RESEARCH ARTICLE

Evaluation of emissions and exposures at workplaces using desktop 3-dimensional printers

There is a paucity of data on additive manufacturing process emissions and personal exposures in real-world workplaces. Hence, we evaluated atmospheres in four workplaces utilizing desktop "3-dimensional" (3-d) printers [fused filament fabrication (FFF) and sheer] for production, prototyping, or research. Airborne particle diameter and number concentration and total volatile organic compound concentrations were measured using real-time instruments. Airborne particles and volatile organic compounds were collected using time-integrated sampling techniques for off-line analysis. Personal exposures for metals and volatile organic compounds were measured in the breathing zone of operators. All 3-d printers that were monitored released ultrafine and fine particles and organic vapors into workplace air. Particle number-based emission rates (#/min) ranged from 9.4×10^9 to 4.4×10^{11} (n = 9 samples) for FFF 3-d printers and from 1.9 to 3.8×10^9 (n = 2 samples) for a sheer 3-d printer. The large variability in emission rate values reflected variability from the printers as well as differences in printer design, operating conditions, and feedstock materials among printers. A custom-built ventilated enclosure evaluated at one facility was capable of reducing particle number and total organic chemical concentrations by 99.7% and 53.2%, respectively. Carbonyl compounds were detected in room air; however, none were specifically attributed to the 3-d printing process. Personal exposure to metals (aluminum, iron) and 12 different organic chemicals were all below applicable NIOSH Recommended Exposure Limit values, but results are not reflective of all possible exposure scenarios. More research is needed to understand 3-d printer emissions, exposures, and efficacy of engineering controls in occupational settings.

By A.B. Stefaniak, A.R. Johnson, S. du Preez, D.R. Hammond, J.R. Wells, J.E. Ham, R. F. LeBouf, K.W. Menchaca, S. B. Martin Jr., M.G. Duling, L.N. Bowers, A.K. Knepp, F.C. Su, D.J. de Beer, J.L. du Plessis

__A.B. Stefaniak__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: Astefaniak@cdc.gov).

__A.R. Johnson__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: AJohnson13@cdc.gov).

__S. du Preez__ is affiliated with North-West University, Occupational Hygiene and Health Research Initiative, Private Bag X6001, Potchefstroom, 2520, South Africa (e-mail: dupreezsonette@nwu.ac.za).

__D.R. Hammond__ is affiliated with National Institute for Occupational Safety and Health, Cincinnati, OH, USA (e-mail: DHammond@cdc.gov).

__J.R. Wells__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: RWells@cdc.gov).

__J.E. Ham__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: JHam1@cdc.gov).

__R.F. LeBouf__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: RLebouf@cdc.gov).

__K.W. Menchaca__ is affiliated with National Institute for Occupational Safety and Health, Cincinnati, OH, USA (e-mail: KMenchaca@cdc.gov).

__S.B. Martin Jr.__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: SMartin1@cdc.gov).

__M.G. Duling__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: MDuling@cdc.gov).

__L.N.Bowers__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: LBowers@cdc.gov).

__A.K. Knepp__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: AKnepp@cdc.gov).

__F.C. Su__ is affiliated with National Institute for Occupational Safety and Health, Morgantown, WV, USA (e-mail: FengChiaoSu@cdc.gov).

__D.J. de Beer__ is affiliated with North-West University, Technology Transfer and Innovation Support Office, Private Bag X6001, Potchefstroom, 2520, South Africa (e-mail: Deon.deBeer@nwu.ac.za).

__J.L. du Plessis__ is affiliated with North-West University, Occupational Hygiene

1871-5532
https://doi.org/10.1016/j.jchas.2018.11.001
Published by Elsevier Inc. on behalf of Division of Chemical Health and Safety of the American Chemical Society.

INTRODUCTION

Additive manufacturing (AM) is the process of joining materials to make parts based upon 3-dimensional (3-d) model data, usually layer-upon-layer.[1] Large industrial-scale AM machines have been in use for decades; however, improvements in technology and availability of lower-cost smaller-scale "desktop" machines have made AM available for use in small businesses, prototyping ("maker") spaces, home-based businesses, and by consumers.[2] There are seven types of AM processes (material extrusion, binder jetting, powder bed fusion, material jetting, directed energy deposition, sheet lamination, and vat polymerization).[1] At this time, the availability of desktop-scale machines is generally limited to material extrusion and vat polymerization processes.[2] The focus of this study is desktop material extrusion machines, more commonly known as "3-d printers" that use fused filament fabrication (FFF) technology, including traditional FFF and sheer 3-d printing – a type of FFF which combines traditional FFF with inkjet printing. These machines feed a solid polymer filament into a heated nozzle to melt the plastic and then extrude it through an orifice onto a build plate to make an object.

Inhalation of emissions from certain filaments used in material extrusion processes is associated with adverse respiratory and cardiovascular health effects. House et al.[3] reported a case of work-related asthma in a worker exposed to emissions during operation of material extrusion processes using an acrylonitrile butadiene styrene (ABS) filament. In a survey of AM workers who primarily used material extrusion processes, 59% reported respiratory symptoms.[4] In an animal toxicology study, rats that inhaled ABS emissions from a desktop FFF 3-d printer developed acute hypertension.[5] At this point in time, it is unclear if these respiratory and cardiovascular endpoints are associated with inhalation of emitted particles, organic vapors, or both. Given these emerging reports of adverse health effects, there is a need to understand the magnitude and characteristics of emissions and exposures from AM processes in workplaces so that informed decisions can be made with regard to risk management.

Numerous studies have measured particle and/or volatile organic compound (VOC) emissions from a single desktop FFF 3-d printer placed in a highly controlled test chamber or clean room.[6–19] Some investigators have evaluated FFF 3-d printer emissions in "real-world" settings, albeit non-industrial locations such as a small room, office, academic laboratory, classroom or library, or college dormitory.[12,15,20–25] Industrial workplaces also use desktop FFF 3-d printers with ABS and polylactic acid (PLA) filaments; however, characteristics of these spaces differ from those of test chambers, clean rooms, offices, libraries, or dormitories. Industries that use FFF 3-d printers for production may have multiple machines that are running different print jobs (size, geometries) using different materials and colors of feedstock filament concurrently over a work shift, a 24-hour period, or multiple days. Further, some of the 3-d printers in a room may be starting a print job, others may be finishing a print job, all while others continue to operate. Unlike a laboratory chamber study, where each 3-d printer or feedstock variable and atmospheric conditions can be controlled, or a room or an office running a well-defined printer scenario, industrial workplaces are less controlled and hence likely to have more complex and variable atmospheres from 3-d printer emissions.

Based on the above-cited literature, it is reasonable to expect that exposures to particles and vapors may occur in industrial settings where desktop FFF 3-d printers are used; however, there is currently little understanding of printer emissions in workplace settings or occupational exposures or on the efficacy of control technologies.[11,26] Hence, we surveyed emissions and measured personal exposures in multiple workplaces using desktop-scale 3-d printers for manufacturing, prototyping, and research to better understand atmospheres in real-world settings; and to assess the efficacy of a custom built ventilation control measure at a manufacturing facility.

METHODS

Assessments were performed at four facilities designated A–D; additional details of these workplaces are provided in the Supplemental file. Table 1 summarizes the types of 3-d printers, consumables, and operating parameters at the time of sampling.

