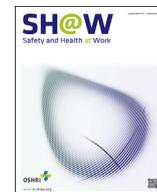




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### Original Article

# Insights Into Emissions and Exposures From Use of Industrial-Scale Additive Manufacturing Machines

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### ABSTRACT

**Background:** Emerging reports suggest the potential for adverse health effects from exposure to emissions from some additive manufacturing (AM) processes. There is a paucity of real-world data on emissions from AM machines in industrial workplaces and personal exposures among AM operators.

**Methods:** Airborne particle and organic chemical emissions and personal exposures were characterized using real-time and time-integrated sampling techniques in four manufacturing facilities using industrial-scale material extrusion and material jetting AM processes.

**Results:** Using a condensation nuclei counter, number-based particle emission rates (ERs) (number/min) from material extrusion AM machines ranged from  $4.1 \times 10^{10}$  (Ultem filament) to  $2.2 \times 10^{11}$  [acrylonitrile butadiene styrene and polycarbonate filaments). For these same machines, total volatile organic compound ERs ( $\mu\text{g}/\text{min}$ ) ranged from  $1.9 \times 10^4$  (acrylonitrile butadiene styrene and polycarbonate) to  $9.4 \times 10^4$  (Ultem). For the material jetting machines, the number-based particle ER was higher when the lid was open ( $2.3 \times 10^{10}$  number/min) than when the lid was closed ( $1.5\text{--}5.5 \times 10^9$  number/min); total volatile organic compound ERs were similar regardless of the lid position. Low levels of acetone, benzene, toluene, and *m,p*-xylene were common to both AM processes. Carbonyl compounds were detected; however, none were specifically attributed to the AM processes. Personal exposures to metals (aluminum and iron) and eight volatile organic compounds were all below National Institute for Occupational Safety and Health (NIOSH)-recommended exposure levels.

**Conclusion:** Industrial-scale AM machines using thermoplastics and resins released particles and organic vapors into workplace air. More research is needed to understand factors influencing real-world industrial-scale AM process emissions and exposures.

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## 1. Introduction

Additive manufacturing (AM) is the process of joining materials to make physical objects from 3-dimensional (3-D) model data, usually layer upon layer [1]. Economic forecasts indicate that AM will continue to grow and gain value in manufacturing [2]. With this growth, there is also potential for AM machines to emit contaminants into occupational environments resulting in worker

exposure [3,4]. Emerging evidence indicates that inhalation of emissions from one type of AM process, referred to as material extrusion, is associated with adverse respiratory and cardiovascular health effects. House et al [5] reported a case of work-related asthma in a worker exposed to emissions from material extrusion of acrylonitrile butadiene styrene (ABS) filament. In a survey of AM workers who primarily used material extrusion machines, 59% reported respiratory symptoms [6]. In an animal toxicology study,

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rats who inhaled ABS emissions from a material extrusion machine developed acute hypertension [7]. It is unclear if these respiratory and cardiovascular endpoints are associated with inhalation of airborne particles, organic vapors, or both.

Herein, desktop scale refers to machines with relatively small build volumes, limited control over applicable build parameters (e.g., build chamber or temperature), and/or slower print speed, whereas industrial scale refers to machines with relatively larger build volumes, defined control over build parameters, and relatively faster print speeds. With few exceptions, emission assessments of AM machines to date have mostly focused on material extrusion, a process by which a solid thermoplastic filament is heated and then extruded through a nozzle onto a build plate to make an object. More specifically, these studies have focused on inexpensive desktop-scale printers using fused deposition modeling (FDM) technology (commonly referred to as “3-D printers”) which were placed in a chamber or small room to simulate a work environment. Studies of these desktop-scale FDM machines indicate that ultrafine particles (UFPs, diameter <100 nm) and volatile organic compounds (VOCs) are released during printing [8–27]. Emerging evidence indicates that UFP and VOC emissions could also occur during operation of industrial-scale material extrusion machines [3]. Another type of AM process is material jetting, in which an object is built by dispensing liquid resin onto a build platform via hundreds of nozzles, curing the polymer using an ultraviolet laser, and repeating the process layer by layer. To our knowledge, only industrial-scale material jetting machines are commercially available, and there are no reports on whether they emit particles or VOCs during operation.

Based on the reviewed literature and the larger scale and throughput of industrial machines, it is reasonable to expect that exposures to particles and vapors may occur in occupational settings where industrial-scale AM processes are used. Despite early indications of potential for adverse health effects from inhalation of these emissions, there is little understanding of the magnitude and characteristics of emissions and exposures from industrial-scale AM processes in workplaces [3,4]. Such data are crucial, so that informed decisions can be made with regard to risk management. Hence, the purpose of this study was to evaluate emissions and exposures in multiple workplaces using industrial-scale material extrusion and material jetting AM processes.

## 2. Methods

Assessments were performed at four facilities designated A–D. Table 1 summarizes the AM machines, consumables (filament or resin type and color) in use at the time of sampling, and machine-operating conditions.

