Aqueous particle generation with a 3D printed nebulizer

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14 Abstract. In this study, we describe the design and testing of a high output stability, constant 15 liquid feed nebulizer using the Venturi principle to generate liquid particles from solutions. This atomizer, the PRinted drOpleT Generator (PROTeGE) was manufactured using 16 17 stereolithography (SLA) printing. Different concentrations of ammonium sulfate solutions were 18 used to characterize the size and number concentration of the generated particles. A comparison 19 of a 3D printed 0.5 mm orifice against a commercially available 0.5 mm brass orifice using the 20 same ammonium sulfate solution was also performed. The particle number concentration 21 generated with the printed orifice was higher, by $\sim 2x$, than the particle number concentration 22 generated with the brass orifice.

23 PROTeGE is also capable of dispersing polystyrene latex spheres (PSLs) for calibration

24 purposes. The particle number concentrations obtained in this study ranged from $\sim 10,000$ cm⁻³

25 for 0.75 μ m to ~100 cm⁻³ for 5.0 μ m PSL particles with a dependence on the concentration of

26 the dispersed solution. For the different concentrated ammonium sulfate solutions particle

number concentrations from ~14,000 cm⁻³ for 0.1 g L⁻¹ to 7,600 cm⁻³ for 5.0 g L⁻¹ were measured. An additional measurement with a Scanning Electrical Mobility System (SEMS) was performed for the 0.6 g L⁻¹ solution to measure particles in the size range of 10 nm to 1000 nm. The generated particle number size distributions (PNSDs) showed a maximum at 50 nm with particle number concentrations of ~40,000 cm⁻³. PROTeGE is easy to manufacture and operate, low in maintenance, and cost-effective for laboratory and field generation of particles from aqueous media in a size range of 10 nm to 5000 nm.

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35 **1 Introduction**

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Reliable and cost-effective particle generation methods are necessary for applications 37 38 where a well-defined mono- or polydisperse particle concentrations and size is required. High concentrations of monodisperse aerosol particles (>10⁶ particles cm⁻³) in the nm to μ m diameter 39 40 size range can be created by instruments utilizing vapor condensation and electrospray 41 techniques. Similar concentrations and size ranges of aerosol particles can be produced from bulk solutions using a variety of instruments such as vibrating-orifice aerosol generators and 42 43 ultrasonic nebulizers. Another common technique used to generate liquid aerosol particles is by pressurized-air nebulization. In this method, compressed air is utilized to shatter a solution 44 45 into small aerosol droplets with a specific size distribution (Swiderska-Kowalczyk et al., 1997). 46 Pressurized-air nebulizers have been used in numerous studies which require the generation of 47 aqueous aerosol particles. For example, Wang et al. (2019) used a nebulizer to create 48 ammonium sulfate seed particles in cloud droplet activation studies. Kong et al. (2018) created 49 aqueous aerosol particles used to study deliquescence and ice nucleation in sea salt particles. 50 These are two of many studies focused on the influence of aerosol particles in the Earth's atmosphere. Pressurized-air nebulizers are also used in pharmaceutical applications to produce 51

52 nanometer-sized drug particles with a specific size distribution (Eerikainen et al., 2003). It is 53 clear that the pressurized-air nebulizer is a ubiquitous instrument for studies or applications 54 requiring aqueous aerosol particle generation. Although effective, commercial particle 55 generation instruments may not be economically feasible for all research and teaching 56 institutions wishing to perform these types of experiments.

