Chemical Insights
An Institute of Underwriters Laboratories Inc.

2019 ANNUAL SUMMARY REPORT

3D Printer Emission Research

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1. INTRODUCTION

Previous research initiatives carried out by Chemical Insights of Underwriters Laboratories Inc. and Georgia Institute of Technology have characterized particle and volatile organic compound (VOC) emissions from consumer 3D printers and developed a standard testing method to allow reproducible quantification of 3D printer emissions (ANSI/CAN/UL 2904). Previous studies showed high levels of particles, especially ultrafine particles (less than 100 nm in size) were emitted during 3D printing. Numerous specific VOCs, including those with health concerns were also identified. The study also showed printing conditions can affect emission levels and characteristics, including printer nozzle temperature, printer and filament brand, filament type (i.e., chemical makeup) and color. Chemical Insights continued the research on 3D printer emissions in 2019 with the following research objectives:

- Assessing particle toxicity using a chemical assay
- Applying ANSI/CAN/UL 2904 method on additional 3D printers and filaments
- Measuring particle and VOC emissions from new filament materials
- Evaluating the impact of additives on particle and VOC emissions
- Investigating metal compositions in raw filament material and in particles

This report summaries the main findings of the research done in the year of 2019, detailed study results on specific objectives are reported separately.

2. METHODS

2.1 Emission measurements in an exposure chamber

Particle and chemical emissions from 3D printers were studied based on the standard method described in ANSI/CAN/UL 2904 (ANSI 2019).

The Chamber: A 6 m^3 stainless steel exposure chamber was used in the experiment. Air flow into the chamber was controlled by an air supply system containing an air compressing unit that produced a 1 air exchange per hour. VOCs and particles were removed from the air before entering the chamber through gas absorption media and a HEPA filter. Supplied air was set to 50% relative humidity and 23 ºC. The design and characterization of the chamber have been previously described (ISO 2007). The chamber was validated for its air tightness, mixing, air change rage and chemical recovery based on procedures described in ASTM D6670 (ASTM 2013) and ISO 16000-9 (ISO 2007). During the experiment, the 3D printer was placed in the middle of the chamber. Air was sampled via ¼ inch inner diameter conductive silicon tubing within 10 cm of the printer. The tubing was about 30 inches long between the point of sampling and instrument, which was located outside the chamber. Reynolds numbers of the flow in sample tubing were below 400, implying laminar flow conditions to minimize particle losses. Particle filter sample during print was collected via conductive silicon tubing from about 10 cm away from the printer to the filter holder or filter cassette outside of the chamber that connected to the vacuum pump at controlled air flow rate.

Particle Measurements: Particle emissions were measured online using a suite of research instruments. The number distributions of particles with diameters from 7 to 300 nm were measured with a scanning mobility particle sizer (SMPS) spectrometer (electrostatic classifier model 3082, differential mobility analyzer model 3081A, condensation particle counter (CPC) model 3789, TSI Inc.). Number concentrations for 206 size channels were recorded over this size range at a sampling interval of 2 minutes. Particle sizes reported are electrical mobility diameters. An optical particle sizer (OPS model 3330, TSI Inc.) was used to measure fine and coarse particles with diameters from 0.3 to 10 µm, with 16 channels of size separation at a sampling interval of 2 minutes. Sizes for this instrument are based on calibrations with commercially available PSL (polystyrene latex) spheres. Particle surface area and mass concentrations were calculated from measured number concentrations assuming particles were spherical with unit density (1 g/cm^3). For each print run, particle measurement started after the printer was turned and warmed up, but before the printer started to extrude filament (i.e., extruder nozzle started to heat up) for at least 10 min, and continued through printing period until 1-hour after the print finished or until the particle concentration decreased to background levels.

VOC Measurements: Chamber air was collected onto sorbent tubes through ¼ inch outer diameter Teflon tubes, which were located about 10 cm on top of the printer to the outside of the chamber connected to a mass flow controller that provided constant flow rates. VOC samples were collected onto Tenax® sorbent tubes at a flow rate of 0.2 L/min and then thermally desorbed for the gas chromatography-mass spectrometric (GC/MS) analysis. Instrumentation included a sample concentrator (Perkin Elmer Model TurboMatrix ATD or TurboMatrix 650), a Hewlett-Packard/Agilent 6890 or 7890 Series Gas Chromatograph and a Hewlett-Packard/Agilent 5973 or 5975 Mass Selective Detector. The analytical methodology is adapted from US EPA Compendium Method TO-17 (US EPA 1999b) and ASTM D6196 (ASTM 2015) and is generally applicable to C_6 – C_{16} organic chemicals with boiling points ranging from 35 ºC (95 °F) to 250 ºC (482 °F). Individual VOCs were identified using a mass spectral database and quantitated using multipoint calibration standards, if available. Total VOC (TVOC) concentrations were determined by adding all individual VOC responses obtained by the mass spectrometer and calibrating the total mass relative to toluene. Solid sorbent cartridges with DNPH (2,4-Dinitrophenylhydrazine) were used to collect formaldehyde and other low-molecular weight carbonyl compounds in the chamber air through the mass flow controller

at a flow rate of 0.5 L/min. The samples were analyzed by high performance liquid chromatography (HPLC) following ASTM D5197 (ASTM 2016) and US EPA Method TO-11A (US EPA 1999a). The mass responses were determined using multi-point calibration curves prepared from standard solutions of hydrazone derivatives of the aldehydes.

2.2 Data analysis

Particle emission rates and total particle emissions during printing were calculated according to ANSI/CAN/UL 2904 (ANSI 2019), which includes a correction for particle loss calculated from the decay curve after the print stopped. SMPS and OPS provide particle size distribution data, along with the integrated total particle concentrations over the instrument detection (or user selected) size ranges. These data were used to calculate particle emission rates and yields, while the size distributions were used to quantify the average mean sizes of the emitted particles. Particle surface area and mass concentrations were calculated assuming particles are spherical with unit density. VOC emission factors and total VOC emissions were calculated using a box model time-varying mass balance equation with a first order total sink factor in accordance to ANSI/CAN/UL 2904 (ANSI 2019).

Chamber measured particle and VOC emission rates were applied to an indoor exposure model and were used to estimate the particle and chemical concentrations in different indoor environments, according to ANSI/CAN/UL 2904 (ANSI 2019). The model was based on a mass balance, assuming the studied room was well-mixed and 3D printing was the only emission source within the room; modeled indoor scenarios included a prototypical office room, a room in a residential house and a classroom in a school.

2.3 Particle toxicity assay

The chemical dithiothreitol (DTT) assay was utilized to estimate the oxidative potential (OP) of 3D printing emitted particles. In this assay, DTT serves as the reducing agent to simulate the interaction between particles and physiological reducing agents and the resulting redox reactions that can occur in vivo when exposed to particles. The particles emitted from 3D printing in the exposure chamber were collected onto 45 mm diameter polytetrafluoroethylene (PTFE) filters at about 10 L/min and then extracted in deionized water before analysis. The analysis procedure followed the semiautomated DTT assay analytical system developed in Gao et al. 2017 to measure total (water-soluble plus water-insoluble) particle OP. Key instruments included a liquid waveguide capillary cell (LWCC, World Precision Instruments Inc.) with an ultraviolet-visible light source (DT-Mini-2, Ocean Optics Inc.) and a multi-wavelength light detector (USB4000, Ocean Optics Inc.). Blank filter samples and positive controls were also analyzed in the same manner. OP was calculated by subtracting sample DTT consumption by that of the blank and normalized by particle mass (OP^{DTT}_m) or sample air volume (OP^{DTT}_v) that passed through the filter.

2.4 Metal analysis

Particle samples for metal analysis were collected from the exposure chamber onto 37 mm diameter mixed cellulose ester (MCE) filters at about 20 L/min. The samples were prepared using microwave assisted acid digestion method (US EPA 2007), to ensure detection of any trace elements in the samples. Metal analysis used an inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900), which can analyze for 28 elements. Pieces of raw filament material were also analyzed with the same method for comparison. Metal analysis was done through a collaboration with US EPA Center for Environmental Solutions and Emergency Response.

2.5 Studied print conditions

The studied printers and filaments were chosen based on their availability and accordance to the study objectives listed above. Details on the printer and filaments tested and some operating conditions are listed in Table 1. Four different printers and 12 different filaments were tested.

TABLE 1. SUMMARY OF PRINTING SCENARIOS

	Printer brand	Filament material	Filament brand	Filament color	Nozzle temperature	Build plate
1	A1	PLA	c	Red	210 °C	50 °C
2	A1	ABS	c	Red	270 °C	100 °C
3	A1	ABS	d	Red	270 °C	100 °C
4	A1	Nylon	i	Natural	270 °C	100 °C
5	D1	PLA	h	Green	215 °C	50 °C
6	D1	PLA	g	Green	215 °C	50 °C
7	D1	Metal PLA	h	Bronze	215 °C	50 °C
8	D1	Metal PLA	g	Bronze	215 °C	50 °C
9	D1	Metal PLA	j	Bronze	230 °C	50 °C
10	E1	Nylon	k	Black	275 °C	Glue, no heat
11	E1	Nylon FR*	k	Black	275 °C	Glue, no heat
12	E2	Metal	k	Gray	220 °C	Heat

**FR- flame retardant*

3. RESULTS AND DISCUSSION

3.1 Particle emission summary

Average particle emission rates (total of all particles emitted divided by print time) and yields (total of all particles emitted divided by mass of filament extruded) for particle number, surface area and mass for all studied printer and filament combinations are shown in Table 2.

