Experimental Evaluations of the Impact of an Additive Oxidizing Electronic Air Cleaner on Particles and Gases

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Abstract: Electronic air cleaning (EAC) technologies have garnered significant attention for use in buildings. Many EAC technologies rely on the addition of reactive constituents to indoor air to react with gas-phase compounds, enhance particle deposition, and/or inactivate microorganisms. However, limited data are available on the efficacy of many EAC technologies and their potential to form chemical byproducts during operation. Here we experimentally evaluate the indoor air quality impacts, specifically targeting particles and gases but not microbial constituents, of a commercially available additive oxidizing EAC that generates positive and negative ions and hydrogen peroxide ($H_2O_2$). Tests were conducted in a large unoccupied test chamber in Chicago, IL and an unoccupied laboratory in Portland, OR under a combination of natural conditions (i.e., without pollutant injection) and perturbation conditions (i.e., with pollutant injection and decay). A combination of integrated and time-resolved measurements was used across both test locations. Chamber tests at lower airflow rates demonstrated that operation of the EAC: (i) had no discernible impact on particle concentrations or particle loss rates, with estimated clean air delivery rates (CADRs) for various particle measures less than ±10 m$^3$/h, (ii) was associated with apparent decreases in some volatile organic compounds (VOCs) and increases in other VOCs and aldehydes, especially acetaldehyde, although a combination of high propagated uncertainty, limitations in test methods (e.g., lack of replicates), and variability between repeated tests limit what quantitative conclusions can be drawn regarding gas-phase organics; (iii) did generate $H_2O_2$, assessed using a crude measure, and (iv) did not generate ozone ($O_3$). Laboratory tests at higher airflow rates, which involved injection and decay of particles and a single VOC (limonene), both simultaneously and separately, demonstrated that: (i) pollutant loss rates for both particles and limonene were slightly lower with the EAC on compared to off, yielding slightly negative pollutant removal efficiencies (albeit largely within propagated uncertainty) and (ii) there was a change in observed concentrations of one potential limonene degradation product, $m/z$ 59 (putatively identified as acetone), with steady-state levels increasing from 10 ppb (air cleaner off) to 15 ppb (air cleaner on). No increases or decreases beyond measurement uncertainty were observed for other analyzed gaseous limonene degradation products. Overall, both chamber and laboratory tests demonstrated negligible effectiveness of this device at the test conditions described herein for removing particles and mixed results for VOCs, including decreases in some VOCs, no discernible differences in other VOCs, and apparent increases in other compounds, especially lower molecular weight aldehydes including acetaldehyde.

Keywords: indoor air cleaning; ionization; hydrogen peroxide; air purifier; clean air delivery rate

1. Introduction

Indoor air cleaning is increasingly recognized as a valuable tool in mitigating indoor air quality issues including airborne transmission of SARS-CoV-2 [1–8], exposure to wildfire smoke [9–11], and exposure to everyday sources of indoor pollutants [12–14]. A wide
variety of air cleaning and filtration technologies are commercially available for use in central heating, ventilation, and air-conditioning (HVAC) systems, including an array of electronic air cleaners (EACs) such as ultraviolet germicidal irradiation (UVGI), plasma generators, hydroxyl radical generators, ionizers, photocatalytic oxidizers, and more [15–19]. Many EACs rely on the addition of oxidizing or reactive constituents to indoor air. To date, limited data are available on the efficacy of many EAC technologies and their potential to form chemical byproducts [20–28].

Several recent experimental characterizations of EAC performance have included (i) large chamber and in-situ field tests of an in-duct bipolar ionization device, which suggested that ionization led to a decrease in some gas-phase organic compounds but an increase in others, most prominently oxygenated VOCs (e.g., acetone and ethanol), with minimal impacts on particles, O$_3$, and NO$_2$ [29], (ii) evaluations of the VOC removal effectiveness and potential for forming gas-phase organic products of a variety of EACs (including two oxidizing plasma air cleaners) in a test duct [30], (iii) demonstration of the formation of oxidized gases and secondary organic aerosols from a commercial oxidant-generating EAC that generates OH radicals and hydrogen peroxide (H$_2$O$_2$) in an office [31], (iv) assessment of the efficacy of bipolar ionization devices for microbial disinfection in air and on surfaces in a variety of test locations [32–34], and (v) measurements of primary emissions, VOC removal efficacies, and VOC byproduct formation of portable oxidation-based air cleaners in an environmental chamber [35]. Each of these showed a variety of mixed results for air cleaner efficacy and/or demonstrated the potential for forming chemical or particle byproducts during operation of some EACs.

To date, the literature on the efficacy and potential for byproduct formation of EACs remains sparse, limited to a narrow range of technologies, and limited to a narrow set of performance metrics. Moreover, no comprehensive test standards to date adequately characterize the net performance, including pollutant removal effectiveness and the potential for byproduct formation across a wide range of constituents, of EACs. Therefore, quantitative information on the impact of many EACs on indoor air remains limited. This work seeks to overcome some of these limitations by experimentally evaluating the indoor air quality impacts of a commercially available additive oxidizing EAC that generates reactive constituents, including positive and negative ions and hydrogen peroxide (H$_2$O$_2$). Tests were conducted in a large unoccupied test chamber at the Illinois Institute of Technology (IIT) campus in Chicago, IL, USA and an unoccupied laboratory at the Portland State University campus (PSU) in Portland, OR, USA.

### 2. Materials and Methods

Experiments were conducted with a commercially available additive oxidizing EAC designed to generate positive and negative ions and hydrogen peroxide (H$_2$O$_2$). A summary of EAC installation details at each test location is provided in Table 1, followed by full experimental details in the following sections. For the chamber experiments in Chicago, IL, USA, many of the experimental methodological details are the same as those recently applied to performance testing of another EAC device; therefore, much of the methodological details provided in Section 2.1 of this paper are the same as those previously published, reprinted from [36] with permission from Elsevier. We utilize much of the same language herein to improve the readability of this paper without requiring reference to the other paper.

| Test Location | Airflow Rate (m$^3$/h) | Duct Dimensions (cm) | Face Velocity (m/s) |
|---------------|------------------------|----------------------|---------------------|
| Chamber (IIT) | 343                    | 61 × 48 × 48         | 2.75                |
| Laboratory (PSU) | 2210              | 170 × 61 × 61        | 1.6 *               |

*Estimated from the measured airflow rate and the cross-sectional area of the duct in which the EAC was installed.
2.1. Chamber Experiments: Chicago, IL, USA

A series of chamber experiments were conducted at the Illinois Institute of Technology campus in Chicago, IL, USA. The EAC was installed following manufacturer installation instructions as closely as possible inside a small custom air-handling unit serving a large aluminum environmental chamber (13.7 m² floor area with volume of 36.7 m³). Figure 1 shows photographs and dimensions of the custom air handling unit, the supply and return ductwork serving the chamber, and the location of the installation of the EAC.

![Figure 1](image_url)

**Figure 1.** Photographs (a,b) and schematic drawings (c,d) of a custom air handling unit and ductwork serving the chamber in recirculation mode, with the ionizing/oxidizing electronic air cleaner (EAC) installed in a plenum, used for experimental in Chicago, IL, USA.

The air handling unit, which was modified from previous work [29] to include return ductwork from the chamber and to operate in a fully recirculating mode, has a 3-speed in-line duct blower (Dayton Model 2RB86) with nominal airflow rates (i.e., at 0 Pa static pressure) of 1058, 1310, and 1563 m³/h at low, medium, and high fan speed settings, respectively. The resistance introduced by the ductwork and heating and cooling coils (which were present but not active in the unit during testing) reduced delivered airflow rates to approximately 250–350 m³/h depending on the fan speed setting. All tests were
conducted at the highest fan speed setting, which was measured to provide ~343 m$^3$/h of recirculating airflow, measured using a pressure matching technique with a DuctBlaster and DG-700 pressure gauge (Energy Conservatory, Minneapolis, MN, USA). This yields approximately nine recirculating air changes per hour, which is comparable to typical recirculation rates measured in residential and light-commercial buildings [37]. The supply airflow rate per floor area (i.e., L/s per m$^2$) is also comparable to those measured in the EPA BASE survey of commercial buildings [38]. The air velocity in the air handler just before the EAC device was measured to be approximately 2.75 m/s at the highest fan speed setting using a Digi-Sense Data Logging Vane Anemometer. Surrounding laboratory air entered the chamber through infiltration through the chamber envelope and the small custom air-handling unit and ductwork, yielding 1.8–2.1 air changes per hour (ACH) with surrounding laboratory air during testing. All tests were conducted without an HVAC filter installed on the recirculating air stream. A small mixing fan was operated in the chamber to achieve well-mixed conditions.

A combination of ‘short-term’ and ‘long-term’ tests were conducted under a mix of ‘natural’ and ‘perturbation’ conditions. ‘Short-term’ tests were hours-long, following a typical schedule of device operation that included running the chamber air handler continuously and then (i) sampling with the EAC device off for approximately 2 h, (ii) switching the EAC device on, allowing approximately 2 h to achieve steady-state conditions and then sampling during the next 2 h, and (iii) switching the EAC device off, again allowing approximately 2 h to achieve a new steady-state condition and then continuing to sample during the next 2 h. ‘Long-term’ tests followed a typical schedule of device operation that included (i) operating the EAC device for approximately 24 h with no activity in the chamber, then (ii) sampling with the EAC on for another 2–4 h, followed by (iii) switching the EAC device off, allowing approximately 2 h to achieve a new steady-state condition, and then sampling for approximately 2 more hours during the ‘EAC off’ condition.

In the ‘natural’ condition tests, constituent concentrations were measured inside and outside the chamber, either simultaneously or alternatingly depending on the instrument, without any intentional pollutant injection. In the ‘perturbation’ condition tests, pollutant concentrations inside the chamber were intentionally elevated, primarily targeting particle injection by burning incense, and then measuring the subsequent decay in particle concentrations [39–42] repeated with and without the EAC device operating in either ‘short-term’ or ‘long-term’ mode. For all types of tests, the air change rate in the chamber was typically measured towards the end of testing using CO$_2$ injection and decay. Figure 2 shows a typical timeline for each type of test, including short- and long-term air cleaner operation and both natural and perturbation tests, with periodic integrated VOC sampling, continuous monitoring of PM and O$_3$, and incense injection and decay. The air in the laboratory space surrounding the chamber was not intentionally well-mixed and while the laboratory space was only intermittently occupied during testing, we could not eliminate or control the activities of personnel in the laboratory space surrounding the chamber during testing.

Analytical Measurements

Continuous monitoring in the chamber experiments included particles (0.01–10 µm) and O$_3$, each alternating every 20 min between inside and outside the chamber during ‘natural’ condition tests and monitoring only inside the chamber during ‘perturbation’ tests. Negative ion concentrations were measured and logged inside the chamber during each test using an Air Ion Counter (AlphaLab, Inc., West Salt Lake City, UT, USA). Particle concentrations were measured using a TSI Model 3910 NanoScan Scanning Mobility Particle Sizer (SMPS; ~0.01–0.4 µm) and a TSI Model 3330 Optical Particle Sizer (OPS; 0.3–10 µm) (TSI, Shoreview, MN). Ozone (O$_3$) was measured using a 2B Technologies Model 211 ozone analyzer (2B Technologies, Boulder, CO, USA). CO$_2$ was measured using Extech SD800 CO$_2$ monitors located inside and outside the chamber (Extech, Nashua, NH, USA). The PM and O$_3$ sampling instruments were each connected to automated switching valves (Swagelok...
Model SS-43GX54-42DCX electrically actuated three-way ball valves) to alternately measure concentrations inside and outside the chamber at 20-min intervals throughout the duration of testing, controlled automatically by an electronic timer (Sestos B3S-2R-24). Measured particle number concentrations were aggregated into three convenient metrics: total particle number concentration in the SMPS size range (0.01–0.4 µm), total particle number concentration in the OPS size range (0.3–10 µm), and estimates of fine particulate matter mass concentrations (PM$_{2.5}$) made using both SMPS and OPS number concentrations and assuming spherical particles and density of 1.5 g/cm$^3$.