Facility A

This building housed a 40 m^3 prototyping space that contained 10 desktop FFF 3-d printers; 9 were from 3D Printing Systems (Rustenburg, South Africa) and one was from Beijing Tiertime Technology Company Ltd. (Beijing, China). These machines used ABS and PLA feedstock filaments (all from 3D Printing Systems). Seven of the 10 printers were in use at the time of sampling. No local exhaust ventilation (LEV) existed for these desktop machines. The room had a recirculating wall-mounted air conditioning unit (equipment to measure flow rate not available for this survey) but no general ventilation. This room was primarily staffed by one employee. Emissions were monitored on one day in this facility.

Facility B

This building housed a 76 m^3 prototyping space with one 3-d printer (UP BOX, Beijing Tiertime Technology, Co Ltd., China). There was no LEV for the machine; the room had a wall-mounted recirculating air conditioner (equipment to measure flow rate not available for this survey) and an open entry (no door) to a staircase that led down to a high bay. Emissions were monitored on one day in this facility.

Facility C

This facility had two rooms that contained 3-d printers. Room C-1 (466 m^3), a research Engineering Laboratory, housed a sheer printer

---

and Health Research Initiative, Private Bag X6001, Potchefstroom, 2520, South Africa (e-mail: Johan.DuPlessis@nwu.ac.za).

Table 1. Summary of Additive Manufacturing Machines by Location.

Location	Machine			Feedstock[b]	Color	Print conditions [°C]	
	Manufacturer[a]	Model	Description			Extruder	Build plate
A	3DPS	UP Mini – 1[c]	Cover off	ABS	Black	250	50
	3DPS	UP Mini – 2	Cover off	PLA	Green	220	60
	3DPS	UP Mini – 3	Cover	N/A	N/A	–[d]	–
	3DPS	UP Mini – 4	Cover	N/A	N/A	–	–
	3DPS	UP Mini – 5	Cover off	ABS	Blue	250	50
	3DPS	UP Mini – 6	Cover off	ABS	Red	250	50
	3DPS	UP Mini – 7	Cover off	N/A	N/A	–	–
	3DPS	UP Mini – 8	Cover off	PLA	Light Blue	220	60
	3DPS	UP Mini2	Cover	ABS	Red	270	80
	B. Tiertime	UP BOX	Cover/filter	PLA	Red	190	60
B	B. Tiertime	UP BOX	Cover/filter	ABS+	White	270	100
C-1	Voxel	Voxel8 sheer	Partial enclosure	PLA	Dark Grey	215	25
				Silver ink	Silver	N/A	N/A
C-2	Makerbot	NextGen 5	No sides/top	PLA	White	215	25
					Yellow	215	25
					Blue	215	25
					Black	215	25
					Green	215	25
D	Ruian Qidi	X-one – 1[c]	No sides/top	PLA	Black	230	60
		X-one – 2	No sides/top		White	240	24
		X-one – 2	No sides/top		Black	200	32
		X-one – 3	No sides/top		Black	240	35
		X-one – 4	No sides/top		Black	240	34
		X-one – 5	No sides/top		Dark blue	240	29
		X-one – 5	No sides/top		Wood	200	30
		X-one – 6	No sides/top		Black	240	35
		X-one – 7	No sides/top		Yellow	200	33
		X-one – 8	No sides/top		Black	230	60
		X-one – 8	No sides/top		Wood	230	60
		X-one – 9	No sides/top		Black	230	60
		X-one – 10	No sides/top		Black	200	28

N/A = parameter not applicable.

[a] 3DPS = 3-D printing systems; B. Tiertime = Beijing Tiertime.

[b] ABS = acrylonitrile butadiene styrene; PLA = poly lactic acid.

[c] Number after hyphen is printer identifier.

[d] – = Printer not operating during sampling period.

(Voxel8 Developer Kit, Somerville, MA, USA), which is a multi-material machine that operates based on material extrusion technology to deposit PLA polymer as well as inkjet technology to dispense liquid conductive metallic silver to build electronic components layer-by-layer. The air exchange rate in the laboratory was 2/hr during sampling. Room C-2 ($320\,m^3$) housed a single FFF 3-d printer (Makerbot, NextGen, 5th Generation, Brooklyn, NY, USA) that was available for use by all facility employees for printing prototypes. Room C-2 is a large space, open to a lounge area, a stairwell, and workstations; the area only had heating and ventilation for occupant comfort. Emissions were monitored on four consecutive days at this facility.

Facility D

This workplace manufactures objects using FFF 3-d printers and injection molding. Sampling was performed over three days at this facility. The Print Room is a $44.5\,m^3$ room that contained 10 desktop 3-d printers (X-one, Ruian Qidi Technology Co., Ltd, Ruian, China). The machines were arranged on shelves, two high by five wide. On the first two days of sampling, there was no LEV for the machines or general exhaust ventilation in the room and the door remained closed unless a worker entered to check on a print job. On the third day of monitoring, a custom-built ventilation enclosure was installed that consisted of hinged acrylic panels that attached to the shelving using bolts. For one portion of the shelving, there was no shelf above the 3-d printer so an aluminum frame was built to enclose them (see Fig. S1 in the Supplemental file). To increase air-tightness, hinged edges of doors were sealed using metallic tape (3M 3381 Foil Tape) and rubber gaskets were used for sealing on the three remaining edges. The air within the enclosure was ventilated using a portable floor fan (Model SS-400-PYT, Sentry Air Systems Inc., Houston, TX) connected to 15.25-cm diameter flexible hose (Model W1036, Woodstock International Inc., Bellingham, WA) to exhaust the air around the printers. The portable floor fan had a variable speed controller rated to move air at up to 19.82 m^3/min (700 cubic feet per minute) and the air was passed through a high efficiency particulate air (HEPA) filter (Model SS-400-HF, Sentry Air Systems Inc., Houston, TX) and a 3.6-kg carbon bed (Model SS-408-CF, Sentry Air Systems Inc., Houston, TX) to remove particles and organic vapors, respectively before discharging the air back into the room. The top and bottom shelves were ventilated using separate exhaust ducts. Particle number concentration and total volatile organic chemical concentrations were monitored inside and outside of the enclosure during 3-d printing. To monitor inside the enclosure, the real-time instruments were placed side-by-side on the shelf between two printers near the middle of the shelving. To monitor outside the enclosure, the same types of instruments were positioned side-by-side at a distance of 0.5 m from the enclosure at the same location as the “inside” instruments. The room had a wall-mounted recirculating air conditioning unit but it was not in use at the time of our survey. Additionally, this facility has a 566 m^3 high bay room that contained a pneumatic injection molding machine that used ABS pellets and was evaluated for comparison of emissions with the desktop FFF 3-d printers.

Room Air Sampling

An isopropanol-based condensation nuclei counter (P-Trak, Model 8525, TSI Inc., Shoreview, MN, USA) capable of counting particles in the size range from about 20 to 1,000 nm was used to determine particle number concentration. In Room C-1 only, an optical particle counter (OPC) (Model 1.108, GRIMM Aerosol Technik GmbH & Co. Ainring, Germany) was used to determine particle size distribution from 300 to 20,000 nm, and a fast mobility particle sizer (FMPS) (Model 3091, TSI Inc) was used to measure particle size distribution from 5.6 to 560 nm. Particle emission rates (described below) were calculated using the P-Trak, OPC, and FMPS data. For Facility D only, an isopropanol-based mobility particle sizer (NanoScan, TSI Inc., Shoreview, MN, USA) was used to measure particle size distribution from 10 to 420 nm. All real-time instruments were factory calibrated prior to use. Measurements were data logged at a frequency of 1 s for the P-Trak and FMPS, 6 s for the OPC, and 60 s for the NanoScan. Conductive silicone tubing (Part No. 3001788, TSI Inc, Shoreview, MN, USA) having length between 0.1 and 0.5 m was connected to the particle sampling instrument inlets (except for the P-Trak at Facility D where 0.5 m of Tygon® tubing was connected to the instrument inlet). No correction was made for particle losses in the sample tubing. For the NanoScan, air was aspirated through the stainless steel aerosol inlet cyclone provided by the manufacturer.