TABLE 2. PARTICLE EMISSION RATES AND YIELDS

Printer	Filament material (brand) color	Emission rate			Yield		
		Number (h^{-1})	Surface (cm^2/h)	Mass (µg/h)	Number (g^{-1})	Surface (cm^2/g)	Mass (µg/g)
A1	PLA (c) red	2.16×10^{10}	3.83	6.71	1.35×10^{9}	0.24	0.42
A1	ABS (c) red	2.08×10^{11}	146	812	1.52×10^{10}	10.6	59.3
A1	ABS (d) red	2.09×10^{12}	372	852	1.42×10^{11}	25.2	57.8
A1	Nylon (i) natural	2.29×10^{10}	19.3	89.6	1.58×10^{9}	1.33	6.18
D1	PLA (h) green	5.44×10^{11}	6.77	8.19	1.50×10^{10}	0.18	0.22
D1	PLA (g) green	3.23×10^{11}	15.6	24.9	8.63×10^{9}	0.42	0.69
D1	Metal PLA (h) bronze	5.54×10^{10}	32.7	108	1.58×10^{9}	0.94	3.12
D1	Metal PLA (g) bronze	1.22×10^{10}	23.5	125	3.23×10^{9}	0.63	3.34
D1	Metal PLA (j) bronze	5.09×10^{12}	230	258	7.90×10^{10}	3.75	4.33
E1	Nylon (k) black	1.56×10^{11}	12.1	15.6	2.25×10^{10}	1.74	2.24
E1	Nylon FR (k) black	5.16×10^{11}	43.4	59.9	7.13×10^{10}	6.00	8.28
E2	Metal (k) gray	7.37×10^{9}	73.5	1370	6.52×10^{8}	6.46	121

The measured emissions were compared to the database obtained from a previous study of 378 tests using the same method, which included 186 runs of ABS filaments, 164 runs of PLA filaments, 15 runs of nylon filaments, 6 runs of HIPS (high impact polystyrene) filaments, 7 runs of PVA (polyvinyl alcohol) filaments. Comparisons between particle number emission rates are shown in Figure 1, yields in Figure 2, and geometric mean diameters (GMD) during print in Figure 3. The lines in the figures indicate the maximum, median, minimum and 25 and 75 percentiles of the database from the 378 tests.

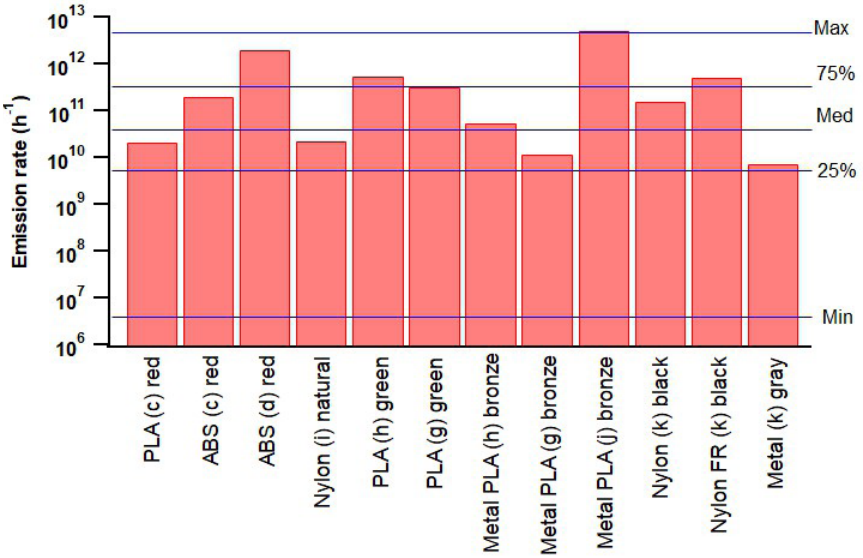

FIGURE 1. AVERAGE PARTICLE NUMBER EMISSION RATES FOR STUDIED PRINTERS AND FILAMENTS, COMPARED TO THE DATABASE FROM A PREVIOUS STUDY.

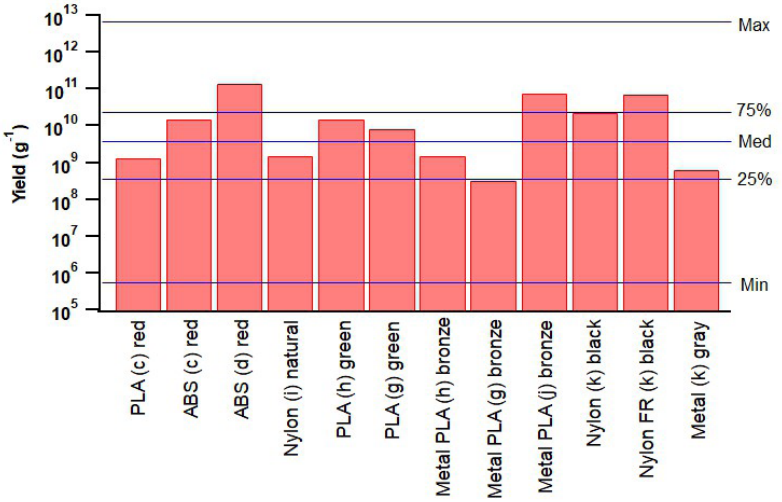

FIGURE 2. AVERAGE PARTICLE NUMBER YIELDS FOR STUDIED PRINTERS AND FILAMENTS, COMPARED TO THE DATABASE FROM A PREVIOUS STUDY.

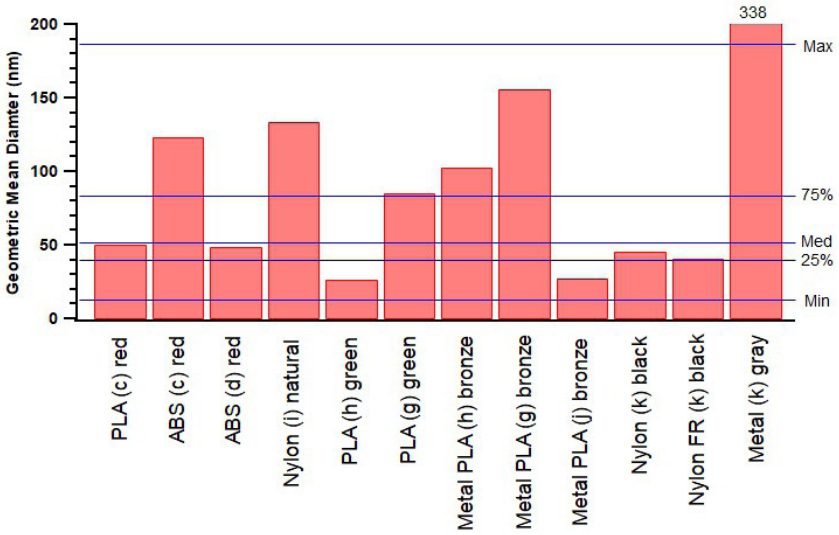

FIGURE 3. PARTICLE AVERAGE GEOMETRIC MEAN DIAMETERS DURING PRINTING FOR STUDIED PRINTERS AND FILAMENTS, COMPARED TO THE DATABASE FROM A PREVIOUS STUDY.

Particle emission rates and yields were generally within the range of the previous study database, except for Metal PLA (j) bronze, which was 13% higher than the maximum emission rate (Figure 1), which was for a high emitter of ABS material. In our previous study (the database for comparison), PLA filaments in general were found to emit less particles than ABS filaments, whereas for these new filaments tested, PLA filaments with special coloring and metal additives can have emission rates and yields higher than the median of the database. Note that regular PLA filament (PLA (c)) emissions were lower than the database median (Figure 1 and 2), whereas two of the three metal PLA filaments were generally above the database median. Figure 3 shows that most of the particle GMDs were less than 100 nm, which is the upper size of ultrafine particles, while specific ABS, nylon, PLA and metal filaments can emit particles with mean size larger than 100 nm. Variations among different filament materials and filament brands were also found, specific comparisons are given in later sections.

3.2 Chemical emission summary

VOC and aldehyde samples were collected and analyzed for new filaments studied, which included two green PLA filaments, three metal PLA filaments, two nylon mixed with carbon fiber filaments and one metal filament. Summary of TVOC emission rates and the most emitted chemicals for each filament are listed in Table 3.

TABLE 3. TOTAL VOC EMISSION RATES AND THE FIVE CHEMICALS WITH THE HIGHEST EMISSION RATES

Printer	Filament material (brand) color	TVOC emission rate (mg/h)	Top 5 chemicals ranked by emission rates
D1	PLA (h) green	0.64	1,4-Dioxane-2,5-dione, 3,6-dimethyl- Octadecane Acetaldehyde Formaldehyde Benzene, chloro
D1	PLA (g) green	0.62	1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)- 2-Oxepanone Ethanone, 1-[4-(1-methylethyl)phenyl]- Acetaldehyde Dodecyl acrylate
D1	Metal PLA (h) bronze	0.76	1,4-Dioxane-2,5-dione, 3,6-dimethyl- Dodecane, 1-chloro Acetaldehyde Methyl methacrylate (2-Propenoic acid, 2-methyl-, methyl ester) Tetradecane, 1-chloro
D1	Metal PLA (g) bronze	0.73	1,4-Dioxane-2,5-dione, 3,6-dimethyl- Acetaldehyde 2-Oxepanone Ethanone, 1-[4-(1-methylethyl)phenyl]- Methyl methacrylate (2-Propenoic acid, 2-methyl-, methyl ester)
D1	Metal PLA (j) bronze	0.73	1,4-Dioxane-2,5-dione, 3,6-dimethyl- Acetaldehyde 1-Dodecanol Crotonic acid Cyclopentanone
E1	Nylon (k) black	2.00	Caprolactam Formaldehyde Benzene, 1-methoxy-2-nitro 1,2,3-Propanetriol, 1-acetate Adipic acid, decyl 2-ethylhexyl ester
E1	Nylon FR (k) black	1.23	Caprolactam Formaldehyde 1,2,3-Propanetriol, triacetate (Triacetin) Benzenemethanol, a,a-dimethyl- Benzene, 1-methoxy-2-nitro-
E2	Metal (k) gray	0.36	Caprolactam Cyclotrisiloxane, hexamethyl Formaldehyde Cyclotetrasiloxane, octamethyl Benzaldehyde, 4-propyl

In general, TVOC emission rates from studied filaments were all below the criteria listed in ANSI/CAN/UL 2904 (10.4 mg/h). TVOC emission rates were found to be associated with filament material and nozzle temperature. Results from this study were compared to the previous data, which included 25 tests with ABS, PLA, nylon, HIPS and PVA filaments (Davis et al. 2019). TVOC emission rates of Nylon (k) and Nylon FR (k) running at 275 °C were the highest among the filaments in this study, which were in between of previous nylon data and were higher than 75th percentile of overall previous data. Levels for PLA based materials running at 210 – 230 °C were comparable and between the median and 75th percentile of previous data. Metal (k) filament running at 220 °C had the lowest TVOC emission rate (less than median of previous data).

