Evaluation of short-term initial performance of a "Molekule Air" portable air cleaner

LBNL Report

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1. EXECUTIVE SUMMARY

The aim of this project was to evaluate and characterize the performance of a MOLEKULE AIR air cleaner unit.[1] The testing protocol comprised the evaluation of an unused Molekule Air unit operating at maximum ("boost" setting) fan speed setting. The device was tested over initial short-term periods of 70-80 h of continuous operation. The tested air cleaner was challenged in separate experiments with a well-characterized mixture of volatile organic compounds (VOCs), and with ozone. All tests were performed at realistic pollutant levels in a 20-m^3 environmental stainless-steel chamber. Variables controlled and measured in this study included the chamber temperature, relative humidity, the composition and concentration of the challenge VOCs, and the concentrations of ozone. Potential formation of byproducts was also investigated to assess the overall performance.

Operation of the air cleaner under clean chamber air conditions, without introduction of VOCs or ozone, demonstrated that the test unit was not a source of those contaminants when new. In experiments where a challenge VOC mixture was injected, the concentrations of all pollutants introduced to the chamber were significantly reduced in periods in which the air cleaner was operated, with a 95% removal efficiency for limonene, 94% for toluene and 55% for formaldehyde. In separate experiments, the removal efficiency for ozone was 95%. No formation of byproducts was observed with the analytical methods used in this study.

2. EVALUATION OF VOC REMOVAL EFFICIENCY

2.1 Choice of VOCs tested in this study

Removal was evaluated for three VOCs which are ubiquitous indoor pollutants:

a) Toluene: commonly emitted by multiple sources, including solvents, paints, construction materials, furniture, and household products. It is also an important outdoor air pollutant, brought indoors through ventilation. While toluene is not particularly harmful at

[1] https://molekule.com/air-purifier-air

commonly found indoor levels, exposure to higher levels may cause reproductive toxicity.[2]

b) Limonene: probably the most common terpenoid used in household products to impart pleasant fragrances (e.g., in cleaners, degreasers, air fresheners). It is also emitted by essential oils diffusers, incense and scented candles. Limonene is a skin irritant and an important precursor to indoor secondary particle formation in the presence of ozone[3].

c) Formaldehyde: a carcinogenic pollutant, commonly found in homes at levels that exceed reference exposure levels for irritation of the eyes and respiratory airways recommended by the State of California[4]. It is emitted by multiple sources that include composite wood products (hardwood plywood, particleboard and medium density fiberboard), household product use, and combustion sources.

These three compounds are commonly used targets for elimination through photocatalytic oxidation.

2.2 Analytical methods for VOCs

Limonene and toluene concentrations were determined by collecting chamber air onto sorbent tubes over a period of approximately 1 hour using a peristaltic pump. The tubes were subsequently analyzed by Thermal Desorption / Gas Chromatography / Mass Spectrometry (TD/GC/MS). Levels of formaldehyde, along with other aldehydes and a few volatile ketones were determined by collecting chamber air samples onto dinitrophenylhydrazine (DNPH)-coated silica cartridges using a peristaltic pump. Cartridges were subsequently extracted and analyzed by High Performance Liquid Chromatography (HPLC). Both analyses follow established EPA methods, and

[2] https://www.atsdr.cdc.gov/phs/phs.asp?id=159&tid=29
[3] Wainman, T.; Zhang, J.; Weschler, C. J.; Lioy, P. J., Ozone and limonene in indoor air: a source of submicron particle exposure. *Environmental health perspectives* **2000,** *108*, (12), 1139-45
[4] https://oehha.ca.gov/air/chemicals/formaldehyde

are current standard practice at LBNL.[5,6] In all cases, samples were collected in duplicates. The values reported correspond to the average, and the experimental error to half the absolute difference between those determinations.