Additionally, 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 energy dispersive X-ray analysis (Quantax, Bruker Scientific Instruments, Berlin, Germany) to identify elemental constituents.

A real-time total organic vapor (TVOC) photoionization detector (RAE Systems, San Jose, CA, USA or Ion Science Inc., Stafford, TX, USA) was used to monitor organic vapor emissions and a real-time gas sensitive semiconductor sensor (Model S500, Ozone Solutions, Hull, IA, USA) was used to monitor ozone concentrations. The TVOC data were used to calculate emission rates (described below). The TVOC monitors were factory calibrated using isobutylene and span checked with isobutylene prior to use. Data was converted from ppb to μg/m^3 isobutylene equivalents based on the molecular weight of isobutylene. 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. 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. Additionally, 450 mL Silonite-coated evacuated canister samples (Model 29-MC450SQT, Entech Instruments Inc., Simi Valley, CA, USA) were collected at Facilities C and D. Details of the canister analytical method are provided in the Supplemental file. Samples for gas-phase carbonyls were obtained by sampling air using a sampling pump calibrated to 4.0 L/min. Air was drawn through 25 mL of deionized water in a 60 mL Teflon bubbler (Savillex, Eden Prairie, MN, USA) or through 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 placed within 1 m of the 3-d printers at breathing zone height. All sampling locations were representative of typical worker locations in the rooms. Background data was collected to assess levels of all analytes for various times (from 5 to 40 min) prior to starting the 3-d printers. Samples were collected during 3-d printing to capture emission release and after printing to capture contaminant decay in the rooms. Sampling durations varied depending on the type of sample collected, the facility, and the build. In general, real-time instruments were used to monitor air for 270–420 min/day; filter cassette samplers were used to collect particles for 68 min–450 min (sample volumes of 0.2–1.4 m^3); TD tubes were used to collect VOCs for 120–420 min (sample volumes of 0.006–0.013 m^3); and bubbler samplers were operated for 65–420 min (sample volumes of 0.3–1.7 m^3).

Personal Sampling

Personal breathing zone samples were collected for metals and VOCs during employee shifts at Facilities A and B and for VOCs at Facility D (no personal samples were collected at Facility C). Previous laboratory studies have identified several metals such as iron, nickel, chromium, and zinc in particles emitted during operation of desktop FFF 3-d printers using ABS and PLA filaments.[14,15,24] Metals were sampled using nanoparticle respiratory deposition (NRD, Zefon International, Inc., Ocala, FL, USA) samplers to determine personal exposure to particles with diameters $<$300 nm.[27] The NRD samplers were operated using a personal sampling pump calibrated to 2.5 L/min and collection substrates were analyzed for metals content using inductively coupled plasma-mass spectrometry (ICP-MS) in accordance with NIOSH Method 7303. VOCs were sampled using passive diffusion badges (TraceAir® 521, Assay Technology, Livermore, CA, USA) and analyzed using GC–MS by NIOSH Methods 1500, 1501, and 2500. Personal sampling at Facilities A and B was approved by the Health Research Ethics Committee of the North-West University (Ethics clearance number: NWU-00004-16-A1). At Facility D, personal breathing zone VOC exposures were measured using a real-time TVOC monitor (Cub, Ion Science Inc.) and 450 mL Silonite®-coated evacuated canister samplers (Entech Instruments, Simi Valley, CA, USA) over a work shift. Canister samples were analyzed at NIOSH using a pre-concentrator/GC–MS system to quantify specific VOCs.[28] Personal sampling at Facility D was performed as part of a NIOSH Health Hazard Evaluation.

Data Analysis

Emission rates (ER) were calculated using a model developed to describe emission from sources in indoor residential and occupational environments, including 3-d printers:[22,29]

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

where, $V =$ the room volume, $C_{peak} =$ peak concentration of the contaminant during printing, $C_{out} =$ 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_{peak} and C_{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 $\overline{C}_{in} =$ the average concentration of the contaminant during printing. Details of the model and calculations are provided in the Supplemental file. For specific VOCs, all concentrations were background-corrected using results of the samples collected prior to 3-d printing.

Temporal changes in particle size distributions (including median and variance) from real-time FMPS measurements were estimated using a two-level Bayesian model with a Markov chain Monte Carlo algorithm developed by Klein Entink et al.[30] We used 1-min averages of FMPS real-time measurements. Analyses were conducted in R 3.3.1 using the "NanoPSDA" package.[31,32]

RESULTS

At all facilities, operation of 3-d printers resulted in an increase in room particle number and VOC concentrations.

Particle and Total Voc Emissions

An example of the influence on 3-d printer emissions on room particle concentration (P-Trak data) is shown in Figure 1. Particle number concentration increased at the start of printing, increased more rapidly when the printer cover was opened, and decayed when the cover was replaced.

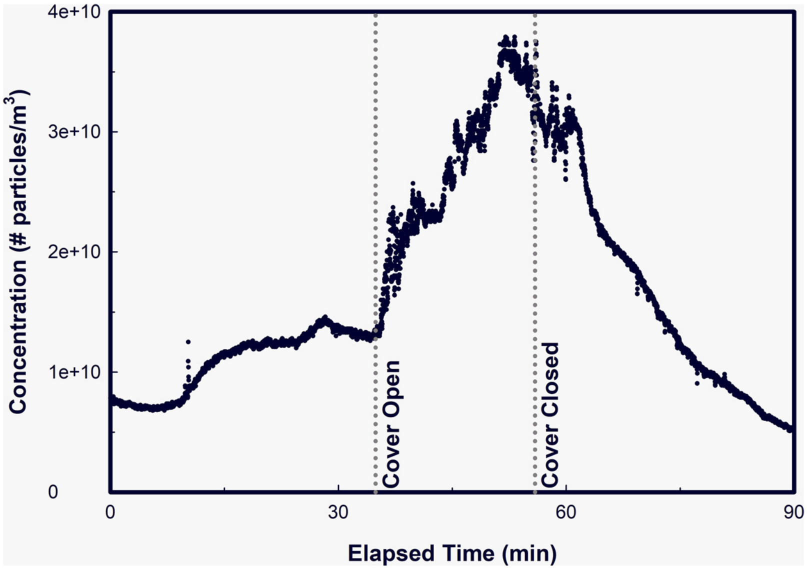

Figure 1. Particle number concentration in Facility B during operation of a desktop 3-d printer. Background monitoring was from t = 0 to 5 min. Number concentration in the room initially rose slowly after printing began (t = 5 min), increased rapidly when the printer cover was opened (denoted by dotted vertical line), and decayed when the cover was closed (denoted by dotted vertical line) and the printer was still operating.

Table 2. Particle and Total Volatile Organic Compound (TVOC) Emission Rates by Facility.

