1 *Article*

2 # Formation of Secondary Organic Aerosols by
3 # Germicidal Ultraviolet Light

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9 **Abstract: Ultraviolet (UV) light with a wavelength of 254 nm has proven to be effective at**
10 **inactivating microorganisms, and thus has been increasingly employed as a method of**
11 **disinfection for indoor environments. Solar UV wavelengths (300 to 400 nm) are known to**
12 **initiate the formation of secondary organic aerosol (SOA) particles from photo-oxidation of**
13 **volatile organic compounds in the atmosphere, but germicidal wavelengths have not been**
14 **extensively studied for indoor environments.   In this work, toluene was exposed to 254 nm UV**
15 **light in a laboratory photoreactor, with varying conditions of the air, the duration of UV**
16 **exposure, and the duration of post-UV time. The number of particles formed in the fine**
17 **particulate matter (PM2.5) size range was measured, and significant levels of particle formation**
18 **were observed for UV exposure periods of as short as 5 minutes. The particle formation ranged**
19 **from 2.4×10^6 particles/m³ for 5 minutes of UV exposure, to 1449.8×10^6 particles/m³ for 15 minutes**
20 **of UV exposure. Particle formation was found to increase with increasing concentrations of gas**
21 **phase toluene, and at relative humidity of approximately 20% and higher. Variations in the**
22 **initial number of particles present did not appear to have a significant effect on the particle**
23 **formation, suggesting that nucleation was not a controlling factor. However, tests in a**
24 **commercial environment showed no significant detectable PM2.5 formation, indicating that**
25 **SOA formation during the intermittent use of germicidal UV may not significantly affect indoor**
26 **air quality.**

27 **Keywords:** fine particulate; PM2.5; UV disinfection; indoor air quality
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29 ## 1. Introduction

30   Ultraviolet (UV) light is increasingly used in residential, commercial, and institutional settings
31 for reduction of surface and airborne bacteria, spores, and viruses, and it uses a mercury lamp with a
32 wavelength of 254 nm to induce damage to the DNA in these cells.   For example, automated UV
33 disinfection has shown good effects in hospitals for reducing environmental biological burdens [1]
34 and infection rates for susceptible patients [2].

35   However, it is well-known from atmospheric chemistry that longer wavelength solar UV
36 (wavelengths from 300 to 400 nm) can promote the generation of aerosol particles [3].   These
37 aerosols are generated by the UV-photooxidation of volatile organic compounds (VOCs) in the
38 atmosphere, which results in less volatile partial oxidation products.   The products tend to
39 condense, possibly on other nano-particulates, and this results in the growth of new or larger aerosol
40 particles, commonly referred to as Secondary Organic Aerosols (SOA).   The degree to which any
41 specific oxidation product contributes to SOA formation depends on the equilibrium established
42 between the gas and particle phases for that compound at the given conditions [4].

43   A concern arises because fine particulate (PM2.5 or particulate matter with diameter less than
44 2.5 μm) is strongly associated with negative health effects such as respiratory and cardiac disease [5].
45 Thus these SOA particles may add to the background burden of PM2.5 in the atmosphere, and
46 especially in indoor environments where germicidal UV devices are used.

47   Therefore, the first objective of this work was to determine if the shorter wavelength germicidal
48   UV was similarly capable of generating SOA, and how the conditions might affect this SOA
49   formation.   Based on this knowledge, the potential impact of UV on particulate concentrations in
50   rooms undergoing automated disinfection could then be assessed to determine if this may be an
51   indoor air quality concern for the use of these devices.
52