**Table 1**  
Summary of additive manufacturing machines by facility

Facility	Machine				Feedstock	Color	Operating conditions (°C)		
	Manufacturer	Model	Type	Description			Extruder	Build plate	Chamber
A	Stratasys	Fortus 250mc	ME	Sealed door	ABS	Ivory	265	95	70
					Support	N/A	265	95	70
	Stratasys	Fortus 900mc	ME	Sealed door	PC	White	270	145	140
B	Stratasys	Objet Connex 350	MJ	Hinged lid	TangoBlack+	Black	N/A	N/A	N/A
					VeroClear	Clear	N/A	N/A	N/A
					Support	N/A	N/A	N/A	N/A
C	Stratasys	Fortus 450mc	ME	Sealed door	PC	White	300	180	180
					Support	N/A	300	180	180
D	Stratasys	Objet Connex 350	MJ	Hinged lid	TangoBlack+	Black	N/A	N/A	N/A
					VeroWhite+	Opaque	N/A	N/A	N/A
					VeroClear	Clear	N/A	N/A	N/A
					Support	N/A	N/A	N/A	N/A

ABS, acrylonitrile butadiene styrene; ME, material extrusion; MJ, material jetting; N/A, parameter not applicable; PC, polycarbonate.

At Facility A, characterization of material extrusion machine emissions and personal air sampling were performed on two consecutive days. This building had several rooms, each containing a different type of AM machine, but we focused on a 66-m<sup>3</sup> room that contained three industrial-scale material extrusion machines (all from Stratasys Inc., Eden Prairie, MN, USA). None of the industrial-scale AM machines in the other rooms were in operation on the sampling days. One machine used ABS filament (Part Number P430) with butyl acrylate–methacrylic acid–styrene polymer support material (SR30), another used polycarbonate filament (PC, Part Number PC10) with methyl methacrylate–methacrylic acid copolymer support material (Part Number SR10), and the third machine used Ultem filament (Part Number 9085) with phenol 4,4'-(1-methylethylidene)bis-polymer with 1,1'-sulfonylbis[4-chlorobenzene] support material (Part Number 9085) (all from Stratasys Inc.). The door to each industrial-scale machine was closed and remained sealed during printing. An air conditioning unit was present in the room but was not operational during sampling. No local exhaust ventilation (LEV) designed to remove emissions directly from the printer source or general ventilation (open windows, etc.) existed in the room. This room was staffed intermittently by one employee.

At Facility B, characterization of material jetting machine emissions and personal air sampling were performed on two consecutive days. This facility contained several rooms, each housing a different type of AM machine, although we only sampled in a 90-m<sup>3</sup> room with an industrial-scale material jetting 3-D machine that had a hinged lid (Objet 350 Connex 3; Stratasys Inc.). On the first day, no other AM machines were in operation, but on the second day, a nylon powder printer was in use in another room. Resins used were a support material (Part Number SUP 705), TangoBlack+ (Part Number FLX980), and VeroClear (Part Number RGD810) all from Stratasys Inc. On both the days, the machine was operated with its lid open. Filtered and conditioned fresh air was supplied to the room via one 32 × 32 cm supply vent (equipment was not available to measure flow rate at the time of the survey); there was no return air vent, but there was a louvre in a wall shared with the building hallway. There was no LEV for the printer. This room was intermittently staffed by one employee.

At Facility C, emissions from an industrial-scale material extrusion machine (Stratasys Inc.) located in a high bay were monitored for one day. This machine was printing PC filament with support material (Part Number PC-S, Stratasys Inc.). Several metal working machines (some of which were operating during sample collection) were also present in the high bay. The AM machine doors remained sealed during operation. This room did not have LEV for the AM machine or the metal working machines; however,

the bay doors were open to the outdoors during printing which provided natural air movement in the room. One employee staffed the high bay, although only intermittently.

At Facility D, emissions from a material jetting machine were monitored on two different days. This research facility contained a 466-m<sup>3</sup> engineering laboratory that housed the same model of material jetting machine (Objet 350 Connex 3; Stratasys Inc.) and used the same support material and resins as Facility B, plus VeroWhite + resin (Part Number RGD835, Stratasys Inc.). This machine had a tight-sealing hinged lid that sealed to enclose the build platform. There was no LEV for the printer. The air exchange rate in the laboratory was 2/hr during sampling.

