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Research Article

Use of 3-Dimensional Printers in Educational Settings: The Need for Awareness of the Effects of Printer Temperature and Filament Type on Contaminant Releases

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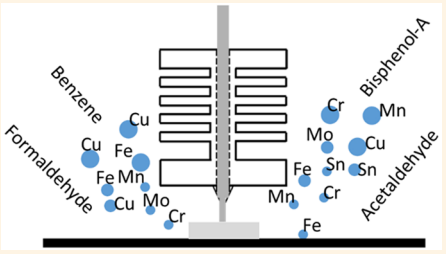
ABSTRACT: Material extrusion-type fused filament fabrication (FFF) 3-D printing is a valuable tool for education. During FFF 3-D printing, thermal degradation of the polymer releases small particles and chemicals, many of which are hazardous to human health. In this study, particle and chemical emissions from 10 different filaments made from virgin (never printed) and recycled polymers were used to print the same object at the polymer manufacturer's recommended nozzle temperature ("normal") and at a temperature higher than recommended ("hot") to simulate the real-world scenarios of a person intentionally or unknowingly printing on a machine with a changed setting. Emissions were evaluated in a college teaching laboratory using standard sampling and analytical methods. From mobility sizer measurements, particle number-based emission rates were 81 times higher; the proportion of ultrafine particles (diameter <100 nm) were 4% higher, and median particle sizes were a factor of 2 smaller for hot-temperature prints compared with normal-temperature prints (all p-values <0.05). There was no difference in emission characteristics between recycled and virgin acrylonitrile butadiene styrene and polylactic acid polymer filaments. Reducing contaminant release from FFF 3-D printers in educational settings can be achieved using the hierarchy of controls: (1) elimination/substitution (e.g., training students on principles of prevention-through-design, limiting the use of higher emitting polymer when possible); (2) engineering controls (e.g., using local exhaust ventilation to directly remove contaminants at the printer or isolating the printer from students); (3) administrative controls such as password protecting printer settings and establishing and enforcing adherence to a standard operating procedure based on a proper risk assessment for the setup and use (e.g., limiting the use of temperatures higher than those specified for the filaments used); and (4) maintenance of printers.



KEYWORDS: *additive manufacturing, ultrafine particles, volatile organic compounds, aldehydes, metals, recycling*

INTRODUCTION

Material extrusion is a type of additive manufacturing process in which feedstock is selectively dispensed through a heated nozzle to build an object. Several variations of material extrusion additive manufacturing exist (see Figure 1a), including fused filament fabrication (FFF), which is the principle of operation for material extrusion-type 3-dimensional (3-D) printers. With FFF 3-D printers, a feedstock polymer filament is heated in an extruder nozzle to just above its glass transition temperature and dispensed onto a build platform, layer-by-layer, to build an object from a computer-aided design software file. FFF 3-D printers are generally smaller and lower in cost and capability than other material extrusion-type additive manufacturing technologies,[1] which makes them popular for use in educational settings.[2,3] FFF 3-D printers are available to students in libraries, dormitories, laboratories, and Makerspaces.[2,4] In these environments, 3-D printing serves multiple purposes, including teaching students about new technologies, serving as a support technology during teaching, and creating assistive technologies. As reviewed by Bharti and Singh, 3-D printing has greatly improved chemical education.[2] For example, 3-D printing is used for teaching crystallography and small molecule structures to chemistry students.[5,6] 3-D printing is also used for learning in other disciplines such as engineering, medicine, and architecture.[4,7,8] Numerous types of polymers are available as FFF 3-D printer feedstock and include acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA),[2] as well as nylon, thermoplastic polyurethane, polycarbonate, polyethylene terephthalate (PET), and glycol-modified PET (PETG). Though less

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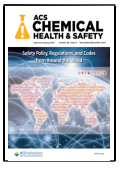