### Short-term tests

| Natural   | Perturbation |
|-----------|--------------|
| Air cleaner off | Air cleaner on | Air cleaner off |
| 2 hours | 4 hours | 4 hours |

### Long-term tests

| Natural   | Perturbation |
|-----------|--------------|
| ... Air cleaner on for 24+ hours | Air cleaner off |
| 2 hours | 4 hours |

Figure 2. Typical timeline of testing and sampling in the chamber experiments in Chicago, IL, USA.

Gas-phase organics were sampled only during ‘natural’ condition tests in which there was no pulsed injection of gas-phase constituents but instead, similar to our prior work, a variety of mostly aged material emission sources were introduced into the chamber prior to testing to simulate a partially furnished office or similar environment with a variety of persistent VOC emission sources. Materials introduced to the chamber included a used table, rug, plastic and metal chairs, two men’s suit jackets, a scarf, window shades, paper posters, foam packaging materials, multiple boxes of dissertations, and a used painting tray. The goal of introducing such material emission sources was to intentionally elevate concentrations of at least some (untargeted/unspecified) gas-phase organics inside the chamber to create a somewhat realistic and steady indoor chemical mixture with which the tested device and its additive constituents would react when operated. Gas-phase organics were monitored by integrated sampling, including (i) VOCs using SUMMA canisters, with off-line analysis conducted following EPA method TO-15 and (ii) aldehydes and carbonyls following EPA method TO-11A using 2,4-Dinitrophenylhydrazine (DNPH) sampling tubes connected to sampling pumps (Buck Elite-5) with off-line analysis conducted via high-performance liquid chromatography (HPLC). Sampling pump flow rates for TO-11A sampling were confirmed to be ~1.75 L/min prior to sampling using a TSI 4040 mass flow meter. Time-integrated VOC and aldehyde samples were collected using the SUMMA canisters and DNPH tubes, respectively, beginning approximately 2 h after any changes to operational conditions were made in the chamber (e.g., before or after the EAC was switched on), so the chamber had time to approach new steady-state conditions by the time of sampling. All sampling devices (except for one CO$_2$ monitor) were located outside the chamber with sampling lines running into the chamber through openings approximately 0.35 m off the floor, which were sealed with cardboard and tape. Particle instruments were connected to rigid stainless steel sampling lines approximately 1.5 m in
length and 0.5 cm in diameter via TSI conductive tubing. The O₃ monitor and SUMMA canisters were connected to flexible PTFE tubing for sampling. Temperature and relative humidity were measured continuously both inside and outside the chamber.

STAT Analysis, a commercial analytical laboratory in Chicago, IL, USA, supplied evacuated SUMMA canisters for VOC sampling and DNPH cartridges for aldehyde sampling. The SUMMA canisters were analyzed via a purge and trap volatile autosampler on an Agilent 6890 gas chromatograph (GC) with an Agilent 5973 mass selective detector (MS). This results in a chromatogram that shows mass spectral data for any detected compound as well as retention time. The commercial laboratory has a calibrated list of compounds that it can quantitate against. DNPH cartridges were also acquired from the same commercial laboratory and returned for analysis, which involved extraction in solvent and analysis on an Agilent 1100 HPLC system against a list of known compounds from the TO-11A list.

Concentrations from DNPH sampling were calculated by dividing mass values provided by STAT Analysis by the volume of the sample (calculated as the pump flow rate times the sample time). STAT Analysis calibrates their analytical systems to the list of compounds in TO-15 and TO-11A.

A single experiment was conducted to investigate the potential production of hydrogen peroxide (H₂O₂) from the air cleaner serving the test chamber, albeit using a method that has not been validated against other techniques. A colorimetric H₂O₂ Dräger-Tube (0.1/a, #81-01-041) was inserted downstream of the air handler in a port in the supply duct [43]. The typical application of this colorimetric sensor involves using a hand pump to pull 20 strokes over a period of approximately 3 min, with each stroke pulling approximately 100 mL. Thus, a typical total sample volume would be 2 L, which yields an average manual flow rate of approximately 666 mL/min over a 3 min period. The detection range on this colorimetric tube is 0.1 to 3 ppm. Therefore, to provide a rough (i.e., semi-quantitative at best) indicator of H₂O₂ production using this approach, we attached the Dräger-Tube to a sample pump, set the flow rate to 660 mL/min, and sampled the air inside the duct and downstream of the air cleaner for approximately 3.5 h until color changes were observed. We then scaled the resulting readings by sample volume to approximate H₂O₂ emission rates as described in Section 3.1.2.

2.2. Controlled Laboratory Experiments: Portland, OR, USA

A series of controlled laboratory experiments were conducted in an unoccupied laboratory on the Portland State University campus in Portland, OR, USA. The laboratory has a floor area 82 m² and a ceiling height of 3.2 m, with a total volume of 263 m³. A schematic of the test environment is shown in Figure 3. The same make and model of EAC used in the chamber experiments (labeled ‘AC’ in Figure 3) was installed in a temporary recirculating air handler constructed from a large cardboard box (170 cm × 61 cm × 61 cm, with a cross-sectional area of 0.37 m²) with a calibrated fan (Blower Door, The Energy Conservatory, Minneapolis, MN, USA) providing approximately 2210 m³/h of airflow through the makeshift air handler (Figure 3a). The airflow rate passing through the makeshift air handler is within the stated range of the manufacturer for target HVAC blower size of 425–11,044 m³/h. The average face velocity in the air handler was calculated to be ~1.6 m/s. The air handler was placed on the floor of the lab. There exists lab benchtops, shelves, and other equipment in the laboratory as shown in the schematic. In addition to the calibrated fan that ran continuously in the air handler, two additional box fans were placed in the laboratory to ensure well-mixed conditions in the space (Figure 3b).
Figure 3. Controlled laboratory experiments in Portland, OR, USA, USA: (a) Schematic of a cardboard duct (170 cm × 61 cm × 61 cm) used as a makeshift air handler for these experiments where the air cleaner (AC) was placed 30 cm away from a plenum fan (60 × 60 cm). The fan airflow rate was set at 2210 m$^3$/h. (b) Schematic of the laboratory where the experiments took place. Location of where injection of particles and limonene were performed is indicated with the red dot, 1 m away from the duct. Monitoring station was installed 2 m away from the duct. Two box fans were also installed in two locations in the laboratory to create a well-mixed environment. (c) Timeline of experiments.

The controlled laboratory experiments followed a timeline shown in Figure 3c, beginning with a period of background measurements in the unoccupied laboratory, followed by injection of a challenge constituent or constituents. Background measurements occurred following a long period of no occupancy and no activity in the lab. A decay period followed pollutant injection. During the first injection and decay, the air cleaner was switched off. Then the process was repeated with the air cleaner turned on. We conducted three injection and decay tests: (1) incense burning only, with the primary aim to elevate particle concentrations and measure their decay; (2) limonene injection only, to measure gas-phase removal effectiveness of the air cleaner; and (3) incense burning and limonene injection combined to evaluate the removal effectiveness for both types of constituents. These test conditions were contrived to evaluate if an increasing air pollution load and complexity influenced the removal rate of VOCs and/or particles.

Injections of air pollutants and an inert tracer were conducted in front of one box fan. Carbon dioxide (CO$_2$) was injected from a compressed gas cylinder (Airgas, 99.99%) until CO$_2$ concentrations were substantially elevated above background levels (>700 ppm). For particle injection and decay tests, four incense sticks (Mainichi-koh, Sandalwood, 14 cm) were burned ~30 cm in front of the fan (red dot on Figure 3b). The sticks were extinguished in a small jar of sand and then placed under the fume hood which was closed during the experiment. For limonene injection and decay tests, pure limonene (L-(-)-limonene, 97%, Sigma Aldrich, Burlington, MA, USA) was used for the injection. 1 mL of the compound was pipetted into a petri dish (10 cm diameter) and placed ~30 cm in front of the fan.
(red dot on Figure 3b) for 5 min. After elevation of limonene concentration in the lab by volatilization from the petri dish, the petri dish was placed in the closed fume hood.

Analytical Measurements

Continuous monitoring of air pollutants occurred at the “monitoring station” located ~2 m from the outlet of the makeshift air handling system (see Figure 3b). The monitoring station included continuous monitoring of CO$_2$ levels to enable determination of the air change rate using a non-dispersive infrared monitor (Licor 840). This instrument has <1 ppm signal to noise ratio and allows confident determination of CO$_2$ at mixing ratios created in the laboratory test space. We measured particulate matter, size-resolved in 29 bins between 0.01 µm and 10 µm, using an optical particle sizer (TSI Model 3330) and a scanning mobility particle sizer (TSI Model 3910 NanoScan SMPS). The ozone concentration was also monitored at the monitoring station using a 2B Technologies Model 106 L ozone analyzer and negative ion counts were measured using an AlphaLab Model AIC2 ion counter. All instruments logged at 1-min intervals.

Time-resolved VOC measurements were performed using a proton transfer reaction–time of flight–mass spectrometer (PTR-ToF1000, Ionicon Analytik GmbH, Innsbruck, Austria) with H$_3$O$^+$ as the reagent ion. The principle of the PTR-ToF-MS has been well-described previously [44–46]. Operating conditions were $T_{\text{drift}} = 60 ^\circ C$, $P_{\text{drift}} = 2.20 \text{ mbar}$, $U_{\text{drift}} = 600 \text{ V}$, resulting in electric field strength to number density ratio $E/N = 135 \text{ Td}$ (Townsend, 1 Td = $10^{-17}$ V-cm$^2$). Signal intensities of impurities such as NO$^+$ ($m/z = 29.9974$), O$_2^+$ ($m/z = 31.9892$), and the water cluster (H$_2$O)H$_2$O$^+$ ($m/z = 37.0289$) were respectively about 0.15%, 1.3%, and 3.7% of the signal of H$_3$O$^+$ ($m/z = 21.0221$). The PTR-ToF-MS scanned across 17–490 amu for compounds with proton affinity higher than that of H$_2$O. Three peaks were used to perform the mass axis calibration: NO$^+$ ($m/z = 29.9974$), C$_3$H$_7$O$^+$ ($m/z = 59.0497$) and a C$_6$H$_4$I$_2$ fragment ($m/z = 203.944$) which is an internal standard continuously injected into the drift tube via a heated permeation device (PerMaScal, Ionicon Analytik GmbH, Innsbruck, Austria). Mass spectra were stored in 1 s intervals. The inlet was maintained at 60 °C and the supplemental inlet flow to the drift tube was set at 100 mL/min.

2.3. Analysis and Parameter Estimation

2.3.1. Natural Condition Tests (IIT Chamber Study)

To evaluate the impacts of EAC operation on constituent concentrations during natural condition tests, including removal efficacy and/or potential byproduct generation, two methods were used. First, inside/outside (I/O) chamber ratios were used with simultaneous air samples and/or alternating measurements inside and outside the chamber to compare EAC on versus off conditions. This approach is intended to provide relative changes attributable to the EAC that account for changes in constituent concentrations (e.g., PM, O$_3$, or gas-phase organics) that may have occurred outside the chamber and that could influence constituent concentrations inside the chamber. Second, the net change in concentrations of gas-phase organic compounds measured between air cleaner on and off conditions was calculated for compounds on the TO-15 and TO-11A analyte lists that were detected above reporting limits (RLs) during the three natural condition tests targeting VOCs and aldehydes. Net changes in concentrations between operational modes were calculated as the difference in differences of the inside minus outside (I–O) chamber concentrations measured during EAC on versus off conditions; i.e., the inside chamber concentration minus the outside chamber concentration measured during EAC on conditions [I–O]$_{\text{on}}$ minus the inside chamber concentration minus the outside chamber concentration measured during EAC off conditions [I–O]$_{\text{off}}$. This approach is intended to yield an approximation of the net change in concentrations of individual compounds during EAC on versus off conditions, where negative values represent net removal of a compound and positive values represent net production of a compound. It is worth noting that both analysis approaches are limited in that they rely on time-integrated samples to
capture time-averaged conditions that might not have been constant over the sampling duration. However, they provide at least exploratory insight into the potential efficacy and/or byproduct formation that could be studied in more depth using time-resolved instrumentation and/or under more tightly controlled experimental chamber tests.