### 2.1. Emissions characterization

The availability of real-time particle sampling instruments was limited, and not all devices were used on all surveys. At Facilities A and C, an isopropanol-based condensation particle counter (CPC, Model 3007; TSI Inc., Shoreview, MN, USA) with a size ranging from 10 to >1000 nm was used to determine particle number concentration. At Facilities B and D, an isopropanol-based condensation nuclei counter (P-Trak, Model 8525; TSI Inc.) with a size ranging from 20 to 1000 nm was used to determine particle number concentration. An optical particle counter (OPC) (Model 1.108; GRIMM Aerosol Technik GmbH & Co. Ainring, Germany) was used to determine particle size distribution from 0.3 to >20 µm. At Facility D only, a real-time fast mobility particle sizer (FMPS) (Model 3091; TSI Inc.) was used to measure particle size distribution from 5.6 to 560 nm. All real-time instruments were factory-calibrated before use. Measurements were data-logged at a frequency of 1 second for the nuclei counters and FMPS and 6 seconds for the OPC. Conductive silicone tubing (Part No. 3001788; TSI Inc.) having a length between 0.1 and 0.5 m was connected to the particle-sampling instrument inlets. According to Jankovic et al [28], losses of nanoscale particle in nonconductive tubing having a length of 0.7 m can be up to 10%. Hence, the use of 0.1- to 0.5-m-long conductive tubing in our studies is expected to minimize particle losses in the sample tubing to <10%, so no correction was made to the measurements. In addition, particles were collected onto 0.8-µm track-etched polycarbonate filters (SKC Inc., Eighty Four, PA, USA) mounted in close-faced 37-mm cassettes by drawing air through the membrane at 4.0 L/min using calibrated sampling pumps. Filters were analyzed using a field emission-scanning electron microscope (FE-SEM, S-4800; Hitachi, Tokyo, Japan) to evaluate size and morphology and by energy-dispersive X-ray analysis (Quantax, Bruker Scientific Instruments, Berlin, Germany) to identify elemental constituents.

For gas-phase emissions, a real-time total organic vapor (TVOC) photoionization detector (RAE Systems, San Jose, CA, USA) was used to monitor organic vapor concentrations, and a real-time gas-sensitive semiconductor sensor (Model S500; Ozone Solutions, Hull, IA, USA) was used to monitor ozone concentrations. The TVOC monitor was factory-calibrated using isobutylene and span-checked with isobutylene before use. Soil vapor intrusion thermal desorption (TD) tubes (Perkin Elmer, Waltham, MA, USA) connected to low-flow sampling pumps (calibrated to 0.050 L/min for 2-hour sample collection or 0.030 L/min for 6-hour sample collection) were used to measure specific VOC concentrations. All sampler inlets were positioned at breathing zone height and collocated with the aerosol monitors. TD tubes were analyzed using a thermal desorption unit (ATD650; Perkin Elmer, Waltham, MA, USA) connected to a gas chromatograph-mass spectrometer (GC-MS) as described in the Supplemental File. In addition, 450 mL of Silonite-coated evacuated canister samples (Model 29-MC450SQT; Entech Instruments Inc., Simi Valley, CA, USA) were collected at

Facility D only [29]. Details of the canister analytical method are provided in the Supplemental File. Both TD tubes and canister samplers were analyzed for 15 different VOCs that have been observed previously in chamber emissions studies of desktop-scale 3-D printers. Background-corrected concentrations for individual VOCs were reported only if the measured level exceeded background. Sampling for gas-phase carbonyl compounds was performed by drawing air using a calibrated sampling pump at 4.0 L/min into either 25 mL of deionized water in a 60-mL Teflon bubbler (Savillex; Eden Prairie, MN, USA) or into 40 mL of deionized water in a 375-mL bubbler depending on sampling duration. After collection, samples were derivatized and analyzed using GC-MS (see Supplemental File).

All real-time and time-integrated sampler inlets were positioned at breathing zone height within 1 m of the AM machines (i.e., at locations representative of where the AM operator normally occupied). Samples to establish background levels of particles and VOCs were collected for up to 30 minutes before the start of printing. Then, samples were collected to capture emissions from the start of printing through the postprinting phase to capture particle and VOC levels in a room. Sampling durations varied depending on the type of sample collected, facility, type of AM process, and size of the object that was built.

### 2.2. Personal sampling

Personal breathing zone samples for metals and VOCs were collected at Facilities A and B only. Prior laboratory studies have reported iron, nickel, chromium, and zinc in particulate emissions from desktop-scale material extrusion printers using ABS and PL filaments [7,21,27]. As such, we used nanoparticle respiratory deposition (NRD, Zefon International, Inc., Ocala, FL, USA) samplers to collect metal-containing particles with diameters from about 15 to 300 nm [30]. NRD samplers were operated using a personal sampling pump calibrated to 2.5 liters/min, and collection substrates were analyzed for metals using inductively coupled plasma-mass spectrometry (ICP-MS) in accordance with National Institute for Occupational Safety and Health (NIOSH) Method 7303. VOCs were sampled using passive diffusion badges (TraceAir 521; Assay Technology, Livermore, CA, USA). Badges were analyzed by gas chromatography-mass spectrometry (GC-MS) by NIOSH Methods 1500, 1501, and 2500. Personal sampling was approved by the Health Research Ethics Committee of the North-West University (Ethics clearance number: NWU-00004-16-A1).