53   **2. Materials and Methods**

54   A diagram of the experimental setup used for this project is shown in Figure 1. The system
55   setup consisted of a custom built UV reactor vessel, containing a UV lamp running the length of the
56   reactor. The air in the system was recirculated using a Cole Parmer Masterflex peristaltic pump, with
57   60 cm of Masterflex size 17 Norprene tubing with (6.4 mm inner diameter). The rest of the tubing
58   used for recirculation was 370 cm of 0.935 cm ID polytetrafluoroethylene (PTFE) tubing. The
59   recirculation rate of the system gas was 415 mL/min, which is equivalent to one vessel air exchange
60   every 63.5 minutes. For the majority of the experiments, the air supplied to the UV reactor was
61   compressed air from the building's system and was passed through an activated carbon/HEPA filter
62   (ZenPure PureFlo Capsule). This ensured that the air was relatively dry with a relative humidity of
63   around 11%, with the filtration removing most particles larger than 0.3 μm diameter.   In addition,
64   some experiments were done with unfiltered compressed air, as well as filtered and unfiltered room
65   air having a relative humidity greater than 11%.
66   The UV reactor vessel was a cylindrical stainless-steel vessel with an inner diameter of 20.3 cm,
67   and a length of 81.3 cm, having an effective volume of 26,359 mL. The UV lamp was a Sterilight
68   model S8RL/4P (Viqua, Guelph ON), a 40 W lamp which produces monochromatic UV light with a
69   wavelength of 254 nm, situated down the centre axis of the reactor.
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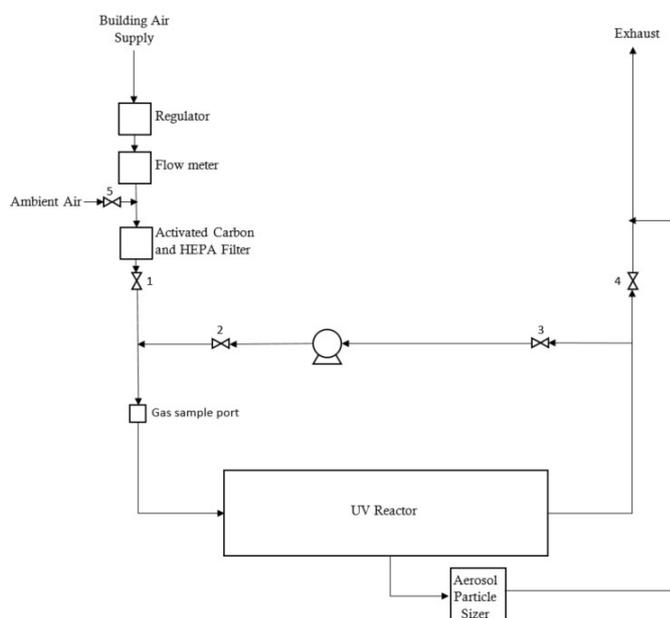
71   **Figure 1:**   schematic of the experimental apparatus used to generate SOA by UV exposure.
72

73   Gas chromatography (GC) was used to monitor the VOC concentrations throughout the
74   duration of the experiments, using an HP 5890 Series II, with a Restek model Rtx-5 10240 fused silica
75   column with an inner diameter of 0.53 mm and a length of 30 m.
76   A TSI Aerosol Particle Sizer (APS) model 3321 was used to monitor the number of aerosol
77   particles present in the system, sampling directly from the UV reactor vessel, as shown in Figure 1.
78   The APS was able to detect particles from 0.5-20 μm in diameter and these particles were sorted into

79 52 size fractions for size distribution analysis, as well as a fraction between 0.3 to 0.5 µm which was
80 aggregated as a size fraction of <0.523 µm.   Samples from the UV reactor were drawn through 86 cm
81 of conductive silicon tubing (inner diameter of 11.2 mm) manufactured by TSI for use with the APS.
82   Toluene was the primary VOC used in the experiments performed and was supplied by VWR
83 International with a minimum purity of 99.5%.
84