The most detected chemicals were mainly associated with filament raw materials thus sharing some similarities among filaments with the same base materials. For all five PLA filaments, the most emitted chemicals (1,4-Dioxane-2,5-dione, 3,6-dimethyl- and 1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3S-cis)-) were isomers of lactide, which can be polymerized to PLA. Acetaldehyde was also present with high emission rates for all five PLA filaments, which is known to be possibly carcinogenic to human by International Agency for Research on Cancer (IARC). Other common high emitted chemicals included alkanes, esters, ketones, arenes, and chloride. Caprolactam is associated with ocular and respiratory toxicity; as the monomer to make nylon, it was the major emitted chemical from nylon filaments from previous findings (Davis et al. 2019), and it was the most emitted VOC from Nylon (k) and Nylon FR (k) filaments as expected. Formaldehyde was shown in top five emitted chemicals for all three brand k filaments, which is a known human carcinogen by IARC. Other major emitted VOCs from nylon mixed with carbon fiber filaments were compounds with benzene ring and nitrogen. Metal (k) filament was found to emit compounds with silicon like siloxanes. Details of emitted chemicals and their health implication are discussed later.

3.3 New filament material

Two new types of filament materials were studied. One was nylon mixed with chopped carbon fibers, which provided high strength and resistance to heat and chemicals (Nylon brand k, and Nylon brand k FR was the same brand, but with flame retardant added). The other one was not a thermoplastic based filament but a metal filament made of stainless-steel powders, which provided even higher strength and resistant to chemicals and corrosion (Metal brand k). Their particle concentrations inside the chamber are shown in Figure 4 and 5.

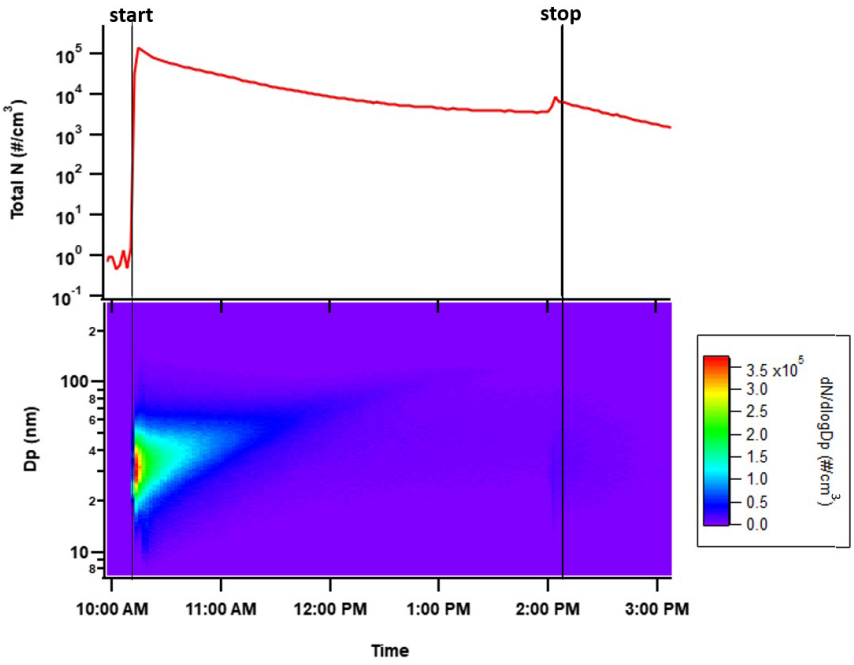

FIGURE 4. TOTAL PARTICLE NUMBER CONCENTRATIONS AND SIZE DISTRIBUTIONS IN THE CHAMBER FOR NYLON (K) BLACK WITH CHOPPED CARBON FIBERS MEASURED BY SMPS. OPS DATA WAS NOT INCLUDED AS PARTICLES IN THAT INSTRUMENT SIZE RANGE ACCOUNTED FOR LESS THAN 0.01% OF TOTAL PARTICLE NUMBER EMISSIONS. VERTICAL LINES INDICATE START AND STOP TIME OF PRINTING.

Figure 4 time series plot shows a similar pattern to what has been previously observed as a typical particle concentration time series; particle concentration peaked at the beginning and then decreased toward an approximate steady state. A smaller peak near when printing ended was also observed; that was also observed previously and depended on printer design. Figure 4 size distribution plot shows a burst of small particles (around 30 nm) when print started, and then the particles grew in size and decreased in concentrations as they went through vapor condensation and particle coagulation.

Particle emission results comparing to previous studied nylon filaments are listed in Table 4. The new filament with chopped carbon fibers (Nylon (k) black) had particle emissions comparable to a high emitting nylon filament. The geometric mean size of particles emitted was less than 50 nm, while GMD for a regular nylon filament was larger than 100 nm. As previously found, particle emissions increased with nozzle extrusion temperature (Zhang et al. 2017); the observed higher particle emissions from this new filament may also be associated with its nozzle temperature, 275 °C, which was 5 °C higher than that of high emitting nylon and 32 °C higher than the regular nylon.

TABLE 4. PARTICLE EMISSION COMPARISON OF NYLON WITH CHOPPED CARBON FIBER FILAMENTS TO PURE NYLON FILAMENTS

	Emission rate (h^{-1})	Emission yield (g^{-1})	GMD (nm)	Nozzle temperature (°C)
Regular emitting nylon	2.16×10^{10}	1.50×10^{9}	123	243
High emitting nylon	2.17×10^{11}	1.56×10^{10}	64.6	270
Nylon (k) black	1.56×10^{11}	2.25×10^{10}	45.7	275

It can be seen in Table 4 and Figures 1 to 3 that roughly higher emission rates and yields were associated with lower GMD. Our aerosol modeling analysis showed that emissions of semi-volatile vapors could either form new particles or condense on pre-existing particles increasing their size and mass (Zhang et al. 2018). The studied high emitters (filaments with high particle emission rates and yields) likely generated high concentrations of semi-volatile vapors that overwhelmed the condensation sink and formed new particles at a rate higher than other regular emitters. This resulted in a greater number of particles with generally smaller particle mean sizes. The outcome is that these high emitting filaments may be especially toxic, because it has been shown that smaller nanoparticles are more toxic than larger-sized particles of the same material and dose (Oberdörster, Ferin, and Lehnert 1994).

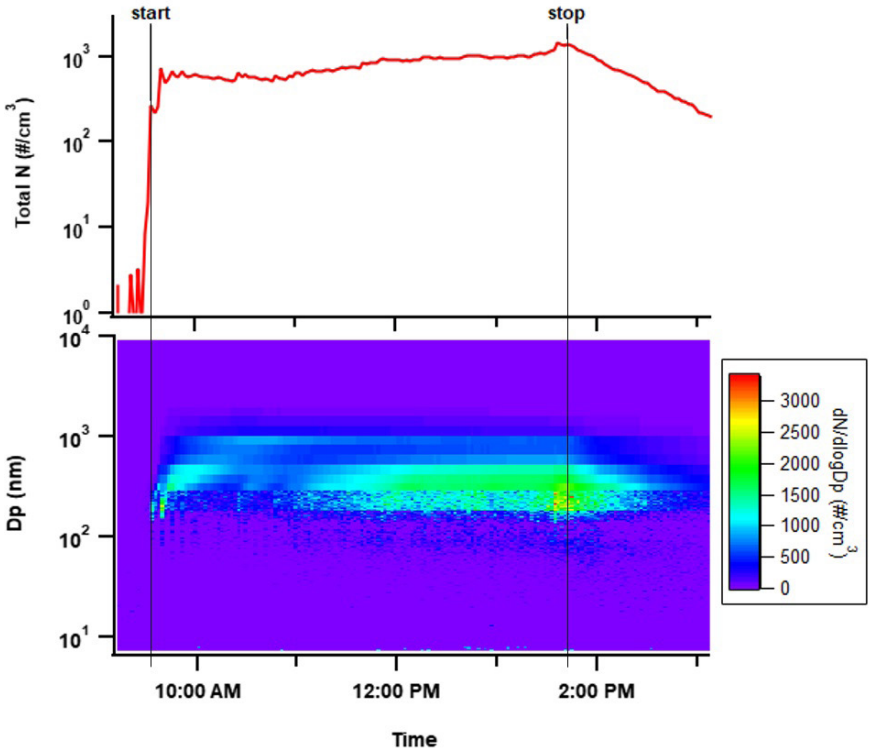

FIGURE 5. TOTAL PARTICLE NUMBER CONCENTRATIONS AND SIZE DISTRIBUTIONS IN THE CHAMBER FOR METAL (K) GRAY MEASURED BY SMPS AND OPS. VERTICAL LINES INDICATE START AND STOP TIME OF PRINTING.