### 2.3. Data analysis

Emission rates (ERs) were calculated using a model developed to describe emission from sources in indoor residential and occupational environments, including AM machine emissions in a room [19,31]:

$$\text{Equation 1. } ER = V \cdot \left[ \frac{C_{\text{peak}} - C_{\text{out}}}{\Delta t} + \overline{AER} + k \cdot \bar{C}_{\text{in}} - AER \cdot C_{\text{out}} \right] \quad (1)$$

In this equation,  $V$  = the room volume,  $C_{\text{peak}}$  = peak concentration of the contaminant during printing,  $C_{\text{out}}$  = the outdoor concentration of the contaminant during printing (assumed to be equal to the background concentration measured in each printer room),  $\Delta t$  = the time difference between  $C_{\text{peak}}$  and  $C_{\text{out}}$ ,  $\overline{AER} + k$  = average total removal rate of the contaminant ( $AER$  = air exchange rate in the room,  $k$  = rate of contaminant loss due to deposition onto surfaces), and  $\bar{C}_{\text{in}}$  = the average concentration of the contaminant during printing. This model accounts for

background particle concentrations in a room, the average rate of removal of particles by air exchange in the room, and loss due to deposition onto surfaces. It is assumed that the average concentration measured during background remains constant during printing, which was reasonable given the characteristics of all rooms (described previously). Details of the model are provided in the [Supplemental File](#).

For the material jetting machines at Facilities B and D, the masses of resin used to printing objects was known to us, which permitted normalization of emissions to mass printed. To determine particle emission yield (particle number or  $\mu\text{g}$  TVOC/g printed), the ER (particle number or  $\mu\text{g}$  TVOC/min) determined using Eq. 1 was multiplied by print time (min) to calculate the total number of particles or mass of TVOC emitted during printing, which was normalized by the mass of printed resin (g printed). Given the limited number of print jobs sampled and the exploratory nature of these surveys, only descriptive comparisons of ERs and yields are given, and no attempt was made to analyze the results statistically.

### 3. Results

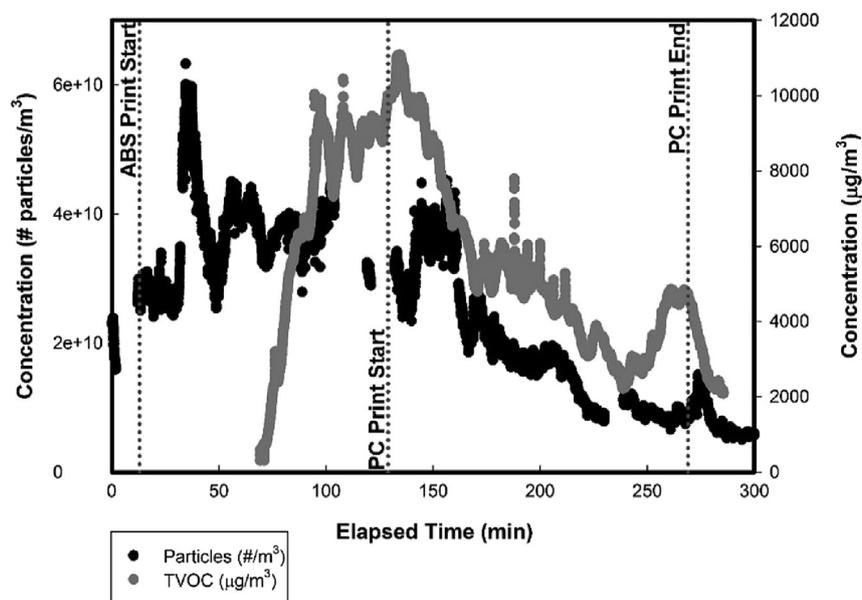
[Fig. 1](#) is a representative example of the influence of material extrusion AM machine operation on room particle number and TVOC concentrations. After background, both particle and organic vapor concentrations increased as printing commenced and decayed after printing was complete. At Facility A, the ERs during material extrusion printing with ABS and PC (Day 1) exceeded that for Ultem (Day 2) based on the number of particles measured using the CPC ( $2.2 \times 10^{11}$  number/min vs.  $4.1 \times 10^{10}$  number/min) and with a diameter  $>0.3 \mu\text{m}$  measured using the OPC ( $2.7 \times 10^5$  number/min vs.  $9.6 \times 10^4$  number/min). The TVOC ER value for printing with ABS and PC was a factor of five lower than when using Ultem™ filament ( $1.9 \times 10^4 \mu\text{g}/\text{min}$  vs.  $9.4 \times 10^4 \mu\text{g}/\text{min}$ ). In Facility C, the high bay door was open during operation of the AM machine, which created natural ventilation and diluted any emissions (i.e., none of the real-time data had a pattern consistent with emissions shown in [Fig. 1](#)). Discussions with facility staff revealed that

opening of the high bay door during printing was a common practice. Hence, consideration should be given to the impact of this type of practice on monitoring efforts in future workplace assessments. In addition, none of these facilities used LEV systems to control emissions, which precluded our ability to assess the efficacy of these systems.

