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**Dynamic Analysis of Particle Emissions from FDM 3D Printers
through a Comparative Study of Chamber and Flow Tunnel
Measurements**

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Highlights

- Flow tunnel provides more accurate particle emission rates and diameters
- Flow tunnel measurements can be used to predict actual environmental conditions
- Printers in chamber generate obvious secondary aerosols (>30 nm)
- Secondary aerosols (>30 nm) from chambers were not observed in field measurements
- Decay rate obtained after printing is insufficient to represent conditions during printing

TOC Art

Keywords: 3D Printing, Particle Emission Rate, Calculation Models, Chamber, Flow Tunnel, Fused Deposition Modelling

Abstract

Ultrafine particle emissions originating from fused deposition modelling (FDM) 3D printers have received widespread attention recently. However, the obvious inconsistency and uncertainty in particle emission rates (PER, #/min) measured by chamber systems still remain, owing to different measurement conditions and calculation models used. Here, a dynamic analysis of the size-resolved PER is conducted through a comparative study of chamber and flow tunnel measurements. Two models to resolve PER from the chamber and a model for flow tunnel measurements were examined. It was found that chamber measurements for different materials underestimated PER by up to an order of magnitude and overestimated particle diameters by up to 2.3 times, while the flow tunnel provided more accurate results. Field measurements of time-resolved particle size distribution (PSD) in a typical room environment could be predicted well by the flow tunnel, while the chamber measurements could not represent the main PSD characteristics (e.g. particle diameter mode). Secondary aerosols (>30 nm) formed in chambers were not observed in field measurements. Flow tunnel was adopted for the first time as a possible alternative for the study of 3D printer emissions to overcome the disadvantages in chamber methods and as means to predict exposure levels.

1. INTRODUCTION

Fused deposition modelling (FDM) 3D printers have been commercialised as desktop printers and are increasingly being used in indoor environments such as offices, labs, and homes.¹ However, studies have shown that the operation of FDM 3D printers emits significant amounts of volatile organic compounds (VOCs) and ultrafine particles (UFP, < 100 nm) through studies involving chambers and typical indoor environments.^{1–24} In fact, the perpetual challenge in evaluating emissions from FDM 3D printers is the inconsistency in reported emission levels and interpretation of data,^{13, 25} both of which are attributed to different measurement conditions and calculation models used.

Specifically, particle emission rates (PER) measured through chambers can vary several orders of magnitude between different studies.¹³ Likewise, for models to estimate PER from raw experiment data, it was recently found that the computed values can be several orders of magnitude apart using different calculation models on the same set of original data by meta-analysis.¹⁷ In particular, almost all studies assumed particle coagulation to be negligible and thus particle loss rate to be constant for chamber studies. However, this may not be the case at high or peak concentration levels and can even result in negative PER for certain periods during printing.^{10,19,26,27} In addition, chamber measurements typically ignore size-resolved particle dynamics¹⁰ as it is extremely difficult to consider changes in particle size distribution during printing. A case in point was demonstrated by Vance *et al.*¹⁹ where particle diameters measured in a chamber (mode: 51 nm) were much larger than that observed in an office (mode: 15.4 nm) for the same printing activity. Accurate information on particle diameter is necessary as nanoparticles between 10 to 30 nm can be deposited in the lower human respiration track.²⁸ In fact, measurements obtained through chamber studies are accumulated particle concentrations,²⁹ which may be slightly different from the dynamic release of particles from printers in a room.

To accurately evaluate emissions from FDM 3D printers for both PER and particle diameters, experiments were designed for a comparative study between chamber and flow tunnel measurements in this study. In order to improve the time resolution of measurements and to obtain real-time relationships

between particle characteristics and the printing process, the flow tunnel is introduced to avoid the prolonged accumulation of particles in a chamber.^{25,30} For the chamber, particle accumulation varies across different chamber dimensions, leading to large variations in the reported PER that have resulted in inconclusive results in the literature. Specifically, two different models (Model 1 and Model 2) will be derived and verified to extract time- and size-resolved PER from chamber experiments, which will be used to examine the reasons behind the observed discrepancies. In addition, the real-time emission characteristics and both time- and size-resolved PER obtained from flow tunnel (with Model 3) are compared against chamber measurements for the same printing activities. Finally, the time- and size-resolved PER measured by chamber and flow tunnel methods are used to predict dynamic particle size distribution (PSD) in a typical room environment (with Model 4), which is verified by actual field measurements.