3. Results

86   Initial blank controls with the UV light turned off confirmed that the presence or absence of
87 toluene in the photoreactor had no detectable effect on particle formation over a period of an hour.
88 Next, using toluene at an initial concentration ranging from 55 to 85 mg/m^3, the effect of UV dose on
89 particulate formation was assessed by running experiments for varying lengths of time with the UV
90 lamp on, followed by a constant hold and recirculation time of 5 minutes. The results are shown in
91 Figure 2, where PM2.5 formation is the difference between initial particulate counts and those at the
92 end of the experiment.   It was observed that in the experimental set-up, no statistically significant
93 particulate formation was detectable until at least 5 minutes of UV exposure was used, and that the
94 counts increased in an apparently non-linear manner beyond the 5 minute exposure time.
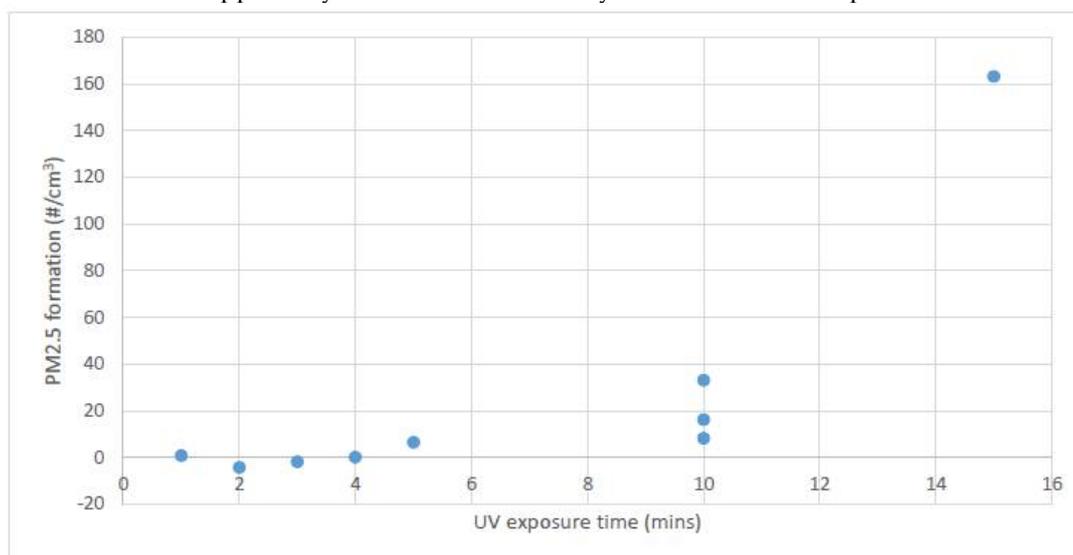
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96 **Figure 2:**   PM2.5 formation (corrected for initial background counts) as a function of UV
97 exposure time, with a constant recirculation time of 5 minutes after UV exposure, for initial toluene
98 concentrations in air of 55 to 85 mg/m^3.
99
100   For the automated UV room disinfection units of interest, the typical exposure time is set for 5
101 minutes as this is generally found to provide a satisfactory disinfection dose [1].   Therefore focusing
102 on the 5 minutes UV exposure, further experiments were performed to assess the particle size
103 distribution within the range measurable by the TSI instrumentation, with the results shown in
104 Figure 3.   These results indicated several points, 1) that injection of the toluene did not create
105 particulate on its own (comparing air blank to air blank with toluene), and 2) that most of the
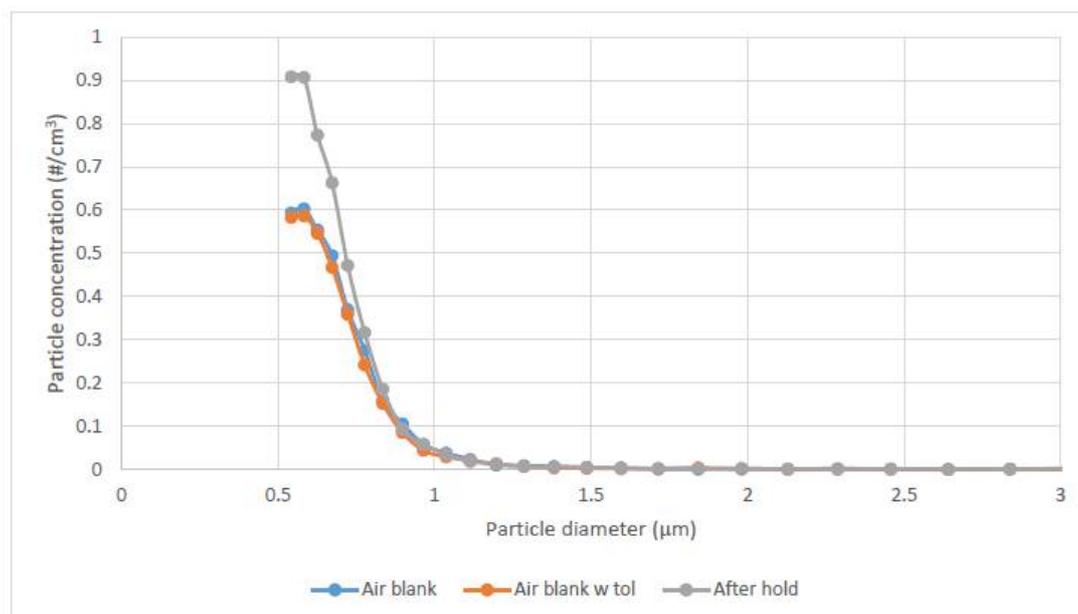106 detectable particulate generation occurred at sizes less than 1 µm.
107