Particle emissions from metal (k) filament are shown in Figure 5. A different pattern from Figure 4; particle concentrations increased as print continued, and the maximum concentration appeared slightly before print stopped. The large peak seen for polymer filaments at the start of the printing (e.g., Figure 4), attributed to homogeneous nucleation of emitted semi-volatile vapors (Zhang et al. 2017), was not seen for this metal filament. The result suggests that for this metal filament, there is no thermodynamic barrier to particle formation, the emitted vapors simply coagulate and grow in size by condensation and coagulation. Figure 3 and 5 also show larger particles were produced by this metal filament and that there was only minor growth in sizes immediately after printing started, in contrast to polymer filaments. The GMD during print was 338 nm, larger than all of those observed previously. The differences of particle emission characteristics from this metal filament indicated the particle formation mechanism may be different from typical thermoplastics studied previously. Although the particles were larger, this metal filament was found to emit less particles in number than typical thermoplastics, with number emission rate and yield close to 25th percentile of previous database. However, the mass yield (particle mass emitted divided by filament mass) can be significantly higher than others since it emitted larger particles (not considering difference in particle density, which could be significantly higher than the assumed 1 g/cm^3 for the metal filaments).

There were 44 different chemicals detected from Nylon (k) black filament and 63 from Metal (k) gray filament, among which 17 and 20 chemicals respectively were listed in health-related regulation and guidance. The sources included ANSI/CAN/UL 2904 (ANSI 2019), IARC classified carcinogenic hazards to humans (IARC 2018), California Office of Environmental Health Hazard Assessment (OEHHA) Proposition 65 (OEHHA 2012), California Department of Public Health (CDPH) Standard Method (SM) (CDPH 2017), American Conference of Governmental Industrial Hygienists (ACGIH®) (ACGIH 2018), and German Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB) (AgBB 2015). Emission levels from Nylon (k) filament were much higher; TVOC emission rate from Nylon (k) filament was over five times of that from Metal (k) filament (Table 3). This was associated with both material and nozzle temperature. For those chemicals with health concern, emission rates of individual chemicals and estimated concentrations for office scenario using the model are shown in Table 5.

TABLE 5. EMISSION RATE (ER) AND MODEL ESTIMATED OFFICE CONCENTRATION (CONC.) FOR EACH CHEMICAL WITH HEALTH CONCERN (ONLY THOSE WITH EMISSION RATES OF 0.01 MG/H AND LARGER ARE INCLUDED)

CAS number	Chemical	Nylon (k) black		Metal (k) gray	
		ER (mg/h)	Conc. (µg/m^3)	ER (mg/h)	Conc. (µg/m^3)
105-60-2	Caprolactam	4.91	236	0.06	3.11
50-00-0	Formaldehyde	0.02	1.16	0.05	2.37
556-67-2	Cyclotetrasiloxane, octamethyl	0.01	0.34	0.03	1.34
91-23-6	Benzene, 1-methoxy-2-nitro-	0.02	0.89		
100-51-6	Benzyl alcohol (Benzenemethanol)	0.01	0.25	0.02	0.73
128-37-0	2,6-Di-tert-butyl-4-methylphenol (BHT)	0.01	0.34		
124-19-6	Nonyl aldehyde (Nonanal)	0.01	0.33	0.01	0.49
106-42-3	Xylene (para and/or meta)	0.01	0.31		
6846-50-0	TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate)	0.01	0.29		
112-31-2	Decanal	0.01	0.27	0.01	0.27
104-76-7	1-Hexanol, 2-ethyl			0.01	0.52
541-02-6	Cyclopentasiloxane, decamethyl			0.01	0.56
540-97-6	Cyclohexasiloxane, dodecamethyl			0.01	0.57
75-07-0	Acetaldehyde			0.01	0.56
107-50-6	Cycloheptasiloxane, tetradecamethyl-			0.01	0.50
100-52-7	Benzaldehyde			0.01	0.27

Only caprolactam from Nylon (k) filament presented with an emission rate larger than 1 mg/h; caprolactam from Metal (k) and other chemicals all had emission rates below 1 mg/h. The estimated office concentration of caprolactam was close to the lowest concentration of interest (LCI) from AgBB (300 µg/m^3). The actual concentration could be higher for less ventilated or smaller spaces, or other emission sources were present. Other detected chemicals included aldehydes and compounds with benzene ring. Though with low emission rates, formaldehyde is a known carcinogen; benzene, 1-methoxy-2-nitro- and acetaldehyde are possibly carcinogenic to humans. One chemical with siloxane was detected from Nylon (k) and more (4 out of 12) from Metal (k), which may be associated with the lubricate applied on the extruder nozzle or silicon may be present in the filament raw material. Siloxanes were also detected from previous study of ABS, PLA, nylon, HIPS and PVA filaments (Davis et al. 2019). New VOCs detected included a possible carcinogen, benzene, 1-methoxy-2-nitro- from Nylon (k) black and cycloheptasiloxane, tetradecamethyl- from Metal (k).

3.4 Filament additives affecting emissions

Past observations have suggested that minor additives in raw filament materials were associated with the variances in particle emission levels, as well as particle chemical composition (Zhang et al. 2017; 2019). We explored this further in our more recent studies, various filament brands with different additives were studied, including coloring dyes, metal powders and a flame retardant (FR).

Effect of Coloring additives: Two green PLA filaments of different brands were compared to a red PLA filament. The comparison of particle concentrations during print from the three PLA filaments is shown in Figure 6. The particle emission time series patterns were similar, with a concentration peak when printing began and a decrease to approximately steady state during printing. Both green color PLA filaments showed higher emission rate and yield than the red PLA (Table 2). However, the green PLA run at a nozzle temperature 5 °C higher than that of the red PLA, which could account for higher emission levels. PLA (g) green filament had a higher peak but lower steady-state concentration than the other two filaments. In addition, all filaments emitted particles with a mean size smaller than 100 nm.

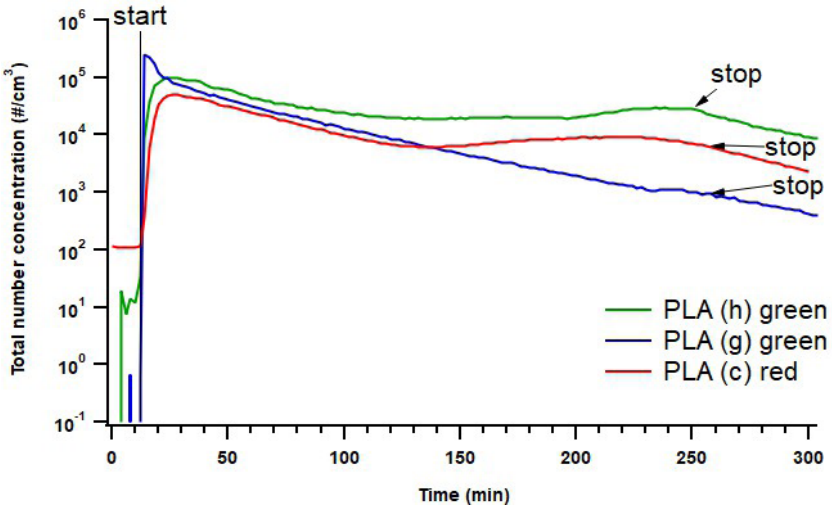

FIGURE 6. PARTICLE TOTAL NUMBER CONCENTRATIONS FOR THREE PLA FILAMENTS. VERTICAL LINE INDICATES WHEN PRINT STARTED AND ARROWS WITH STOP INDICATE WHEN PRINT STOPPED.

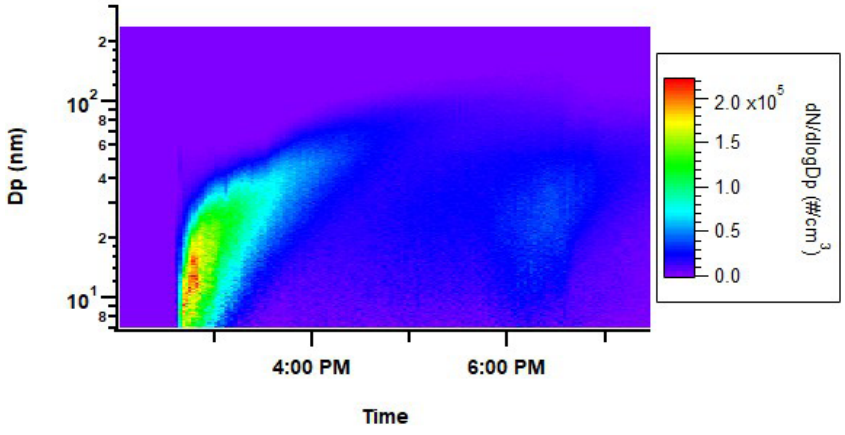

FIGURE 7. PARTICLE SIZE DISTRIBUTION OF PLA (H) GREEN FILAMENT. VERTICAL LINES INDICATE WHEN PRINT STARTED AND STOPPED.