2. MATERIALS AND METHODS

2.1. Study Design

2.1.1. Standard Chamber Measurements

Figure 1. 2D schematics for (a) side view of a standard cubic chamber measurement system, (b) side view of a flow tunnel measurement system with flow from left to right, and (c) top view of a typical room measurement. The 3D schematics and actual images of the chamber and flow tunnel systems are shown in Figures S1 and S2 in Supporting Information.

A chamber with inner volume of 1 m^3 was constructed out of stainless steel to minimize wall losses in accordance to UL 2904 and ASTM D6670,^{26,31} as shown in Figure 1(a). The chamber was operated above atmospheric pressure to prevent leakage of room air into the chamber. Eight inlets and outlets were designed and evenly distributed on the four side walls and a fan was installed on the top cover to promote mixing within the chamber. Air change per hour (ACH) of the chamber was set to 3 h^{-1} for most cases, as higher ACH will result in air velocities near the printer nozzle to be higher than that in typical room conditions, as shown in Table S1 in Supporting Information. An activated carbon HEPA filter with 99.97% filtration efficiency at $0.3 \mu\text{m}$ (Carbon Cap 150, Whatman, GE Healthcare Life Sciences) was used to remove particles and VOCs from the compressed air supply. The background values of total particle concentration (10 - 420 nm) in the chamber were less than $200 \text{ \#/cm}^3$. Environmental conditions

including temperature and relative humidity as well as air velocity near the printer nozzle are summarized in Table S1 for the chamber, flow tunnel and room.

2.1.2. Flow Tunnel Measurements

In order to overcome the disadvantage of particle accumulation in chambers, instantaneous emissions were measured in a flow tunnel where particles emitted by each print layer were continuously carried along the ‘mixing section’ to the sampling point. The flow tunnel was mostly constructed out of acrylic material except for the contraction cone that was made of fiberglass, as shown in Figure 1(b). The ‘mixing section’ and ‘second mixing and stable section’ were used to ensure uniform mixing of particles at the sampling point. The shape of the contraction cone was a cubic curve to quickly stabilize the flow.³² The length from the start of the ‘second mixing and stable section’ to the sampling point (1.3 m) was about seven times larger than its width or height (0.184×0.184 m) to achieve a completely developed flow.³³ Reynolds number (Re) at the sampling point was ~3200, which can be assumed to be fully developed turbulent flow (> 2900), where the turbulence can further promote mixing before sampling.³⁴

Air velocity was measured along the cross section of the sampling point using a hot wire anemometer (ST732, *SENTRY*), which was found to be 0.3 m/s at the centre and averaged 0.271 m/s across six different points. An isokinetic and sealable sampling probe was used to capture particle emissions at the sampling point, as shown in Figure S1(c). The inlet diameter of the isokinetic sampling probe (7.28 mm) was designed according to the inlet flux of NanoScan SMPS (0.75 L/min).³⁵ Both activated carbon and HEPA (99.95%) filters were installed at the inlet of the flow tunnel to remove particles and VOCs in the supply air, ensuring background particle concentration levels to be less than 400 #/cm³ for all the experiments. Near the printer nozzle, air velocity was about 0.1 m/s that is common in typical room environments.

2.1.3. Room Measurements

Observations from flow tunnel and chamber were used to predict concentration levels and particle

characteristics in a typical room (volume: 53.9 m³, ACH: ~3.3) as shown in Figure 1(c). The ACH was estimated by the flow rate of incoming air (~176.7 m³/h) and room volume. The printer was positioned near the center of the room on a table of height 1 m and air sampling was performed at two positions away from the 3D printer (0.5 m and 2.5 m).