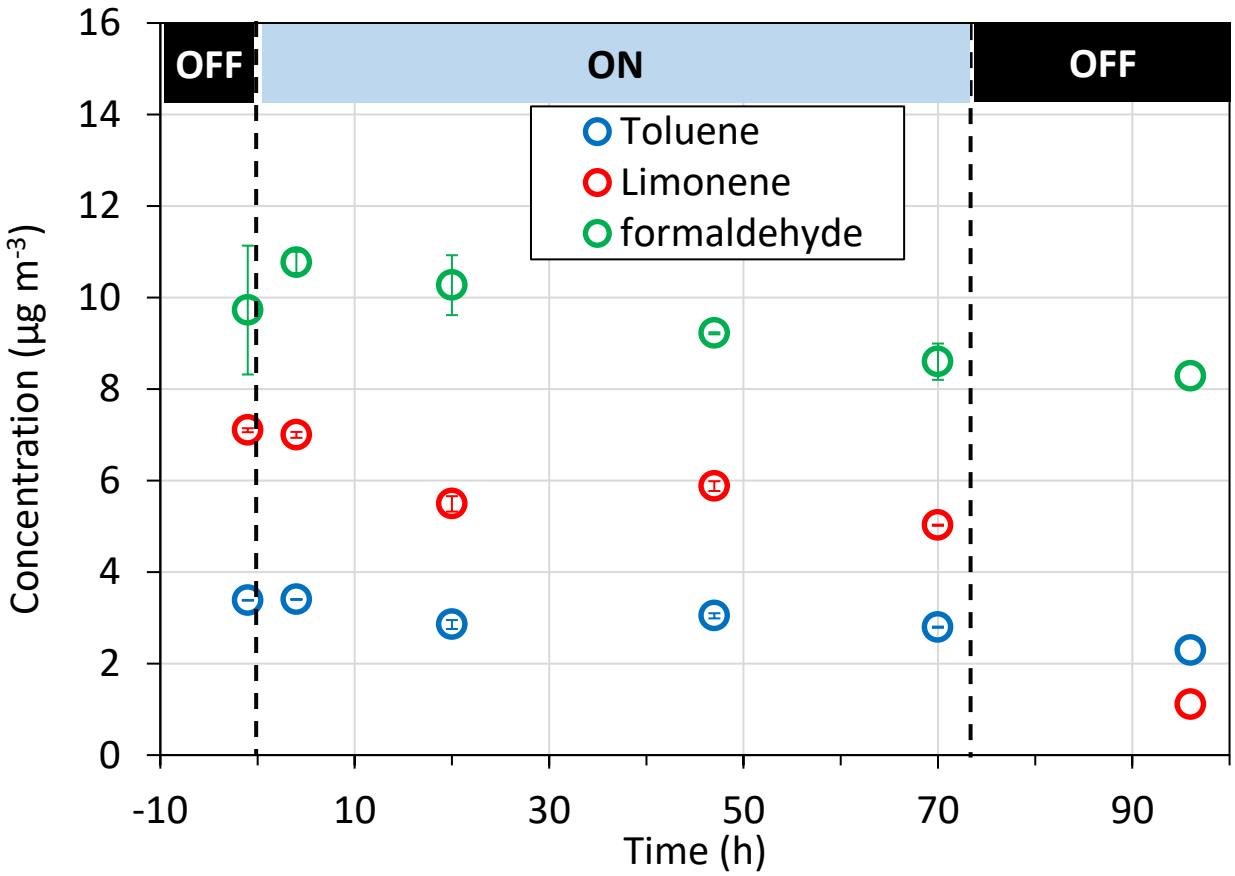
2.3 Investigation of VOC emissions from the air cleaner

The experiment was performed using LBNL's 20-m^3 stainless-steel indoor environmental chamber. For the purpose of evaluating potential VOC emissions by the unit, this test was carried out without the catalytic filter, which was removed from the air cleaner. By doing this, it was possible to measure VOC emissions arising from the operation of the air cleaner (e.g., from a heating fan, or other plastic components). The air cleaner was placed inside the ventilated chamber, and tests comprised alternating periods in which the unit was turned on and off. An initial test cycle was performed to evaluate potential emissions of VOCs by the unit. It comprised an initial equilibration period with the air cleaner turned off, during which samples were taken, followed by a 72-h period with the Molekule Air unit operating continuously, in which several samples were collected. Finally, a 20-h period with the air cleaner turned off allowed to measure additional samples. Chamber temperature was kept at 25 °C, and relative humidity at 35 %. The chamber air exchange rate was 0.23 h^{-1}. No significant increment in chamber concentrations were recorded for the three tested pollutants, nor for other VOCs, during the period in which the air cleaner (without the photocatalytic filter) was running. Concentrations during that period were comparable to those measured with the air cleaner off, immediately before and after operation, and corresponded to chamber background levels. Results from this test are shown in Figure 1.

[5] U.S. EPA. Method TO-1, Revision 1,0: Method for the Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS); Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency (U.S. EPA): Cincinnati, OH, 1984

[6] U.S. EPA. Compendium Method TO-11A - Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by HPLC [Active Sampling Methodology]; Office of Research and Development, U.S. Environmental Protection Agency (U.S. EPA): Cincinnati, OH, 1999.