Figure 3: Particle size distribution for 5 minutes UV exposure followed by 5 minutes recirculation (hold) post-UV.

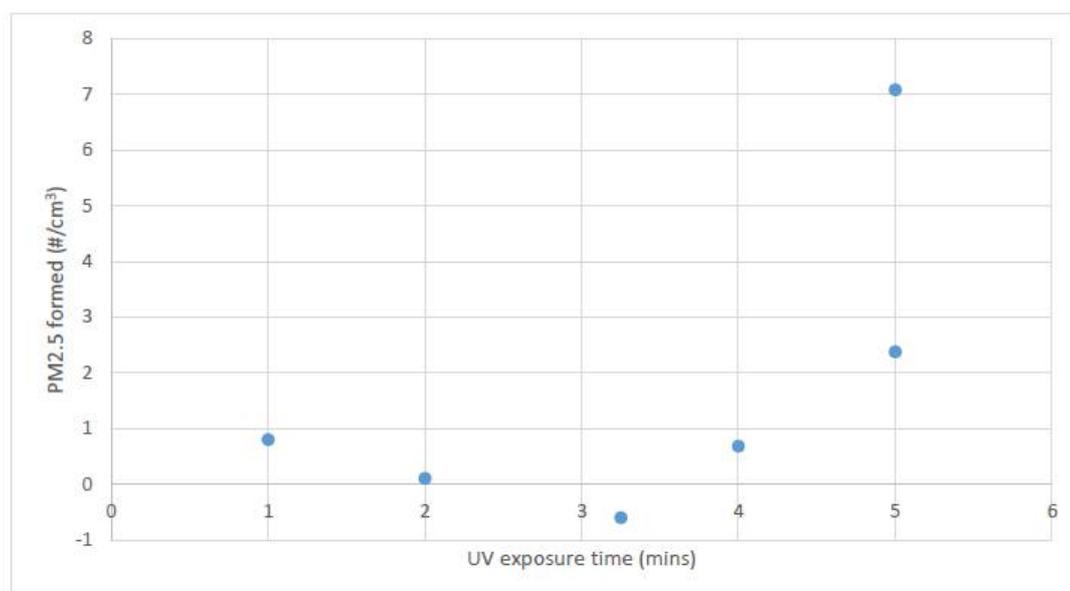**Figure 4:** PM2.5 counts after a constant total time (6 minutes), with varying UV exposure times.

It was expected that the UV exposure would initiate particulate formation by creating less volatile partial oxidation products of toluene, and that particulate growth would then play a role that would be related to total residence time.   To test for this effect, a constant residence time of 6 minutes was used, with varying UV exposure times up to 5 minutes (the typical UV disinfection unit dose time).   The results are shown in Figure 4, which re-confirms the results in Figure 2 whereby at least 5 minutes of UV dose were required for measurable particulate formation.   It was concluded that under these experimental conditions, the effect of the hold time after UV exposure was not a significant factor in particulate counts.   The particle size distribution for 5 minutes exposure time in Figure 4 was similar to that shown in Figure 3 (therefore not shown again), also indicating the UV exposure time plays a more significant role than the total time available for particulate generation and growth.