Facility	Details[a]	P-Trak (#/min)	TVOC (μg/min)
A	Various	9.7×10^{10}	3.3×10^{6}
B	ABS (white)	7.3×10^{10}	1.2×10^{5}
C-1	PLA (gray)/Ag ink	1.9×10^{9}	3.1×10^{4}
C-1	PLA (gray)/Ag ink	3.8×10^{9}	1.6×10^{4}
C-1	PLA (gray)/Ag ink[b]	2.1×10^{11}	2.3×10^{4}
C-2	PLA (white)	5.5×10^{9}	1.3×10^{4}
	PLA (yellow)	n.s.	2.1×10^{3}
	PLA (yellow)	n.s.	3.1×10^{3}
	PLA (blue)	1.2×10^{10}	4.6×10^{3}
	PLA (black)	1.9×10^{10}	1.5×10^{4}
	PLA (black)	9.0×10^{10}	4.4×10^{4}
	PLA (green)	9.4×10^{9}	2.6×10^{4}
D	Various	1.7×10^{11}	1.1×10^{4}
	Various	4.4×10^{11}	7.9×10^{3}

n.s. = not sampled (instrument was not available at the time of printing).

[a] ABS = acrylonitrile butadiene styrene; PLA = poly lactic acid; Various = more than one printer or type of feedstock used during sampling (see Table 1 for filament types and colors).

[b] Print job failed.

Table 2 summarizes the calculated ERs for the 3-d printers based on the P-Trak data. Number-based particle ER values ranged from 2×10^{9} particles/min (sheer printer, Facility C) to 4×10^{11} (material extrusion, Facility D). Room C-2 contained a single desktop FFF 3-d printer that was used to build prototype objects with five different colors of the same brand of PLA filament under the same print conditions over four days (white, blue and green were printed once whereas yellow and black colors were printed twice). Number-based emission rates for these print jobs varied by a factor of nine, i.e., from 1×10^{10} particles/min to 9×10^{10} particles/min. On the first two days of sampling at Facility D, number-based ER values were 2 to 4×10^{11} particles/min and the average geometric mean (GM) mobility particle size in the Print Room was 38 nm on the first day and 33 nm on the second day. On the third day at Facility D, the effectiveness of the ventilated enclosure was assessed while all 10 printers were operating. Outside of the enclosure, the particle number concentration (P-Trak) in the room air reached 1.42×10^{5} particles/cm^3 of air before the enclosure doors were sealed and the fan turned on. Within 30 min, particle number concentration in the room decreased to 418 particle/cm^3 of air, which is a 99.7% reduction (Figure 2). TVOC concentration followed a similar pattern and decreased 53.2%. From the NanoScan measurement, the average particle size outside the enclosure was 40 nm and the reduction of particle number concentration was 99.7%. Inside the enclosure, particle number concentration (P-Trak) peaked at 2.61×10^{5} particles/cm^3 and decreased to 4,050 particles/cm^3 within 50 min, which is a 98.4% reduction in particle concentration whereas TVOC concentration decreased by 69.5% (data not shown). During warm-up of the injection molding machine with ABS in the high bay at Facility D, the number-based ER was 2.5×10^{7} particles/min (NanoScan) and the average particle size was 102 nm but there was no

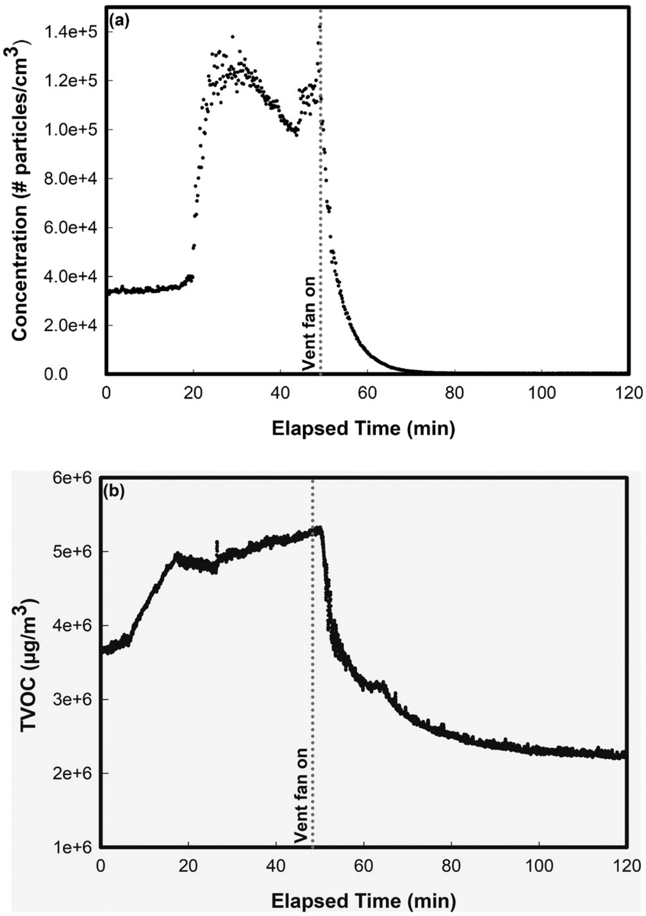

Figure 2. Reductions of (a) particle number and (b) total volatile organic compound (TVOC) concentration in the Print Room at Facility D during use of a ventilated enclosure to capture emissions. Particle number concentration decreased 99.7% and TVOC concentration decreased 53.2%.

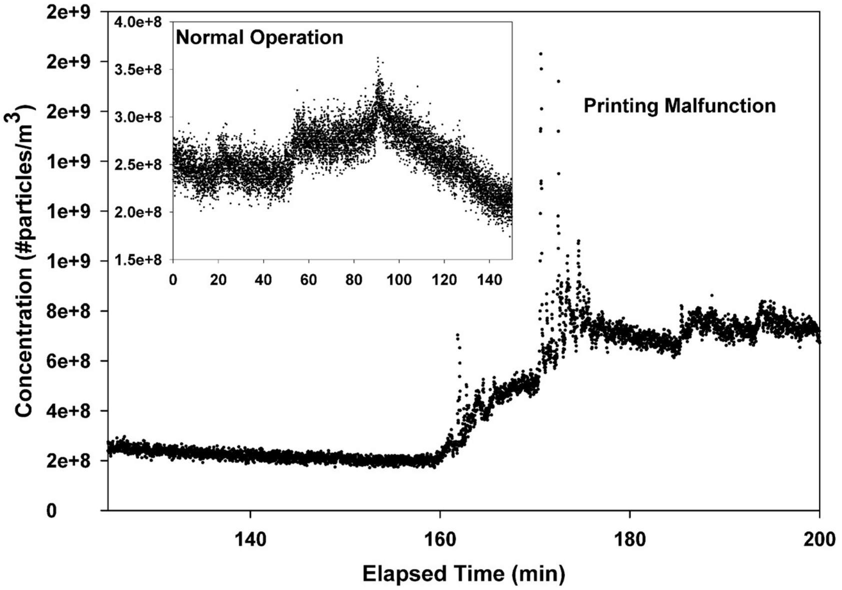

Figure 3. Particle number concentration profile (P-Trak data) in Room C-1 during operation of a sheer 3-d printer. The inset shows particle concentration during background (t = 0 to 40 min) and normal operation. The main plot shows a rapid increase in concentration during print failure (t = 160 to 200 min).

appreciable change relative to background during molding (Fig. S2 in the Supplemental file).

On the second day of the survey at Facility C, the sheer printer in room C-1 was operating normally but after 65 min, there was an error, which caused a rapid increase in particle concentration as measured by the P-Trak (Figure 3). On the third day of the survey at Facility C, the sheer printer operated normally. When the sheer printer was operating normally, the calculated particle number-based ER values were 2 to 4 × 10^9 particles/min (P-Trak; Table 2) and 1 × 10^5 particles/min (OPC, diameter >0.3 μm); however, when the print failed, these ER values increased to 2 × 10^{11} particles/min (P-Trak) and 1 × 10^6 (OPC) particles/min. Particle ER values calculated from the FMPS data were higher during normal operation (2 to 3 × 10^{11} particles/min) compared to when the print failed (7.4 × 10^{10} particles/min). Evaluation of the FMPS data for the day the sheer printer failed revealed temporal changes in the particle size distribution (Figure 4). Electron microscopy analysis of filter samples collected on the days when the sheer printer was operating normally identified nanoscale particles; iron, but not silver, was detected in particles (Figure 5).