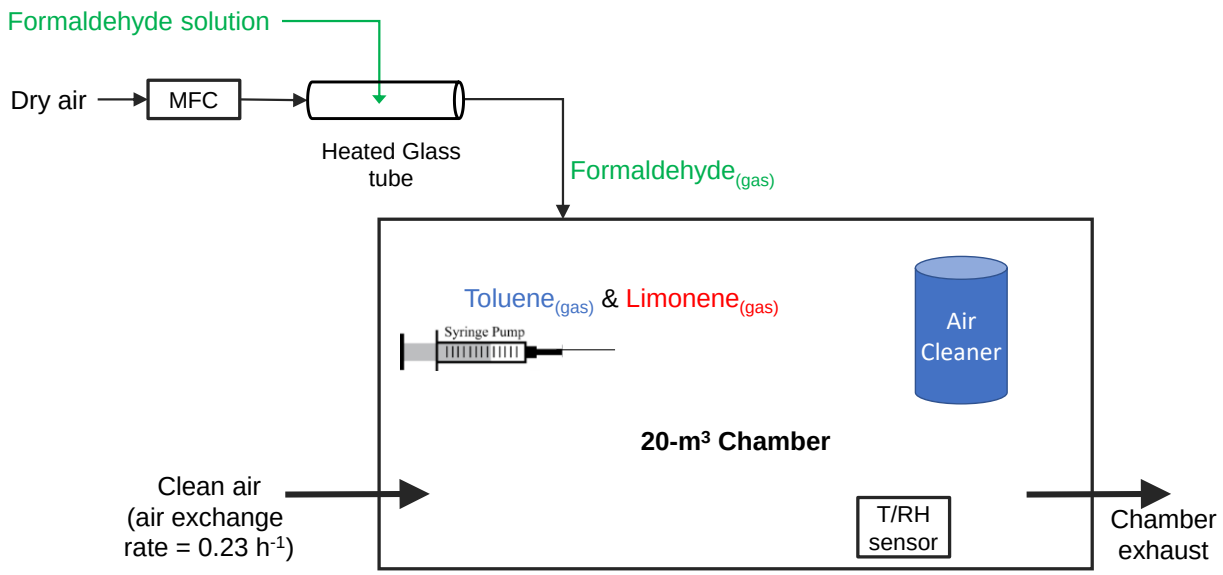
***Figure 1**: Evaluation of potential VOC emissions in clean chamber air*



2.4 Removal efficiency of VOCs

In order to evaluate the air cleaner performance, the three challenge VOCs were introduced continuously, and allowed to reach steady-state levels. Toluene and limonene (both liquids) were pre-mixed and introduced in a syringe pump that delivered a constant flow directly into the chamber. In the case of formaldehyde a 37% aqueous solution was injected continuously into a heated glass tube, where it evaporated in a flow of dry air that delivered a constant flow of gas phase formaldehyde into the chamber. Fast evaporation of the liquids into the ventilated chamber led to a stable steady-state gas phase concentration over the studied period (with the air cleaner "off" and "on"). The experimental setup is described in Figure 2.

***Figure 2**: Evaluation of potential VOC emissions in clean chamber air*



The gas phase concentration of each of the three contaminants was determined four times during the experiment: in two measurements before the air cleaner was operated, and another two carried out after the air cleaner operation. The values reported in Table 1 correspond to averages of those four determinations. The reported experimental error is the standard deviation of those determinations. The relative standard deviation (RSD), indicating individual measurement precision, was between 5% and 12%, which is very reasonable for these kinds of studies. The main reason for the reported variability in chamber concentration could be related with fluctuations in the delivery of the liquids by the syringe pumps, for example due to the presence of small bubbles in the liquid. Overall, the concentrations reported here are realistic, and could represent a polluted indoor environment in North America.[7]

[7] Hodgson, A. T., Levin, H. Volatile organic compounds in indoor air: A review of concentrations measured in North America since 1990. LBNL Report Number 51715. https://buildings.lbl.gov/publications/volatile-organic-compounds-indoor-air

Compound	**Concentration ($\mu g\ m^{-3}$)**	**Relative standard deviation (RSD)**	**Concentration (ppb)**
Toluene	144 ± 7	5 %	38 ± 2
Limonene	147 ± 17	12 %	26 ± 3
Formaldehyde	84 ± 8	10%	68 ± 6
TOTAL VOCs	**374 ± 32**	**8 %**	**132 ± 11**