2.3.2. Perturbation Tests (IIT Chamber Study and PSU Lab Study)

Perturbation tests allowed for solving for pollutant loss rates under each tested condition. To solve for the total pollutant loss rate constant ($\lambda + k$) from a perturbation test, where the pollutant is either particle or gas-phase constituents, we used a first-order log-linear regression solution to a well-mixed mass balance incorporating the measured time-resolved pollutant concentration data minus that measured during background conditions, applied only to the decay period, as shown in Equation (1).

$$-ln \frac{C_t - C_{bg}}{C_0 - C_{bg}} = (\lambda + k)t$$

where $C_t$ and $C_0$ are the measured pollutant concentrations inside the sampling location (i.e., inside the chamber in the chamber study or at the monitoring location in the laboratory study) at time $t$ and $t = 0$, respectively, and $C_{bg}$ is the average pollutant concentration measured in the same location during approximately steady-state conditions either immediately prior to or after the particle injection and decay periods.

For each test using CO$_2$ as a tracer gas, $\lambda$ was estimated by regressing the natural logarithm of the indoor and outdoor (laboratory study) or inside and outside chamber (chamber study) CO$_2$ concentrations versus time, as shown in Equation (2).

$$-ln \frac{Y_{in,t} - Y_{out}}{Y_{in,0} - Y_{out}} = \lambda t$$

where $Y_{in,t}$ and $Y_{in,0}$ are the CO$_2$ concentrations (ppm) measured at the indoor sample location at time $t$ and $t = 0$, respectively, and $Y_{out}$ is the average CO$_2$ concentration (ppm) measured outdoors (laboratory study) or outside the chamber (chamber study) using a second previously calibrated monitor.

The air change rate measured at each perturbation test was subtracted from the estimated first-order loss rate constant for each pollutant measure (e.g., PM$_{2.5}$, total SMPS number, or total OPS number concentration for particles, or limonene concentrations for gas-phase perturbation tests) to generate an estimate of non-ventilation loss rates attributable to a combination of deposition in the chamber, any heterogeneous or homogeneous reactions, and/or removal by the air cleaner (if switched on) ($k$). Differences in loss rates ($\lambda + k$) and/or non-ventilation loss rates ($k$) between test conditions were then compared to explore the magnitude of air cleaning effect, to estimate clean air delivery rates (CADRs) following Equation (3) [39,40,47], and to estimate the removal efficiency ($\eta$) of the air handling unit and air cleaning/filtration configuration following Equation (4) [41,42].

$$\text{CADR} = (k_2 - k_1)V$$

$$\eta = \frac{(k_2 - k_1)V}{Q}$$

where $\eta$ is the single-pass removal efficiency of any air cleaning device installed in the recirculating air handling unit ($\cdot$), $k_1$ and $k_2$ are non-ventilation loss rate constants from two different test conditions (i.e., with and without the air cleaner operating), $V$ is the volume of the chamber (m$^3$), and $Q$ is the air flow rate through the recirculating air handling unit (m$^3$/h).
3. Results and Discussion

3.1. Chamber Experiments: Chicago, IL, USA

Table 2 provides a description of chamber experiments that were conducted in Chicago, IL, USA. Three sets of both short-term and long-term operation tests included (i) natural condition tests targeting only gas-phase organics (VOCs and aldehydes), (ii) natural condition tests targeting only particles and O₃, and (iii) perturbation tests targeting only particles. The mean (standard deviation, SD) temperatures and relative humidity values were similar between inside and outside the chamber, and the chamber air change rate ranged ~1.9–2.1 h⁻¹.

Table 2. Summary of chamber tests performed.

| Test Date     | Test Condition | Operation Duration | Constituents Measured | Temp. (°C) ᵃ | RH (%) ᵃ | ACH h⁻¹ | Neg. Ions ᵃ (ions/cm³) |
|---------------|----------------|--------------------|-----------------------|---------------|----------|---------|------------------------|
|               |                |                    |                       | In            | Out      | In      | Out        | EAC off | EAC on |
| Natural       |                |                    |                       |               |          |         |            |           |         |
| Condition Tests: VOC/aldehydes during short-term and long-term operation |
| 4 May 2021    | Natural        | Short-term         | VOC/aldehydes        | 27.0 (0.2)    | 27.1 (0.1) | 31 (3)  | 32 (3)    | 2.07     | 1150 (940) | 1370 (1720) |
| 8 May 2021    | Natural        | Short-term         | VOC/aldehydes        | 22.7 (0.3)    | 22.9 (0.6) | 24 (2)  | 25 (3)    | 2.00     | 1380 (1040) | 4850 (2920) |
| 5 July 2021   | Natural        | Long-term          | VOC/aldehydes        | 30.5 (0.7)    | 28.5 (0.6) | 39 (1)  | 46 (1)    | 1.87     | 950 (150)   | 2470 (2130) |
| Natural       |                |                    |                       |               |          |         |            |           |         |
| Condition Tests: PM and O₃ during short-term and long-term operation |
| 2 July 2021   | Natural        | Short-term         | PM and O₃            | 29.1 (0.6)    | 27.8 (0.6) | 36 (2)  | 41 (2)    | 1.92     | 790 (510)   | 4220 (1680) |
| 15 July 2021  | Natural        | Long-term          | PM and O₃            | 28.4 (0.3)    | 28.2 (0.6) | 48 (2)  | 51 (3)    | n/a      | 770 (130)   | 930 (240)  |
| Perturbation  |                |                    |                       |               |          |         |            |           |         |
| Tests: PM injection and decay following long-term operation |
| 7 July 2021   | Perturbation    | Short-term         | PM                    | 29.5 (0.3)    | 29.2 (0.5) | 41 (1)  | 44 (3)    | 1.93     | 610 (110)   | 1200 (330) |
| 12 July 2021  | Perturbation    | Long-term          | PM                    | 27.7 (0.4)    | 27.6 (0.6) | 51 (1)  | 54 (2)    | 1.94     | 800 (190)   | 580 (260)  |

ᵃ Mean values (with standard deviation in parentheses).

3.1.1. Negative Ion Production

Figure 4 shows two examples of negative ion concentration profiles measured over time inside the test chamber, including one long-term and one short-term natural condition test. Positive ions were not measured. Background (air cleaner off) negative ion levels were typically less than 2000 ions/cm³ and increased to as high as ~14,000 ions/cm³ with the air cleaner operating. Long-term operation (Figure 4a) tended to yield an early spike in ion production and then a decline to lower levels over time, eventually returning close to background. Figure 4b shows sustained elevations in negative ion concentrations during the short-term test with the EAC on. These data suggest that this test setup resulted in intermittent ion production from the EAC during longer operational periods. This effect is also reflected in Table 2, which summarizes mean (SD) negative ion concentrations measured with the EAC on and off during each test. The mean negative ion concentration during EAC operation ranged from 580 to 4850 ions/cm³ across all short-term and long-term tests. The mean negative ion concentration with the EAC off was 920 ions/cm³, averaged across all tests. Short-term operation of the EAC yielded higher mean negative ion concentrations than long-term operation (i.e., mean of 2910 ions/cm³ vs. 1330 ions/cm³). Worth noting, the mean ion concentrations during PM perturbation tests in Table 2 exclude periods in which particle injection and decay occurred because incense injection led to a temporary scavenging of ion concentrations in the chamber, presumably as both PM and VOC emissions from
incense provided reaction sites for emitted ions; once PM concentrations decayed back to background levels, ion concentrations rebounded back to previous levels. For example, the mean negative ion concentration during periods of incense injection ranged from 110 to 330 ions/cm³, with an average of 240 ions/cm³.

Figure 4. Example negative ion concentration profiles over time for (a) long-term (24+ h operation) test followed during ‘natural’ conditions (i.e., no pollutant injection) and (b) short-term (4-h operation) test during ‘natural’ conditions (i.e., no pollutant injection).

3.1.2. H2O2 Production

During the single H2O2 production potential test, the Dräger-Tube was inspected after 0.5 h of sampling and some brown coloration was observed, extending to ~0.1 ppm on the tube (Figure 5). The tube was then re-inserted and continued to sample until 3.5 h elapsed, at which point the brown coloration was observed to be extended to ~2.5–3.0 ppm on the tube. Here we use 2.5 ppm as a conservative estimate of the resulting reading. At 0.5 and 3.5 h of sampling time at a sample flow rate of 660 mL/min, a total sample volume of ~19.8 L and ~138.6 L was collected, respectively, representing ~10x and ~69x more sample volume than a 3-min 100 mL/pump hand pump approach would have collected. Thus, these sample volume ratios were used to dilute the concentration readings from each sample, resulting in an estimated equivalent of ~0.01 ppm (~10 ppb) and ~0.036 ppm (~36 ppb) for the 0.5-h and 3.5-h sample times, respectively. These estimated molar concentrations were then converted to mass concentrations assuming a MW of H2O2 of 34 g/mol, yielding ~14 and ~51 µg/m³, respectively. Finally, these concentration estimates were converted to estimates of H2O2 generation rates by multiplying the resultant concentration by the recirculating airflow rate in the air handler (343 m³/h). This approach resulted in estimates of H2O2 generation rates of ~5 mg/h at the 0.5-h sample and ~17 mg/h at the 3.5-h sample. While these approximations are at best semi-quantitative and rely on a number of assumptions such as linear scaling of the visual concentration reading to collected sample volume, they suggest that (i) there was indeed H2O2 production during EAC operation and (ii) the magnitude of H2O2 production may be on the order of mg/h from this EAC operating in this test chamber configuration.

3.1.3. Natural Condition Chamber Tests: Particulate Matter (PM)

Figure 6 shows mean (SD) inside/outside (I/O) chamber concentration ratios for three PM metrics, including the total number concentration in the SMPS size range (‘total SMPS’, 0.01–0.4 µm), the total number concentration in the OPS size range (‘total OPS’, 0.3–10 µm), and estimated PM2.5 mass concentration, from one short-term test and one long-term test conducted under natural (i.e., non-injection) conditions. It should be noted that while these integrated measures of total particle number and mass concentrations include data from all particle size bins from the SMPS and OPS instruments, the three largest size bins from the SMPS instrument typically recorded zero number concentrations. This is a known limitation in the instrument resulting from the use of a unipolar charger but does not...
meaningfully affect these comparisons. In Figure 6a, I/O chamber ratios for all particle metrics were similar with the EAC off and with the EAC on following short-term operation, with differences in mean I/O ratios less than 0.02 and largely within uncertainty (i.e., one standard deviation of the mean). Mean (SD) I/O chamber ratios from this test with the EAC off and on, respectively, were 0.62 (0.03) and 0.62 (0.01) for total SMPS particle number concentrations, 0.35 (0.02) and 0.33 (0.01) for total OPS particle number concentrations, and 0.45 (0.02) and 0.46 (0.01) for estimated PM$_{2.5}$ mass concentrations. Figure 6b also shows that there were again only small differences (less than 0.04) in mean I/O chamber ratios for the three particle metrics between EAC off conditions and after the EAC operated longer term (for over 24 h), largely within overlapping uncertainties. Mean (SD) I/O chamber ratios from this test with the air cleaner off and on, respectively, were 0.63 (0.02) and 0.66 (0.02) for total SMPS particle number concentrations, 0.52 (0.03) and 0.48 (0.02) for total OPS particle number concentrations, and 0.39 (0.01) and 0.36 (0.02) for estimated PM$_{2.5}$ mass concentrations. Combined, these data suggest that the EAC operation had an overall negligible impact on particle concentrations in the chamber, as tested.