TVOC ER values varied by three orders of magnitude among facilities (Table 2). For the sheer printer, TVOC ER values were 2 to 3 × 10^4 μg/min regardless of operating status (normal, failure).

Quantification of Individual VOCs

Table 3 summarizes the levels of individual VOCs that were quantified during FFF 3-d printing in room air at Facilities A, B, and D (concentrations of all VOCs measured using TD tube samples in Facility C were similar to background levels). The types of VOCs and their concentrations varied among facilities. In Facility D, an employee cleaned the printer beds with isopropyl alcohol during sample collection, so not all of the measured airborne concentration of this chemical was from 3-d printer emissions. At Facility D, the TVOC concentration in the high bay increased from about 4000 to 72000 μg/m^3 upon adding ABS pellets to the pre-heated hopper; however, there was no appreciable change in concentration during injection molding. Table S1 summarizes the background-corrected concentrations of individual VOCs measured during warm-up and operation of the injection molding machine. At the start of warm-up, only two VOCs (ethanol and isopropanol) were quantified in workplace air. Upon reaching the set point temperature of the machine, an additional three VOCs (acetaldehyde, methyl methacrylate, and *m*,*p*-xylene) were quantifiable. During operation of the injection molding machine, a total of eleven VOCs were measured and concentrations were elevated relative to warm-up.

Ozone and Carbonyl Formation

During 3-d printing, average ozone concentrations in Facilities A–D ranged from 10 to 17 μg/m^3. 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 they were not emitted or formed during these printing processes.

Personal Exposures to Metals and VOCs

Employees at Facilities A and B were exposed to low levels of aluminum (0.01–0.02 mg/m^3) and to low levels of VOCs (Table 4). At Facility D, personal real-time TVOC monitoring revealed multiple peaks that corresponded to entering the print room or specific tasks (Fig. S3). From the canister samples, employee personal exposure included eight VOCs, most of which differed from those measured at the other facilities (in mg/m^3): acetaldehyde (0.01–0.02 mg/m^3), acetone (0.05–0.12 mg/m^3), ethanol (0.04 mg/m^3), isopropyl alcohol (2.7–9.8 mg/m^3), methyl methacrylate (0.002 mg/m^3), methylene chloride (0.0006 mg/m^3), toluene 0.002 (mg/m^3), and *m*,*p*-xylene (0.001–0.003 mg/m^3). All personal VOC levels were well below applicable NIOSH Recommended Exposure Limit (REL) values.[34]

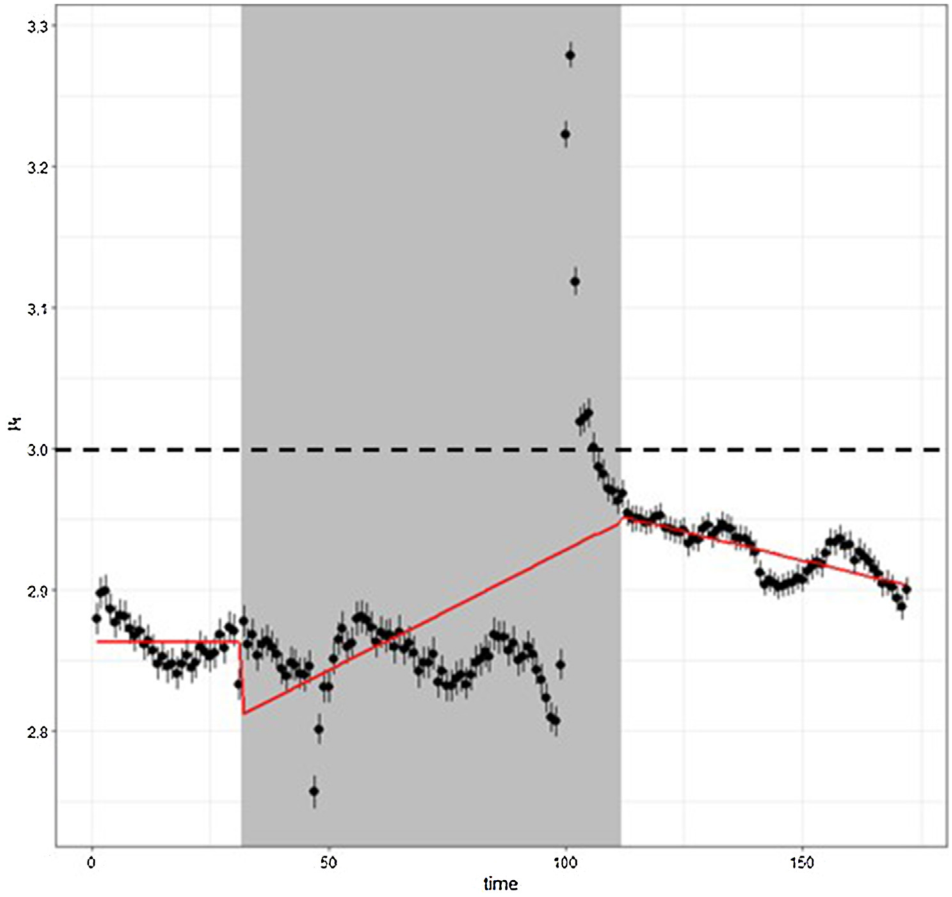

Figure 4. Time series plots (in minutes) of the mean (μ_t) particle size (y-axis) versus time in minutes (x-axis) during the background, printing, and post-print failure phases of a sheer 3-d printer. The gray area indicates the printing period including the print failure. The white areas preceding and after the gray area are the background and post-print failure phases, respectively. Black dots are mean values with Bayesian 95% credible intervals, and red lines are regression model-fitted trends. The y-axis is on a log-scale. The horizontal dashed line at $\mu_t = 3.0$ corresponds to $\exp(3.0) = 20$ nm, the lower size cut-off of the P-Trak instrument. The mean particle size during printing before the failure was $\mu_t = 2.9$ (18 nm). The mean particle size during the print failure reached $\mu_t \sim 3.3$ ($\sim$ 26 nm) before decaying.

DISCUSSION

In this study, 23 desktop 3-d printers (22 FFF and one sheer type) were evaluated at four different workplaces involved in prototyping, research, and manufacturing.

Particle and Total VOC Emission Rates

Particle number-based ER values calculated from P-Trak instrument data (Table 2) were consistent with values previously reported for ABS and PLA filaments in test chambers and rooms.[6–8,10,11,14–19,22–24] Emission characteristics were variable, and at least part of this variability is attributed to differences in the unique combinations of 3-d printer design (e.g., no side walls), feedstock type (ABS, PLA), feedstock color, print characteristics (shape, geometry), and printing conditions (Table 1) during monitoring.[6–8,10,11,14–19,22–24] The calculated number-based ER values were highest in Facilities A (7 printers operating normally) and D (10 printers operating normally), which is consistent with Stephens et al.[23] and Bharti and Sing[20] who reported that particle emissions in educational facilities increased as the number of printers operating increased up to five.