128   The potential role of nucleation sites on SOA generation and growth was assessed by
129   comparing the UV-induced SOA formation with air that was either initially HEPA filtered or not.
130   The HEPA filtered air contained approximately 5×10^6 particles/m^3 as measured by the APS
131   instrument after injection of toluene to a concentration of 58 mg/m^3, while the unfiltered air
132   contained approximately 10×10^6 particles/cm^3 under the same initial conditions.   After 5 minutes of
133   UV exposure and 1 minute of recirculation, the change in particulate concentration was measured,
134   as displayed in Figure 5.   There was some indication that filtered air tended to produce smaller
135   particle sizes under similar UV exposure conditions, however the difference was not highly
136   significant in either numbers or differences in particle size distribution.   This suggests that
137   nucleation sites did not play a large role in SOA formation, at least under the conditions used in
138   these experiments.
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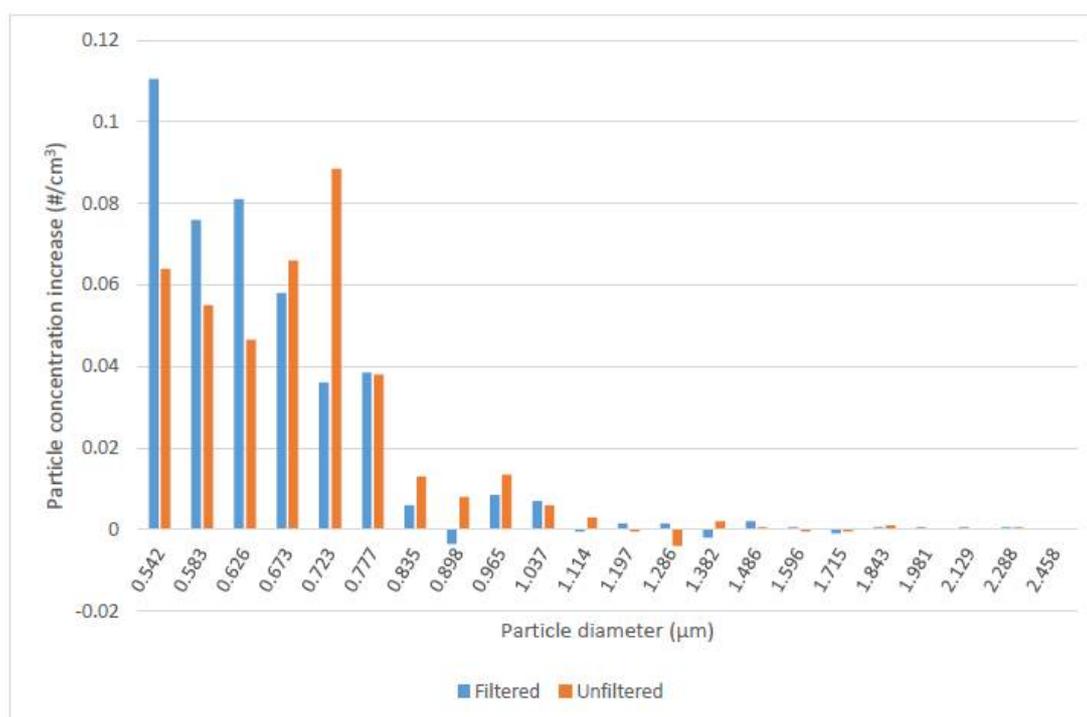
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141   **Figure 5:**   effect of HEPA filtered versus unfiltered compressed air on generation of particulate