57 Advances in 3D printing have made it possible to rapidly fabricate high-resolution (µmscale) devices. Stereolithography, a form of 3D printing technology, creates objects in layers 58 59 through the use of photopolymerization. In conjunction with Computer Aided Design (CAD), 60 or Computer Aided Manufacturing (CAM) software, an ultraviolet (UV) laser is used to trace 61 a pre-programmed design on to the surface of a photopolymer contained in a vat. The resin is 62 photochemically solidified and forms a single layer of the desired object. The Form 2 SLA 3D printer (Formlabs, Inc.), used in this work, is capable of creating objects with a layer thickness 63 of 25 µm. 64

65 The Form 2 was previously used to fabricate PRIZE, a compact fluidized bed aerosol generator (Roesch et al. 2017). It was found that PRIZE was able to successfully disperse 66 67 aerosol particles from dry material without creating artifact particles (particles generated from 68 the material used to fabricate the generator). The impetus for this study, similar to the study 69 presented in Roesch et al. 2017, was to fabricate a low-cost, constant pressure nebulizer, using 70 a SLA 3D printer, PROTeGE. In the following two sections we describe how PROTeGE is 71 designed and manufactured. The experimental setup and performance tests using different PSL 72 and ammonium sulfate solutions is discussed. Three types of experiments were conducted to 73 demonstrate the performance of PROTeGE: (1) an aerosol production experiment using four 74 different sizes of PSL's, (Polysciences Inc., NIST traceable) ranging from 0.75 to 5.0 μ m, (2) 75 experiments where different concentrations of ammonium sulfate solutions were dispersed and 76 monitored over time with an optical particle sizer (OPS, Model 3330, TSI Inc.) and for the 0.6 g L⁻¹ also with a SEMS (BMI Inc.), (3) an experiment comparing the performance of a printed 77

78 0.5 mm orifice to a 0.5 mm commercial brass orifice using the same ammonium sulfate solution

- 79 of 0.6 g L⁻¹.
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- 81
- 82 2 Methods
- 83 2.1. Design

84 PROTeGE was designed using a CAD program (Solidworks 2015, Dassault Systems). There 85 are two versions: the first is printed as a single part including a 0.5 mm diameter orifice (Fig. 86 1), while the second, featuring the same inner and outer dimensions, has an exchangeable nozzle 87 to use various machined orifice diameters. The 0.5mm (0.02 in) orifice used in the comparison 88 is a commercially available brass nozzle (Part Number 2943T887, McMaster-Carr) that is 89 threaded into the pressurized air inlet of PROTeGE (Fig. 1d). This modular feature enables 90 rapid exchange of nozzles with a different orifice diameter using the same printed unit. In 91 contrast, the exclusively printed version of PROTeGE has a fixed orifice diameter for 92 continuous and simple operation. Both versions are based on the generator designs of May, 93 1973 and Liu & Lee, 1975. Unlike the repurposing of existing nebulizers built for other uses, such as medical applications (Reisner et al., 2001), PROTeGE was designed specifically for 94 95 research applications e.g. instrument calibration and particle generation, similar to other 96 custom-built nebulizers (Wex et al., 2015). In contrast to other generation systems, which are 97 typically machined, PROTeGE is made from photopolymer resin (e.g. FLGPCL02, Formlabs 98 Inc.), weights only \sim 50 g, and can therefore feature smaller overall dimensions.

99 The front inlet to PROTeGE is a 6.35 mm (0.25 in) barbed tube to connect to a pressurized 100 airflow. The inlet is end-capped by the orifice. Directly following, and perpendicular oriented 101 to the orifice, is the liquid feed 3.18 mm (0.125 in) inlet to the dispersible solution. Excess 102 liquid from the nebulizing process exit the chamber through a 6.35 mm outlet at the bottom, 103 dripping directly back into the feed bottle. Aqueous particles exit the chamber through the 9.53 104 mm (0.375 in) aerosol outlet at the top. The overall dimensions of PROTeGE are 17 x 45 x 65

105 mm (width, depth, height). Designed CAD files were converted to style files (.stl) to be readable

106 by the 3D printer software (PreForm, Formlabs Inc.).

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108 2.2. Manufacturing

109 The manufacturing and post-processing of the parts was performed as described by Roesch et 110 al., 2017 using the same 3D printer software, clear photopolymer resin (FLGPCL02, Formlabs 111 Inc.) and 3D SLA printer (Form 2, Formlabs Inc.). Modifications were made to the dimensions 112 of the default contact points of the printing scaffolding; in this study scaffolding was reduced 113 to 0.45 mm due to the overall smaller geometry of PROTeGE (i.e., lower mass needing to be 114 supported). Using a resolution of 100 μ m, eight complete PROTeGEs can be printed on the 115 build surface at the same time, taking ~8 h.