2.2. 3D Printers and Filaments

A commercially available FDM 3D printer without enclosure was adopted in this study (UP Plus 2, Tiertime) and the thickness for each layer of print was set to 2 mm. As shown in Table 1, a total of 29 filament materials (diameter: 1.75 mm) were investigated in the flow tunnel, where each case was repeated at least two times. Seven materials were then chosen and used to compare between flow tunnel and chamber, which were repeated for three times. For the prediction and comparison of particle characteristics in a typical room, five materials were selected with at least two repeats.

Table 1. Summary of filament materials, printing conditions, and particle emission yields (PEY).

Test method	Material	Colour	Density ^a (g/cm ³)	Brand	Nozzle /bed temp. ^b	PEY (#/g)
Chamber	ABS1 ^c	natural	1.02	Esun	260/90°C	1.08E+11
	ABS2	white	1.12	Polymaker	260/90°C	1.01E+11
	ABS5	white	1.02	Esun	260/90°C	9.70E+10
	ABS6	white	1.04	Ecomaylene	260/90°C	1.75E+11
	ABS7	black	1.04	Ecomaylene	260/90°C	1.46E+11
	PVA1	yellow	1.33	OEM	220/50°C	4.08E+11
	PLA1	natural	1.21	Ecomaylene	220/50°C	-
Room	ABS2	white	1.12	Polymaker	260/90°C	-
	ABS5	white	1.02	Esun	260/90°C	-
	ABS6	white	1.04	Ecomaylene	260/90°C	-
	ABS7	black	1.04	Ecomaylene	260/90°C	-
	PVA1	yellow	1.33	OEM	220/50°C	-
Flow tunnel	ABS1 ^d	natural	1.02	Esun	260/90°C	1.06E+12
	ABS2 ^d	white	1.12	Polymaker	260/90°C	5.12E+11
	ABS5 ^d	white	1.02	Esun	260/90°C	1.67E+11
	ABS6 ^d	white	1.04	Ecomaylene	260/90°C	2.30E+11
	ABS7 ^d	black	1.04	Ecomaylene	260/90°C	2.52E+11
	PVA1 ^d	yellow	1.33	OEM	220/50°C	1.66E+12
	PLA1 ^d	natural	1.21	Ecomaylene	220/50°C	2.48E+08
	PLA2	natural	1.2	Polymaker	220/50°C	2.42E+09

PVA2 (S1)	natural	1.37		220/50°C	3.39E+09
PC2	transparent	1.19		260/90°C	6.38E+11
PETG2	transparent	1.25		240/70°C	4.48E+09
Polywood2	wood	0.8		220/50°C	5.59E+09
ASA2	white	1.1		260/90°C	9.63E+11
TPU2 (TPU95)	white	1.22		230/60°C	1.84E+10
ABS3	natural	1.04		260/90°C	7.03E+11
PLA3	natural	1.24		210/50°C	1.97E+09
PVA3	natural	1.25		210/50°C	4.59E+10
PA3	white	1.12	Esun	260/90°C	3.39E+11
ASA3	natural	1		260/90°C	7.39E+11
Wood3	natural	0.7		220/50°C	1.59E+10
TPU3 (95A)	white	1.15		220/50°C	1.61E+10
ABS4	transparent	1.04		260/90°C	3.31E+12
PLA4	white	1.22		220/50°C	2.19E+10
PA4	natural	1.12		260/90°C	2.13E+12
PC4	transparent	1.12		260/90°C	1.57E+12
PETG4	white	1.24	Gizmo Dorks	240/80°C	1.50E+11
HIPS4	white	1.05		260/90°C	1.74E+12
CF-ABS4 ^c	black	1.02		260/90°C	2.51E+12
TPU4 (95A)	white	1.2		230/30°C	1.39E+10