Figure 5. Results from colorimetric sampling with a H$_2$O$_2$ Dräger-Tube installed downstream of the air cleaner: before sampling, after 0.5 h, and after 3.5 h of sampling.
3.1.4. Natural Condition Chamber Tests: Ozone (O\(_3\)) Concentrations

Figure 7 shows inside/outside (I/O) chamber concentration ratios for ozone (O\(_3\)) measured during two natural condition tests in the test chamber, including one short-term and one long-term test. There were negligible differences in median I/O O\(_3\) ratios measured during EAC on and off conditions, with a slight decrease in the median value with the EAC on during the short-term test and a slight increase in the median value with the air cleaner on during the long-term test. These results suggest that the device does not produce O\(_3\) as tested. Table 3 also summarizes mean (SD) O\(_3\) concentrations measured inside and outside the chamber simultaneously with gas-phase organics sample collection during three natural condition tests that targeted VOCs and aldehydes, as well as resulting mean I/O ratios and propagated uncertainty (i.e., relative SD for inside and outside chamber concentrations added in quadrature). The mean O\(_3\) concentrations inside and outside the chamber ranged from ~1–8 ppb and ~4–14 ppb, respectively, varying by test day, but did not vary by more than ~1 ppb when comparing across EAC on versus off conditions.
Table 3. Summary of mean (SD) ozone (O$_3$) concentrations measured inside and outside the chamber during three natural condition tests targeting gas-phase organics (VOCs and aldehydes).

| Date       | Duration | Air Cleaner Off | Air Cleaner On |
|------------|----------|-----------------|----------------|
|            |          | Inside Chamber  | Outside Chamber| Mean |
|            |          | (ppb)           | (ppb)          | I/O  |
|            |          | Mean I/O        | Mean I/O       | Ratio|
|            |          | Ratio           | Ratio          |      |
| 4 May 2021 | Short-term| 3.8 (0.4)       | 8.9 (0.4)      | 0.43 | 4.0 (0.6) | 8.1 (1.4) | 0.50 (0.11) |
| 8 May 2021 | Short-term| 7.9 (1.8)       | 13.7 (1.8)     | 0.58 | 7.8 (1.6) | 13.5 (1.8) | 0.57 (0.14) |
| 5 July 2021| Long-term | 1.6 (0.4)       | 4.0 (0.4)      | 0.40 | 2.2 (0.6) | 5.1 (1.5)  | 0.43 (0.17) |

3.1.5. Natural Condition Chamber Tests: Gas-Phase Organics

Figures A1–A3 show all analytes targeted by TO-15 (VOCs) and TO-11A (aldehydes) analyses and their resulting concentrations (in units of ppbv, for VOCs on the TO-15 list) and masses recovered (in units of µg for aldehydes on the TO-11A list) in all inside and outside chamber samples collected during the three natural condition test days, including two short-term tests and one long-term test. Analytes and their concentrations/masses are reported directly as received on the analytical reports provided by the commercial analytical lab. Figures A4 and A5 show estimates of analytical uncertainties reported by the commercial analytical lab for analytes on the TO-15 and TO-11A list, respectively. Analytical uncertainty in TO-15 analytes is based on the standard deviation of recovery spikes at the 95% confidence interval (with a coverage factor of 2) from 40 calibration runs. Analytical uncertainty in TO-11A analytes is based on the standard deviation of recovery spikes at the 95% confidence interval (with a coverage factor of 2) from 12 calibration runs. The average uncertainty in the TO-15 analyte list was ~20%, with a minimum of ~15% to a maximum of ~74%. The average uncertainty in the TO-11A analyte list was ~14%, ranging from a minimum of ~5% to a maximum of ~76%. In both lists, there were two outlier compounds with estimated uncertainties well above the next highest uncertainty of ~27%: acetone from the TO-11A list (~76%, compared to ~17% on the TO-15 list) and propene from the TO-15 list (~74%). Acetone was the only compound that appeared in both analyte lists; only acetone from the TO-15 list was used due to its much lower uncertainty and upon the recommendation of the commercial laboratory.

Tables A1–A3 show resulting concentrations and estimated analytical uncertainties (in units of µg/m$^3$) for the TO-15 and TO-11A analytes that were quantified above reporting limits (RLs) in at least one air sample collected from inside or outside the chamber during the three natural condition tests that targeted gas-phase organics. Integrated concentrations for aldehydes were calculated by dividing the reported mass recovered (µg) by the estimated sample volume (pump flow in m$^3$/h x sample time in h). To provide consistent units across gas-phase organic analytes, integrated molar concentrations from canister VOC samples (ppbv) were converted to mass concentrations (µg/m$^3$) using the ideal gas law assuming constant atmospheric pressure of 1 atm and the average air temperature recorded at each sample location during sampling (from Table 2).

Also shown in Tables A1–A3 are: (i) inside/outside (I/O) chamber concentration ratios measured during air cleaner on and off conditions, (ii) percentage differences in I/O ratios between air cleaner on and off conditions, (iii) absolute inside minus outside (I-O) chamber concentration differences measured during air cleaner on and off conditions, and (iv) the absolute differences in I-O chamber concentration differences (i.e., net change) measured between air cleaner on and off conditions. Increases in I/O ratios and differences in I-O concentrations between air cleaner on and off conditions are labeled with red text in Tables A1–A3 while decreases or unknown impacts are shown in black text. Estimates of propagated analytical uncertainty are also provided for I/O concentration ratios, I-O concentration differences, and differences in I-O concentration differences (i.e., net changes) that could be quantified (i.e., for those compounds with quantifiable concentrations above
RLs in at least two samples). Propagated uncertainties are estimated by adding relative uncertainties (for I/O ratios) and absolute uncertainties (for I–O concentration differences) in quadrature.

A detailed discussion of VOCs, including aldehydes, is provided in the Appendix A and briefly summarized here. Overall, these data suggest that there was typically a decrease in I/O chamber concentration ratios and the differences in inside chamber concentrations minus outside chamber concentrations for some VOCs on the TO-15 analyte list and an increase in others during both short- and long-term operation of the air cleaner compared to air cleaner off conditions, although a combination of a lack of consistency in findings across tests and high estimates of propagated uncertainty in these measurements limits the conclusions that can be drawn. Instead, we suggest that the results for VOCs from the TO-15 analyte list be interpreted largely as a screening analysis for potential impacts, but deep insights on the impacts of the air cleaner on these compounds cannot be drawn.

However, there was more consistency in observed changes in aldehyde concentrations from the TO-11A analyte list during air cleaner operation compared to air cleaner off conditions, as increases in both I/O chamber concentration ratios and differences in inside chamber concentrations minus outside chamber concentrations were observed for both total aldehydes and acetaldehyde in all three tests, although the magnitude of differences was within propagated uncertainty for two tests and greater than propagated uncertainty for one test. It is also worth noting that non-discernible differences observed within estimates of propagated uncertainty for compounds on either analyte list suggests a lack of demonstrable efficacy for those compounds in these chamber tests.

To illustrate the observed net changes in aldehydes and their associated propagated uncertainties, Figure 8 shows the net production or removal of gas-phase organics measured during air cleaner on and off conditions for compounds on the TO-11A analyte list that were detected above reporting limits (RLs) in samples collected during the three natural condition tests. Positive values represent net production and negative values represent net removal; error bars show propagated uncertainties. There was a relatively consistent net increase in the sum of quantified compounds on this list of approximately +5–6 µg/m³ during all three tests, albeit within propagated uncertainty for two of the three tests and just outside uncertainty for the other test. Multiplying the net change in total aldehyde concentrations by the chamber volume and air change rate during each test yields a rough approximation of the total aldehyde generation rate (and estimated propagated uncertainty) during air cleaner operation of ~430 (490) µg/h, ~390 (280) µg/h, and ~420 (630) µg/h during the 4 May, 8 May, and 5 July tests, respectively. While the estimated total aldehyde generation rate across these three tests is relatively consistent (~390–430 µg/h), the high propagated uncertainty in this measure crosses 0 µg/h in two of the three tests. Despite the high uncertainty, the apparent net production of low molecular weight aldehydes (e.g., acetaldehyde) is reasonably plausible given our understanding of the potential impacts of ionization and oxidation chemistry resulting from additive EAC operation. However, further work should strive to reduce uncertainty in such estimates.

3.1.6. Chamber Perturbation Tests: Particulate Matter (PM)

Figures 9 and 10 show results from one short-term and one long-term perturbation test targeting particles via injection and decay of incense. We aimed to have at least one natural logarithm removal from initial particle concentrations to use for the linear regressions to solve for loss rates (via Equation (2)). This resulted in between about 25 and 60 min of decay per test. Only data from the first ~25 min were used for the regressions with total OPS and PM_{2.5} concentrations from the short-term perturbation test with the air cleaner off because the regression became sub-linear after that, most likely due to transient changes in the ambient lab air concentration that were not measured. Regression results are also summarized in Table 4, along with estimates of clean air delivery rates (CADR) made using Equation (3) and single-pass particle removal efficiencies made using Equation (4). Uncertainties in CADRs are estimated using the standard errors from regression coefficients.
added in quadrature with the square of the chamber volume. Uncertainties in removal efficiencies are estimated by adding the standard errors from regression coefficients in quadrature with the uncertainty in the DuctBlaster air flow rate measurement (3%) [48]. It is worth noting that both estimates of uncertainty are most likely underestimated because there are other non-quantifiable sources of uncertainty such as the uncertainty in the selection of the background concentration inside the chamber.

Figure 8. Net change of aldehyde concentrations (and propagated uncertainties) measured during air cleaner operation compared to air cleaner off conditions for compounds on the TO-11A analyte list that were detected above reporting limits (RLs) in samples collected during the three natural condition tests (two short-term and one long-term). Positive values represent net production and negative values represent net removal. Net changes are calculated as the differences in differences of inside minus outside (I–O) chamber concentrations measured during EAC on versus off conditions.

Figure 9. First-order particle loss rate constants ($\lambda + k$) from a short-term perturbation test (7 July 2021) after the air cleaner operated for a few hours and after the air cleaner was switched off: (a) total number concentrations measured by the SMPS (0.01–0.4 µm), (b) total number concentrations measured by the OPS (0.3–10 µm), and (c) estimated PM$_{2.5}$ mass concentrations.
The air change rates in the chamber were measured to be 1.93 h⁻¹ and 1.94 h⁻¹ on these two test days, respectively. Total particle loss rate constants (\(\lambda + k\)) ranged from ~2.0 to ~2.6 h⁻¹ depending on particle metric and test condition. Subtracting the air change rate from total particle loss rate constants yields deposition loss rate constants in the chamber of approximately 0.1 to 0.7 h⁻¹ depending on particle metric and test condition, with generally slightly higher loss rate constants for the smaller total SMPS size range. The observed magnitude of chamber deposition loss rate constants and slight size-dependence are in line with expectations based on prior chamber studies. Moreover, while it may be somewhat counterintuitive that loss rate constants were similar for each of the three particle metrics, which span a wide range of sizes from 10 nm to 10 \(\mu\)m, it is not unexpected given the nature of the aerosol injection source. Incense burning resulted in a relatively narrow size distribution concentrated mostly around 0.05 to 0.5 \(\mu\)m and thus loss rate constant estimates for each metric all converge around similar values.

Table 4. Summary of first-order loss rate constants and estimated single-pass removal efficiencies of the EAC resulting from short-term (7 July 2021) and long-term (12 July 2021) chamber perturbation tests targeting only particle injection and decay.

| Experiment | Air Cleaner On | Air Cleaner Off | CADR | \(\eta\) |
|------------|---------------|----------------|------|-------|
| Short-term (7 July) | | | | |
| Total SMPS | \(2.55\) (0.02) | \(2.52\) (0.01) | 1.1 (0.8) | 0.3% (3.1%) |
| Total OPS | \(2.50\) (0.00) | \(2.42\) (0.02) | 2.6 (0.7) | 0.8% (3.1%) |
| PM\(_{2.5}\) | \(2.38\) (0.01) | \(2.35\) (0.02) | 1.1 (0.9) | 0.3% (3.2%) |
| Long-term (12 July) | | | | |
| Total SMPS | \(2.45\) (0.02) | \(2.61\) (0.01) | \(-4.6\) (0.8) | \(-1.3%\) (3.1%) |
| Total OPS | \(2.41\) (0.01) | \(2.53\) (0.01) | \(-4.6\) (0.4) | \(-1.3%\) (3.0%) |
| PM\(_{2.5}\) | \(2.33\) (0.01) | \(2.55\) (0.02) | \(-8.1\) (0.7) | \(-2.4%\) (3.1%) |

- Parameter estimate (with propagated uncertainty in parentheses) 
- A single CO\(_2\) injection and decay was used to characterize the air change rate on this test day, relevant for both air cleaner on and off conditions.
Overall, there were no discernible differences in loss rate constants for each particle metric and size range between EAC on and off conditions during either short-term or long-term air cleaner operation. Estimates of CADRs for the three particle metrics range from approximately $-8$ to $3 \text{ m}^3/\text{h}$ based on these differences in loss rates. Estimated single-pass removal efficiencies based on these differences in loss rates range from approximately $-3\%$ to $+1\%$, with each estimated efficiency value falling within the quantified uncertainty of approximately $3\%$. Given the (unquantified) uncertainties introduced by making assumptions for background concentrations inside the chamber during particle injection and decay (which were not measurable and are thus assumed based on conditions observed either immediately prior to injection or an hour or more after the decay period), the appropriate practical interpretation of these observed small differences in loss rate constants, CADRs, and single-pass removal efficiencies is that the values were negligible, or functionally, near zero. In other words, operation of this air cleaner in the test chamber resulted in no discernible differences in particle loss rates, CADRs, or single-pass removal efficiencies, which is also consistent with the small differences in I/O chamber concentration ratios observed during natural condition tests.