A custom UV box was used to post-cure the printed parts. Inside the box, the printed parts were 116 117 placed on a slow-moving turntable to be illuminated equally from all sides by 28 high-power LEDs emitting at 405 nm. It should be noted that the curing time depends on the size and wall 118 119 thickness of the printed part; one hour per mm wall thickness is suggested. The post-curing 120 time for PROTeGE was ~1 h. For more detailed information see the manufacturing section in 121 Roesch et al., 2017. The cost to produce one PROTeGE is around ~\$2.50 depending on the type 122 of resin and the percentage of scaffolding used. The commercial brass nozzle costs <\$10, so a 123 total PROTeGE costs under \$15. For users with no access to a 3D printer, it is also possible to 124 upload the .stl file for PROTeGE (provided at <u>https://www.thingiverse.com/thing:4444498</u>) to 125 an online print service. Pictures of PROTeGE and post processing details for the instrument are 126 also provided on the data repository as well as supplement to this study.

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128 **2.3. Experimental setup**

129 A schematic of the experimental setup including the relevant flow rates used in this study is 130 shown in Fig. 2. Dry, filtered, pressurized air was used as the carrier gas. The input flow rate of 1.7 L min⁻¹ (at 35 psi) into PROTeGE was controlled by a rotameter (MR3A, Omega 131 132 Engineering). A high velocity jet is created by the expansion of the pressurized air through the 133 orifice. As a result, the pressure behind the orifice drops, the liquid is pulled upward from the 134 feed bottle, and the high velocity jet disperses the liquid solution into droplets. Large droplets 135 that are unable to follow the streamlines through the aerosol outlet are removed by impaction 136 at the curved wall; these drip back as excess liquid into the feed bottle through a drain outlet at 137 the bottom of PROTeGE. For these experiments, the droplets from the aerosol outlet were 138 subsequently dried using a silica gel drier. Downstream, the flow of residuals (remaining solid 139 cores of the droplets) was split into two flows. The first is sent to the OPS, to determine PNSDs 140 in the size range of 0.3 to 10 µm and the remainder through a filter (IDN-4G, Parker) open to 141 lab. Unless otherwise noted, all experiments presented here were performed using the brass 142 nozzle with a 0.3 mm orifice and the previously stated pressures and flow rates.

143

144 **3. Results**

In this study three types of experiments were conducted: (1) an aerosol production experiment using four different sizes of PSL's, ranging from 0.75 to 5.0 μ m, (2) an application experiment where different concentrated ammonium sulfate solutions were dispersed and monitored over time with the OPS and for the 0.6 g L⁻¹ also with the SEMS, (3) a comparison experiment on the performance of a printed 0.5 mm orifice versus a 0.5 mm commercial brass orifice using the same ammonium sulfate solution. For all experiments the PNSDs of the droplet residuals (i.e., after drying) were measured with the OPS.

Prior to each experiment, PROTeGE was immersed in a jar with Destilled De-ionized (DDI)
18.2 MΩ•cm Millipore water and sonicated for 10 minutes in an ultrasonic bath to ensure clean

154 inner surfaces. Afterwards, PROTeGE was dried using pressurized nitrogen and connected to

155 the setup. Each of the four samples was prepared in a separate 100 ml glass bottle, using 80 ml of DDI water plus multiple drops of the respective PSL solution (0.75 µm, 1.5 µm, 2.0 µm, 5.0 156 157 µm). The generated number concentration of PSL particles strongly depends on the 158 concentration of the prepared PSL sample. Therefore, the higher the concentration of the 159 solution, the higher the generated particle number concentration. A time-series measurement of 160 420 seconds was performed for each of the four PSL samples. The obtained PNSDs showed particle number concentrations of ~10,000 cm⁻³ for 0.75 µm PSL particles, ~1,000 cm⁻³ for 1.5 161 μm PSL particles, ~800 cm⁻³ for 2.0 μm PSL particles to ~100 cm⁻³ for 5.0 μm PSL particles 162 163 (Fig. 3). All four investigated PSL samples showed a narrow PNSD except the 5.0 µm PSL sample where a fraction of sub-micrometer particles was detected (Fig. 3d). This fraction of 164 165 particles likely originates from the solution matrix in which the PSLs are suspended. Overall 166 the generated PNSDs were stable over their measured period of time while only the 1.5 μ m 167 PSL sample showed a slight decrease. These data show that the curved design of the chamber 168 enables PROTeGE to disperse PSL particles with diameter up to 5.0 micrometer.