The sheer printer extruded PLA filament and metallic ink but the number-based ER values (P-Trak data) were within the range observed for most colors of PLA filaments printed using desktop FFF 3-d printers (Table 2). Hence, from an ER standpoint, sheer printing appears to be similar to desktop material extrusion FFF 3-d printing (when operating normally). The sheer printer also emitted particles with sizes >300 nm (OPC data). Previous studies of desktop FFF 3-d printers using ABS or PLA filaments in a test chamber and a clean room have also observed the emission of particles with sizes >300 nm.[13,17,19] A detailed investigation of the mechanisms of aerosol formation for particles with sizes >300 nm was beyond the scope of this workplace exposure assessment study.

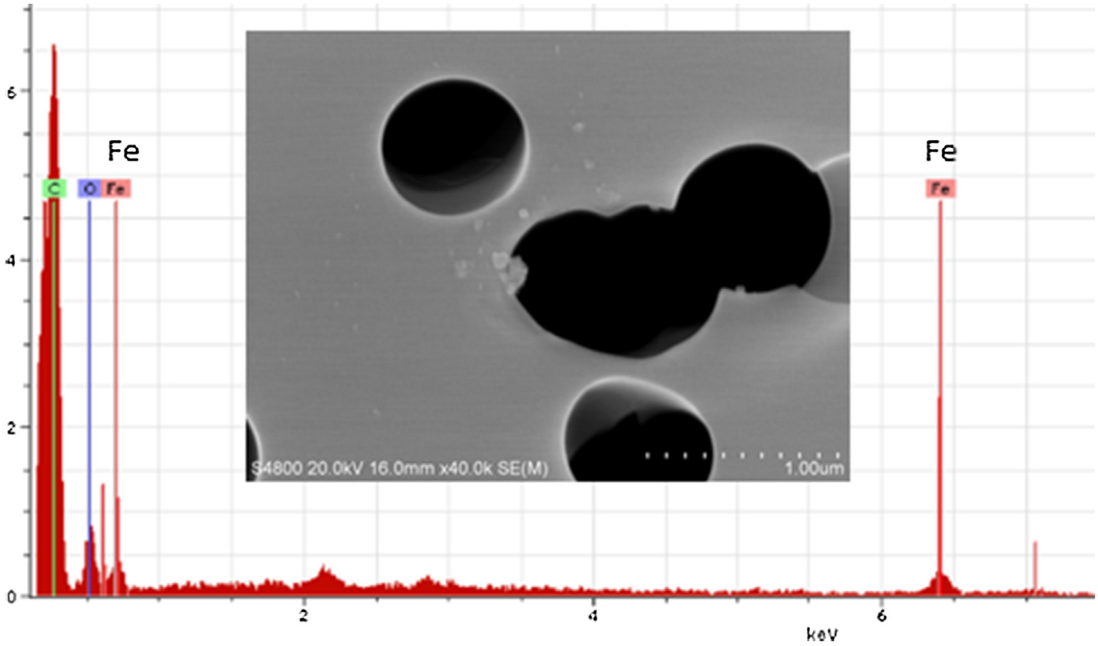

Figure 5. Field emission-scanning electron micrograph of particles collected in Room C-1 during operation of the sheer printer illustrating the presence of nanoscale particles (inset). Elemental analysis using energy dispersive X-ray analysis identified iron but not silver.

Table 3. Background-corrected Concentrations of Volatile Organic Compounds (μg/m^3) During 3-d printing by Facility.

Facility	Sample	min	Chemical[a]								
			Acetaldehyde	Acetone	Benzene	Hexane	IPA	MC	MMA	Toluene	*m*,*p*-Xylene
A	1	99	<LOD	98.7	1.6	2.2	122.2	1.2	<LOD	1.5	<LOD
B	1	75	<LOD	–	–	–	–	–	<LOD	–	–
	2	75	<LOD	457	8.2	7.7	4637	–	<LOD	–	–
D	1	355	83.1	222.0	<LOD	<LOD	23413	6.3	3.1	4.0	4.7
	2	360	43.0	272.9	11.1	<LOD	40765	9.2	3.7	<LOD	<LOD

– = Background-corrected value below zero.

[a] IPA = isopropyl alcohol, MC = methylene chloride, MMA = methyl methacrylate <LOD = below analytical limit of detection (all in μg/m^3): acetaldehyde = 12.6, benzene = 2.7, hexane = 4.8, methyl methacrylate = 2.2, *m*,*p*-xylene = 0.6.

Vance et al.[16] reported the formation of particles with size of almost 500 nm by agglomeration for a desktop FFF 3-d printer using a wood-infused PLA filament. Particle concentrations of $10^8/m^3$–$10^{10}/m^3$ under ambient conditions were observed for the sheer printer in Room C-1. As noted by Hinds, agglomeration is generally not likely to be significant when particle concentration is less than $10^{12}/m^3$ (i.e., the time to reduce the initial number concentration of particles in Room C-1 by half would be on the order of days).[35]

On the day that the sheer printer build failed, the number-based ER values calculated from the P-Trak and OPC instrument data increased but the ER value calculated from the FMPS data decreased. Inspection of the temporal changes in FMPS size distribution data on the day of the printer failure (Figure 4) revealed an increase in GM particle size from the printing phase to the failure (i.e., from about 20 nm–26 nm). These data indicate that during normal operation, the GM size of emitted particles is about 20 nm, which is similar to the lower limit of measurement for the P-Trak. Hence, the higher ER calculated from the P-Trak measurements for the print failure reflects the release of particles with size of about 26 nm, which can be measured reliably by the instrument. Whether the printer operated normally or failed, the emitted GM size of emitted particles was about 20–26 nm, which is within the measurement range of the FMPS. Further inspection of Figure 4 reveals that there were fewer small particles emitted during the print failure. Hence, the lower ER calculated from the FMPS

Table 4. Time-weighted Average Personal Exposures to Volatile Organic Compounds at Facilities A and B.

Facility	Employee	Task[a]	min	TWA exposure (mg/m^3)						
				Acetone	Pentane	Hexane	Cyclohexane	Ethanol	IPA[b]	Naphthas
A	1	ABS and PLA printing	162	0.10	0.01			0.01		1.45
	1	ABS and PLA printing + AVP + ethanol cleaning	200	2.70	0.15	0.16		0.10	0.03	1.33
	2	ABS printing	125	1.88	0.11	0.19	0.03	0.03		2.14
	2	ABS and PLA printing	80	0.05	0.03	0.22	0.02	0.01	0.15	2.09
B	5	ABS printing	80	0.04	0.04				0.35	2.83
		NIOSH REL		590	350	1050	1050	1900	980	400

[a] ABS = acrylonitrile butadiene styrene, PLA = polylactic acid, AVP = acetone vapor polishing (see reference[26] for more information).

[b] IPA = isopropyl alcohol.

Empty cell = level below analytical detection limit.

measurements for the print failure reflects that fewer, but larger particles were formed during this event and measured by the instrument.

Preliminary evaluation of a custom-built ventilated enclosure demonstrated its utility in reducing particle number and TVOC concentrations in the Print Room at Facility D by 99.7% and 53.2%, respectively. The reason that particles were removed more effectively than vapors was likely due to difference between the HEPA filter compared to the carbon bed that was used with the air cleaner. HEPA filters are designed to remove at least 99.97% of 0.3 μm size particles (the most penetrating particle size) compared to the activated carbon portion of the air cleaner, which was rated by weight rather than efficiency and may not have been as effective at removing gaseous pollutants. The approach used herein was to ventilate both rows of 3-d printers by enclosing the shelves holding the printers. Kwon et al. evaluated several different control measures for a 3-d printer in a test chamber, including a suction fan coupled to a filter mounted on the printer extruder and an enclosure ventilation fan with filter media attached to the ventilation hole built into the 3-d printer. They reported that an enclosure ventilation fan with a HEPA filter performed best, removing 99.95% of particles from the chamber.[11] Collectively, our data and that of Kwon et al. suggest that removal of contaminants by ventilation or by filtration are both promising approaches to controlling 3-d printer emissions.