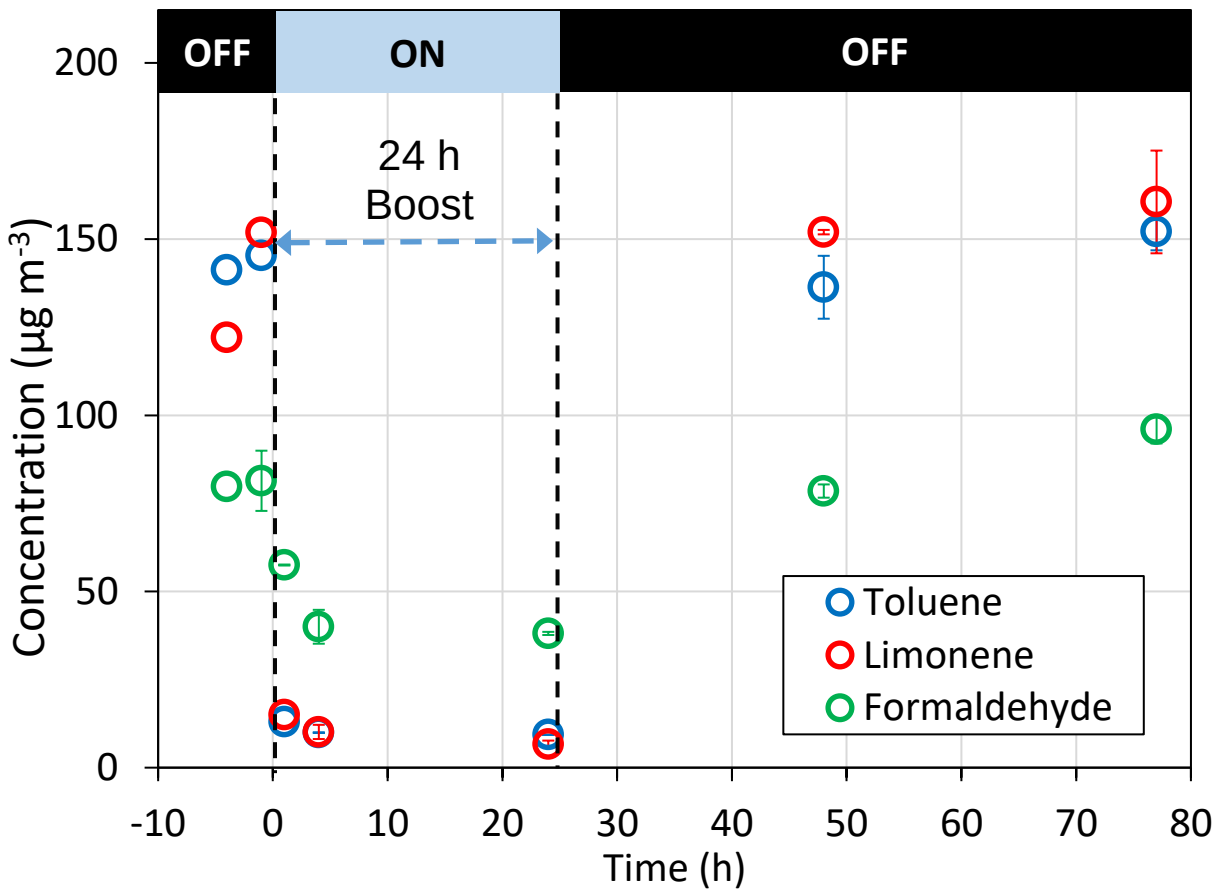
***Table 1**: Average VOC chamber concentration determined with the air cleaner OFF (n=4)*

Figure 3 presents the chamber VOC concentrations measured during the experimental period with the air cleaner initially turned off, followed by a 24-h period with the air cleaner operating in boost mode, and a subsequent 48-h period with the air cleaner turned off. A quick reduction of toluene and limonene levels was observed during the first hours of operation of the air cleaner, reaching low concentrations that were maintained during the 24-h period. Formaldehyde also decreased, but at a relatively slower rate, and reaching a steady-state concentration that was higher than those of the other two compounds.

Formation of oxidation byproducts was examined by inspection of the GC/MS and HPLC chromatograms of samples collected in periods during which the air cleaner was operated and background periods with the air cleaner turned off. Benzaldehyde, a characteristic byproduct of toluene oxidation, was not found in any of the samples. In addition, other common oxidation byproducts, such as acetaldehyde, acetone and acrolein, were either not detected or, if detected, were at the same levels before, during and after device operation (hence, not produced by operation of the air cleaner). Examination of GC/MS chromatograms suggested presence of background levels of siloxanes in chamber air, probably emitted by plastic gaskets and other materials present in the chamber, not related with the air cleaner. The

chromatograms did not show the presence of other chemicals, including compounds that were not used as analytical standards.