^aDensities obtained from manufacturers or calculated according to the length of a filament sample and the corresponding mass. ^bHighest printing temperatures of filaments as recommended by manufacturers were used. Each spool of filament was named by its material and an Arabic number (e.g. ABS1). ^cABS1 was another spool of Esun ABS filament, which was different from ABS3. ^dFor flow tunnel, the materials shown in the first group were used for comparison with chamber and room measurements, while other filaments were grouped by brands. Acrylonitrile-butadiene-styrene (ABS), polyvinyl alcohol (PVA), polylactic acid (PLA), polycarbonate (PC), polyethylene terephthalate-co-1,4-cyclohexylenedimethylene terephthalate (PETG), polyamides (PA) (also known as Nylon), acrylonitrile styrene acrylate (ASA), thermoplastic polyurethane (TPU), high-impact polystyrene (HIPS), Carbon Fibre ABS (CF-ABS).

2.3. Sampling Instruments and Procedure

A combination of particle sizers including TSI 3910 NanoScan SMPS (size range: 10-420 nm; sheath air: 0.75 L/min) and TSI 3330 OPS (size range: 0.3-10 µm) was used to measure particle size distribution between 10 nm and 10 µm. Measurements were recorded for the background (for at least 5 minutes), printing phase (about 25 minutes) and post-printing phase (at least 5 minutes for flow tunnel; 30 minutes for chamber and room). The sampling interval was one minute in all cases. The object printed

was a cube with 100% infill and raft (shown in Figure S3) given that its shape has little influence on the magnitude of PER.¹⁰ The printing phase was defined from the time when PER begins to rise to the end of material extrusion. Note that particle number concentrations measured by the OPS were negligible (< 0.1%) for all the tests, as compared to that by SMPS.

2.4. Data Analysis

For the chamber, a dynamic model for size-resolved PER (Model 1) with constant particle decay rate coefficient (K_0 , min⁻¹) is proposed and compared with a widely used Model 2 based on log-linear regression analysis (K_1 , min⁻¹).^{10,13,19,26,27,36,37} A detailed derivation is provided for the two models and it was found that Model 1 is mathematically connected to Model 2. For the flow tunnel, Model 3 is proposed to calculate the time- and size-resolved PER. In the room experiments, the predictions of time-resolved PSDs using data from the chamber or flow tunnel were performed using Model 4. Schematics of Model 1 and Model 2 are shown in Figure S4, and all four models are summarized in Table S2.

2.4.1. Time- and Size-resolved Particle Emission Rates in Chamber

Total particle number emission over a print activity is the integral of time-resolved PER, $E(t)$, over the whole printing phase. Particle emission yield is defined as the total particle number per unit mass of filament consumed (#/g). A dynamic model for particle number balance assuming well-mixed conditions is used to derive the models, which can be expressed as,¹⁹

$$V \frac{dC(t)}{dt} = E(t) + Q_{in}C_{in}(t) - \beta VC_{out}(t) - Q_{out}C_{out}(t) \quad (1)$$

where V is the volume of the chamber (cm³), C_{out} is particle concentration (#/cm³) flowing out of the chamber that is equal to the concentration in the chamber $C(t)$. C_{in} is particle concentration flowing into the chamber, which is the same as background concentration levels. Q_{in} and Q_{out} are the flow rates of air into and out of the chamber, respectively (cm³/min). β is total particle loss coefficient (min⁻¹), including

the effects of particle diffusion, gravitational deposition, coagulation, breakage, wall losses, etc.