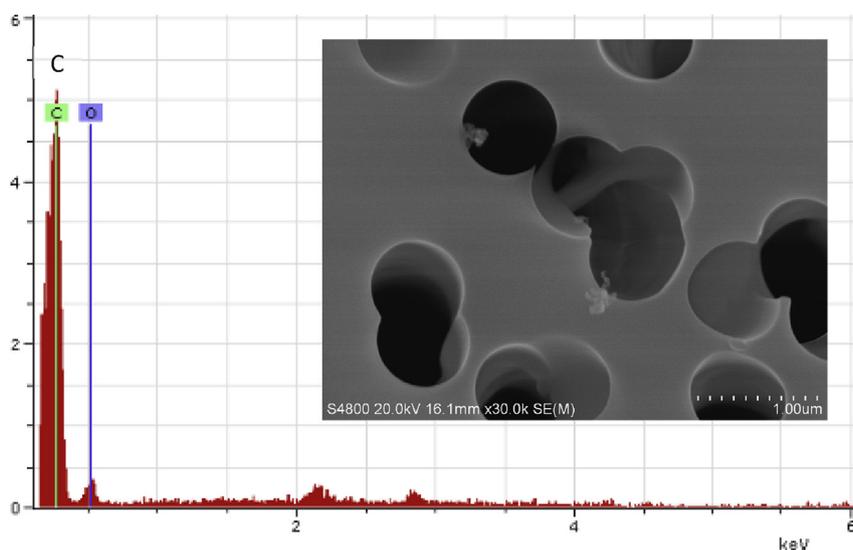
[Fig. 2](#) is an FE-SEM image of particles collected in Facility D while operating a material jetting machine. Particles were clusters of UFPs composed of carbon. As shown in [Table 2](#), the number-based particle ER values were in an order of magnitude higher when the material jetting machine was operated with the lid open (Facility B) than when it was closed (Facility D), whereas the TVOC yield values were similar regardless of the lid position. The FMPS instrument was only available while sampling in Facility D, and the calculated particle number ER values were higher than calculated using the P-Trak data. The higher rates are attributed to the fact that the FMPS can measure particle sizes down to 5.6 nm, but the P-Trak has a minimum size cutoff of 20 nm and hence cannot count these smaller particles measured by the FMPS. The mass of resin consumed during printing was known, and total particle and TVOC emissions were normalized to mass to determine yields values ([Table 2](#)). Number-based particle yield values for the P-Trak and OPC were higher when the printer lid was open than when it was closed; TVOC yield values were similar regardless of the lid position.

#### 3.1. Quantification of individual VOCs

Six different VOCs (acetone, benzene, styrene, toluene, *m,p*-xylene, and *o*-xylene) were measured on TD tube area samples during operation of the industrial-scale material extrusion machines at Facilities A and C. Concentrations of any individual VOC were at most 6% of their applicable NIOSH Recommended Exposure Limit (REL). At Facility A, during printing with ABS and PC (Day 1), the concentrations of individual VOCs were higher in the morning, reflecting a build-up of contaminants in the room during printing (e.g., acetone ranged from 5.7 to 33.1  $\text{mg}/\text{m}^3$ ), and decreased in the afternoon after the print jobs were complete (e.g., acetone ranged



**Fig. 1.** Real-time particle and total volatile organic compound (TVOC) concentrations in Facility A. Initially, one machine was printing using acrylonitrile butadiene styrene (ABS) filament, and after about 120 minutes, a second machine began printing using polycarbonate (PC) filament. Background monitoring was from  $t = 0$  to 5 min. ABS printing began at  $t = 5$  min and continued for 650 min (plot truncated at  $t = 300$  min for brevity, but decay trend continued for the remainder of sampling). PC printing was from  $t = 120$  to 260 min.



**Fig. 2.** Field emission–scanning electron micrograph and energy-dispersive X-ray analysis spectra of particles collected during industrial-scale material jetting additive manufacturing printing (Facility D).

from 2.5 to 15.7 mg/m<sup>3</sup>). On the second day, just Ultem filament was extruded, and only acetone (0.4 mg/m<sup>3</sup>) was quantified above background.

Results of TD tube area samples revealed that five different VOCs (acetaldehyde, acetone, benzene, ethanol, toluene and *m,p*-xylene) were common to room air during operation of the material jetting machines in Facility B (lid open) and Facility D (lid closed). In general, concentrations of these VOCs were similar between facilities regardless of the position of the machine lid and were at most 1.4% of their applicable NIOSH REL. The one exception was acetaldehyde (range, 14–214 μg/m<sup>3</sup>), which NIOSH considers a potential occupational carcinogen and does not have an REL [32]. Ethanol was used to clean the build platform on the material jetting machine in Facility B before operation, and the measured concentration was 10.6 mg/m<sup>3</sup> on that day, indicating that tasks in addition to printing could influence AM operator exposure.