142   at various sizes with 5 minutes UV exposure and 1 minute recirculation (initial toluene
143   concentrations 55 to 85 mg/m^3).
144
145   The foregoing results were obtained using compressed plant air with a low relative humidity of
146   approximately 11% at room temperatures.   To explore the role of water in SOA formation, further
147   experiments were conducted with room air which varied in relative humidity from day to day.   The
148   air was drawn into the UV reactor using an air sampling pump, and was either HEPA filtered or not,
149   to further examine the effects of nucleation sites for SOA growth.   For constant initial toluene
150   concentrations and UV exposure times, the number of particles produced was measured by
151   comparing particle counts before and after UV, with the results summarized in Figure 6.
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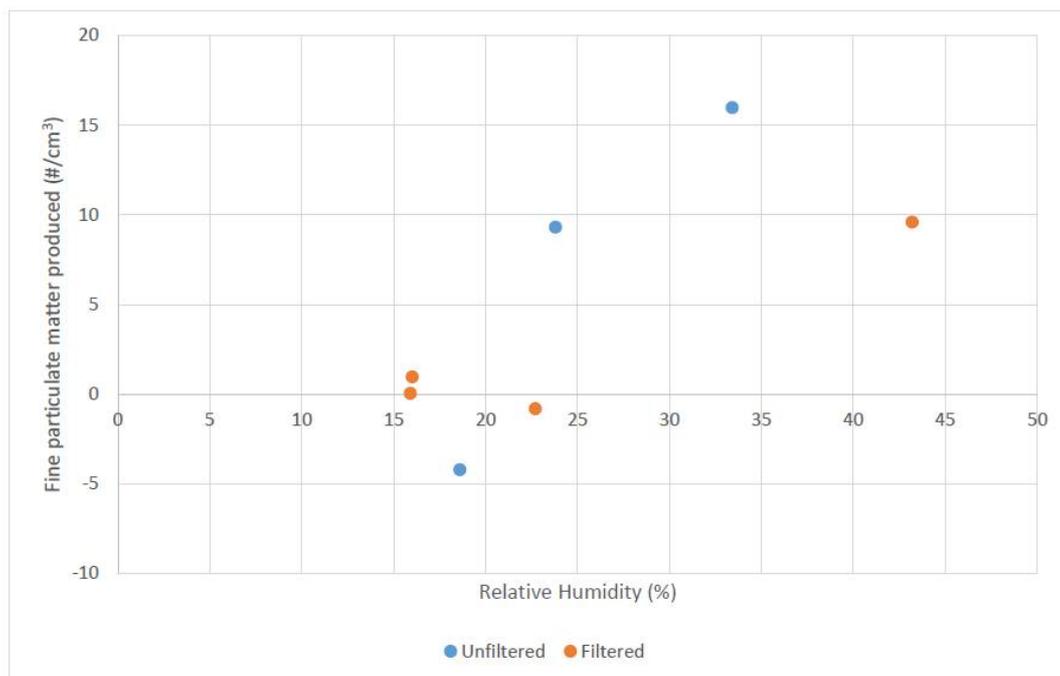
Figure 6: PM2.5 production for filtered and unfiltered room air at different relative humidities. Initial toluene concentration was between 55 and 85 mg/m^3, with 5 minutes UV exposure and 1 minute hold time before sampling.