If C_{in} is negligible ($< 200 \text{ \#/cm}^3$) and the sum of the last two terms in Eq. (1) is represented by $kVC_{out}(t)$, Eq. (2) can be obtained in the form,^{27,38}

$$V \frac{dC(t)}{dt} = E(t) - kVC(t) \quad (2)$$

The particle decay rate coefficient k can be expressed as the sum of the ACH ($\alpha = Q_{out}/V$) and β , as shown in Eq. (3). As such, k accounts for multiple channels of particle losses as defined by its constituents.³⁶

$$k = \alpha + \beta \quad (3)$$

PER can be obtained from Eq. (2) in discrete form as given by,

$$E(t_n) = V \left[\frac{C(t_n) - C(t_{n-1})}{\Delta t} + k \frac{C(t_n) + C(t_{n-1})}{2} \right] \quad (4)$$

where $C(t_n)$ and $C(t_{n-1})$ are particle concentrations in the chamber during printing at the current and previous time steps, respectively. $\Delta t = t_n - t_{n-1}$ and $n = \{2, 3, 4, \dots, N\}$ for N number of measurements in the printing phase. k is obtained using size-resolved particle number concentration during the post-printing phase (also known as decay) and is assumed to be applicable in the printing phase.

Model 1. Here, k is assumed to be a constant (K_0) throughout the whole measurement period and can be derived from Eq. (4) with $E(t) = 0$ during the post-printing phase to arrive at,

$$K_0 = \left[\frac{C(\hat{t}_1) - C(\hat{t}_1 + \Delta t)}{\Delta t} \right] / \bar{C} \quad (5)$$

where $\hat{t}_1$ is at least 15 mins after the end of printing according to the standards.²⁶ K_0 can be seen as the average value of k over a large interval.

Model 2. Alternatively, k can be obtained using a log-linear regression analysis (K_1) on the size-resolved particle number concentration in the decay phase that was extensively adopted in many studies.^{13,26,27,37}

$$K_1 = \frac{\ln[C(\hat{t}_1)/C(\hat{t}_1 + \Delta t)]}{\Delta t} \quad (6)$$

where $\hat{t}_1$ shares the same meaning as in Model 1. Combining Eq. (5) and (6), K_0 can be expressed as a function of K_1 ,

$$K_0 = \frac{2[e^{K_1\Delta t} - 1]}{\Delta t[e^{K_1\Delta t} + 1]} \quad (7)$$

Substituting Eq. (7) into (4) with $k = K_0$, we arrive at the following,

$$E(t_n) = \left[V \cdot \frac{C(t_n) - C(t_{n-1}) \cdot e^{K_1\Delta t}}{\Delta t \cdot e^{K_1\Delta t}} \right] \frac{2}{e^{K_1\Delta t} + 1} \quad (8)$$

Notably, $2/[\exp(K_1\Delta t)+1]$ is approximately unity (~ 0.96) since $K_1 (< 0.1$ for ACH of 3) is small and Δt is finite which is determined by the sampling interval of the instrument during printing (1 min for SMPS). Thus, the condensed form of Eq. (8) with only the terms in the square bracket remaining was also obtained from the deconvolution analysis on emission rate and a single exponential decay function by Schripp *et al.*³⁸ The derivation here provides another route to obtaining the same equation based on particle number balance.

2.4.2. Time- and Size-resolved Particle Emission Rates in Flow Tunnel Method

Model 3. Time- and size-resolved $E(t)$ (#/min) in the flow tunnel is obtained using Eq. (9) for each size bin.

$$E(t) = vA[C(t) - C_b] \quad (9)$$

where A is the cross-sectional area (cm^2) and v is the average flow velocity (cm/min), both measured along the cross section of the sampling point in the flow tunnel. C_b and $C(t)$ are background and printing particle concentration levels at the sampling point, respectively ($\#/\text{cm}^3$).

2.4.3. Predicted Time-resolved Particle Size Distribution in Room Measurements

Model 4. The time-resolved PSD in a typical room can be predicted through iterative computation using Eq. (10) on each size bin that is captured by the SMPS. Similar to the derivation process for the chamber, Eq. (10) is derived from the Eq. (1) assuming well-mixed conditions in the room and $\beta = 0$ and given by,

$$C(t_n) = \frac{2E(t_n)\Delta t}{V(2 + \alpha\Delta t)} + \frac{2 - \alpha\Delta t}{2 + \alpha\Delta t}C(t_{n-1}) + \frac{2\alpha\Delta t}{2 + \alpha\Delta t}C_b \quad (10)$$

where V is room volume (i.e. $53.9 \times 10^6 \text{ cm}^3$); α is the ACH of room (i.e. 0.055 min^{-1}); C_b is background concentration in a room ($\#/\text{cm}^3$); $C(t_{n-1})$ starts from C_b ; $E(t_n)$ ($\#/\text{min}$) are from the results in flow tunnel or chamber.