### 3.2. Ozone and carbonyl formation

Among all facilities, the background-corrected ozone concentrations were highest in Facility A during operation of the industrial-scale material extrusion machines using ABS and PC (37 μg/m<sup>3</sup>) and Ultem (43 μg/m<sup>3</sup>) filaments. Ozone concentration when running PC at Facility C was 10 μg/m<sup>3</sup>. During operation of the

material jetting machines, room ozone concentrations rapidly increased from about 15 μg/m<sup>3</sup> to 30 μg/m<sup>3</sup> at the start of printing in Facility B (lid open), remained elevated during operation (average = 26.3 μg/m<sup>3</sup>), and decayed rapidly when printing ceased. When the material jetting machine was operated with the lid closed, ozone emissions followed the same pattern as when the lid was open; however, average concentrations were 9–11 μg/m<sup>3</sup>. The NIOSH REL for ozone is 200 μg/m<sup>3</sup> and is a ceiling value.

Ozone may react with unsaturated VOCs to form new compounds, including carbonyls [33]. While carbonyl compounds were observed (e.g., glyoxal, methylglyoxal, and 4-oxopentanal) from the collected air samples in the parts per billion range, no concentrations were observed to be greater than background levels, indicating that they were not emitted or formed during these printing processes.

### 3.3. Personal exposures to metals and VOCs

Tasks besides operation of AM machines occurred in Facilities A and B (e.g., cleaning build plates with alcohol), and employees sometimes left the machine rooms to work in other areas. As such, measured personal exposures to metals and VOCs are not solely from AM machine emissions. Personal 8-hour time-weighted average (TWA) exposures to metals measured using NRD samplers did not exceed 0.01 mg/m<sup>3</sup> for aluminum (REL = 5 mg/m<sup>3</sup> as respirable size particles) or 0.01 mg/m<sup>3</sup> for iron (REL = 5 mg/m<sup>3</sup>) at any facility.

At Facility A, personal exposures to organic vapors during material extrusion with ABS, PC, and Ultem included acetone (0.04–1.88 mg/m<sup>3</sup>), pentane (0.04–0.11 mg/m<sup>3</sup>), cyclohexane (0.01–0.04 mg/m<sup>3</sup>), ethanol (0.03–0.08 mg/m<sup>3</sup>), and naphtha (2.06–2.31 mg/m<sup>3</sup>); however, concentrations were well below their RELs of 590, 350, 1050, 1900, and 400 mg/m<sup>3</sup>, respectively. In addition, low levels of hexane (0.15–0.19 mg/m<sup>3</sup>) and benzene (0.03–0.02 mg/m<sup>3</sup>) were measured in the breathing zone when printing with ABS and Ultem, but not PC filament. At Facility B, personal exposures during material jetting machine operation also included low levels of these same chemicals, i.e., acetone (0.02–0.08 mg/m<sup>3</sup>), pentane (0.01–0.06 mg/m<sup>3</sup>), ethanol (0.52–2.02 mg/m<sup>3</sup>), and naphtha (1.53–1.71 mg/m<sup>3</sup>), as well as isopropyl alcohol (0.07–0.52 mg/m<sup>3</sup>; REL = 980 mg/m<sup>3</sup>).

**Table 2**

Emission rates and yields for industrial-scale material jetting additive manufacturing machines at Facilities B and D

Facility	Lid	Day	Metric <sup>†</sup>	Particle number <sup>†</sup>			TVOC
				P-Trak	FMPS	OPC	
B	Open	1	Rate	2.3 × 10 <sup>10</sup>	n.s.	1.1 × 10 <sup>5</sup>	2.8 × 10 <sup>4</sup>
			Yield	2.1 × 10 <sup>10</sup>	n.s.	9.8 × 10 <sup>4</sup>	2.5 × 10 <sup>4</sup>
D	Closed	1	Rate	1.5 × 10 <sup>9</sup>	2.1 × 10 <sup>12</sup>	8.5 × 10 <sup>3</sup>	4.5 × 10 <sup>4</sup>
			Yield	4.1 × 10 <sup>8</sup>	6.0 × 10 <sup>11</sup>	2.4 × 10 <sup>3</sup>	1.3 × 10 <sup>4</sup>
	Closed	2	Rate	5.5 × 10 <sup>9</sup>	1.8 × 10 <sup>11</sup>	1.1 × 10 <sup>4</sup>	2.5 × 10 <sup>4</sup>
			Yield	7.7 × 10 <sup>9</sup>	2.6 × 10 <sup>11</sup>	1.5 × 10 <sup>4</sup>	3.5 × 10 <sup>4</sup>

FMPS, fast mobility particle sizer; n.s., not sampled (instrument was not available for use at this facility); OPC, optical particle counter; TVOC, total volatile organic compound.

<sup>†</sup> P-Trak range, 20–1000 nm; FMPS range, 5.6–560 nm; OPC range, 0.3–>20 μm.

<sup>†</sup> Rate units: number (number/min), TVOC (μg/min); yield units: number (number/g printed), TVOC (μg/g printed).