***Figure 3**: Measured VOC concentrations upon continuous injection of toluene, limonene and formaldehyde*

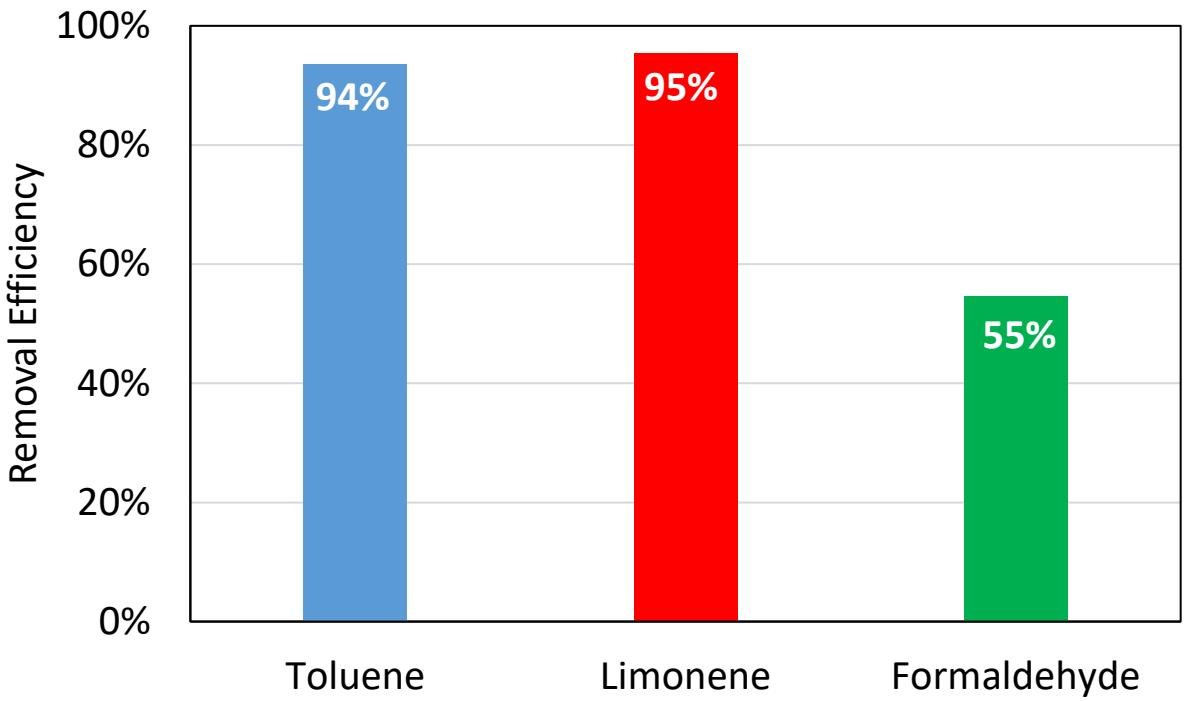


The removal efficiency (*RE*) of each of the three VOCs was calculated as:

$$RE(\%) = \frac{C_{off} - C_{on}}{C_{off}} \times 100 \qquad (1)$$

where C_{off} and C_{on} are the chamber concentrations measured with the air cleaner turned off and on, respectively. The corresponding *RE* values are reported in Figure 4.

