, is presented for each experiment in Figure 5.

Volatile decay measurements for the control experiment (no device) had greater variance among individual VOC decay rates compared to the experiment with the OH radical device fan on without air cleaning (Table 3), presumably because operating the additional fan increased mixing of VOCs within the chamber. A one-way ANOVA determined that \overline{AER}_{eq} rates were not equal across all four experiments ($p=2.73 \times 10^{-14}$). A Tukey's honest significant test determined that only the activated carbon device had a significantly higher VOC reduction rate, based on \overline{AER}_{eq} . Comparison of the OH radical device with OH generation OFF and ON did have a significant effect. With OH radical generation, the device had a slight improvement in reducing VOCs per a 2-way t-test ($p=0.001$), indicating that OH radicals were reducing volatile concentrations, although at levels insignificant compared to the activated carbon device.

In terms of CADR, both the control experiment (no air cleaning) and the OH radical device with fan ON and OH generation OFF, produced CADR values less than 0, meaning that the CO_2 in the chamber decayed slightly faster than the VOCs. These negative values are likely due to measurement uncertainty resulting from taking the difference of two exponential decay coefficients ($\overline{AER}_{eq} - AER_{vent}$) obtained from least-squares linear regression fits. Also, calculations assume the chamber is well mixed, adding further uncertainty. The negative values indicate that VOC atmospheric and surface losses were negligible over the course of the experiment.

The OH radical generator had a calculated CADR of $6.32 \text{ m}^3/\text{hour}$. While this demonstrates that there is evidence that the OH radical generator is accelerating the decay of the VOCs, the CADR is very small for practical building applications. For reference, an air cleaner operating at $6.32 \text{ m}^3/\text{hour}$ in a typical home with volume of 375 m^3 would require nearly 60 hours to clean the entire air volume. (Chan, 2005) This is consistent with the conclusion of Chen et al that found that an air ionization device tested did not significantly remove any VOCs tested other than limonene. (Chen, 2005) For comparison, the activated carbon device CADR was $72.10 \text{ m}^3/\text{hour}$, which is 11 times the CADR of the OH radical generator and would clean the same home's air volume in 5.2 hours. This is consistent with the range of CADR for VOC removal by portable sorption filtration measured by Chen et al. (Chen, 2005) A full technical description of the OH radical device was not available to us, so we are unable to theorize why this air cleaning system reduced VOCs at a lower rate relative to the carbon filter. We kindly remind readers that the results herein should not be misinterpreted by readers as a comparison of these technologies to reduce VOCs. Instead, these two devices were used only for demonstrative purposes of this method.

OH radicals remove volatile compounds through oxidation reactions, forming new VOCs, some of which may also be of health concern. Thereby, an OH radical device may inadvertently remove one set of toxicants by generating another. The least-oxidized first-

generation products for compounds like BTEX by oxidation would convert benzene to phenol (54% yield), toluene to cresol (19% yield) and xylenes into xylenol (15% yield). Other volatile products, such as benzaldehyde and tolualdehyde, are also created through oxidation of toluene and xylene but in smaller yields (6%).(Bates, 2021) Fragmentation and autooxidation generates highly oxidized, small products like glyoxal, methylglyoxal, and 2-butenedial.(Bates, 2021) We mined the GC-MS datasets from the OH radical device with generator ON for evidence of these oxidation products, and none were found. These oxidized compounds were likely lost to surfaces or were generated at levels below limits of detection. Still, this method can be further adapted to increase detection sensitivities to monitor possible formation of volatile byproducts, such as through sorbent-packed micro-preconcentrators(McCartney et al., 2017b) or through more sensitive detectors such as a triple quadrupole mass spectrometer.

4. Conclusions

We demonstrated a chamber measurement method for air cleaner VOC removal performance with two important features 1) the control and continuous real-time characterization (using CO₂ decay methods) of AER with the outdoors and 2) periodic sampling of VOCs using solid phase micro extraction (SPME) fibers which were then analyzed off-site to determine concentration of specific VOCs in the sampled air, enabling calculation of specific chemical removal rates in terms of the CADR. The SPME fiber analysis method worked as desired, however it should be noted that sorbent packed sampling tubes are likely a suitable alternative depending on available materials and equipment. In the future, the SPME-GC-MS measurement method could be replaced with portable and fast gas phase chemical separation and detection technology such as ion mobility spectrometry (IMS). Our current and future work involves development of a portable air monitoring unit with a chemical pre-concentrator chip to replace the SPME fibers, and using an IMS detector to replace the gas chromatograph.(Fung et al., 2019, McCartney et al., 2017a) This device aims to be a portable, rapid, real time chemical detection device that can easily cover a universal range of chemicals including the VOCs.