During injection molding, particle concentration in the high bay at Facility D increased rapidly when the reservoir containing ABS pellets was heated from 40 to 235 °C to melt the thermoplastic but did not change appreciably during molding (Fig. S1). The calculated particle ER during warm-up period (2.5×10^7 particles/min) was at least three orders of magnitude lower than observed for the desktop 3-d printers using ABS filaments (Table 2).

VOC Concentrations in Workplace Air

Nine different VOCs were quantified in workplace air at Facilities A, B, and D during 3-d printing with ABS and PLA filaments (Table 3). Of these chemicals, all but hexane, isopropyl alcohol, and methylene chloride have been quantified previously in emissions from desktop 3-d printers using ABS and PLA filaments in chamber or room studies or from thermogravimetric evaluation of these types of filaments.[8,10,14,15,36] Interestingly, Azimi et al.[6] evaluated emissions from ABS and PLA filaments during operation of a desktop-scale FFF 3-d printer in a chamber and reported concentrations of 18 different VOCs, but all were different from those quantified in these facilities. Zhang et al. reported that for PLA, printer brand contributed more to particle emissions variation than filament brand and filament color, but effects were not statistically significant. In that same study, for ABS, both printer brand and filament brand had statistically significant effects on particle emissions, while filament color did not. The authors did not report chemical emissions in their study; however, particle formation was believed to be from condensation of organic vapor emissions.[18] Hence, printer brand and/or filament brand likely also influence VOC emissions and help explain the variation observed in chemical emissions among published literature. Differences in the mass of polymer used in the injection molding machine and FFF 3-d printers preclude direct comparison of individual VOC concentration values; however, some similarities in identities of VOCs are noteworthy. During warm-up of the injection molding machine at Facility D, the number of detectable VOCs increased from two to five. When ABS pellets were heated to their melt temperature and extruded 11 different VOCs were identified in the high bay air. All VOC concentrations were elevated compared with the warm-up (Table S1), indicating that efforts to control exposures may be more efficacious if implemented for the extrusion step of the injection molding process (and addition of polymer to the preheated machine as described below). Seven of these VOCs were common to those identified during operation of desktop FFF 3-d printers using ABS and PLA filaments in the previously cited studies (acetaldehyde, acetone, benzene, isopropyl alcohol, methyl methacrylate, toluene, and *m*,*p*-xylene). In addition, styrene (an asthmagen) was identified in high bay air; this chemical has been measured in several chamber studies of desktop 3-d printer emissions.[6,8,14,15,36] Consistent with these data, He et al.[37] reported exposures to benzene, ethylbenzene, methyl methacrylate, toluene, *m*,*p*-xylene, and styrene in workplace air at an ABS plastic recycling workshop. When ABS pellets were added to the pre-heated injection molding machine, TVOC levels increased from a background level of about 4,000 to over 72,000 µg/m^3. Both injection molding and material extrusion additive manufacturing technologies used similar processes to heat the thermoplastic. Though Deng et al.[7] reported that pre-heating the extruder nozzle of a desktop 3-d printer before loading with ABS filament reduced particle emissions by 75%, the injection molding data presented here indicates that such practice could result in organic vapor emissions.

Ozone and Carbonyl Reaction Product Formation

Regardless of facility, all ozone concentrations were below the NIOSH REL ceiling value of 200 µg/m^3.[34] The carbonyl compounds observed were present in both the background and during 3-d printing, 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 our previous laboratory chamber experiment which indicated the formation of carbonyls during printing.[14] Given an average ozone concentration of 20 µg/m^3 and an average ozone rate constant of (1×10^{-16} cm^3/molecules/s) for alkenes containing 1 to 2 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, B, and D and the rate was 2.0/hr for Location C-1. One possible explanation for why new carbonyl compounds were not formed during printing could be that the precursors to carbonyl formation were removed by air exchange before reactions occurred.

Personal Exposures to Metals and VOCs

Measured personal exposures to aluminum and iron and individual VOCs were well below their corresponding NIOSH RELs.[34] Note that we used the NRD sampler to measure personal exposure to metal-containing particles with diameters <300 nm because these particle sizes are often observed in emissions from FFF 3-d printers[18] and have high probability of depositing in the alveolar region of the lung;[38] however, the mass per particle decreases as size decreases. As such, exposures to these metals could be higher if they were measured using a cassette or cyclone samplers with a larger inlet size cut-off rather than the NRD sampler. A total of twelve different VOCs were quantified on personal samples collected from employees at Facilities A, B, and D (acetone, acetaldehyde, pentane, hexane, cyclohexane, ethanol, isopropyl alcohol, methyl methacrylate, methylene chloride, naphtha, toluene, and *m*,*p*-xylene). He et al.[37] measured personal exposures of workers during an extrusion process at an ABS plastics recycling facility and also identified cyclohexane. It is unknown whether the source of naphtha exposures in Facilities A and B is the 3-d printers. 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 in foundries to improve the drying and removal process of the metal from the sand cast.[39,40] At Facility B, the source of naphtha may be from metal working fluids from the metal machines that were operating in another room at the facility during sampling. Personal real-time TVOC monitoring of an employee at Facility D demonstrated that entering the print room as well as post-processing of finished parts resulted in spikes in exposure. Additionally, the cleaning of printer beds by other employees in the print room resulted in exposure to the employee being monitored when in the vicinity of the cleaning task. The highest 8-hour TWA personal exposure concentrations for any individual VOC was <10% of its applicable NIOSH REL. Though these personal exposures are well below applicable RELs, it is important to note that they reflect conditions at the time of sampling and any changes to work processes, including building-related factors (changes to ventilation, etc.), machine-related factors (number, type, etc.), and feedstock-related factors (thermoplastic, color, etc.) could change these exposures.

CONCLUSIONS

An evaluation of 23 desktop 3-d printers at four different workplaces involved in prototyping, research, and manufacturing confirmed that these AM processes contribute to workplace particle and VOC pollution. Particle number-based ERs ranged from 10^9 to 10^{11} particles/min and organic chemical concentrations in workplace air varied widely. Emission levels were influenced by the 3-d printer design, characteristics of the feedstock, and build parameters. Preliminary evaluation of a custom-built ventilated enclosure demonstrated the utility of a control technology in reducing printer-emitted particle number and TVOC concentrations. The health significance of exposure to small particles and/or organic chemicals emitted by 3-d printers is currently unknown, though emerging evidence indicates they may induce adverse respiratory or cardiovascular effects. At the time of sampling in these facilities, personal exposures to select metals and organic chemicals were well below NIOSH RELs. Further workplace evaluation is warranted to understand factors that influence emissions and to extend knowledge gained from chamber testing experiments and to quantify exposures in larger populations of workers to better understand risk potential. Additionally, research on best practices for 3-d printing workspace design and layout and the efficacy of engineering controls will be beneficial.