#### 4. Discussion

In general, particle ERs, regardless of the type of AM process, were five to six orders of magnitude higher for particle number measured using condensation nuclei counters (P-Trak or CPC) than using the OPC instrument, indicating that the dominant particle size was below 300 nm in these workplaces. Industrial-scale material extrusion machines can extrude filaments such as Ultem which need higher build temperatures than possible in most desktop-scale machines. In Facility A, particle number–based ER values were lower, but TVOC ER values were higher when Ultem filament was printed relative to ABS and PC filaments (Table 2). To our knowledge, this was the first evaluation of Ultem filament, and these data provide important insights into the emissions profile of this material. In a previous study of material extrusion machines, a CPC was used to evaluate printer door seals and cooling fan outlets during printing but did not identify these locations as emission points [3]. As such, additional evaluations of industrial-scale AM machines are needed to understand emission points.

Results from the other observations of the same model of material jetting AM machine using the same consumables Facilities B and D suggested a decrease in particle number–based emissions when the machine was operated with its lid closed, but no impact on TVOC emissions. One potential explanation for this observation is that particles may deposit on the interior surfaces of the machine lid by electrostatic or thermophoretic mechanisms when it is in the down position, but organic vapors do not adhere to the lid. Additional sampling is necessary to confirm this explanation. At Facility B, operation of a nylon powder printer in a different room on the second day resulted in entrainment of particles into the room containing the material jetting machine, which precluded measurement of its emissions that day. Despite the absence of a thermal process, and even with the machine lid closed, particle and TVOC ER values for the material jetting machines were similar to those for the material extrusion machines. Investigation of aerosol formation mechanisms were beyond the scope of the current investigation, although one possible explanation for the observed UFP emissions is that liquid resin droplets were broken apart during jetting from the printer nozzles (approximate diameter of 50  $\mu\text{m}$ ) onto the build surface. Hence, an important finding of this study is that feedstock materials in liquid form can emit aerosols and vapors, and closure of the machine lid may not fully contain emissions.

It is somewhat difficult to compare the ER and yield results from our study with existing reports in the literature for other AM processes because most prior studies were performed in controlled laboratory chambers, and different measurement methods and equations have been used among investigators to express these metrics for particles and chemicals. For example, chamber studies of desktop-scale “3-D” printers using ABS filament report ERs that range from  $2 \times 10^8$  number/min [21] to  $2 \times 10^{11}$  number/min [14]. ERs measured for PC in chamber studies range from  $3 \times 10^9$  number/min [34] to  $\sim 4 \times 10^{10}$  number/min [9]. The upper end of the rates for ABS are on the same order of magnitude, but the rates for PC are an order of magnitude lower than we observed at Facility A during simultaneous printing with these filaments ( $2.2 \times 10^{11}$  number/min). A few studies have reported ER data for desktop-scale 3-D printers using ABS filament in different types of nonindustrial rooms (classrooms, laboratories, and offices) and estimates range from 1 to  $2 \times 10^{11}$  number/min [16,22] which is consistent with our observations. Data on TVOC ERs for ABS and PC are limited to chamber studies of desktop 3-D printers. Reported ER values for ABS range from 10  $\mu\text{g TVOC}/\text{min}$  [21] to 64  $\mu\text{g TVOC}/\text{min}$  [12], and for PC, only Azimi et al [9] have reported an ER (3  $\mu\text{g TVOC}/\text{min}$ ); these values are three orders of magnitude lower than that we measured in Facility A ( $1.9 \times 10^4$   $\mu\text{g TVOC}/\text{min}$ ) during industrial-scale AM.

##### 4.1. Chemical concentrations in workplace air

At Facilities A and C, benzene, styrene, toluene, *m,p*-xylene, and *o*-xylene were measured during operation of the material extrusion AM machines with ABS and PC filaments. Acetone was measured when printing with ABS, PC, and Ultem filaments at Facility A (but not when printing with PC filament at Facility C). Wojtyla et al [35] used thermogravimetric analysis to evaluate decomposition products of ABS filament and reported that acetone was a component of emissions. Azimi et al [9] evaluated emissions from ABS and PC filaments using a desktop-scale FDM machine in a chamber but did not report the release of acetone. Other chamber/room studies of desktop-scale FDM machines have reported release of benzene, styrene, toluene, *m,p*-xylene, and *o*-xylene [9,12,14,20,21]. These reports indicate that desktop-scale FDM machines can be somewhat informative for understanding VOC emissions from industrial-scale material extrusion machines printing with ABS and PC filaments (although high-temperature filaments, such as Ultem, can currently be printed using industrial-scale machines only). Quantification of styrene, albeit at low levels, during operation of the industrial-scale material extrusion machines using ABS and PC filaments is of interest because it may be an asthmagen [36]. At Facilities B and D, six different VOCs were quantified in room air during operation of material jetting machines. Among these vapors, acetaldehyde is of interest as this chemical is categorized as a potential occupational carcinogen by NIOSH [32].

Given these results for material extrusion filaments and material jetting resins evaluated in this study and the ever-expanding options for feedstock materials on the commercial market, there is a need for more research to understand VOC emissions from AM machines using these materials. A standard laboratory method to quantify or categorize filament emissions (particle and chemical) could be useful for manufacturers for product stewardship and informative to consumers when making decisions on consumable purchases. Such considerations are components of a broader life cycle assessment strategy for AM [37].