The method was demonstrated with an AER_{vent} of 1 h⁻¹ with two air cleaners selected to serve as a case study: an OH radical generator and an activated carbon air cleaner. Future work could examine if similar results are obtained at a range of AER seen in homes, where the 10–90th percentile of all homes is estimated to range from 0.2 – 1.5 h⁻¹.(Chan, 2005) It was shown that the particular activated carbon air cleaner device tested had a CADR an order of magnitude greater than the OH radical generator device tested (72.10 vs 6.32 m³/hour). Future work could include testing replicates of air cleaning devices as well as additional types and brands of air cleaning devices. The results are consistent with previous findings that activated carbon air cleaners are more effective at removing VOCs than OH radical generator air cleaners.(Stone et al., 2012, Zeng et al., 2021, AHAM, 2021, Chen, 2005)

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This work was supported by: NIH NCATS 1U18TR003795 [CED], 4U18TR003795 [CED], 1U01TR004083 [CED] and UL1 TR001860 [CED]; NIH award UG3-OD023365 [CED]; NIH award 1P30ES023513-01A1 [CED]; the Department of Veterans Affairs award I01 BX004965-01A1 [CED]; the University of California Tobacco-Related Disease Research Program award T31IR1614 [CED], and Panasonic Life Solutions Company of America contract A21-3577 [CED]. The contents of this manuscript are solely the responsibility of the authors and do not necessarily represent the official views of the funding agencies.

Abbreviations

AER	air changes per hour
BTEX	benzene, toluene, ethyl benzene and xylene
CADR	Clean air delivery rate
CIS	Cooled injection system
MERV	Minimum efficiency reporting value
OH	Hydroxyl
SIM	Selected ion monitoring
SPME-GC-MS	Solid phase microextraction-gas chromatography-mass spectrometry
VOC	Volatile organic compound

Nomenclature

AER_{eq}	Equivalent air exchange rate [h^{-1}] (total ventilation and air cleaning) measured for individual volatile organic compound decay
\overline{AER}_{eq}	Equivalent air exchange rate [h^{-1}] averaged for decay of nine volatile organic compounds
AER_{vent}	Ventilation air exchange rate [h^{-1}] measured with carbon dioxide decay
C_o	Initial carbon dioxide concentration [ppm] at start of the chamber experiment
$C(t)$	Carbon dioxide concentration [ppm] as a function of time
t	Time [h]
V	Chamber volume [m^3]
VOC_{bg}	Background volatile organic compound concentration [ppb]

VOC_0	Initial volatile organic compound at the start of the chamber experiment [ppb]
$VOC(t)$	Volatile organic compound concentration as a function of time [ppb]

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Highlights

- Method to evaluate air cleaner volatile organic compound removal performance
- Clean air delivery rate for removal of volatile organic compounds
- CADR of carbon filter was eleven times the hydroxyl radical generator tested