3. RESULTS AND DISCUSSIONS

3.1. Comparison of Dynamic Size Distribution of Particle Emissions in Flow Tunnel and Chamber

Taking ABS6 as an example, as shown in Figure 2(a) and 2(b), total particle number concentration (TPNC) was relatively stable for the duration of printing in the flow tunnel, except for an initial peak due to the overheating of filaments.¹³ The diameter of the particles emitted during printing remained relatively constant between 10 to 30 nm for ABS6. In contrast, for printing in the chamber under the same conditions in Figure 2(c)-(d) and Figure 3(a), TPNC rapidly increased to a peak at the fourth minute of printing, followed by a relatively stable concentration till the end of printing. Moreover, the mean diameter of particles in the chamber rose from ~20 to 40 nm as printing progressed. This particle growth phenomenon was evident from the ‘torch shape’ of PSD in Figure 2(d). Secondary aerosol with particle

225 diameters larger than ~20 nm was largely generated due to particle accumulation in the chamber, which
226 was not reflective of actual characteristics of particle emissions (mode of particle diameter < 20 nm based
227 on flow tunnel). The difference between chamber and flow tunnel measurements was observed for all the
228 seven materials, as shown in Figures S5-S24. In the chamber, particle growth was observed even for
229 materials that were low in emissions levels (< 2000 #/cm³) or using higher ACH (5/h) (Figures S20 and
230 S23). As compared to other materials, particle growth was most obvious for ABS1 and ABS2, which
231 surprisingly witnessed a rapid linear reduction of TPNC after the initial peak during printing (Figures
232 S12-14 and S18-19). This was also observed by Zhang *et al.*¹³ using a chamber for ABS filaments.

233 **Figure 2.** Comparison of dynamic particle concentration and diameter for ABS6 in (a) & (b) flow tunnel, and (c) &
234 (d) chamber measurement (ACH: 3/h). Repeated experimental data are shown in Figures S10 and S22.

235 Specifically, as shown in Figure 3(a), secondary aerosols with particle diameters ranging between

32 and 74 nm were generated in sequence during printing in the chamber for ABS6. Particle emissions in the smaller size bins of 10 to 23 nm decreased significantly between 15 to 25 min, suggesting that they could be the source of particle growth. At about 25 min, saturation of PSD was observed and the absorbing ability of existing particles in the chamber for the smallest particles decreased. As a result, the smaller size bins of 10 to 23 nm reached a balance between newly generated particles and particle loss from 25 min onwards till the end of printing. For post-printing phase, it was interesting that the mode of particle diameters did not continuously increase, further suggesting that particle growth was related to newly generated particles (< 20 nm) during printing, as shown in Figure 2(c). To capture the loss rate of smallest particles, the printing activity was deliberately halted after two minutes into the printing phase, and the loss rate of the smallest particles (10-13 nm) was highest in its decay process, as demonstrated in Figure 3(b) and Figure S22(g)-(h). The large secondary aerosol in size bin from 56 to 74 nm was not generated due to insufficient time for particle growth. Although particle growth was clearly related to the newly generated small particles, its dynamic mechanism cannot be solely attributed to particle coagulation/agglomeration, considering that the condensation of VOCs on the existing particles (i.e. heterogeneous nucleation) may exist as well.²⁹

Figure 3. Size-resolved and total particle number concentration (TPNC) in chamber (ACH: 3/h) as well as particle decay rate coefficient K_0 in Model 1 during and post-printing for (a) ABS6 and (b) ABS6 with only two minutes of printing. Note that K_0 estimated during printing was higher than 0.34 due to newly generated particles. Given that K_1 in Model 2 was found to be the same as K_0 in Model 1, only the latter is shown here. (c) Comparison of time-resolved PER based on total particles between Model 1 and Model 2 in chamber for ABS6 with one negative PER observed.