3.2. Controlled Laboratory Experiments: Portland, OR, USA

3.2.1. Negative Ion Production

Figure 11 shows time-series concentrations of negative ions measured at the monitoring station during injection and decay tests in the controlled laboratory study. There existed a strong spatial gradient of ions in the laboratory environment, despite the presence of substantial mixing airflow provided by the three recirculating fans in the space. During brief spatial mapping of the ion concentration in the laboratory in a preliminary experiment where the air cleaner was on and no challenge compounds were injected, we observed negative ion concentrations exiting the duct of $\sim 3 \times 10^6 \text{ ions/cm}^3$, $\sim 2.5 \times 10^4 \text{ ions/cm}^3$ at the monitoring station, and $\sim 8 \times 10^3 \text{ ions/cm}^3$ at the northwest and northeast corners of the laboratory. During experiments where challenge pollutants were injected, we located the ion monitor at the monitoring station identified in Figure 3 throughout the experiments. Shown in Figure 11 is that negative ion concentrations are substantially elevated during all periods of air cleaning operation compared to background periods, though the trend and range of values differed across the three experiments. The air exchange rate was stable across the two days of experiments (Table 4), as were materials and activities in the laboratory. We speculate that differences in negative ion concentration across the three experiments reflect the differing challenge mixtures across the experiments. For example, it is consistent that the experiment with the highest mass loading of challenge pollutants (limonene and incense simultaneously) had the lowest measured ion concentration as there existed more reaction sites for ions and products of ion chemistry to interact with.

3.2.2. Controlled Laboratory Study Perturbation Tests

An example of the injection and decay that occurred during perturbation tests in the controlled laboratory study is shown for limonene in Figure 12a. From the regression of the decay period post-injection, we estimate the total loss of limonene due to the sum of the air change of the space ($\lambda$) and other loss processes ($k$), such as chemical reactions initiated by the air cleaner (Figure 12b). As can be observed in Figure 12, we aimed to elevate the challenge concentration substantially above that of the background level. This serves to reduce the uncertainty associated with the background steady-state levels which were taken from a period of monitoring prior to the initiation of the experiment (e.g., 0–45 min in Figure 12a) and used in calculation of the decay constants for both the air cleaner on and air cleaner off tests. Regressions were conducted (as in Figure 12b) to determine loss rate constants. For all particle constituents and limonene, regression $R^2$ values were >0.99. In some cases, as in Figure 12b, there appeared to be small deviations from the first-order model applied here that we speculate is a result of imperfect mixing and/or a changing background condition over the course of the experiment.
Figure 11. Ion concentrations (negative mode) measured during controlled laboratory studies at Portland State University over day 1 (panel (A)) and day 2 (panel (B)). On day 1, a perturbation was conducted over a 200 min period using incense burning to elevate particle concentrations, also causing increases in some VOCs. On day 2, two perturbation tests were conducted over a 400 min period: first using limonene followed by simultaneous incense burning and limonene injection.

Figure 12. Example of a perturbation test with limonene injection: (a) time series of the limonene concentration with the air cleaner off shaded in grey and the air cleaner on shaded in green; (b) regression of the natural logarithm of the limonene concentrations versus time as shown in Equation (2).

A summary of experimental outcomes for the three different challenge mixtures is shown in Table 5, including decay constants for particulate and gas-phase species. Note that the air change rate of the laboratory was measured three times across the two days. The cylinder used to elevate CO₂ concentrations simultaneous to the challenge mixture was exhausted during the day 2 (Limonene injection only) experiment. The triplicate measurement of air change rate across the two days shows little variation, which is expected due to the engineered mechanical ventilation system in the laboratory (providing ~6.4–6.8 ACH of outdoor air). The equivalent air change per hour provided to the space through the makeshift duct that includes the electronic air cleaner (8.4 h⁻¹) exceeds that provided to the space by ventilation, indicating an air cleaner with high equivalent single pass efficiency would meaningfully reduce concentrations of target pollutants in the space.
Table 5. Summary of experimental results from controlled laboratory studies at Portland State University.

| Experiment and Constituent | Air Cleaner On | Air Cleaner Off | CADR | η |
|----------------------------|----------------|----------------|------|---|
|                             | λ + k (h⁻¹)    | λ (h⁻¹)ₐ       | Neg. Ions b (ions/cm³) | λ + k (h⁻¹) | λ (h⁻¹)ₐ | Neg. Ions b (ions/cm³) | (m³/h) | (%) |
| Day 1: Incense burning     |                |                |      |    |
| PN₀.01-0.03                 | 5.67 (0.05)    | 6.84           | 16,604 (7298)   | 5.72 (0.05) | 6.42 | 486 (114) |               | 117 |
| PN₀.03-10                  | 7.10 (0.06)    | 13,494 (3406)  | 1038 (109)      | 6.22 (0.01) | 6.46 | 9672 (3938) |               | 117 |
| PN₂.5                      | 7.10 (0.06)    | 6.29 (0.01)    | 6.29 (0.01)     | 6.57 d        | 6.57 d | 665 (149) | 1376 (117) | 117 |

Day 2: Limonene injection only
- Limonene 6.23 (0.01) 6.57 d 13,494 (3406) 6.22 (0.01) 6.46 1038 (109) 29 (86) 1.3 (3.9)
- Limonene 5.25 (0.04) 6.57 d 9672 (3938) 6.20 (0.05) 6.57 d 665 (149) 68 (88) 3.1 (4.0)
- Limonene 5.91 (0.05) 6.57 d 6.20 (0.05) 6.57 d 665 (149) 77 (88) 3.5 (4.0)
- Limonene 6.14 (0.01) 6.29 (0.01) 6.29 (0.01) 6.57 d 665 (149) 37 (86) 1.7 (3.9)

| Experiment and Constituent | Air Cleaner On | Air Cleaner Off | CADR | η |
|----------------------------|----------------|----------------|------|---|
|                             | λ + k (h⁻¹)    | λ (h⁻¹)ₐ       | Neg. Ions b (ions/cm³) | λ + k (h⁻¹) | λ (h⁻¹)ₐ | Neg. Ions b (ions/cm³) | (m³/h) | (%) |
| Day 2: Incense burning and limonene injection |                |                |      |    |
- PN₀.01-0.03                 | 5.51 (0.05)    | 6.20 (0.05)    | 6.20 (0.05)     | 6.57 d        | 665 (149) | 77 (88) 3.5 (4.0)
- PN₀.03-10                  | 5.91 (0.05)    | 6.20 (0.05)    | 6.20 (0.05)     | 6.57 d        | 665 (149) | 77 (88) 3.5 (4.0)
- PN₂.5                      | 5.91 (0.05)    | 6.20 (0.05)    | 6.20 (0.05)     | 6.57 d        | 665 (149) | 77 (88) 3.5 (4.0)
- Limonene 6.14 (0.01) 6.29 (0.01) 6.29 (0.01) 6.57 d 665 (149) 37 (86) 1.7 (3.9)

* Uncertainty in air change rate is taken as 0.23 h⁻¹, the standard deviation of the three measurements of air change rate made during day 1 and day 2 (limonene, air cleaner on) experiments. b Mean values (with standard deviation in parentheses) c Error propagated for terms in Equation (3) and 4 with the larger of the standard error for parameter estimates or the standard deviation across multiple measurements. d Air change rate used is the average of three prior measurements of CO2 decay during day 1 experiments and day 2 (limonene, air cleaner on experiments).

Table 5 also estimates the total pollutant loss rate constants (λ + k) and air change rate (λ). These parameters allow calculation of CADR and equivalent single-pass pollutant removal efficiency (η) using Equations (3) and (4), respectively. Shown in Table 4 is that, for all experiments conducted, the CADR and η of the air cleaner operating in the space are slightly negative, with uncertainty either including or nearly including zero. This implies that the operation of the EAC does not discernably impact the rate of removal of particle constituents or limonene (the test VOC) from this test space.

Comparisons of total loss rates shown in Table 5 across experiments offer some insight and guidance for future experimentation. For example, PN₀.03-10 and PN₂.5 total loss rates are greater than air change during day 1 experiments. During day 2 experiments where particles and limonene were injected, we observed PN₀.03-10 and PN₂.5 loss rates that are less than air change alone. Further experimentation is necessary to discern whether this reduction in particle loss rate is due to formation from chemistry involving limonene or simply variation in background particle removal processes. For PN₀.01-0.03, the total loss rate constant (λ + k) is lower than air change alone for all experiments. We speculate that there exists a source from the coagulation of sub-10-nm particles that are likely generated during the incense burning (similar to the observations of Patel et al. [49]) and are not measured at their initial size by the Nanoscan SMPS. In the case of limonene, we observe total loss rates (λ + k) that are very near air change alone.

3.2.3. Byproduct Formation in the Controlled Laboratory Study

Shown in Figure 13A are time-averaged concentrations of potential limonene oxidation products measured during the limonene only injection and decay experiment. From the reaction between limonene and oxidants such as O₃ or OH radicals, a variety of carbonyl compounds, including ketones, carboxylic acids, and aldehydes may be formed [50–52]. Since the purported mechanism of the air cleaner studied in this work is the generation of oxidant species (H₂O₂) and positive and negative ions that may subsequently lead to generation of oxidants (e.g., radicals), we report in Figure 13A possible VOC reaction products from oxidation of limonene. We time-average the concentrations of the reported
species over periods of measurement with the air cleaner off and with the air cleaner on; note that corresponding timeseries are reported in Figure A2 in Appendix A. Shown in Figure 13B is the putative identification of each compound based on the measured experimental m/z, assignment of chemical formula, and plausible associated chemical. Note that compound identification in PTR-TOF-MS based on exact mass is subject to uncertainty.

Figure 13. Panel (A): Mean concentration of several VOCs of interest as potential byproducts of limonene oxidation during the perturbation test presented in Figure 12 (injection of limonene) when the air cleaner was off (blue bars) and when the air cleaner was on (yellow bars). Error bars correspond to the standard deviation over each period of the perturbation test. The 10 first and last minutes of each period (on or off) are excluded for the calculation to avoid the uncertainty due to the researcher entering and exiting the space to turn the device off or on. Panel (B): Table of putative identification based on the exact mass measured by the PTR-TOF-MS.

There appeared to be, in general, little observable formation of oxygenated byproducts generated as a result of limonene oxidation due to EAC operation. We believe this can be explained by a combination of the observed low effective removal efficiency of the EAC for limonene (Table 4) and the high air change rate (~6 h⁻¹) of the space, which, in general, serves to suppress indoor homogeneous chemistry [53].

For one compound, m59 (putatively identified as acetone), we observe a ~51% increase in the mean steady-state concentration when the EAC is on compared to off, greater than the reported uncertainty. Note that for m59 and m31, we observed rapid increases and decays in concentrations beginning at around t = 160 min (see Figure 12 for relevant timeline), approximately 50 min after the injection of limonene with the air cleaner operating. We do not attribute these later increases and decays to EAC operation, as they occurred after a period of near steady-state in both traces and with no observable change in the experiment or air cleaner operation; these data are not included in the reported averages and standard deviations in Figure 13. We believe these events are indicative of chemical use in an adjoining space to our laboratory or in the supply air provided to the laboratory. Including these transient events would result in larger increases in concentrations of these compounds compared to what is shown in Figure 13. Additional explanation and time-series data from the experiment are shown in Figures A7 and A8.