***Figure 4**: VOC removal efficiency*

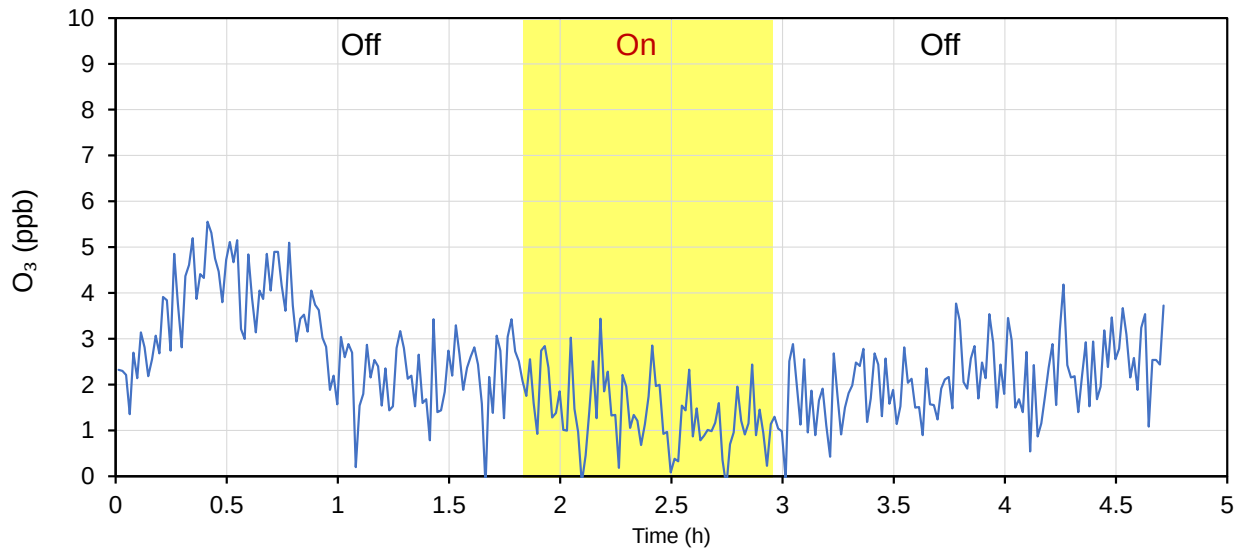


3. EVALUATION OF OZONE REMOVAL

During a preliminary test, it was verified that operation of the air cleaner in clean air did not produce ozone, as shown in Figure 5. Chamber ozone concentration remained at background levels during air cleaner operation. Chamber temperature was kept at 23 °C, and relative humidity at 40 %. A separate test was carried out in the presence of a high but realistic level of ozone, in the range 77 – 88 ppb, to assess the air cleaner's ability to eliminate indoor ozone with the air cleaner operating at a boost fan speed. Due to ozone's reactivity, it was not possible to reach a steady-state concentration as described for the VOCs, but rather a continuously increasing level due to quenching/inactivation of reactive materials present in the chamber. Ozone can react with chemicals adsorbed on chamber walls (primarily from previous experiments, but also from deposition of pollutants and aerosols present in background air). For that reason, ozone levels measured during periods of operation of the air cleaner were compared

with those recorded during off periods before and after the test. Ozone was measured continuously using a photometric analyzer (Model 2B Tech 202).

***Figure 5**: Chamber ozone concentration with air cleaner ON and OFF, without introduction of additional ozone*



3.1 Ozone generation system and experimental setup

Ozone was produced continuously using a high capacity corona-discharge generator (Yanco Industries M/N GE30/FM100) that was fed with pure oxygen (O_2) at a flow of 60 cm^3 min^{-1}. The high-concentration ozone flow was diluted with clean air, and subsequently split between a flow that was injected in the chamber and an excess line that was venting in a fume hood. The desired chamber concentrations were achieved by adjusting the relative flows being introduced in the chamber and vented. The delivery system is described in Figure 6, and the experimental setup for ozone tests is shown in Figure 7.