3.2. Particle Decay Rate Coefficient in the Models of Chamber Method

Comparing Models 1 and 2 for the chamber, there was insignificant differences in the predicted PER between the two models for all cases considered, as shown in Figure 3(c) for ABS6 and Figures S31-S37 for other materials. Taking size bin of 10-13 nm for ABS6 as an example, the particle decay rate coefficient during printing ($K_0 > 0.34$) was larger than that in the decay phase ($K_0 = \sim 0.11$) in Figure 3(a). For ABS2 with stronger particle growth, the value of K_0 for small particles (10-23 nm) was even larger than one during printing, resulting in the rapid disappearance of these particles, as shown in Figures S30(b) and S19. In fact, particle decay rate coefficient is time-varying and determined by the combined influence of newly generated particles and existing PSD in the chamber. The observations clearly illustrate that even though the definition of K_0 includes the effects of particle coagulation and other dynamics, the value of K_0 obtained through the decay process cannot represent actual particle losses during the printing phase, which is usually ignored in the literature. This requires a dynamical population balance model considering both particle coagulation and heterogeneous nucleation so that information on each size bin can be extracted to obtain the accurate PER in the chamber measurements.³⁹

3.3. Comparison of Particle Emission Rates in Flow Tunnel and Chamber Measurements

Comparing the chamber and flow tunnel measurements in time- and size-resolved PER for ABS6 in Figures 4(a) and (b), it was evident that the chamber method provided unrealistic observation of particle emissions from a printer. For ABS1 and ABS2, the chamber method even resulted in a large number of instances with negative PER in Figure 5(a), Figures S31 and S34. Negative PER obtained from chamber measurements were also observed in another study.¹⁰ Particle diameters during the initial and final stages of printing were higher than the remaining times of printing as shown in Figure 4(b), which was due to the overheating of filament in the nozzle.¹³

Figure 4. Comparison of time- and size-resolved particle emission rates (E , #/min) for ABS6 (a) in chamber (Model 1; ACH: 3/h) and (b) flow tunnel measurement (Model 3). Repeated experimental data is shown in Figure S38.

Moreover, as summarized in Figure 5 and Table 1 for all cases tested, the statistical PER and mean particle emission yield obtained using chamber was ~ 1.3 -10 times lower than that of the flow tunnel, with the former further overestimating particle diameters by ~ 1.5 -2.3 times. Despite inherent variability of PER between similar printing activities, there was strong evidence of particle growth in chambers, which resulted in the underestimation of PER and overestimation of particle sizes. In essence, materials that exhibited continuously ‘decreasing’ (e.g. ABS1 and ABS2) TPNC after an initial peak gave larger underestimations of PER than that for materials with ‘relatively stable’ (e.g. ABS6 and PVA1) or continuously ‘ascending’ TPNC.

Figure 5. Comparison of (a) statistical particle emission rates (10-420 nm) and (b) the statistical mode of particle diameters for ABS1, ABS2, PVA1, ABS5, ABS6, and ABS7 in flow tunnel, chamber (ACH: 3/h), and room measurements (except for ABS1). Boxes indicate the inter-quartile range with median (50%) in between. The top and bottom of whiskers represent 5th and 95th percentile. The maximum and minimum values are shown in squares.