ACKNOWLEDGEMENTS

The authors thank K.L. Dunn and G. Roth at NIOSH for critical review of this manuscript prior to submission to the journal. 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. The contents of this article, including any opinions and/or conclusions expressed, are solely those of the authors. Funding for this project was provided by NIOSH intramural funds (ABS, ARJ, DH, JRW, JEH, RFL, KWM, SBM, MGD, LNB, AKK, FCS) and the South African Department of Science and Technology (SDP, DJDB, JDP). The funding sources had no involvement in the study design; collection, analysis and interpretation of the data; writing of the report; or the decision to submit the article for publication.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jchas.2018.11.001.

REFERENCES

1. International Organization for Standardization/ASTM International. *Additive Manufacturing – General Principles – Terminology (ISO/ASTM 52900) Standard*; International Organization for Standardization/ASTM International: Geneva, Switzerland, 2015.
2. Anon. *Wohlers 3D Printing and Additive Manufacturing State of the Industry: Annual Worldwide Progress Report.* Ft. Collins, CO, 2016.
3. House, R.; Rajaram, N.; Tarlo, S. M. *Occup. Med.* **2017**, *67*(8), 652.
4. Chan, F. L.; House, R.; Kudla, I.; Lipszyc, J. C.; Rajaram, N.; Tarlo, S. M. *Occup. Med.* **2018**, *68*(3), 211.
5. Stefaniak, A. B.; LeBouf, R. F.; Duling, M. G.; Yi, J.; Abukabda, A. B.; McBride, C. R.; Nurkiewicz, T. R. *Toxicol. Appl. Pharmacol.* **2017**, *335*(1).
6. Azimi, P.; Zhao, D.; Pouzet, C.; Crain, N. E.; Stephens, B. *Environ. Sci. Technol.* **2016**, *50*(3), 1260.
7. Deng, Y.; Cao, S. J.; Chen, A.; Guo, Y. *Build. Environ.* **2016**, *104*(311).
8. Floyd, E. L.; Wang, J.; Regens, J. L. *J. Occup. Environ. Hyg.* **2017**, *14*(7), 523.
9. Geiss, O.; Bianchi, I.; Barrero-Moreno, J. *J. Aerosol Sci.* **2016**, *96*(24).
10. Kim, Y.; Yoon, C.; Ham, S.; Park, J.; Kim, S.; Kwon, O.; Tsai, P. J. *Environ. Sci. Technol.* **2015**, *49*(20), 12044.
11. Kwon, O.; Yoon, C.; Ham, S.; Park, J.; Lee, J.; Yoo, D.; Kim, Y. *Environ. Sci. Technol.* **2017**, *51*(18), 10357.
12. Mendes, L.; Kangas, A.; Kukko, K.; Mølgaard, B.; Säämänen, A.; Kanerva, T.; Flores Ituarte, I.; Huhtiniemi, M.; Stockmann-Juvala, H.; Partanen, J.; Hämeri, K.; Eleftheriadis, K.; Viitanen, A. K. *J. Ind. Ecol.* **2017**, *21*(Suppl. 1), S94.
13. Rao, C.; Gu, F.; Zhao, P.; Sharmin, N.; Gu, H.; Fu, J. *Sci. Rep.* **2017**, *7*(1).
14. Stefaniak, A. B.; LeBouf, R. F.; Yi, J.; Ham, J. E.; Nurkewicz, T. R.; Schwegler-Berry, D. E.; Chen, B. T.; Wells, J. R.; Duling, M. G.; Lawrence, R. B.; Martin, S. B., Jr.; Johnson, A. R.; Virji, M. A. *J. Occup. Environ. Hyg.* **2017**, *14*(540).
15. Steinle, P. *J. Occup. Environ. Hyg.* **2016**, *13*(121).
16. Vance, M. E.; Pegues, V.; Van Montfrans, S.; Leng, W.; Marr, L. C. *Environ. Sci. Technol.* **2017**, *51*(17), 9516.
17. Yi, J.; LeBouf, R. F.; Duling, M. G.; Nurkiewicz, T. R.; Chen, B. T.; Schwegler-Berry, D.; Virji, M. A.; Stefaniak, A. B. *J. Toxicol. Environ. Health A*, **2016**, *79*(453).
18. Zhang, Q.; Wong, J. P. S.; Davis, A. Y.; Black, M. S.; Weber, R. J. *Aerosol Sci. Technol.* **2017**, *51*(11), 1275.
19. Zhou, Y.; Kong, X.; Chen, A.; Cao, S. *Proc. Eng.* **2015**, *121*(506).
20. Bharti, N.; Singh, S. *J. Chem. Ed.* **2017**, *94*(7), 879.
21. Simon, T. R.; Aguilera, G. A.; Zhao, F. *ASME 2017 12th International Manufacturing Science and Engineering Conference, MSEC 2017 Collocated with the JSME/ASME 2017 6th International Conference on Materials and Processing*, **2017**.
22. Stabile, L.; Scungio, M.; Buonanno, G.; Arpino, F.; Ficco, G. *Indoor Air*, **2017**, *27*(2), 398.
23. Stephens, B.; Azimi, P.; El Orch, Z.; Ramos, T. *Atmos. Environ.* **2013**, *79*(334).
24. Zontek, T. L.; Ogle, B. R.; Jankovic, J. T.; Hollenbeck, S. M. *J. Chem. Health Safety*, **2017**, *24*(2), 15.
25. McDonnell, B.; Jimenez Guzman, X.; Dolack, M.; Simpson, T. W.; Cimbala, J. M. *Solid Freeform Fabrication 2016: Proceedings of the 26th Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference*, Austin, TX, 2016, p. 2456.
26. du Preez, S.; Johnson, A. R.; LeBouf, R. F.; Linde, S. J. L.; Stefaniak, A. B.; Du Plessis, J. *Rapid Proto. J.* **2018**, *24*(5), 865.
27. Cena, L. G.; Anthony, T. R.; Peters, T. M. *Environ. Sci. Technol.* **2011**, *45*(15), 6483.
28. LeBouf, R. F.; Stefaniak, A. B.; Virji, M. A. *J. Environ. Monit.* **2012**, *14*(3), 977.
29. He, C.; Morawska, L.; Hitchins, J.; Gilbert, D. *Atmos. Environ.* **2004**, *38*(21), 3405.
30. Klein Entink, R. H.; Bekker, C.; Fransman, W. F.; Brouwer, D. H. *J. Aerosol Sci.* **2015**, *81*(62).
31. Klein Entink, R. *NanoPSDA*. Analysis of Time Series of Particle Size Distribution Data in Nano Exposure Assessment. 2014.
32. R-Code Team. *R: A Language and Environment for Statistical Computing*. 2016.
33. Weschler, C. J. *Indoor Air*, **2011**, *21*(3), 205.
34. NIOSH. *NIOSH Pocket Guide to Chemical Hazards*; DHHS (NIOSH): Cincinnati, OH, 2007.
35. Hinds, W. C. *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*; John Wiley & Sons, Inc.: New York, 1999.
36. Wojtya, S.; Klama, P.; Baran, T. *J. Occup. Environ. Hyg.* **2017**, *14*(6), D80.
37. He, Z.; Li, G.; Chen, J.; Huang, Y.; An, T.; Zhang, C. *Environ. Int.* **2015**, *77*(85).
38. ICRP. *International Commission on Radiological Protection. Publication 66: Human respiratory tract model for radiological protection*; Pergamon: Oxford, UK, 1994.
39. HA-International. *Material Safety Data Sheet*. 2006. Available at http://www.sfm.state.or.us/cr2k_subdb/MSDS/TECHNISET_NF_RESIN.PDF.
40. HA-International. *Introduction to Foundry Coatings*. 2017. Available at http://ha-international.com/pdf/Refractory%20Coating%20OverviewV1.pdf.