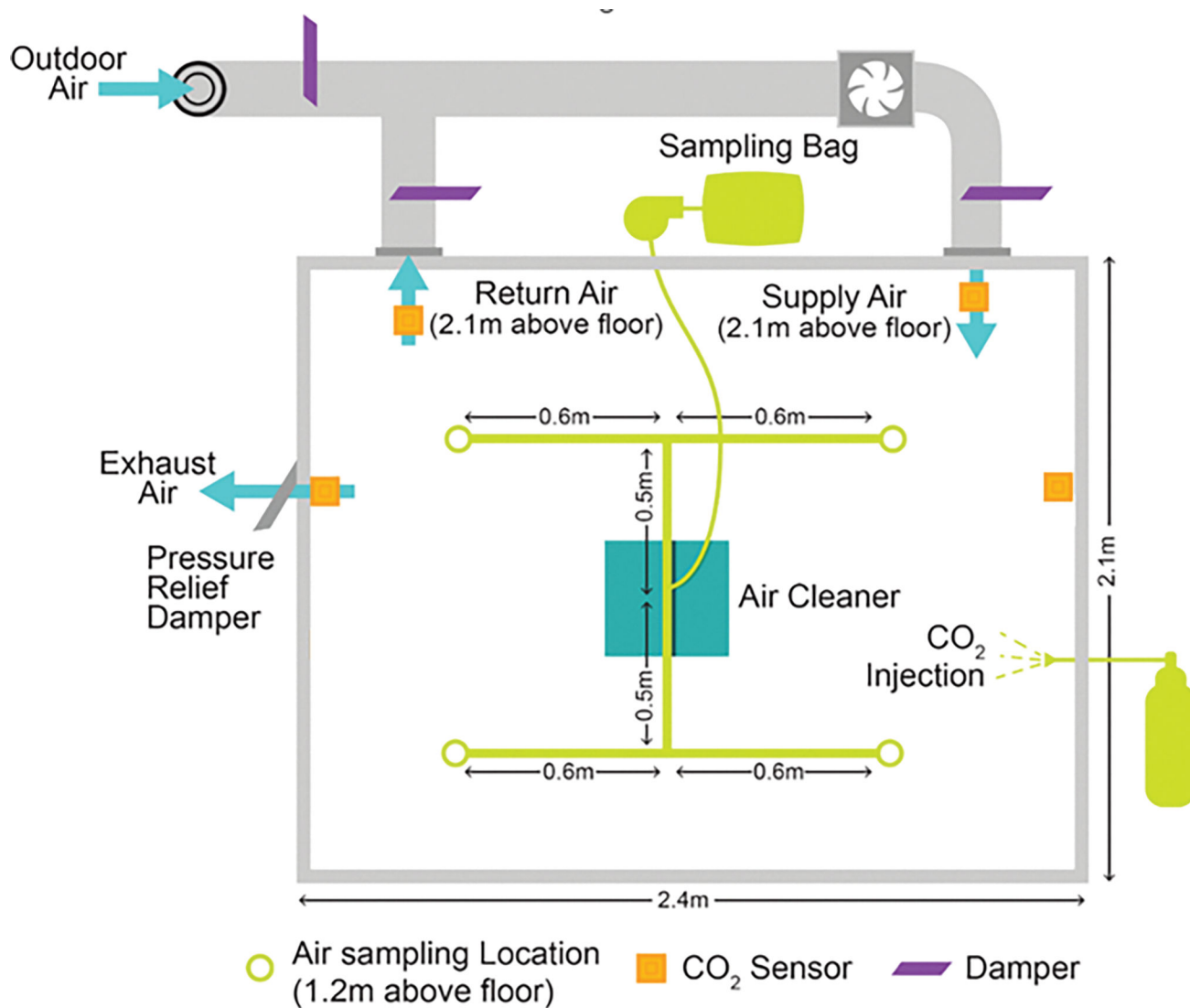


Figure 1. Visualization of the chamber and schematic of the air sample extraction tubing with the inlets. CO₂ sensors at 1.2 m above the floor unless otherwise specified