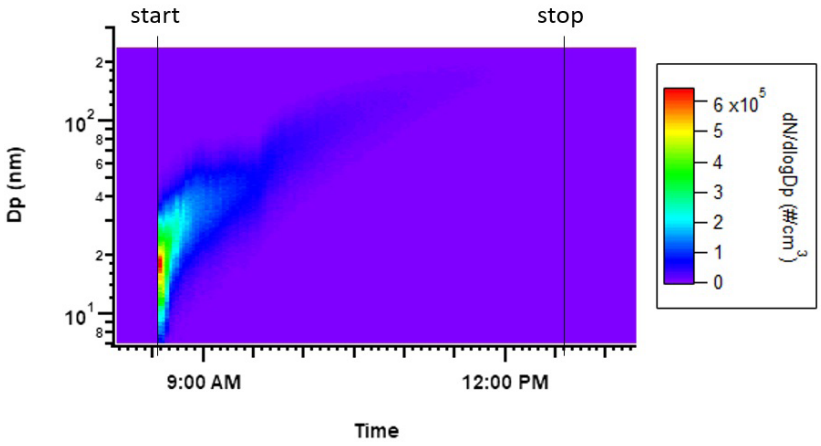

FIGURE 8. PARTICLE SIZE DISTRIBUTION OF PLA (G) GREEN FILAMENT. VERTICAL LINES INDICATE WHEN PRINT STARTED AND STOPPED.

Particle size distributions also showed the burst of small particles in the beginning of print and growth of emitted particles during print (Figure 7 and 8). For brand h PLA, it is noteworthy that non-zero concentrations of particles were detected all the way down to the lowest measurement size of the SMPS (limited by CPC used) of 7 nm, suggesting particles smaller than 7 nm were emitted in the first 10 minutes of print. This filament also had a smaller GMD (Figure 3).

37 different chemicals from PLA (h) green filament and 47 from PLA (g) green filament were detected, among which 19 and 24 chemicals respectively were listed in health-related regulation and guidance. Their TVOC emission rates were comparable with a difference of 3% (Table 3).

TABLE 6. EMISSION RATE (ER) AND MODEL ESTIMATED OFFICE CONCENTRATION (CONC.) FOR EACH CHEMICAL WITH HEALTH CONCERN (ONLY THOSE WITH EMISSION RATES OF 0.01 MG/H AND LARGER ARE INCLUDED)

CAS number	Chemical	PLA (h) green		PLA (g) green	
		ER (mg/h)	Conc. (μg/m³)	ER (mg/h)	Conc. (μg/m³)
75-07-0	Acetaldehyde	0.03	1.48	0.03	1.52
50-00-0	Formaldehyde	0.02	0.78	0.02	1.06
100-18-5	Benzene, 1,4-bis(1-methylethyl)-			0.02	0.88
108-90-7	Benzene, chloro	0.01	0.65		
85-44-9	Phthalic anhydride (1,3-Isobenzofuran-randione)	0.01	0.54		
100-42-5	Styrene			0.01	0.54
112-31-2	Decanal	0.01	0.42	0.01	0.38
141-32-2	Butyl acrylate (2-Propenoic Acid, butyl ester)			0.01	0.39
80-62-6	Methyl methacrylate (2-Propenoic acid, 2-methyl-, methyl ester)			0.01	0.39
105-60-2	Caprolactam	0.01	0.30	0.01	0.29
124-19-6	Nonyl aldehyde (Nonanal)	0.01	0.29	0.01	0.27
106-42-3	Xylene (para and/or meta			0.01	0.29
100-51-6	Benzyl alcohol (Benzenemethanol)			0.01	0.27
100-52-7	Benzaldehyde	0.01	0.27		
104-76-7	1-Hexanol, 2-ethyl	0.01	0.26		

In general, emission rates of individual chemicals were low, in orders of 0.01 mg/h (Table 6). About 50% of the listed chemicals were overlapped between the two filament brands with comparable emission rates, including aldehydes and caprolactam. Acetaldehyde and styrene are possibly carcinogenic to humans. Methyl methacrylate is an irritant that was detected from PLA of a certain manufacturers. A newly detected VOC was found from PLA (g) green, which was benzene, 1,4-bis(1-methylethyl)-.

Effect of Metal additives: Three metal PLA filaments that had different percentages of metal powder added were also studied for particle and VOC emissions. Metal PLA (h) bronze was a pure PLA filament that had a metallic bronze look but actually contained no metal powder. Metal PLA (g) bronze was a PLA based filament with approximately 25% metal powder added. Metal PLA (j) bronze was a PLA based filament with approximately 80% bronze power added, therefore the density of this filament was about 3 times of other common thermoplastic filaments (3.9 g/cm^3). This filament also required a relatively higher nozzle temperature (230 °C) than the other two (215 °C). A comparison of particle concentrations during print from these filaments is shown in Figure 9. The particle size distributions are shown in Figure 10 to 12.

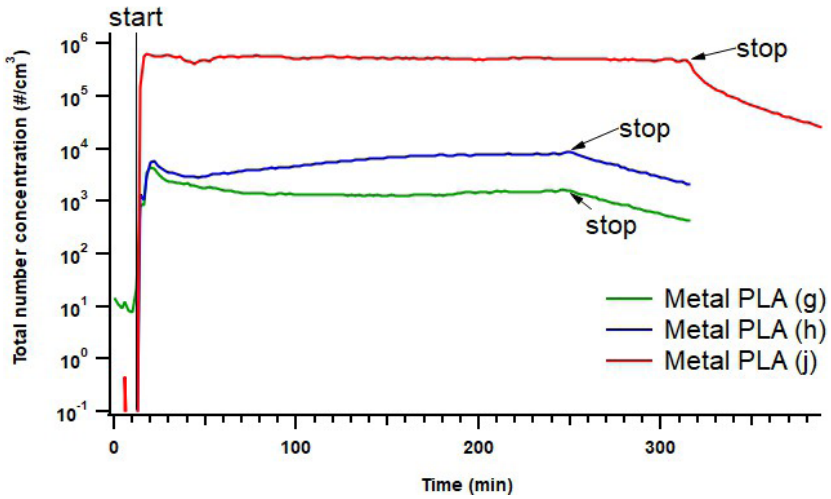

FIGURE 9. PARTICLE TOTAL NUMBER CONCENTRATIONS FOR THREE METAL PLA FILAMENTS. VERTICAL LINE INDICATES WHEN PRINT STARTED AND ARROWS WITH STOP INDICATE WHEN PRINT STOPPED. METAL PLA (H) CONTAINED NO METAL POWDER, (G) CONTAINED 25% AND (J) 80% BRONZE POWDER. METAL PLA (J) OPERATED AT AN EXTRUSION NOZZLE TEMPERATURE OF 230 °C, COMPARED TO 215 °C FOR THE OTHER TWO PLA FILAMENTS SHOWN.

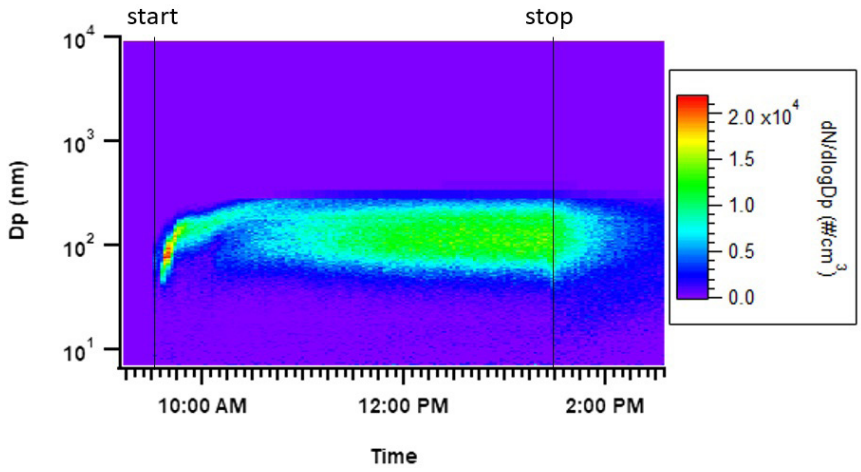

FIGURE 10. PARTICLE SIZE DISTRIBUTION OF METAL PLA (H) BRONZE FILAMENT. VERTICAL LINES INDICATE WHEN PRINT STARTED AND STOPPED. THIS FILAMENT CONTAINED NO METAL POWDER AND NOZZLE TEMPERATURE WAS 215 °C.

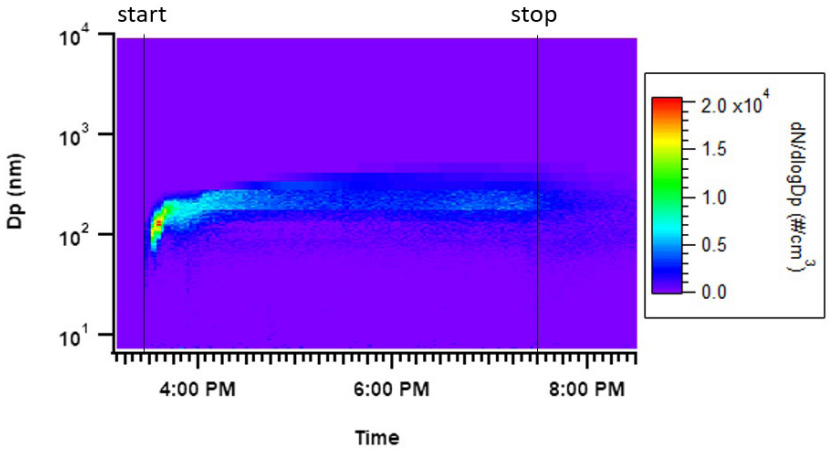

FIGURE 11.PARTICLE SIZE DISTRIBUTION OF METAL PLA (G) BRONZE FILAMENT. VERTICAL LINES INDICATE WHEN PRINT STARTED AND STOPPED. THIS FILAMENT CONTAINED 25% BRONZE POWDER AND NOZZLE TEMPERATURE WAS 215 °C.