Small increases of 6% and 9%, respectively, of several byproducts possibly attributed to the air cleaner operation are observed for m45 (putatively identified as acetaldehyde) and m73 (putatively identified as butyraldehyde). These results are in general alignment with observations of aldehyde production in the chamber studies in Chicago (shown
However, observed increases for these compounds (m45 and m73) in the controlled laboratory study are within experimental uncertainty, potentially because of the higher air change rate in this space. We observed clear increases in higher molecular weight constituents (m127, m139 and m153 putatively attributed to 6-methyl-5-hepten-2-one (6-MHO), 4-AMCH, limonene oxide (C10H16O) respectively) during limonene injection (Figure A3); however, we do not attribute the increases in these compounds due to EAC operation as they accumulate during injections with both EAC on and off periods. Instead, we believe this result is explained by the reaction of limonene with ozone present in the laboratory from outdoors; O3 concentrations were measured between 20–25 ppb across the periods shown in Figure 13. Indoor/outdoor (I/O) O3 ratios during the three experiments are presented in Figure A9 in Appendix A. No significant difference in O3 I/O ratio is observed when the device was operating compared to when it was off. This implies the device did not produce quantities of ozone sufficient to alter ozone levels compared to background conditions.

4. Conclusions

Here we describe a set of experimental evaluations of the impacts of a commercially available additive oxidizing electronic air cleaner (EAC) that generates positive and negative ions and hydrogen peroxide (H2O2) on particulate matter and gases in two different test settings, including a large unoccupied test chamber and an unoccupied controlled laboratory. Between the two test locations, the device was tested at both higher and lower airflow rates, with both time-integrated and time-resolved air sampling of various constituents, and under both natural and perturbation test conditions. Despite the differences in test approaches, there were several similarities in results, and some differences. For example, both chamber and laboratory tests demonstrated that the unit did not increase loss rates for particles and did not yield discernible differences in several measured VOCs. Chamber tests further demonstrated that while the concentrations of some VOCs apparently decreased during EAC operation, others increased, especially aldehydes (e.g., acetaldehyde), although many comparisons were within propagated uncertainties. Controlled laboratory tests further demonstrated that loss rates for a single VOC (limonene) did not increase during a perturbation test with the EAC operating and that there was an increase in observed concentrations of one potential limonene degradation product, m/z 59 (putatively identified as acetone), with steady-state levels increasing from 10 ppb (air cleaner off) to 15 ppb (air cleaner on). Although limitations exist in each test approach, this work provides novel performance data for this EAC and highlights the need for continued improvements in air cleaner performance test standards that characterize both effectiveness and the potential for byproduct formation under realistic test conditions.

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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest.

**Appendix A**

**Appendix A.1. VOCs including Aldehydes from the Chamber Study**

Cells highlighted in yellow in Figures A1–A3 show analytes in a sample that were quantified above the reporting limit (RL). TO-11A analytes from DNPH samples are shown in units of µg and the total collected air volumes for each sample are shown in m³ (pump flow × sample time); integrated concentrations are calculated as mass (µg) over volume (m³). Conversions of integrated mass concentrations from canister VOC samples (i.e., from ppb_v to µg/m³) were calculated using the ideal gas law assuming constant atmospheric pressure of 1 atm and the average air temperature recorded at each sample location during sampling (from Table 2). Figures A4 and A5 show estimates of analytical uncertainties reported by the commercial analytical lab for analytes on the TO-15 and TO-11A lists, respectively.

In Tables A1–A3, if an analyte was detected above reporting limits (RLs) in all four samples (i.e., inside and outside chamber during both air cleaner on and off conditions), then I/O chamber concentration ratios were calculated and a percent difference between air cleaner on and off conditions was quantified. For example, in the first short-term test (Table A1), the I/O ratio of formaldehyde increased from 1.73 to 1.99 between air cleaner off and on conditions, suggesting a 15% increase in the I/O ratio of formaldehyde attributable to air cleaner operation. Conversely, the I/O ratio of propene decreased from 8.67 to 3.80 between air cleaner off and on conditions, suggesting a 56% decrease in the I/O ratio of propene attributable to air cleaner operation. I-O concentration differences were calculated only for compounds for which both inside and outside concentrations were above RLs. Furthermore, in Tables A1–A3, if an analyte was detected above its RL in at least one sample but fewer than four samples, then a semi-quantitative or purely qualitative assessment of I/O ratio and difference in I/O ratio between air cleaner on and off conditions was conducted. For example, in the first short-term test (Table A1), the I/O ratio of benzene increased from an unknown I/O ratio with the air cleaner off (both inside and outside chamber samples were below RL) to at least 64 with the air cleaner on (i.e., 124 µg/m³ inside and <1.9 µg/m³ outside), suggesting an increase, albeit unquantifiable, in the I/O ratio of benzene attributable to air cleaner operation during this test. Conversely, the I/O ratio of valeraldehyde decreased from at least 3.0 with the air cleaner off (i.e., 3.3 µg/m³ inside divided by a value smaller than the RL of 1.1 µg/m³ outside the chamber) to 0.85 (i.e., 2.2 µg/m³ divided by 2.6 µg/m³) with the air cleaner on, suggesting a decrease, albeit not precisely quantifiable, in the I/O ratio of valeraldehyde attributable to air cleaner operation during this test.

Table A1 shows that during the first (4 May 2021) short-term test there was a quantifiable decrease in the I/O chamber ratio for four VOCs (acetone, isopropyl alcohol, propene, and toluene, with magnitudes ranging from −4% to −56%, with only isopropyl alcohol comparisons falling outside the propagated uncertainty in I/O ratios) and a likely, but not directly quantifiable, increase in the I/O chamber ratio for at least six VOCs (2-butanone, benzene, carbon disulfide, ethylbenzene, m,p-xylene, and total xylenes) on the TO-15 analyte list during air cleaner operation compared to air cleaner off conditions. There were apparent increases in I/O ratios, albeit not directly quantifiable, for benzene, ethylbenzene, and m,p-xylene, each of which were below RLs in the air cleaner off conditions, and then detected above RLs inside the chamber during air cleaner operation but were not detected in concurrent samples from outside the chamber, suggesting a generation process occurred in the chamber during air cleaner operation. However, such findings for these compounds are not repeated in each of the other two tests, which suggests that factors unrelated to air cleaner operation, such as an inexplicable issue in sampling or analytical protocols that we are unable to ascertain, may have contributed to the detection of these compounds during
this test. The largest decreases in I/O ratios (for isopropyl alcohol and propene) were also supported by the I–O net change analysis, which also contribute to a net reduction of the sum of all VOCs on the TO-15 analyte list detected above RLs (although only isopropyl alcohol was outside propagated uncertainty). A slight decrease in the I/O ratio for acetone in this analysis (−15%, within propagated uncertainty) corresponded to a +33 µg/m³ net increase in I–O concentration difference, presumably because of a relatively large change in outside chamber concentrations that occurred during sampling and was obscured in the I/O comparison (although 33 µg/m³ is within propagated uncertainty for this measure of ~43 µg/m³).

Table A1 also shows there was an increase in the I/O chamber ratio of four compounds on the TO-11A analyte list during air cleaner on compared to off conditions, including formaldehyde (+15%), acetone (+51%), acetaldehyde (+52%), and butyraldehyde (+250% or greater). The acetaldehyde and butyraldehyde I/O comparisons were greater than propagated uncertainty. There was a likely decrease in valeraldehyde I/O ratios, and no change in hexaldehyde I/O ratios (i.e., within propagated uncertainty). The sum of all quantified aldehydes from the TO-15 analyte list suggests that the I/O chamber ratio of total aldehydes increased by approximately 11% during this short-term test with the air cleaner on compared to off. The net change analysis also supports the I/O ratio analysis, with a net increase in the sum of total aldehydes quantified of approximately +6 µg/m³ during air cleaner operation compared to air cleaner off conditions, largely driven by net increases in acetaldehyde, formaldehyde, and butyraldehyde (changes in acetaldehyde and butyraldehyde were greater than propagated uncertainty and changes in formaldehyde concentrations were near propagated uncertainty). However, this net change in total aldehydes was within propagated uncertainty for this measure of ~7 µg/m³, suggesting the magnitude of increase was not significant.

Table A2 shows that during this short-term test there was a quantifiable decrease in the I/O chamber ratio in two VOCs (acetone and toluene, with magnitudes ranging from −34% to −51%), a likely decrease in one VOC (dichlorodifluoromethane), and a quantifiable increase in one VOC (isopropyl alcohol, +14%) on the TO-15 analyte list during air cleaner operation compared to air cleaner off conditions. Only the change in I/O ratio for toluene was greater than propagated uncertainty. The I–O net concentration changes in Table A2 show a large net increase in isopropyl alcohol of +619 µg/m³ (greater than propagated uncertainty), net increases in propene of at least +44 µg/m³ and in acetone of +10.5 µg/m³ (albeit within propagated uncertainty), and small net decreases in toluene and dichlorodifluoromethane. It is worth noting again that results for VOCs from the TO-15 analyte list were quite different between these two short-term tests, which limits the conclusions that can be drawn from this analysis.

Table A2 also shows there was an increase in the I/O chamber ratio of two compounds on the TO-11A analyte list, including formaldehyde (+8%, but within propagated uncertainty) and acetaldehyde (+51%, greater than propagated uncertainty). There was a quantifiable decrease in I/O ratios of hexaldehyde (−11%, but within propagated uncertainty) and butyraldehyde was essentially unchanged (−2%, also within propagated uncertainty). The sum of all quantified aldehydes from the TO-11A analyte list suggests that the I/O chamber ratio of total aldehydes by approximately 21% higher during this short-term test with the air cleaner on compared to off, although the difference is again within propagated uncertainty for this measure. Similar to results from the first short-term test, the net change analysis also supports the I/O ratio analysis for compounds on the TO-11A list, with a net increase in the sum of total aldehydes quantified of approximately +5 µg/m³ during air cleaner operation compared to air cleaner off conditions, largely driven by net increases in acetaldehyde (which were greater than propagated uncertainty) and formaldehyde (which were within propagated uncertainty). Overall, the magnitude of increase was slightly greater than propagated uncertainty in this measure of ~4 µg/m³, suggesting the increase was detectable just outside of our range of uncertainty.
A potential explanation for the observed differences in the types and magnitude of changes in VOCs and aldehydes between the two short-term tests is that despite having similar operational conditions, mean negative ion concentrations differed by a factor of approximately 3.5 between the two tests, from ~1370 ions/cm$^3$ on 4 May to ~4850 ions/cm$^3$ on 8 May. It is unclear what contributed to these large differences in ion production from the tested device under otherwise similar conditions. The air temperature inside and outside the chamber was lower on the second test day, while relative humidity and chamber air change rates were similar between the two tests. Additionally, as shown in Table 3, mean O$_3$ concentrations inside and outside the chamber were somewhat higher on 8 May than on 4 May, but were not meaningfully different between EAC on and off conditions on either test day. Thus, these results suggest that additional ion production during the second short-term test may have contributed to additional VOC scavenging but also to higher aldehyde production through ion-initiated reactions in the chamber. Moreover, the observed differences do not appear driven by other factors such as ozone-initiated chemistry in the test space. However, only limited conclusions can be drawn from these data, especially for VOCs, as replicate samples were not included for resource constraints and changes in VOCs are not consistent across what should have otherwise been replicate experiments. Outcomes for aldehydes for these two tests were more consistent, but still within or near propagated analytical uncertainty.

Next, Table A3 shows that during the long-term operational test on 5 July 2021, there was a quantifiable decrease in the I/O chamber ratio in two VOCs (acetone and toluene, −10% to −14%, although both were within propagated uncertainty), a likely decrease in one VOC (naphthalene), a quantifiable increase in one VOC (isopropyl alcohol, +45%, greater than propagated uncertainty), and a likely increase in three VOCs (chloromethane, trichloroethene, and m,p-xylene) on the TO-15 analyte list during air cleaner operation compared to air cleaner off conditions. The I–O net concentration change analysis in Table A3 shows a smaller net increase in isopropyl alcohol of +33 µg/m$^3$ (within propagated uncertainty), a net increase of chloromethane of at least +121 µg/m$^3$, a net decrease in naphthalene of at least 14.5 µg/m$^3$, and a small net decrease in acetone (−2.4 µg/m$^3$, within propagated uncertainty).