In addition to the PSL measurements, ammonium sulfate experiments with different solution concentrations (0.1 g L⁻¹, 0.6 g L⁻¹, 5.0 g L⁻¹) and an experiment to determine the performance of the printed 0.5 mm orifice versus the 0.5 mm brass orifice using the same ammonium sulfate solution of 0.6 g L⁻¹ were conducted. The three solutions were again prepared in separate 100 ml glass bottles using DDI 18.2 MQ•cm Millipore water. The cleaning procedure of PROTeGE was identical to the one described above for the PSL experiments.

For the lowest concentration of aqueous ammonium sulfate solution (0.1 g L⁻¹) the maximum particle number concentration of ~14,000 cm⁻³ was observed in the 0.3 μ m bin of the OPS (Fig. 4a). The overall width of the generated PNSDs ranged from 0.3 μ m up to 0.6 μ m. Compared to the higher concentrated solutions of 0.6 g L⁻¹ and 5.0 g L⁻¹ this is rather narrow. Dispersing the 0.6 g L⁻¹ solution of ammonium sulfate generated PNSDs in the range of 0.3 μ m up to 1.5 μ m with a maximum particle number concentration of ~8,200 cm⁻³ in the 0.5 μ m detection bin of 181 the OPS (Fig. 4b). For the highest concentration of 5.0 g L^{-1} the generated PNSDs ranged from

182 1.0 μ m to 2.4 μ m with a maximum particle number concentration of ~7,600 cm⁻³ (Fig. 4c).

For the 0.6 g L⁻¹ solution an additional experiment using the SEMS instrument was performed.
The size range was scanned from 10 nm to 1000 nm with a resolution of 60 bins and a sampling

rate of 1 second per bin. The maximum particle number concentration of of only and a simpling rate of 1 second per bin. The maximum particle number concentration was found at ~50 nm with ~40,000 cm⁻³. The average PNSD for a 420 second sampling period is shown in Fig. 4d. During the experiment the generated size distributions did not change over time. Combining the obtained size distributions from SEMS and OPS shows that PROTeGE is capable of generating particles as small as 10 nm up to 2.4 μ m based on the dispersed ammonium sulfate solution. The higher the concentration of the solution the larger the generated particles. Also compositions that were used in this study may deviate from stock solutions.

192 Overall, the generated particle number concentrations for the different tested ammonium sulfate 193 solutions are high enough (> 1,000 cm⁻³) to operate particle size selection instruments 194 downstream of PROTeGE, e.g. a differential mobility analyzer (DMA), assuming \sim 10% of the 195 introduced particles are selected as monodisperse aerosol particles.

In order to investigate the performance of an integrally printed 0.5 mm orifice versus the 196 197 commercial brass nozzle the same 0.6 g L⁻¹ ammonium sulfate solution was used. Visual 198 observations of the printed 0.5 mm orifice showed that there were sometimes imperfections and 199 asymmetries in the roundness of the printed orifice. It was therefore necessary to post-drill the 200 printed orifice with a 0.5 mm bit by hand, which was done for the PROTeGE used in experiment described here. The generated particle number concentration with the printed orifice was 201 ~4,500 cm⁻³versus ~2,400 cm⁻³ for the brass nozzle with minimal difference in PNSD shape. 202 The printed nozzle exhibited a broader shoulder from 0.3 µm to 0.5 µm with higher particle 203 204 number concentrations than the brass nozzle. The latter showed a decline with the highest particle number concentration at 0.3 µm leveling out to 1.0 µm. Overall, the width of both 205 206 PNSDs ranged from 0.3 μ m to 1.0 μ m (Fig. 5).