***Figure 6**: Ozone generation, dilution and delivery system*

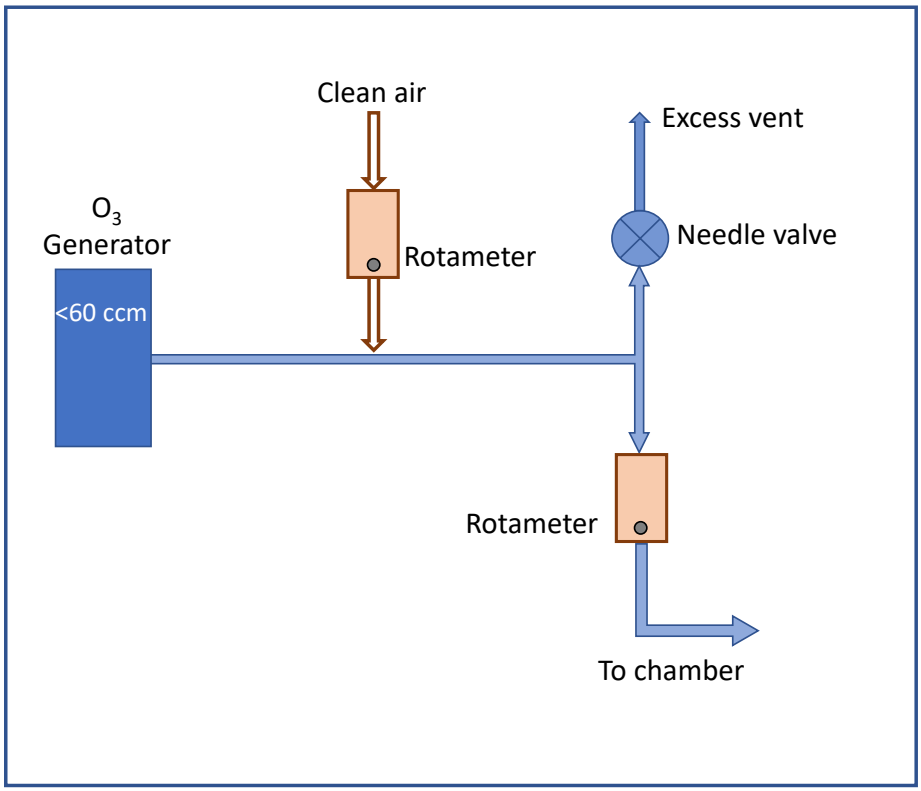
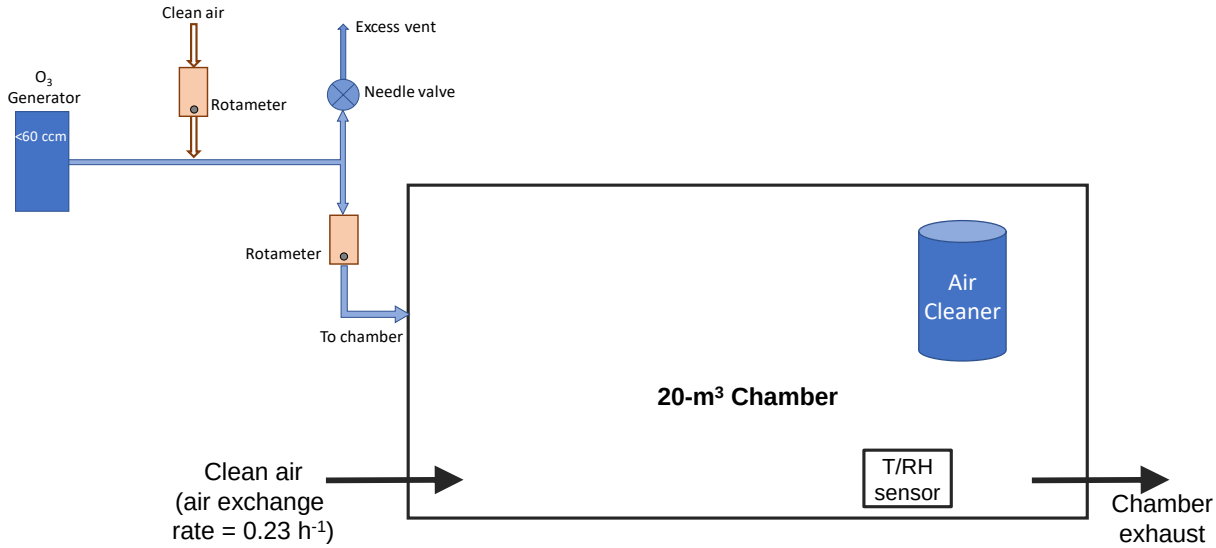