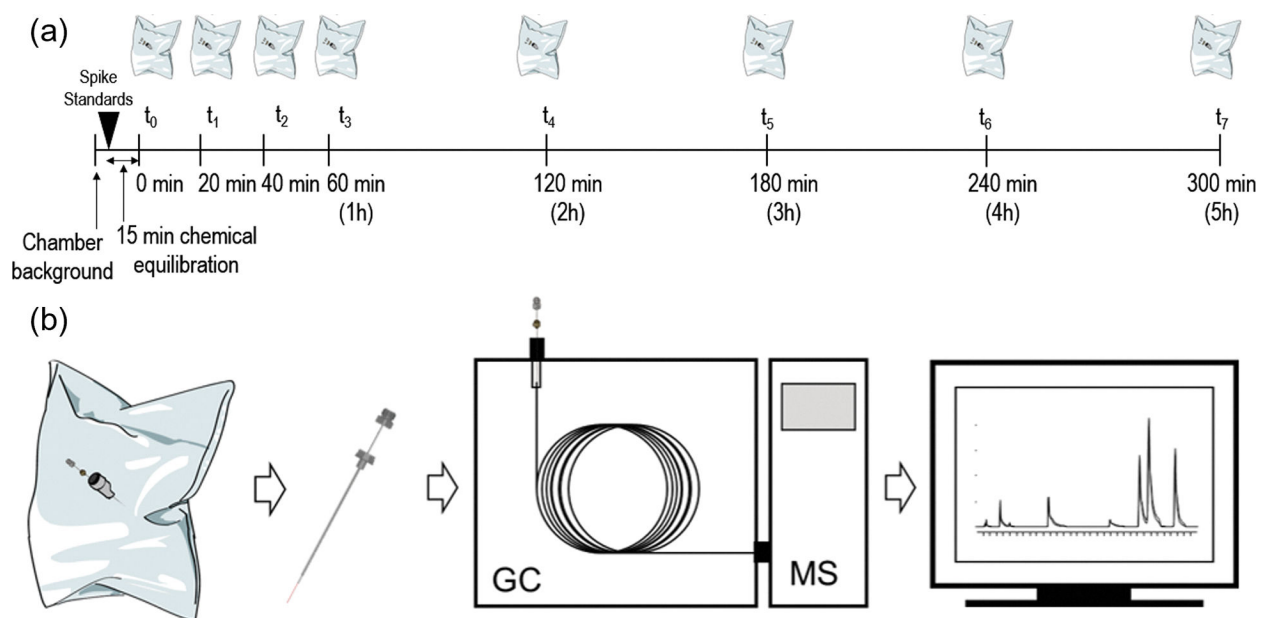


Figure 2.

(a) Sampling timeline from the chamber to the Tedlar bags for subsequent SPME-GC-MS analysis. Only one experiment (the control with no air cleaning device) was extended beyond t_5 time point to take additional data at t_6 and t_7 . (b) Schematic of the GC-MS analysis of SPME fiber with the VOCs extracted from Tedlar bags