208 **4. Conclusion**

209 In this study, we described the design and the performance of a low-cost particle generator – 210 PROTeGE. The experiments presented here show the PROTeGE capability for generating four 211 different sizes of PSL particles between 0.75 µm and 5.0 µm with resulting particle number 212 concentrations between 100 cm⁻³ and ~10,000 cm⁻³. This enables PROTeGE to be used as a simple and cost-effective particle generation unit for calibration purposes. In addition, we show 213 214 the results of experiments using different concentrations of ammonium sulfate solutions. The 215 generated PNSDs ranged from 10 nm up to 2.4 µm, based on the dispersed solution, with stable 216 output concentrations demonstrating that particle size selection instruments can be used 217 downstream of PROTeGE. Finally, we compared the performance of a commercially machined brass 0.5 mm orifice to a 3D printed 0.5 mm orifice. Both nozzles showed PNSDs ranging from 218 219 $0.3 \ \mu m$ to $1.0 \ \mu m$ with a broader shoulder for the printed nozzle between $0.3 \ \mu m$ and $0.5 \ \mu m$ 220 compared to the brass orifice. Also the total particle number concentration generated with the 221 printed orifice was almost two times higher than the total particle number concentration 222 generated with the brass orifice.

Due to the low cost of PROTeGE (~\$15, material costs) multiple generators can be used in parallel to reduce experimental time while running more samples. If one is in doubt about the usage of certain liquids with PROTeGE, please refer to the MSDS of the resin or contact the manufacturer for details about chemicals having dissolving properties on SLA 3D printed materials. Electro-plating the 3D printed generator will give it metal-like properties for better resistance against chemical attack.

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Data availability: The .stl files for PROTeGE are available at
<u>https://www.thingiverse.com/thing:4444498</u> and also as supplement to this study.

233	Authors contribution: MR and DJC contributed both equally to the manuscript. The
234	experiments were conducted by MR.
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236	Competing interests: The authors declare that they have no conflict of interest.
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- F., Zaveri, R. and Zheng, G.: Cloud droplet activation of secondary organic aerosol is mainly
- controlled by molecular weight, not water solubility, Atmos. Chem. Phys. 19, 941-954, 2019.
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278 279 Figure 1: Dimensioned drawings of PROTeGE: (a) side view; (b) front view; (c) detailed view of the inlet section with the printed 0.5mm orifice; (d) detailed view of the inlet section with the exchangeable nozzle/orifice. PROTeGE consists 280 281 of: (1) a pressurized air inlet, (2) a printed 0.5mm orifice, (3) a liquid feed inlet, (4) a central impaction chamber, (5) the drain outlet, (6) an aerosol outlet, and an optional (7) exchangeable orifice.

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284 285 286 Figure 2: Schematic of the experimental setup used in this study. A dry pressurized air flow (PA) was passed through a rotameter (R) to control the flow rate and a filter (F) upstream of PROTeGE (P). Generated droplets were dried with

silica gel (D) before the flow of particles was directed into an OPS with excess flow discarded through a filter (F).



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Figure 3: Total particle number concentrations and particle number size distributions as function of time for different
sized polystyrene latex spheres generated with PROTeGE and detected by the OPS: (a) 0.75 μm; (b) 1.5 μm; (c) 2.0 μm;
(d) 5.0 μm where the black arrow denotes the PSL size and the small particles represent atomized matrix material (see
text for details).





310 311 Figure 4: Total particle number concentrations and particle number size distributions as a function of time of aqueous ammonium sulfate particles: (a) 0.1 g L^{-1} ; (b) 0.6 g L^{-1} ; (c) 5.0 g L^{-1} ; (d) Average particle number size distribution from 10 nm to 1000 nm measured with the SEMS for aqueous ammonium sulfate particles of 0.6 g L^{-1} .