3.4. Prediction of Field Measurements using Data from Flow Tunnel and Chamber

In the room measurements, there was no obvious difference in particle concentration for different distances between the SMPS and printer (0.5 or 2.5 m apart), which was an indication of well-mixed condition, as shown in Figures S25 and S26 for ABS6. The mode of particle diameters in the room for ABS6 was 11.5 nm throughout the printing process as shown in Figure 6(c), which was the same as that measured in the flow tunnel (in Figure 2(a)) for ABS6. Similar observations were made for all the five materials tested, as summarized in Figure 5(b). Comparing the predicted PSD by the chamber (Figure

6(a)) and flow tunnel (Figure 6(b)) against room measurements (Figure 6(d)), good agreement can be observed for the flow tunnel, while the chamber failed to represent the main PSD characteristics (e.g. the mode of particle diameters). The same conclusion can be reached for all other materials, as shown in Figures S40-S43. Furthermore, as shown in Figure 6(c), the predicted TPNC by flow tunnel was more accurate than that by chamber for ABS6, and the latter also significantly underestimated TPNC for ABS2, as shown in Figure S40. From Figure 6(c), it is obvious that the slope of predicted TPNC was similar to that of measured TPNC in the room in the post-printing phase, which was determined by the ACH in the room.

Figure 6. Predictions of time-resolved particle size distribution (PSD) in a typical room using Model 4 by (a) chamber (ACH: 3/h) or (b) flow funnel measurement for ABS6. Repeated predictions are shown in Figures S39. (c) Comparison of predicted and measured total particle number concentration (TPNC) with error bars resulting from averaging repeats in each condition, and (d) time-resolved PSD measured in the room (ACH: 3.3/h) for ABS6, with

repeated experimental data shown in Figures S25 and S26.

3.5. Particle Emissions by Flow Tunnel for Multiple Materials

Statistical analysis of PER and mean particle diameters for 29 materials are illustrated in Figure 7. Evidently, most of the ABS, PA, HIPS, PC, and ASA displayed higher PER than PLA, Wood, PVA, TPU, and PETG. The median values of the ‘high emission’ materials in Figure 7(a) ranged from $\sim 2 \times 10^{10}$ to $\sim 6.8 \times 10^{11}$ #/min. For comparison, the distribution of PER from a database of 94 chamber experiments for various combinations of printers and materials (majority: ABS and PLA) by Georgia Tech is shown as the last box plot in Figure 7(a), witnessing lower PER below 10^{10} #/min.²⁶ For particle diameter, all materials emitted ultrafine particles below 100 nm, as shown in Figure 7(b). The medians of mean particle diameters measured by the flow tunnel for ABS ranged from ~ 20 to 30 nm, which were smaller than that reported in chamber measurements (~ 40 to 60 nm).¹³ PVA materials witnessed maximum particle diameters among all the materials and the TPNC for a range of materials obtained from the flow tunnel are shown in Figures S44-S65.

Figure 7. (a) Statistical particle emission rates (10–420 nm) for 29 materials using the flow tunnel, and (b) Mean particle diameters during printing. Boxes indicate the inter-quartile range with medians in between. The top and bottom of whiskers represent 5th and 95th percentile. The maximum and minimum values are shown in squares. High emission for median above 10¹⁰ #/min; Middle emission for median from 10⁸ to 10¹⁰ #/min; Low emission for median below 10⁸ #/min.

In conclusion, chamber method underestimated PER (even reaching negative values) by about 1.3–10 times, and overestimated particle diameters by about 1.5–2.3 times for different materials. Secondary aerosol characteristics were widely reported in the literature, but it was found in this study that secondary aerosols (> 30 nm) resulting from the chamber method were not observed in a typical room environment. The particle growth phenomenon in the chamber was clearly related to newly generated small particles. Decay rate obtained after printing was insufficient to represent conditions during printing, and thus a dynamic population balance model is required for chamber method. The flow tunnel method, as a possible alternative for the study of 3D printer emissions to overcome the disadvantages in chamber methods, provided more accurate predictions of particle emission rates and diameters as verified through field measurements in a typical room. Even though the current observations are only for particle emissions from a desktop 3D printer, the findings clearly expose the need to consider differences in aerosol characteristics resulting from a small chamber or a typical room for any potential emission source.

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ASSOCIATED CONTENT

Supporting Information Available: Additional text, two tables and 65 figures with descriptions of experimental conditions, data analysis methods and ancillary results. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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