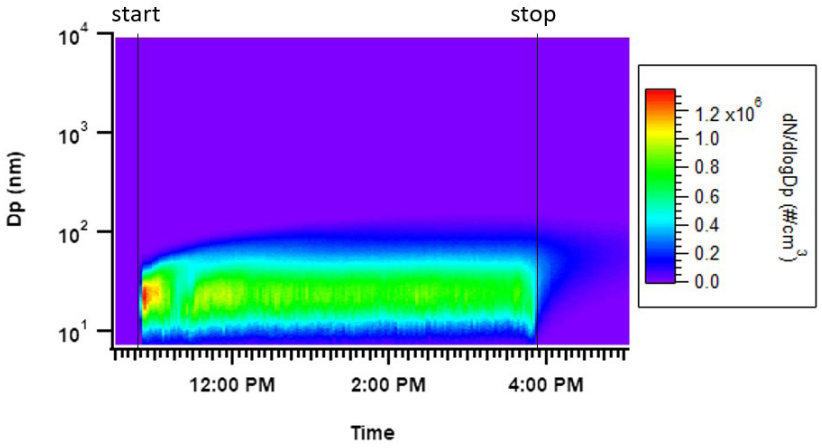

FIGURE 12. PARTICLE SIZE DISTRIBUTION OF METAL PLA (J) BRONZE FILAMENT. VERTICAL LINES INDICATE WHEN PRINT STARTED AND STOPPED. THIS FILAMENT CONTAINED 80% BRONZE POWDER AND NOZZLE TEMPERATURE WAS 230 °C.

These three PLA filaments showed similar trend as regular PLA filaments, see Figure 6, when operated at similar nozzle temperatures. However, the higher particle emissions of both total number and yield, and lower GMD (mean particle size) for the PLA containing 80% bronze powder may be associated with the higher nozzle temperature. Metal PLA (h), a pure PLA filament with metallic coloring, emitted slightly higher levels of particles than PLA (c) red filament (Table 2).

42 different chemicals from Metal PLA (h) bronze filament, 57 from Metal PLA (g) bronze filament, and 55 from Metal PLA (j) bronze were detected respectively, among which 21, 27 and 25 chemicals respectively were listed in health-related regulation and guidance. Their TVOC emission rates were also comparable with differences no larger than 4% (Table 3).

TABLE 7. EMISSION RATE (ER, MG/H) AND MODEL ESTIMATED OFFICE CONCENTRATION (CONC., MG/M^3) FOR EACH CHEMICAL WITH HEALTH CONCERN (ONLY THOSE WITH EMISSION RATES OF 0.01 MG/H AND LARGER ARE INCLUDED)

CAS number	Chemical	Metal PLA (h) bronze		Metal PLA (g) bronze		Metal PLA (j) bronze	
		ER	Conc.	ER	Conc.	ER	Conc.
75-07-0	Acetaldehyde	0.07	3.17	0.10	4.96	0.22	10.6
80-62-6	Methyl methacrylate (2-Propenoic acid, 2-methyl-, methyl ester)	0.05	2.35	0.03	1.28		
120-92-3	Cyclopentanone					0.03	1.38
100-42-5	Styrene			0.03	1.27		
50-00-0	Formaldehyde	0.02	0.98	0.02	0.95	0.02	1.03
29911-28-2	2-Propanol, 1-(2-butoxy-1-methyle-thoxy)- (Dipropylene glycol monobutyl ether)	0.02	1.02			0.02	0.80
100-51-6	Benzyl alcohol (Benzenemethanol)	0.01	0.31	0.02	0.91	0.01	0.36
109-99-9	Furan, tetrahydro (THF)					0.02	0.82
100-18-5	Benzene, 1,4-bis(1-methylethyl)-			0.02	0.76		
112-31-2	Decanal	0.01	0.41	0.01	0.49	0.01	0.62
124-19-6	Nonyl aldehyde (Nonanal)	0.01	0.26	0.01	0.41	0.01	0.39
141-32-2	Butyl acrylate (2-Propenoic Acid, butyl ester)			0.01	0.37		
105-60-2	Caprolactam					0.01	0.36
71-36-3	1-Butanol (N-Butyl alcohol)	0.01	0.31				
75-98-9	Propanoic acid, 2,2-dimethyl					0.01	0.29
25265-77-4	2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate					0.01	0.27
540-97-6	Cyclohexasiloxane, dodecamethyl			0.01	0.26		
100-52-7	Benzaldehyde			0.01	0.25		
107-50-6	Cycloheptasiloxane, tetradecamethyl-			0.01	0.24		

Formaldehyde, a carcinogen, was detected from all three metal PLA filaments with comparable emission rates (Table 7). Though these emission rates may seem low, CDPH SM has chronic Reference Exposure Level (REL) of formaldehyde at 9 µg/m^3, which may easily be reached with multiple 3D printers operating simultaneously or a single printer operating in a smaller or less ventilated space. Acetaldehyde, as a possible carcinogen, was also detected from all metal PLA filaments with emission rates varied from below 0.1 mg/h for Metal PLA (h) to above 0.2 mg/h for Metal PLA (j). Other possible carcinogens included styrene from Metal PLA (g) and tetrahydrofuran from Metal PLA (j). The other three common chemicals among metal PLA filaments were benzyl alcohol, decanal and nonanal, which were also detected from the two green PLA filaments. In general, emission rate of individual chemical was in orders of 0.01 mg/h. Two siloxanes were emitted from Metal PLA (g) filament, which may be associated with raw filament composition or other sources. Newly found VOCs were benzene, 1,4-bis(1-methylethyl)- from Metal PLA (g), 2-propanol, 1-(2-butoxy-1-methylethoxy)- from Metal PLA (h) and (j) and tetrahydrofuran (THF) from Metal PLA (j), among which THF is a possible carcinogen. Cycloheptasiloxane, tetradecamethyl- from Metal PLA (g) was also seen from metal filament in this study.

Effect of Flame Retardant: Filament Nylon FR (k) black and Nylon (k) black were both made of nylon and chopped carbon fiber, but Nylon FR (k) had an additional flame retardant (FR) chemical added. The total particle number concentrations and size distributions during print of this filament are shown in Figure 13. The particle emission pattern was similar to the filament without FR additives shown in Figure 4, but with higher levels. Nylon FR (k) black produced about 3 times higher particle number emission rate and yield compared to Nylon (k) black, printing at the same nozzle temperature, suggesting that the FR resulted in increased emissions. The GMD of the filament with FR was slightly smaller than that without FR (Figure 3).

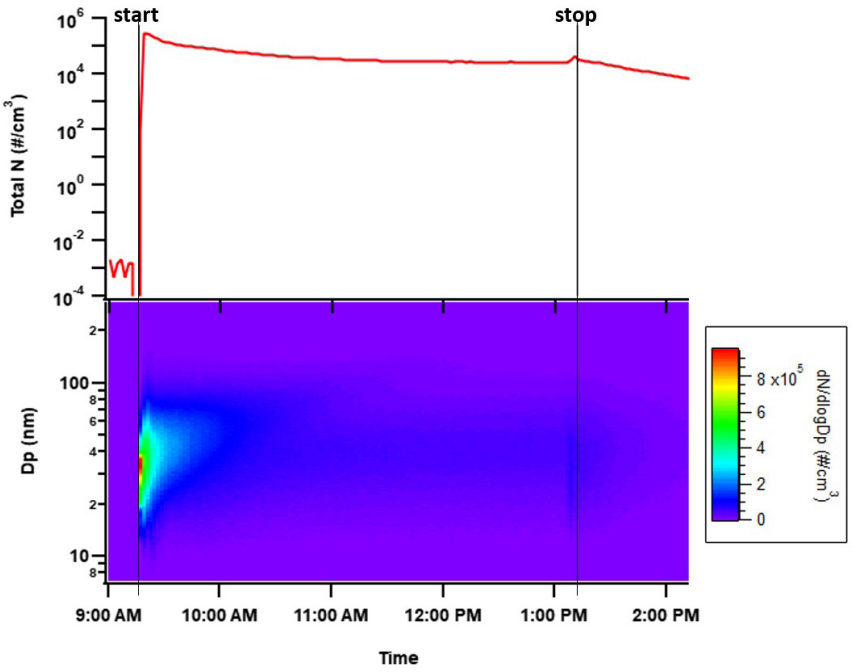

FIGURE 13. TOTAL PARTICLE NUMBER CONCENTRATIONS AND SIZE DISTRIBUTIONS IN THE CHAMBER FOR NYLON FR (K) BLACK MEASURED BY SMPS. OPS DATA WAS NOT INCLUDED SINCE PARTICLES IN THAT SIZE RANGE CONTRIBUTED LESS THAN 0.01% OF TOTAL PARTICLE NUMBER EMISSIONS. VERTICAL LINES INDICATE START AND STOP TIME OF PRINTING.

41 different chemicals were detected from Nylon FR (k) black filament, and 17 from them were listed in health-related regulation and guidance.

TABLE 8. EMISSION RATE (ER) AND MODEL ESTIMATED OFFICE CONCENTRATION (CONC.) FOR EACH CHEMICAL WITH HEALTH CONCERN (ONLY THOSE WITH EMISSION RATES OF 0.01 MG/H AND LARGER ARE INCLUDED).

CAS number	Chemical	Nylon FR (k) black	
		ER (mg/h)	Conc. (µg/m³)
105-60-2	Caprolactam	1.75	84.3
50-00-0	Formaldehyde	0.02	0.90
91-23-6	Benzene, 1-methoxy-2-nitro-	0.01	0.34
107-98-2	2-Propanol, 1-methoxy-	0.01	0.26
124-19-6	Nonyl aldehyde (Nonanal)	0.01	0.26
112-31-2	Decanal	0.01	0.24

There were 6 chemicals in the health-related lists with emission rates of 0.01 mg/h or higher, which were also detected from Nylon (k) black filament except 2-propanol, 1-methoxy- that was first seen in this study (Table 8 and 5). Formaldehyde is a carcinogen and 2-propanol, 1-methoxy- is a possible carcinogen. The emission rate of caprolactam was larger than 1 mg/h, resulting in the estimated office concentration to be larger than OEHHA's 8-hour REL (7 µg/m³); caprolactam is associated with ocular and respiratory toxicity. Other chemicals all had emission rates in order of 0.01 mg/h.