Table A3 also shows there was an increase in the I/O chamber ratio of acetaldehyde from the TO-11A analyte list during air cleaner operation (+22%, greater than propagated uncertainty), while I/O ratios of formaldehyde (+5%), butyraldehyde (+2%), and hexaldehyde (+1%) slightly increased but were within propagated uncertainty. Valeraldehyde (0%) was unchanged. The sum of all quantified aldehydes from the TO-11A analyte list suggests that the I/O chamber ratio of total aldehydes increased by approximately 8% during this long-term test during air cleaner on compared to off conditions, which was within propagated uncertainty for this measure. The net change analysis for compounds on the TO-11A list shows a net increase in the sum of total aldehydes quantified of approximately +6 µg/m$^3$ during air cleaner operation compared to air cleaner off conditions, again driven by net increases in acetaldehyde (which was greater than propagated uncertainty) and formaldehyde (which was within propagated uncertainty). However, the net change in total aldehydes of +6 µg/m$^3$ was within propagated uncertainty for this measure of ~9 µg/m$^3$. Mean negative ion concentrations were 2470 ions/cm$^3$, ranking in between the two short-term tests.

Overall, the net change in I–O concentration differences between EAC on and off conditions for the sum of quantified VOCs on the TO-15 list ranged from a large net decrease (May 7 short-term test: −1313 µg/m$^3$) to a large net increase (8 May short-term test: +663 µg/m$^3$) to a small net increase (5 July long-term test: +165 µg/m$^3$). These comparisons may be only moderately useful, as there are limitations to this net change analysis for compounds on the TO-15 analyte list, as well as the sum total of those compounds quantified, including: (i) the TO-15 VOC analyte list is limited to compounds that the commercial lab quantitates against and thus does not yield a complete measure of total carbon that may be available for conversion/reaction and (ii) there was only a small number of compounds that
were observed above RLs in enough samples to be useful for quantification (e.g., toluene, propene, isopropyl alcohol, and acetone). There were also large uncertainties associated with most comparisons except isopropyl alcohol.

To further demonstrate the measured differences in aldehydes from the during air cleaner operation, Figure A6 summarizes the I/O chamber concentration ratios and propagated uncertainties calculated during the air cleaner on and off conditions, as well as the percent difference between air cleaner on and off conditions, for five compounds on the TO-11A analyte list that were detected above RLs in most samples collected across the three natural condition tests.

Figure A1. TO-15/TO-11A analytes and reported concentrations: 4 May 2021 short-term test.
Figure A2. TO-15/TO-11A analytes and reported concentrations: 8 May 2021 short-term test.
Figure A3. TO-15/TO-11A analytes and reported concentrations: 5 July 2021 long-term test.
| TO-15 Analyte            | Analytical Uncertainty (%) |
|-------------------------|----------------------------|
| 1,1,1-Trichloroethane   | 15.7%                      |
| 1,1,2,2-Tetrachloroethane | 18.7%                    |
| 1,1,2-Trichloroethane   | 19.0%                      |
| 1,1-Dichloroethane      | 19.7%                      |
| 1,1-Dichloroethene      | 19.0%                      |
| 1,2,4-Trichlorobenzene  | 26.7%                      |
| 1,2,4-Trimethylbenzene   | 17.1%                      |
| 1,2-Dibromoethane       | 17.1%                      |
| 1,2-Dichlorobenzene     | 17.1%                      |
| 1,2-Dichloroethane      | 17.9%                      |
| 1,2-Dichloropropane     | 20.2%                      |
| 1,3,5-Trimethylbenzene  | 17.1%                      |
| 1,3-Butadiene           | 21.1%                      |
| 1,3-Dichlorobenzene     | 16.7%                      |
| 1,4-Dichlorobenzene     | 17.1%                      |
| 1,4-Dioxane             | 16.3%                      |
| 2-Butanone              | 19.7%                      |
| 2-Hexanone              | 17.6%                      |
| 4-Ethyltoluene          | 15.0%                      |
| 4-Methyl-2-pentanone    | 15.4%                      |
| Acetone                 | 17.0%                      |
| Benzene                 | 19.9%                      |
| Benzyl chloride         | 21.3%                      |
| Bromodichloromethane    | 17.4%                      |
| Bromoform               | 16.3%                      |
| Bromomethane            | 20.7%                      |
| Carbon disulfide        | 22.6%                      |
| Carbon tetrachloride    | 17.1%                      |
| Chlorobenzene           | 17.3%                      |
| Chloroethane            | 20.5%                      |
| Chloroform              | 18.4%                      |
| Chloromethane           | 23.9%                      |
| cis-1,2-Dichloroethene  | 18.7%                      |
| cis-1,3-Dichloropropene | 16.4%                      |
| Cyclohexane             | 19.2%                      |
| Dibromochloromethane    | 17.4%                      |
| Dichlorodifluoromethane | 20.6%                      |
| Ethyl acetate           | 19.9%                      |
| Ethylbenzene            | 17.4%                      |
| Freon-113               | 20.6%                      |
| Freon-114               | 20.7%                      |
| Heptane                 | 19.4%                      |
| Hexachlorobutadiene     | 25.5%                      |
| Hexane                  | 20.5%                      |
| Isopropyl Alcohol       | 14.9%                      |
| m,p-Xylene              | 17.8%                      |
| Methyl tert-butyl ether | 18.0%                      |
| Methylene chloride      | 18.3%                      |
| Naphthalene             | 26.4%                      |
| o-Xylene                | 18.2%                      |
| Propene                 | 73.7%                      |
| Styrene                 | 16.5%                      |
| Tetrachloroethene       | 18.1%                      |
| Tetrahydrofuran         | 21.0%                      |
| Toluene                 | 19.6%                      |
| trans-1,2-Dichloroethene| 20.5%                      |
| trans-1,3-Dichloropropene | 17.8%                  |
| Trichloroethene         | 18.0%                      |
| Trichlorofluoromethane  | 20.6%                      |
| Vinyl acetate           | 27.1%                      |
| Vinyl chloride          | 19.9%                      |
| Xylenes, Total          | 17.9%                      |

**Figure A4.** Analytical uncertainties in analytes on the TO-15 list.
Table A1. The experiment. In the case of m59, the signal increased by nearly an order of magnitude from near-steady state levels with the air cleaner on with no observable change to the chemistry initiated by the air cleaner would cause these compounds rapidly increase in 2 min followed by decay to prior steady-state levels. We believe these signals may have been impacted by usage of these chemicals in an adjacent space to the laboratory or space in 2 min followed by decay to prior steady-state levels. We believe these signals may have been impacted by usage of these chemicals in an adjacent space to the laboratory or space that is shared in the air handler that serves the lab.

Figure A5. Analytical uncertainties in analytes on the TO-11A list.

Figure A6. Inside/outside (I/O) chamber concentration ratios measured during air cleaner on and off conditions, as well as the percent difference between air cleaner on and off conditions, for five compounds on the TO-11A analyte list that were detected above reporting limits (RLs) in nearly every sample collected during the three natural condition chamber tests (two short-term and one long-term).

Appendix A.2. VOC Measurements in the Controlled Laboratory Study

Shown in Figure A7 are time-series data that accompany Figure 13 for the limonene-only experiment. For both compounds m31 and m59 we excluded data after t = 160 min from the calculation of the mean concentration reported in Figure 13, as it is implausible that the chemistry initiated by the air cleaner would cause these compounds rapidly increase from near-steady state levels with the air cleaner on with no observable change to the experiment. In the case of m59, the signal increased by nearly an order of magnitude in 2 min followed by decay to prior steady-state levels. We believe these signals may have been impacted by usage of these chemicals in an adjacent space to the laboratory or space that is shared in the air handler that serves the lab.
Table A1. Resulting concentrations and calculated inside/outside (I/O) chamber concentration ratios for TO-15/TO-11A analytes above reporting limits (RL) in at least one air sample from the 4 May 2021 short-term natural condition test. Symbols “likely ↑” and “likely ↓” denote likely, albeit not directly quantifiable, increases and decrease, respectively.

| Analyte | MW (g/mol) | 4 May 2021-Short-Term (Negative Ions: –1370 ions/cm³) |
|---------|------------|-----------------------------------------------------|
|         |            | Air Cleaner Off | Air Cleaner On | I/O Concentration Ratio | Concentration Difference (µg/m³) |
|         |            | Inside Chamber  | Outside Chamber | EAC Off | EAC On | % Change | Inside–Outside (I–O) |
| TO-15 List |           |                 |                 | EAC Off | EAC On |          | EAC Off | EAC On | EAC On-Off |
| 1,2-Dichloroethane | 99.0 | 3.8 (0.7) | <2.5 | 2.6 (0.5) | <2.5 | >1.5 | >1.0 | unknown | >1.3 | >0.1 | <−1.2 |
| 2-Butanone | 72.1 | <4.4 | <4.4 | 8.2 (1.6) | <4.4 | unknown | >1.9 | likely ↑ | unknown | 3.8 (1.6) | unknown |
| Acetone | 58.1 | 137 (23) | 37.7 (6.4) | 196 (33) | 63.7 (11) | 3.6 (0.9) | 3.1 (0.7) | −15% | 99 (24) | 132 (35) | +33 (43) |
| Benzene | 78.1 | <1.9 | <1.9 | 123.7 (25) | <1.9 | unknown | >65 | likely ↑ | unknown | 121.8 (25) | unknown |
| Carbon disulfide | 76.1 | <1.9 | <1.9 | 4.9 (1.1) | <1.9 | unknown | >2.6 | likely ↑ | unknown | 3.0 (1.1) | unknown |
| Dichlorodifluoromethane | 120.9 | <3.0 | <3.0 | 3.1 (0.6) | unknown | <1.0 | unknown | unknown | −0.1 (0.6) | unknown |
| Ethylbenzene | 106.2 | <2.6 | <2.6 | 24.1 (4.2) | <2.6 | unknown | >9.2 | likely ↑ | unknown | 21.5 (4.2) | >+20 |
| Isopropyl Alcohol | 60.1 | 3418 (509) | 439 (65) | 2173 (323) | 634 (25) | 7.8 (1.6) | 3.4 (0.7) | −56% | 2979 (513) | 1538 (337) | −140 (613) |
| m,p-Xylene | 106.2 | <5.2 | <5.2 | 16.8 (3.0) | <5.2 | unknown | >3.2 | likely ↑ | unknown | >11.6 | unknown |
| Propene | 42.1 | 222 (164) | 25.6 (18.9) | 130 (96) | 34.2 (25.2) | 8.7 (9.0) | 3.8 (4.0) | −56% | 197 (165) | 95.7 (99) | −101 (192) |
| Tetrachloroethene | 165.8 | <4.1 | 18.2 (3.3) | <4.1 | <4.1 | <0.23 | unknown | likely ↓ | −14.1 (3.3) | unknown | unknown |
| Toluen | 92.1 | <7.5 | <7.5 | 4.1 (0.8) | <7.5 | 1.8 (0.5) | 1.75 (0.5) | −4% | 3.4 (1.7) | 3.4 (1.8) | 0 (2.4) |
| Trichloroethene | 131.4 | <3.3 | 3.4 (0.6) | <3.3 | <3.3 | <1.0 | unknown | unknown | −0.1 (0.6) | unknown | unknown |
| Sum VOCs > RL | n/a | 3788 (698) | 528 (95) | 2687 (489) | 740 (132) | 7.2 (1.8) | 3.6 (0.9) | −49% | 3260 (704) | 1947 (506) | −1313 (867) |
| TO-11A List |           |                 |                 | EAC Off | EAC On |          | EAC Off | EAC On | EAC On-Off |
| Acetaldehyde | 44.1 | 6.0 (0.3) | 4.9 (0.3) | 10.1 (0.6) | 5.5 (0.3) | 1.2 (0.1) | 1.9 (0.2) | +52% | 1.1 (0.4) | 4.6 (0.7) | +3.6 (0.8) |
| Butyraldehyde | 72.1 | 5.2 (0.4) | 2.9 (0.2) | 4.9 (0.4) | <1.1 | 1.8 (0.2) | >4.4 | +250% | 2.2 (0.5) | >3.8 | +1.5 (0.6) |
| Formaldehyde | 30.0 | 21.1 (1.8) | 12.1 (1.0) | 24.3 (2.1) | 12.2 (1.1) | 1.7 (0.2) | 2.0 (0.24) | +15% | 8.9 (2.1) | 12.1 (2.3) | +3.2 (3.1) |
| Hexaldehyde | 100.2 | 7.7 (0.7) | 7.6 (0.7) | 8.5 (0.8) | 8.4 (0.8) | 1.0 (0.1) | 1.0 (0.13) | 0% | 0.1 (1.0) | 0.1 (1.1) | 0 (1.4) |
| Valeraldehyde | 86.1 | 3.3 (0.4) | <1.1 | 2.2 (0.3) | 2.6 (0.3) | >3.0 | 0.9 (0.2) | likely ↓ | −2.2 | −0.4 (0.4) | <−2.6 (0.6) |
| Total aldehydes | n/a | 43.2 (3.7) | 27.7 (2.3) | 50.1 (4.1) | 28.8 (2.4) | 1.6 (0.6) | 1.7 (0.6) | +11% | 15.6 (4.3) | 21.3 (4.8) | +5.7 (6.5) |
Table A2. Resulting concentrations and calculated inside/outside (I/O) chamber concentration ratios for TO-15/TO-11A analytes above reporting limits (RL) in at least one air sample from the 8 May 2021 short-term natural condition test. Symbols “likely ↑” and “likely ↓” denote likely, albeit not directly quantifiable, increases and decrease, respectively.