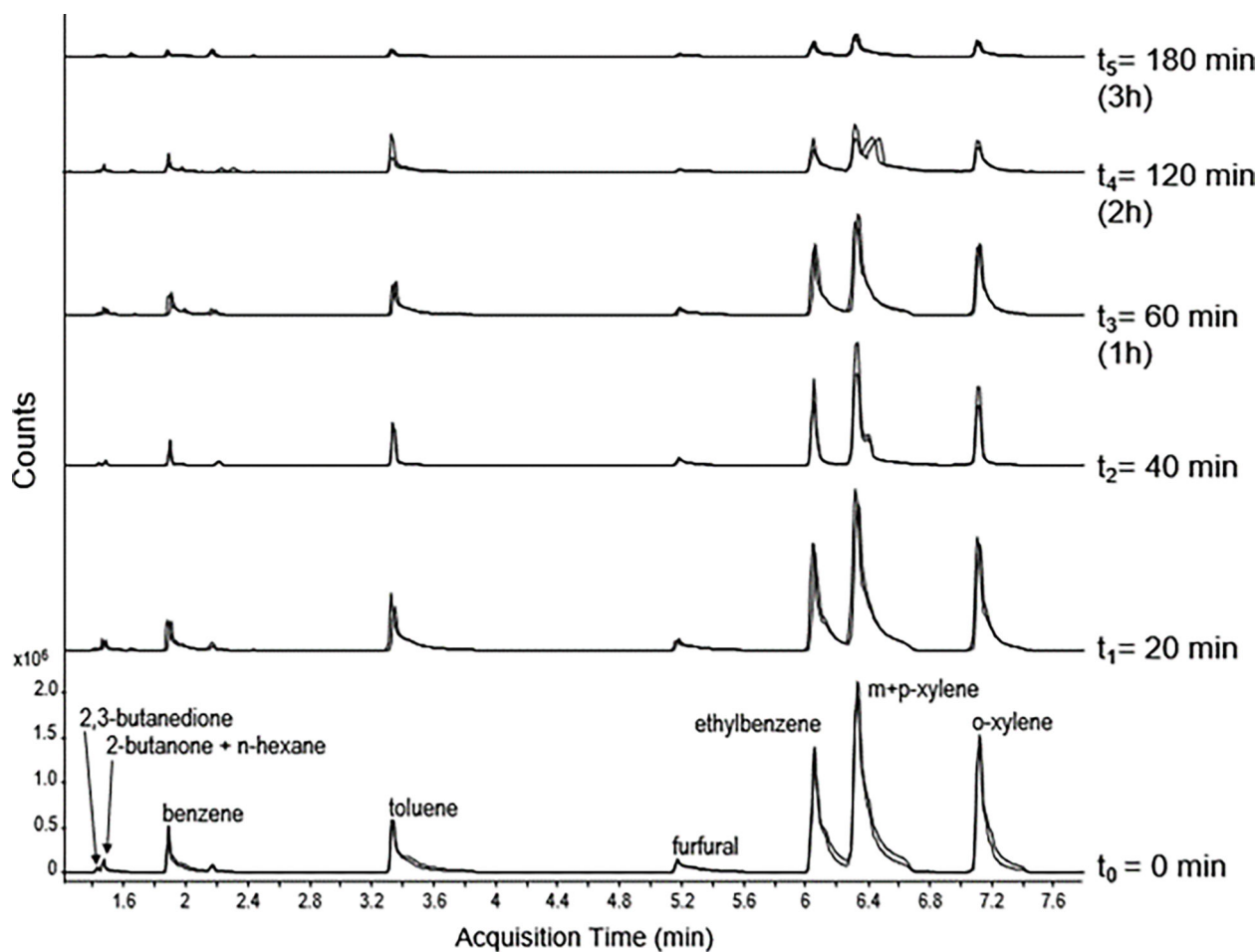


Figure 3. Gas chromatographs of experimental VOCs at different sampling time points, showing natural reduction of chemicals in the chamber (no air cleaning device used).

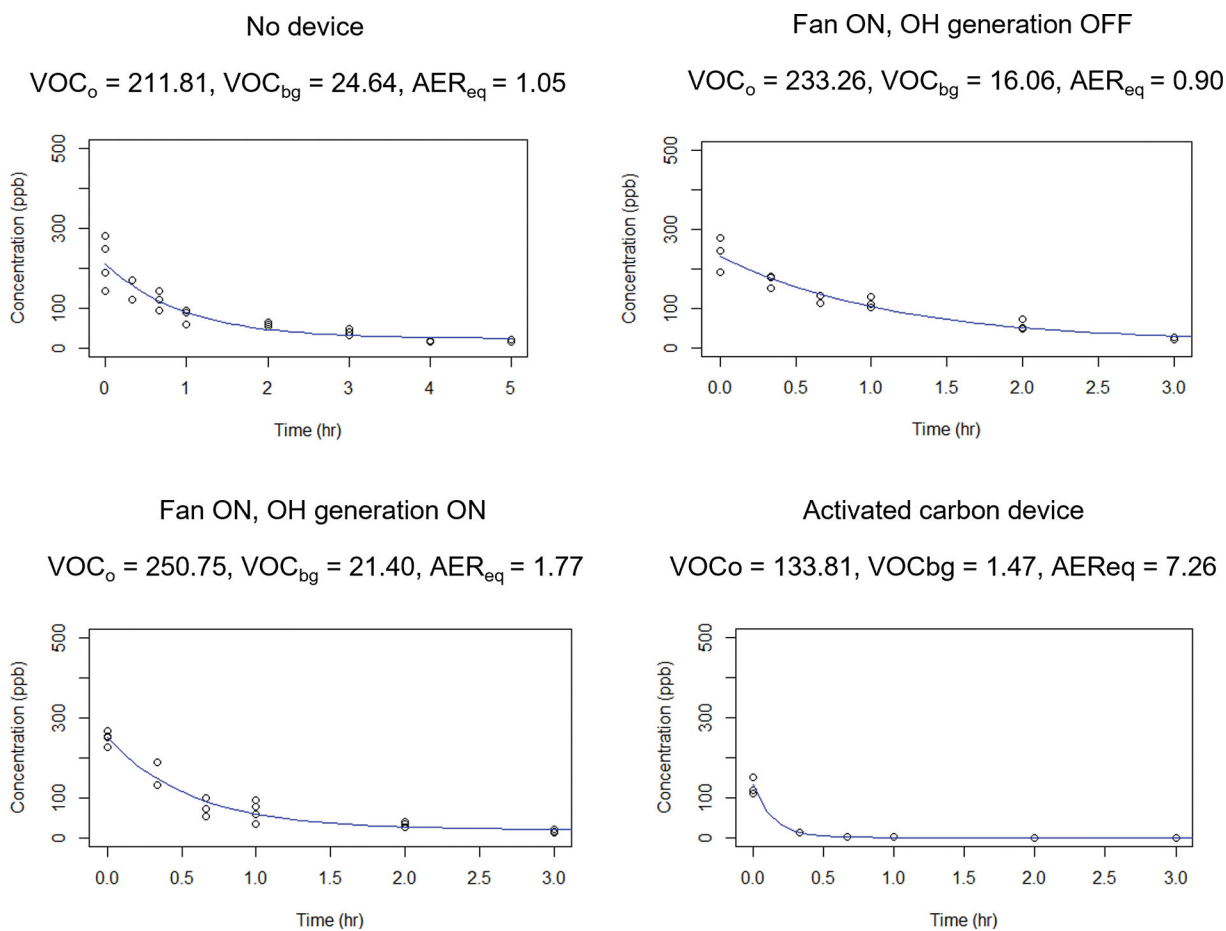


Figure 4.