Effect of Nozzle Temperature: Nozzle temperature was found to have an exponential relationship with particle emissions for the same filament (Zhang et al. 2017). In Table 9, Pearson correlation coefficient was calculated for PLA-based filaments and overall filaments tested. The effect of nozzle temperature was less clear when comparing among different filament materials and filament brands, as these factors were also affecting emissions. Therefore, comparison for all filaments showed weaker correlation than PLA-based filaments. However, the correlation was largely driven by the one or two high emitting points. Nylon (k) black filament was found to have comparable particle emissions as the high emitting nylon that running at nozzle temperature of 270 °C.

TABLE 9. PEARSON CORRELATION COEFFICIENT (R) AND P-VALUE FOR NOZZLE TEMPERATURE VS. DIFFERENT PARTICLE EMISSION PARAMETERS

	Particle number emission rate	Particle number yield	GMD
5 PLA-based filaments			
R	0.997	0.989	-0.535
p-value	<0.05	<0.05	0.35
All 8 filaments			
R	-0.019	0.545	-0.363
p-value	0.97	0.16	0.38

VOC emissions were also affected by nozzle temperature; the higher nozzle temperature, the higher TVOC emission rates (Figure 14). The Pearson correlation coefficient of nozzle temperature and TVOC emission rate was 0.86 with a p-value of 0.005.

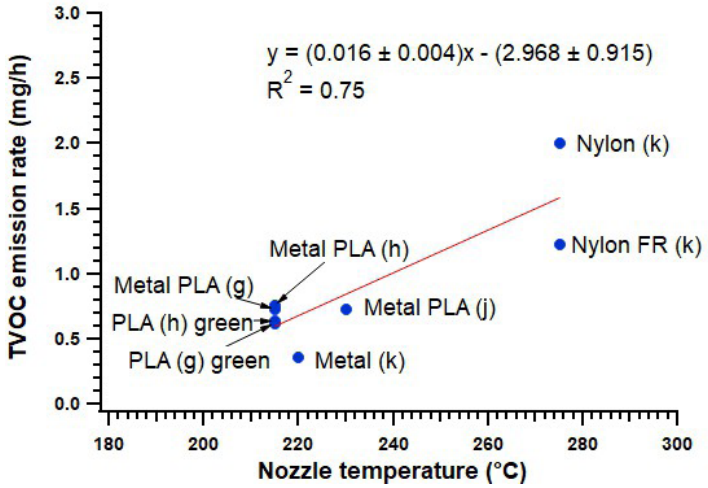

FIGURE 14. EFFECT OF NOZZLE TEMPERATURE ON TVOC EMISSION RATE.

3.5 Particle toxicity

The DTT assay was applied to particle samples collected from four different filaments, which included two ABS (brand c and d), one PLA (brand c) and one Nylon (brand i). Detailed results are published in Zhang et al. 2019. All four particle samples analyzed showed statistically significant higher responses than blanks.

The measured OP^{DTT}_{m} of particles showed similar response levels for similar doses, which were comparable or relatively lower than those of ambient fine particulate matters ($PM_{2.5}$) (Figure 15). However, exposure to 3D printing may be higher than typical ambient $PM_{2.5}$ levels, especially in poorly ventilated spaces or in close proximity to the operating printers.

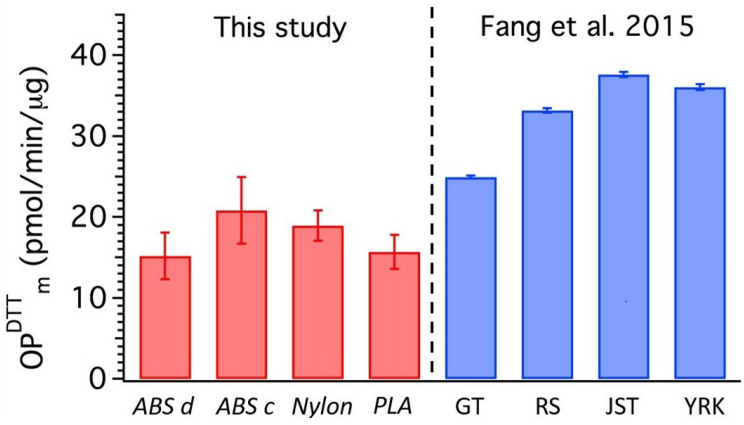

FIGURE 15. OP^{DTT}_M MEASURED BY DTT ASSAY FOR THE FOUR PARTICLE SAMPLES, COMPARED TO OP^{DTT}_M OF AMBIENT AIR $PM_{2.5}$ RESULTS FROM DIFFERENT MONITORING SITES (FANG ET AL. 2015). ERROR BAR FOR THIS STUDY REPRESENTS STANDARD DEVIATION OF THREE REPEATED MEASUREMENTS, ERROR BAR FOR FANG ET AL. 2015 REPRESENTS STANDARD DEVIATION OF DATA FOR EACH MONITORING SITE (GT, RS, JST AND YRK).

Potential adverse health effects depend not only on OP^{DTT}_m, but also on actual exposure levels, or particle concentrations, which were included in the parameter of OP^{DTT}_v. First, particle concentrations in different indoor environments were calculated using the emission factors obtained from the chamber study and the indoor air model, and then OP^{DTT}_v was calculated by OP^{DTT}_m times predicted particle concentration. When considering emission levels (Figure 16), ABS filaments had higher responses than the PLA filament due to their much higher emission levels (Table 2).

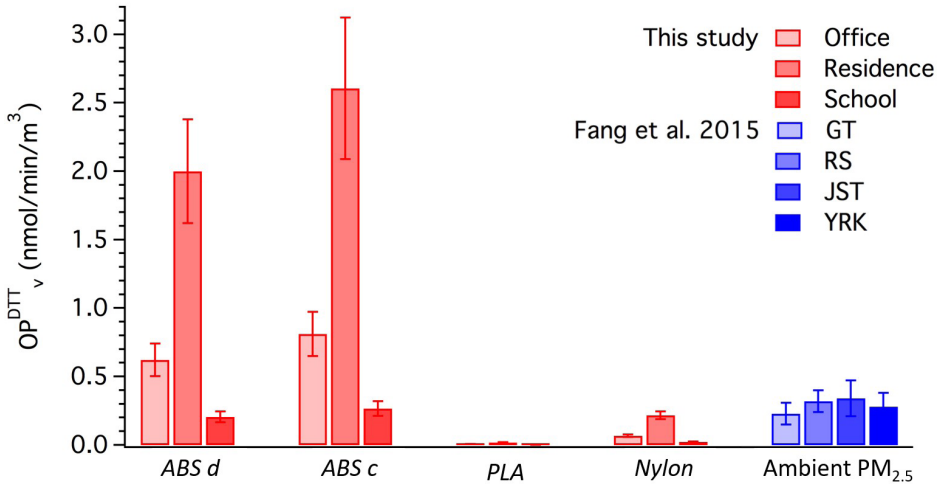

FIGURE 16. OP^{DTT}_V CALCULATED USING OP^{DTT}_M MEASURED IN CHAMBER STUDY AND MODEL PREDICTED 3D PRINTER PARTICLE CONCENTRATIONS IN OFFICE, RESIDENCE, AND SCHOOL SETTINGS FOR EACH FILAMENT IN RED, COMPARED TO PREVIOUS AMBIENT AIR $PM_{2.5}$ STUDY AT VARIOUS MONITORING SITES IN BLUE.

The school classroom environment showed the lowest OP^{DTT}_v due to a larger space and better ventilation, while the residential home had the smallest space and lowest ventilation, resulting in the highest OP^{DTT}_v (Figure 15). In addition, estimated exposure to ABS filament emissions in office and residential settings had a higher OP^{DTT}_v than ambient $PM_{2.5}$, while the school estimated exposure was comparable to ambient data; PLA showed much lower OP^{DTT}_v than ambient $PM_{2.5}$ due to its much lower emission level (Figure 16).

3.6 Metal composition of filaments and particles

Preliminary results from ICP-MS metal analysis has been obtained for the three metal PLA filaments; bronze metal PLA brand h, g and j, on both the filament material and emitted particles. Note that bronze is a mixture containing mostly copper, with tin the next major metal, and lower levels of a range of other elements such as aluminum, manganese, nickel or zinc, and sometimes non-metals or metalloids such as arsenic, phosphorus or silicon.

All 23 elements detected from raw filaments are listed in Table 10. < MDL means concentrations was below method detection limit (MDL) for all three replicates, and any value in italic was above MDL, but below method reporting limit (MRL) for at least two of the replicates. For Metal PLA (h) bronze, a pure PLA filament, there was no Cu detected, but low level of Sn was present in the filament. In addition, other common metal additives like Na, Mg, Al, Ca, K, Ti were detected; especially Fe was detected in high concentrations, which can present as a coloring dye. As expected, Cu was detected in high levels in Metal PLA (g) bronze and Metal PLA (j) bronze, which contained 25% to 80% of bronze powder, while Sn levels in Metal PLA (g) bronze seemed to be lower than expected. In Metal PLA (g) bronze, other metals like Na, Ca, and Zn were also detected in moderate levels. Metal PLA (j) bronze had low levels of other elements except for Ni and P.