### 8 May 2021-Short-Term (Negative Ions: −4850 ions/cm³)

| Analyte                        | MW (g/mol) | TO-15 List | Concentration (µg/m³) | I/O Concentration Ratio | Concentration Difference (µg/m³) |
|--------------------------------|------------|------------|-----------------------|-------------------------|---------------------------------|
|                                |            | Inside Chamber | Outside Chamber | Inside Chamber | Outside Chamber | EAC Off | EAC On | % Change | EAC Off | EAC On | EAC On-Off |
| 2-Butanone                     | 72.1       | 7.7 (1.5) | <4.5 | 4.5 (0.9) | <4.5 | >1.7 | >1 | unknown | >3.2 | >0 | unknown |
| Acetone                        | 58.1       | 88.5 (15.0) | 22.5 (3.8) | 124.4 (21.2) | 47.8 (8.1) | 3.9 (0.9) | 2.6 (0.6) | −34% | 66.1 (16) | 76.6 (23) | +10.5 (28) |
| Dichlorodifluoromethane        | 120.9      | 3.9 (0.8) | 3.6 (0.7) | <3.0 | 3.6 (0.7) | 1.1 (0.3) | <0.8 | likely ↓ | 0.3 (1.1) | >−0.6 | >−0.9 |
| Isopropyl Alcohol              | 60.1       | 1783 (265) | 346 (52) | 2476 (368) | 421 (63) | 5.2 (1.1) | 5.0 (1.2) | +14% | 1436 (270) | 2055 (374) | +619 (461) |
| Propene                        | 42.1       | 46.8 (34.5) | <10.4 | 107.5 (79.2) | 17.3 (12.8) | >4.5 | 6.2 (6.5) | unknown | >36.4 | 90.2 (80) | >+44 |
| Toluene                        | 92.1       | 7.6 (1.5) | 2.3 (0.4) | 6.1 (1.2) | 3.7 (0.7) | 3.3 (0.9) | 1.6 (0.5) | −51% | 5.3 (1.6) | 2.4 (1.4) | −3.0 (2.1) |
| **Sum VOCs >RL**               | n/a        | 1937 (319) | 375 (57) | 2718 (471) | 493 (85) | 5.2 (1.2) | 5.5 (1.3) | +7% | 1562 (324) | 2225 (479) | +663 (578) |
| TO-11A List                    |            |            |            |            |            |            |            |            |            |            |            |
| Acetaldehyde                   | 44.1       | 4.7 (0.3) | 3.2 (0.2) | 7.8 (0.4) | 3.5 (0.2) | 1.5 (0.1) | 2.2 (0.2) | +51% | 1.5 (0.3) | 4.3 (0.5) | +2.8 (0.6) |
| Butyraldehyde                  | 72.1       | 4.2 (0.4) | 2.1 (0.2) | 3.9 (0.3) | 2.0 (0.2) | 2.0 (0.2) | 2.0 (0.2) | −2% | 2.1 (0.4) | 1.9 (0.4) | −0.2 (0.5) |
| Formaldehyde                   | 30.0       | 12.7 (1.1) | 6.4 (0.5) | 14.5 (1.2) | 6.7 (0.6) | 2.0 (0.2) | 2.2 (0.3) | +8% | 6.4 (1.2) | 7.8 (1.4) | +1.4 (1.8) |
| Hexaldehyde                    | 100.2      | 4.7 (0.4) | 3.6 (0.3) | 5.3 (0.5) | 4.6 (0.4) | 1.3 (0.2) | 1.2 (0.2) | −11% | 1.1 (0.5) | 0.7 (0.6) | −0.4 (0.8) |
| Valeraldehyde                  | 86.1       | <1.1 | 1.7 (0.2) | <1.1 | <1.1 | <0.7 | unknown | unknown | >−0.6 | unknown | unknown |
| **Total aldehydes**            | n/a        | 26.3 (2.1) | 17.0 (1.4) | 31.4 (2.5) | 16.7 (1.4) | 1.5 (0.8) | 1.9 (0.8) | +21% | 9.3 (2.6) | 14.7 (2.8) | +5.4 (3.8) |
Table A3. Resulting concentrations and calculated inside/outside (I/O) chamber concentration ratios for TO-15/TO-11A analytes above reporting limits (RL) in at least one air sample from the 5 July 2021 long-term natural condition test. Symbols “likely ↑” and “likely ↓” denote likely, albeit not directly quantifiable, increases and decrease, respectively.

| Analyte                      | MW (g/mol) | 5 July 2021-Long-Term (Negative Ions: −2470 ions/cm³) | Concentration (µg/m³) | I/O Concentration Ratio | Concentration Difference (µg/m³) |
|------------------------------|------------|-------------------------------------------------------|------------------------|-------------------------|----------------------------------|
|                              |            | Air Cleaner Off | Air Cleaner On | Inside–Outside (I–O) | EAC Off | EAC On | % Change | Inside–Outside (I–O) | EAC Off | EAC On | EAC On-Off |
| TO-15 List                   |            | Inside Chamber | Outside Chamber | Inside Chamber | Outside Chamber | EAC Off | EAC On    | % Change | EAC Off | EAC On | EAC On-Off |
| 2-Butanone       | 72.1       | 7.8 (1.5) | 5.8 (1.1) | <11.0 | 7.0 (1.4) | 1.3 (0.4) | <1.6 | unknown | 2.0 (1.9) | unknown | unknown |
| Acetone             | 58.1       | 72.3 (12.3) | 37.5 (6.4) | 76.9 (13.1) | 44.6 (7.6) | 1.9 (0.5) | 1.7 (0.4) | −10% | 34.7 (13.8) | 32.3 (15.1) | −2.4 (21) |
| Benzene            | 78.1       | <1.9 | <1.9 | <4.7 | 2.9 (0.6) | unknown | <1.6 | unknown | unknown | unknown | unknown |
| Chloroethane       | 64.5       | 2.3 (0.5) | <1.6 | <3.9 | <1.6 | >1.4 | unknown | unknown | >0.7 | unknown | unknown |
| Chloromethane      | 50.5       | 6.5 (1.6) | <3.1 | 127.7 (30.5) | <3.1 | >2.1 | >41 | likely ↑ | >3.4 | >124.6 | >121 |
| Dichlorodifluoromethane | 120.9   | <3.0 | 4.6 (1.0) | <7.3 | 3.8 (0.8) | <0.7 | <1.9 | unknown | >−1.6 | unknown | unknown |
| Ethylbenzene       | 106.2      | <2.6 | <2.6 | 6.4 (1.1) | 2.9 (0.5) | unknown | 2.2 | unknown | unknown | 3.5 (1.2) | unknown |
| Isopropyl Alcohol  | 60.1       | 386 (57) | 340 (51) | 200 (30) | 121 (18) | 1.1 (0.2) | 1.7 (0.3) | +45% | 45.9 (77) | 78.8 (35) | +33 (84) |
| m,p-Xylene        | 106.2      | <5.1 | <5.1 | 21.7 (3.9) | <5.1 | unknown | >4.2 | likely ↑ | unknown | >16.6 | unknown |
| Naphthalene        | 128.2      | 17.0 (9.1) | 5.7 (1.5) | <7.7 | 10.9 (2.9) | 3.0 (1.1) | <0.7 | likely ↓ | 11.3 (4.7) | >−3.2 | >−14.5 |
| Propene            | 42.1       | 12.3 (9.1) | 22.1 (16.3) | <25.3 | <10.4 | 0.6 (0.6) | unknown | unknown | −9.8 (18.7) | unknown | unknown |
| Toluene            | 92.1       | 7.8 (1.5) | 5.2 (1.0) | 8.1 (1.6) | 6.3 (1.2) | 1.5 (0.4) | 1.3 (0.4) | −14% | 2.6 (1.8) | 1.8 (2.0) | −0.7 (2.7) |
| Trichloroethene    | 131.4      | <5.2 | <3.2 | 14.2 (2.6) | <3.2 | unknown | >4.4 | likely ↑ | unknown | >11.0 | Unknown |
| Sum VOCs > RL      | n/a        | 512 (88) | 421 (78) | 455 (83) | 200 (33) | 1.2 (0.3) | 2.3 (0.6) | +87% | 91 (118) | 256 (89) | +165 (148) |
| TO-11A List        |            |            |            |            |            |            |            |            |            |            |            |
| Acetaldehyde       | 44.1       | 9.0 (0.5) | 8.2 (0.5) | 14.7 (0.8) | 11.0 (0.6) | 1.1 (0.1) | 1.3 (0.1) | +22% | 0.8 (0.7) | 3.7 (1.1) | +2.9 (1.3) |
| Butyraldehyde      | 72.1       | 5.0 (0.4) | 4.0 (0.3) | 5.2 (0.4) | 4.1 (0.3) | 1.2 (0.2) | 1.3 (0.2) | +2% | 0.9 (0.5) | 1.1 (0.6) | +0.2 (0.8) |
| Formaldehyde       | 30.0       | 27.0 (2.3) | 19.6 (1.7) | 33.6 (2.9) | 23.3 (2.0) | 1.4 (0.2) | 1.4 (0.2) | +5% | 7.4 (2.9) | 10.3 (3.5) | +2.9 (4.5) |
| Hexaldehyde        | 100.2      | 9.0 (0.8) | 8.7 (0.8) | 8.5 (0.8) | 8.1 (0.7) | 1.0 (0.1) | 1.1 (0.1) | +1% | 0.3 (1.1) | 0.4 (1.0) | +0.1 (1.5) |
| Valeraldehyde      | 86.1       | 4.5 (0.6) | 4.1 (0.5) | 4.5 (0.6) | 4.0 (0.5) | 1.1 (0.2) | 1.1 (0.2) | 0% | 0.4 (0.8) | 0.4 (0.8) | 0.0 (1.1) |
| Total aldehydes    | n/a        | 54.5 (4.6) | 44.7 (3.8) | 66.5 (5.5) | 50.6 (4.2) | 1.2 (0.7) | 1.3 (0.9) | +8% | 9.8 (6.0) | 16.0 (6.9) | +6.1 (9.2) |
Figure A7. Evolution of the concentration of several VOCs of interest as potential byproducts of limonene oxidation from low molecular weight (panel (A)) to higher molecular weight (panel (B)) as a function of the time during the perturbation test presented in Figure 12 (injection of limonene) when the air cleaner was off and when the air cleaner was on.

Figure A8. Evolution of the concentration of several VOCs of interest as potential byproducts of limonene oxidation as a function of the time during the perturbation test presented in Figure 12 (injection of limonene) when the air cleaner was off and when the air cleaner was on.
Appendix A.3. Ozone Measurements in the Controlled Laboratory Study

![Figure A9. Indoor/outdoor (I/O) ozone concentration ratios over the three experiments performed in the controlled laboratory study averaged over the periods were the air cleaner (AC) was off or on. The error bars represent the standard deviation. Indoor concentrations were measured at the monitoring station in the laboratory as indicated in the schematic of Figure 3. Outdoor concentrations were obtained from hourly monitoring data at the Portland SE Lafayette station from the Oregon Department of Environmental Quality (https://orai.deq.state.or.us (accessed on 1 November 2021)).](image-url)

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