As indicated in Figure 6, particle formation was relatively low for low humidities, similar to the results shown in Figure 2 where compressed air was used as the medium with approximately 11% relative humidity. However, as humidity approaches and exceeds 25%, there appears to be a discrete jump in particulate formation. The chemistry of SOA formation from toluene and similar compounds is quite complex [4] and water vapour or aerosol plays a role in the yield of SOA under solar UV wavelengths [6]. The results in Figure 6 indicate that SOA formation with germicidal UV will be somewhat higher at typical indoor air humidity levels (30 to 45%) compared to drier air. As noted by Ng et al. [7], quantifying SOA mass yields is a very challenging experimental problem, and this was not attempted in this work. However, the trends shown here are consistent with expectations from previous research using solar UV wavelengths.

As indicated in the UV reactor experiments, SOA formation appeared to be possible and measurable under the conditions that might be expected in a room UV disinfection cycle, although the impact was relatively small. To test this SOA formation under more representative and realistic room disinfection conditions, particle sampling was undertaken in a bathroom that had been fitted with an automated UV disinfection device, the same as the one described by Hunt and Anderson [1]. The APS instrument was used to take samples before, during and after UV disinfection in the bathroom, with the results shown in Figure 7.
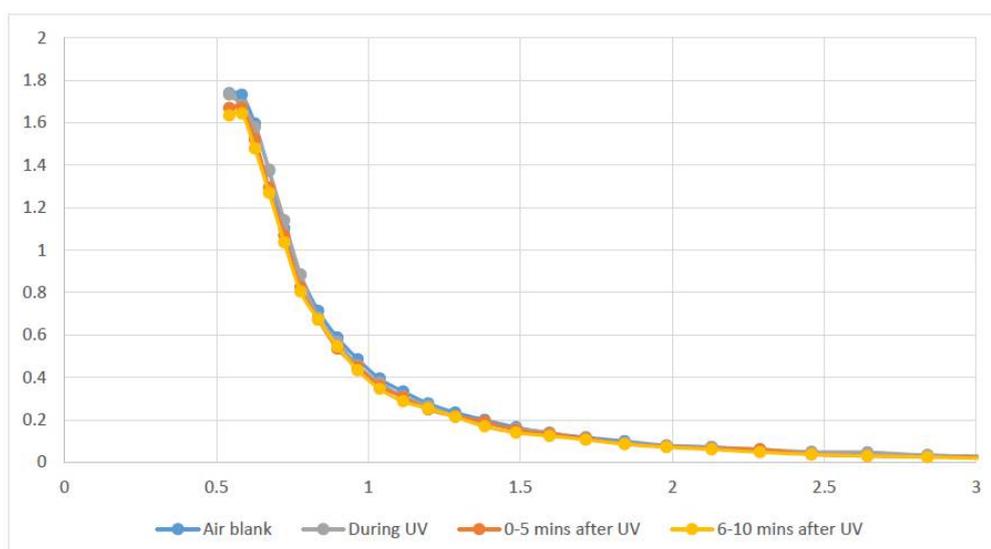
Figure 7: Particulate size distribution in bathroom with above-door automated UV system, before (Air blank), during and after an automated 5 minute UV disinfection cycle. Most points are collinear and superimposed.

The air in the room was like that found in a typical commercial office building, with no noticeable odor and relatively low particle counts. Although it was not feasible to measure the volatile organic compound concentrations, literature reports that such office environments typically have a sum of common VOC concentrations ranging from 64 to 76 $\mu g/m^3$ [8]. As can be seen in Figure 7, under the tested conditions there was no significant change in either the numbers or size distribution of particulates in the room during or after a disinfection cycle.

4. Discussion

Although the UV reactor experiments indicate that some SOA formation is possible or likely, the conditions in these experiments have several important differences from those found in the room environment where UV disinfection is used. First, the concentrations of VOC (toluene) were around 50 to 85 mg/m^3, which is up to three orders of magnitude higher than VOC concentrations typically found in commercial and institutional environments [9]. Secondly, the average UV fluence rate within the reactor was relatively high (19.5 mW/cm^2) compared to the wide range of fluence rates that will be found in a room, depending on the distance to the UV lamps. For this room, the average fluence rate was very roughly estimated to be approximately 0.14 mW/cm^2 using a simplified geometrical technique for annular photoreactors reported by Bolton [10]. This mean fluence rate estimate is consistent with the measured values on surfaces in a similar room, reported to range from 0.01 to 0.1 mW/cm^2 depending on the distance from the UV lamp to the surface in the room [1].

It can be concluded from this work that germicidal UV disinfection devices are capable of generating SOA in ways that follow the trends identified in atmospheric chemistry for solar UV wavelengths (300 to 400 nm). Presumably the mechanisms will be similar, with photo-oxidation causing the formation of partially oxidized toluene by-products with lower vapour pressure, which then condense to form new or larger particulates in the gas phase. This mechanism will depend to some extent on the nature of the VOC, its UV absorption spectrum, its oxidation pathway and the vapour pressure and partitioning behaviour of the oxidation products. Therefore it would be worthwhile to examine the behaviour of other VOCs under UV germicidal wavelengths. However, based on the preliminary tests performed in a room, the practical impact on PM2.5 concentrations for realistic situations in commercial and institutional spaces is possibly minimal, especially

212 compared to other internal and external sources of fine particulate that may impact the air quality in
213 these rooms.
214

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216 acquisition, William Anderson; Investigation, Eureka Choi; Methodology, Eureka Choi and Zhongchao Tan;
217 Resources, Zhongchao Tan; Supervision, William Anderson and Zhongchao Tan; Writing – original draft,
218 Eureka Choi; Writing – review & editing, William Anderson.

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224 the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or
225 in the decision to publish the results.
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