TABLE 10. METAL CONCENTRATIONS IN RAW FILAMENTS

	Metal PLA (h) bronze No bronze (µg/g)	**Metal PLA (g) bronze 25% bronze (µg/g)**	**Metal PLA (j) bronze 80% bronze (µg/g)**
Sodium (Na)	52.8 ± 0.5	72.6 ± 7.1	*17.9 ± 1.1*
Magnesium (Mg)	90.4 ± 1.8	*4.40 ± 0.30*	22.3 ± 0.8
Aluminum (Al)	421 ± 4	32.3 ± 0.5	*6.40 ± 1.90*
Silicon (Si)	450 ± 8	*19.2 ± 1.1*	35.5 ± 2.5
Phosphorus (P)	< MDL	*22.5 ± 1.0*	2448 ± 108
Potassium (K)	240 ± 4	6.26 ± 6.84	< MDL
Calcium (Ca)	88.4 ± 0.9	264 ± 3	< MDL
Titanium (Ti)	133 ± 44	< MDL	1.12 ± 0.02
Chromium (Cr)	1.40 ± 0.11	*0.53 ± 0.15*	1.14 ± 0.32
Manganese (Mn)	2.91 ± 0.05	< MDL	< MDL
Iron (Fe)	**1272 ± 9**	*19.0 ± 1.2*	*19.1 ± 1.6*
Cobalt (Co)	*0.06 ± 0.001*	< MDL	1.97 ± 0.06
Nickel (Ni)	*0.37 ± 0.06*	< MDL	261 ± 10
Copper (Cu)	< MDL	**18000 ± 336**	**708000 ± 32900**
Zinc (Zn)	< MDL	6040 ± 103	23.6 ± 0.3
Arsenic (As)	< MDL	< MDL	20.6 ± 0.4
Strontium (Sr)	*0.11 ± 0.002*	0.27 ± 0.004	*0.10 ± 0.04*
Molybdenum (Mo)	*0.08 ± 0.001*	< MDL	< MDL
Cadmium (Cd)	< MDL	*0.06 ± 0.005*	< MDL
Tin (Sn)	37.2 ± 0.6	31.3 ± 0.3	**89800 ± 4200**
Antimony (Sb)	< MDL	< MDL	5.21 ± 0.15
Barium (Ba)	0.91 ± 0.10	< MDL	0.92 ± 0.04
Lead (Pb)	< MDL	< MDL	24.1 ± 0.4

Particles emitted from these filaments were also analyzed using the same method, detected element concentrations in emitted particles are listed in Table 11. B, Si, Cu, and Sn were detected in higher levels than the other elements, from all these filaments, whether they contained bronze powder or not. Concentrations of Si were significantly higher than other elements. Boron, which was not detected in any of the filament raw materials, was present in all particle samples. This indicated components from sources other than filaments may be transferred to particles, potential sources may include printer parts such as the extruder nozzle, gears feeding the filament or electrical wires.

TABLE 11. METAL CONCENTRATIONS IN EMITTED PARTICLES (BLANK WAS SUBTRACTED FROM SAMPLE)

	Metal PLA (h) bronze No bronze (µg/g)	Metal PLA (g) bronze 25% bronze (µg/g)	Metal PLA (j) bronze 80% bronze (µg/g)
Boron (B)	45.4	176	116
Silicon (Si)	4900	12300	8820
Calcium (Ca)	147	-	44.8
Manganese (Mn)	0.62	0.83	4.85
Copper (Cu)	139	393	210
Arsenic (As)	1.15	0.64	4.52
Strontium (Sr)	1.55	1.55	0.75
Tin (Sn)	92.1	170	112
Lead (Pb)	4.59	10.3	5.68

Using measurement results from filament and particle, ratio of metal partitioned from filament to particle was calculated based on emission rate using the equation below, assuming elements in particle were from filament (Table 12).

$$Ratio_X = \frac{metal\ X\ in\ emitted\ particle}{metal\ X\ in\ raw\ filament} = \frac{\frac{\mu g\ metal\ X\ in\ particle}{g\ particle} \times \frac{g\ particle\ emitted}{g\ filament\ used}}{\frac{\mu g\ metal\ X\ in\ filament}{g\ filament}}$$

$$= \frac{data\ in\ table\ 6\ for\ metal\ X \times particle\ mass\ emission\ yield\ for\ the\ filament}{data\ in\ table\ 5\ for\ metal\ X}$$

$$= \frac{\mu g\ metal\ X\ in\ particle}{\mu g\ metal\ X\ in\ filamnet} \times \frac{10^6\ \mu g}{g} = \frac{\mu g\ metal\ X\ in\ particle}{g\ metal\ X\ in\ filamnet} = ppm$$

TABLE 12. RATIO (PPM, OR MG/G) OF METAL TRANSFERRED FROM FILAMENT TO PARTICLE

	Metal PLA (h) bronze No bronze	Metal PLA (g) bronze 25% bronze	Metal PLA (j) bronze 80% bronze
Boron (B)	Not present in filament	Not present in filament	Not present in filament
Silicon (Si)	39.1	2480	825
Calcium (Ca)	5.97	-	Not present in filament
Manganese (Mn)	0.76	Not present in filament	Not present in filament
Copper (Cu)	Not present in filament	0.08	0.001
Arsenic (As)	Not present in filament	Not present in filament	0.73
Strontium (Sr)	52.6	22.3	25.8
Tin (Sn)	8.89	21.0	0.004
Lead (Pb)	Not present in filament	Not present in filament	0.78

Si was found to have the highest ratio, 39.1 ppm for brand h, 2480 ppm for brand g and 825 ppm for brand j, assuming all Si in particles was from filaments. However, Si is widely used in industrial and consumer products including lubricant and may be released during print. Sr was detected in low levels in both filament and particle, but it had a relatively high transfer ratio for all filaments (22.3 to 52.6 ppm). Sn showed an 8.89 ppm partition ratio for brand h and 21.0 ppm for brand g, but was very low (0.004 ppm) for brand j that had the highest Sn concentration in the filament. Partition for Cu was also low with 0.08 ppm for brand g and 0.001 ppm for brand j. Other elements that had low concentrations in filaments also had low partition ratios. The results indicated bronze powder (mainly copper and tin) was not likely the source or driving factor of particle emissions for metal added PLA filaments, but as discussed above, other unknown additives were producing particles with a combined effect of nozzle temperature.

4. CONCLUSION

Continuous research on particle emissions from 3D printing using methods established in prior research (Zhang et al. 2017) have found that thermoplastic filaments tended to emit higher levels of small particles comparing to metal filaments, when printing at comparable nozzle temperatures. Thermoplastic based filaments that contained various additives were often operated at differing nozzle temperatures, which affectd particle emissions, but in some cases additives had additional effects and in other cases no effects. Green PLA filaments were found to emit more particles than a red PLA filament at 5 °C higher nozzle temperature. The metal PLA printing at a higher nozzle temperature was found to have more particle emissions than the other PLA-based filaments. Flame retardants resulted in an increase of particle emission rate and a slightly decrease in particle mean size when printing at the same nozzle temperature as the same base material filament without flame retardants. A filament of nylon with added carbon fibers was found to have comparable emissions as a pure nylon filament running at comparable nozzle temperature, but higher than a nylon filament running at lower temperature. In general, as found in our previous research, a higher nozzle temperature was associated with higher emissions, however other factors, such as different filament materials, filament brands and additives also affected particle emissions in complex ways. Generation and analysis of larger data sets are needed to sort out which parameter have the greatest effect on particle emissions, which is a future research topic.

The most emitted individual VOCs were associated with filament base material, including lactide from PLA-based filaments and caprolactam from nylon-based filaments. Total VOC emission rates were associated with filament material and nozzle temperature, with the highest for nylon-based filaments run at 275 °C, and then PLA-based filaments run at 210 – 230 °C, and lowest for the metal filament run at 220 °C. Emitted chemicals with health concern mostly included formaldehyde, acetaldehyde, decanal, nonanal, some siloxanes and caprolactam. 6 VOCs with health concern not seen from the previous study were detected. Benzene, 1,4-bis(1-methylethyl)-, 2-propanol, 1-(2-butoxy-1-methylethoxy)-, and tetrahydrofuran (THF, possible carcinogen) were from PLA-based filaments; benzene, 1-methoxy-2-nitro- (possible carcinogen) and 2-propanol, 1-methoxy- were from nylon-based filaments; and cycloheptasiloxane, tetradecamethyl- from both the 80% bronze PLA and the metal filament. In general, emission rates of total VOC and individual VOCs were lower than the criteria listed in ANSI/CAN/UL 2904.

Particles emitted from ABS, PLA and nylon filaments were found to induce adverse health impacts as assessed via a cell-free toxicity assay. Results combining indoor air modeling showed exposure to 3D printer emit particles can be a larger health concern than ambient fine particles when operating in poorly ventilated or confined areas, which indicated the importance of dilution as a way of reducing exposures. In addition, particle size is essential in understanding particle health impacts. Our study found filaments with high particle number emission rates and yields were usually associated with lower particle mean sizes, which may result in more health concerns, as small particles are easier to transport and pass through cell membranes. This is a possible topic for future research focusing on the health impact of emitted particles and ways of assessing it.

Metals like copper and tin were not likely to be transferred from filament to particle as they tended to remain in the solid phase rather than evaporate or emitted from filament. This indicated the particle emissions may be associated with additives other than metals. However, other sources like printer parts or chemicals may contribute to particle composition like boron and silicon. More study is needed to understand the source of metals in 3D printer-emitted particles. Additional metal analysis will study the metal composition of particles emitted from the metal filament and compare the differences between a polymer based filament and a metal powder based filament. Future study will also investigate particle toxicity and the relationship between particle metal composition and particle toxicity.

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