Example decay curves for benzene shown for each air cleaning test. The complete set of results for all nine VOCs are included in the supplementary material.

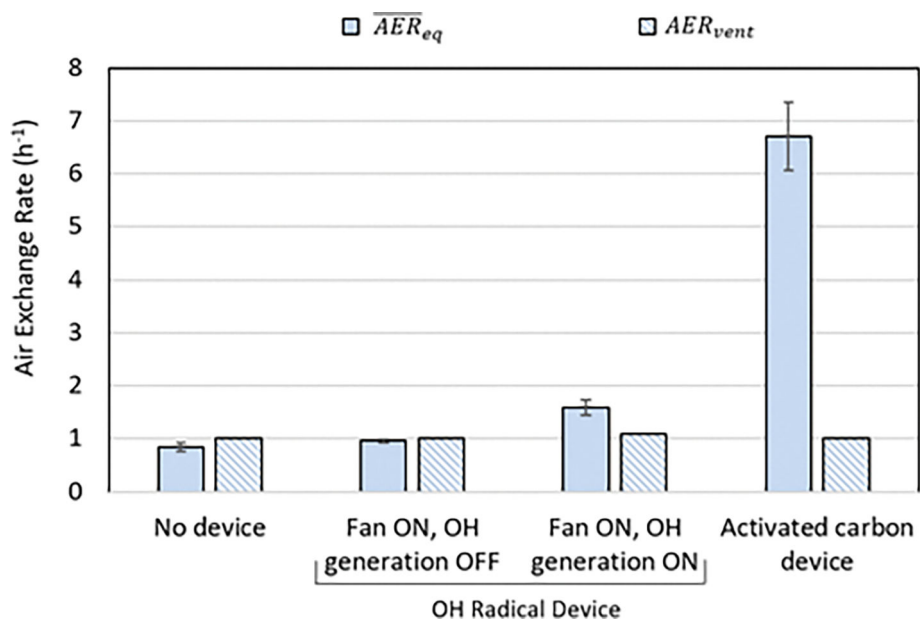


Figure 5. Air changes per hour for the CO₂ decay and the average of all VOC decays for each experiment. The error bars represent the standard error of the mean.

Table 1.

List of experimental VOCs:

• 1-pentene	• toluene
• 2,3-butanedione	• m-xylene
• 2-butanone	• p-xylene
• benzene	• o-xylene
• ethylbenzene	• furfural (2-furaldehyde)

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Table 2.

Calculated AER_{eq} for decay of each VOC (includes outdoor air ventilation, atmospheric and surface losses, and air cleaning), \overline{AER}_{eq} for all VOCs, AER_{vent} measured from CO₂ decay, and CADR for the OH radical generator and activated carbon device.

VOC, AER_{eq}	OH Radical Device			Activated carbon device
	No device	Fan ON, OH generation OFF	Fan ON, OH generation ON	
2,3-butanedione	0.68	0.86	1.18	10.67
2-butanone	0.92	1.10	1.63	8.36
benzene	1.05	0.90	1.77	7.26
ethylbenzene	0.72	0.96	1.35	6.49
furfural	0.55	0.84	1.25	4.85
n-hexane	1.18	1.17	2.67	4.22
o-xylene	0.65	0.97	1.36	6.14
p+m-xylene	0.67	0.94	1.31	6.42
toluene	1.13	0.90	1.77	5.93
\overline{AER}_{eq} (shown in Figure 5)	0.84	0.96	1.59	6.70
Std Error of the Mean \overline{AER}_{eq}	0.08	0.04	0.15	0.64
AER_{vent} (from CO ₂ decay, Figure 5)	1.018	1.005	1.09	1.018
$\overline{AER}_{eq} - AER_{vent}$	-0.18	-0.05	0.50	5.69
Clean Air Delivery Rate (m ³ /hr)	<0	<0	6.32	72.10