##### 4.2. Ozone and carbonyl reaction product formation

Regardless of machine type, elevated levels of ozone were measurable in all printer rooms. The exact mechanism by which ozone was formed by the AM machines is not known. For the material jetting machines, the ultraviolet laser wavelength used to cure resin is above 200 nm and would not be capable of forming ozone. Given that elevated levels of ozone were measured in all printer rooms, one plausible source is the electrical components of the AM machines. Carbonyl compounds observed were present in both the background and during the printing process, suggesting that the printing process did not emit new carbonyl compounds into the indoor environment. This trend was observed in all samples collected from the varying locations and was in contrast to a previous laboratory chamber experiment, which indicated the formation of carbonyls during printing [20]. Given an average ozone concentration of 20  $\mu\text{g}/\text{m}^3$  and an average ozone rate constant of  $1 \times 10^{-16}$   $\text{cm}^3$  molecules<sup>-1</sup> s<sup>-1</sup> for alkenes containing one to two carbon–carbon double bonds, the pseudo-first-order rate constant is 0.090/hr. We assumed an average air exchange rate of 0.22/hr for Facilities A–C, and the rate was 2/hr for Facility D. Hence, one possible explanation for why new carbonyls did not form during printing could be that the precursors to carbonyl formation were removed by air currents before reactions occurred.

##### 4.3. Personal exposures to metals and VOCs

Measured personal exposures to metals and individual VOCs were well below their corresponding NIOSH RELs. For metals, NRD

samplers were used to measure personal exposure to metal-containing particles with diameters <300 nm because these particle sizes have high probability of depositing in the alveolar region of the lung [38]; however, the mass per particle decreases as size decreases. Hence, mass exposures to these metals could be higher if they were measured using a sampler that collects larger size particles which may be useful in future studies. In addition, it is important to note that the surface-to-volume ratio rapidly increases as particle size decreases, meaning that more atoms are on the surface of nanoscale particles and available to react with biological systems, making surface area an important metric for pulmonary inflammation for exposure to insoluble and poorly soluble particles [13]. Seven different VOCs were quantified on personal samples collected from employees at Facility A (acetone, pentane, hexane, benzene, cyclohexane, ethanol, and naphtha) during material extrusion AM processes. He et al [39] measured exposures of workers during an extrusion process at an ABS plastics recycling facility and also identified benzene and cyclohexane. At this time, it is unknown whether the source of naphtha exposure is the AM machines. Facility A also contains a sand binder jetting machine (not in use at the time of our survey), and naphtha is often used as a carrier or reducer in sand-casting processes to improve the drying and removal process of the metal from the sand cast [40,41].

At Facilities A and B, ethanol was used as a cleaning solvent and was measured on all personal samples. du Preez et al [3] reported that postprocessing of ABS- and PL-printed objects using vapor polishing resulted in personal exposures to acetone and chloroform, respectively. Graff et al [4] evaluated preprinting and postprinting tasks associated with laser sintering printing of metal powders and reported that these tasks resulted in elevated concentrations of particles. Hence, exposures to emissions during operation of AM machines is just one contributor to total exposure among AM operators, and consideration should be given to understanding all contributing sources in these workplaces. Personal exposures to VOCs were all well below their applicable RELs. It is important to note that the measured exposures reflect conditions at the time of sampling and that any changes to work processes, including building-related factors (changes to ventilation, etc.), machine-related factors (number, type, etc.), and feedstock-related factors (thermoplastic, resin, etc.), could change VOC concentrations.

## 5. Conclusions

Overall, particle number-based ERs in these industrial workplaces were on the order of  $10^9$ – $10^{10}$  number/min for material jetting machines (P-Trak data) and  $10^{10}$ – $10^{11}$  number/min for material extrusion machines (CPC data). ERs calculated from OPC data were several orders of magnitude lower, suggesting that emitted particles had sizes predominantly below 300 nm regardless of the AM process in use. Low levels of metals and organic chemicals were measurable in all workplaces. Notably, material jetting machine resin feedstock released particles and VOCs at levels similar to or greater than some material extrusion machines that use heat to melt feedstock material. The health significance of these exposures is currently unknown, although available literature indicates that inhalation of ABS filament emissions during operation of a material extrusion AM machine may be associated with work-related asthma in workers and acute hypertension in rodents. At this time, it is unknown if potential adverse effects are attributable to VOCs, UFP, or both VOCs and UFP. Hence, further workplace evaluations could help to understand factors that influence emissions from these and other types of AM processes and to quantify exposures in larger populations of AM operators. Such information is necessary to understand risk potential and identify

effective control technologies, if deemed to be necessary. The real-time monitoring instruments and sampling techniques used in this study provided useful information on emissions and exposures in diverse workplaces and could serve as a model to standardize approaches for future workplace assessments.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.shaw.2018.10.003>.

## Disclaimer

The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention.

## Conflict of interest

The authors declare no conflict of interest.

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