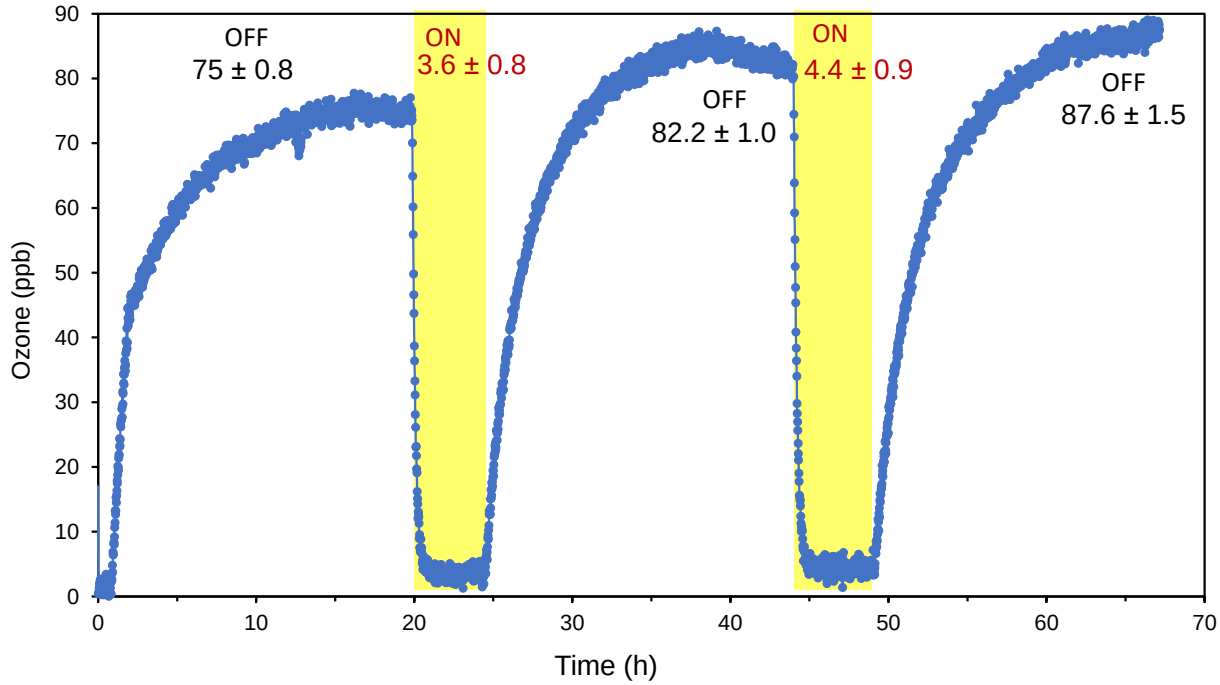
***Figure 7**: Experimental setup for ozone injection in a room-sized environmental chamber*



3.2 Ozone removal efficiency

Results corresponding to two air cleaning operation cycles, and their respective background periods with the air cleaner turned off, are shown in Figure 8. Ozone concentration increased constantly during the background periods, reaching relatively stable levels over the final 10 hours of measurements in each case. The background concentrations were determined for those relatively constant periods. As the chamber surfaces were being quenched, the levels reached during the first, second and third background period were increasingly higher. By contrast, ozone concentration showed a fast reduction immediately after the air cleaner was turned on, remaining at very low levels over the duration of the air cleaning operation period. Once the air cleaner was turned off, ozone levels increased again. The corresponding ozone concentration in each segment are reported in Table 2, together with the removal efficiency for each of the two periods during which the air cleaner was operated. Removal efficiency was calculated using equation (1). Due to the changes in background levels, the value of each C_{off} was determined as the average of two OFF periods occurring immediately before the ON period, and after reaching a relatively stable level once the air cleaner had been turned off.

***Figure 8**: Chamber ozone concentration during tests*



Air cleaner setting	Experiment time	Ozone concentration (ppb)	Removal efficiency
OFF	10 – 20 h	75 ± 1	
ON	20 – 25 h	3.6 ± 0.8	95 %
OFF	35 – 45 h	82 ± 1	
ON	45 – 50 h	4.4± 0.9	95 %
OFF	60 – 70 h	88± 2	

***Table 2:** Average ozone chamber concentration determined with the air cleaner OFF and ON, and ozone removal efficiency*

4. DISCUSSION

The Molekule Air performance was evaluated by determining the following parameters:

a) the presence of any emission of organic contaminants or ozone during operation in a clean chamber environment,

b) the removal efficiency of challenge pollutants over several hours of continuous operation, reaching steady-state conditions, and

c) the formation of secondary byproducts of the PECO process, such as ozone and volatile carbonyls.

The following is the summary of findings:

a) no measurable amounts of VOCs nor ozone were emitted when the air cleaner was operated in a clean chamber (i.e., in the absence of added contaminants).
b) The removal efficiency of toluene, limonene and ozone were very high, reducing the levels of those contaminants by more than one order of magnitude.
c) The removal efficiency of formaldehyde was high (55%), particularly considering that many photocatalytic air cleaners often become a source of this chemical due to incomplete decomposition of other compounds.[8]
d) No secondary byproducts were observed when the air cleaner was operated in the presence of a challenge VOC mixture.

These results suggest that the air cleaner has enough capacity to remove indoor gaseous pollutants at levels that are typically present indoors, without producing harmful byproducts.

[8] Hodgson, A.T., Destaillats, H., Sullivan, D.P., Fisk, W.J. Performance of ultraviolet photocatalytic oxidation for indoor air cleaning applications. *Indoor Air* 2007, 17, 305-316.