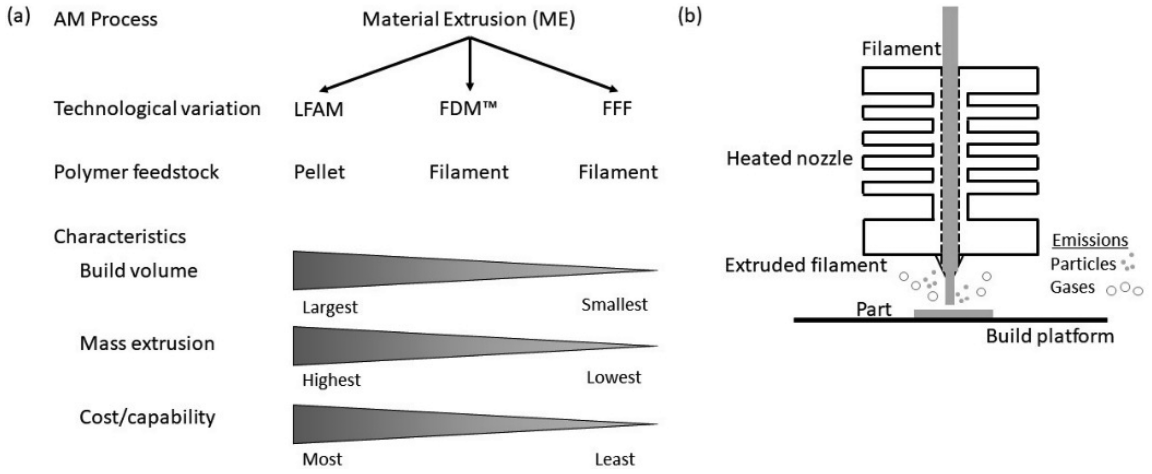

Figure 1. (a) Material extrusion-type additive manufacturing. AM = additive manufacturing, LFAM = large format additive manufacturing, FDM = fused deposition modeling, FFF = fused filament fabrication. (b) Schematic of an FFF 3-D printer extruder nozzle.

common, high impact polystyrene (HIPS), high- and low-density polyethylene (HDPE, LDPE), polypropylene (PP), and T-lyne polymers are also used as feedstock, in part because their waste can be converted into FFF 3-D printing feedstock.[9]

During use, FFF 3-D printers emit billions of particles per minute and numerous gases.[10−12] The primary source of these contaminants is the thermal degradation of the polymer filament in the heated extruder nozzle (Figure 1b).[13,14] Libraries, dormitories, classrooms, and Makerspaces in educational settings are often designed for occupant comfort, not contaminant control. This design consideration is important because an FFF 3-D printer could be placed in a room with or without general ventilation, which might not be sufficient to exhaust emissions, thereby resulting in exposure to users and bystanders. Additionally, if the ventilation system in the space does not directly exhaust emissions to the outdoors, contaminated air could be recirculated throughout the room or building.

Exposure to FFF 3-D printer emissions poses a potential threat to human health. It is known that an association exists between exposure to ambient and indoor ultrafine particles (aerodynamic diameter less <100 nm; UFP) and increases in diastolic blood pressure.[15] A large portion of particles emitted from FFF 3-D printers are ultrafine particles (UFP), i.e., have a diameter less than 100 nm (nm).[16] A single 3 h nose-only exposure to emissions released during FFF 3-D printing with an ABS filament (79 nm mean particle size) caused rats to develop acute hypertension characterized by elevated diastolic blood pressure.[17] Particles released during FFF 3-D printing can also contain metals, such as possible immune sensitizers (e.g., chromium and nickel), asthmagens (e.g., caprolactam), and endocrine disruptors (e.g., bisphenols).[10,18,19] Gases released during FFF 3-D printing include, but are not limited to, asthmagens (e.g., methacrylates) and potential occupational carcinogens (e.g., aldehydes).[10,11,20,21]

■ USE OF FFF 3-D PRINTERS IN EDUCATIONAL SETTINGS

Prevention of exposures from the use of FFF 3-D printers in educational settings requires more data on (1) emission characteristics for various types of polymers, (2) the impact of waste generation and recycling, and (3) the impact of printer settings on emissions.

FFF 3-D Printer Emissions Characteristics. Particle number concentration increased in a college library with the number of FFF 3-D printers operating using PLA polymer filament.[2] In another study, particle and total volatile organic compound (TVOC) concentrations in a college office, dormitory, library, and club space varied during FFF 3-D printing with ABS and PLA polymer filaments.[4] Laboratory test chamber studies have evaluated emissions from HIPS polymer and reported the release of UFP and gases.[10,11,18,21,22] Despite efforts to recycle HDPE, LDPE, and PET polymers,[9] to our knowledge, there are no data available on FFF 3-D printing emission characteristics of HDPE, LDPE, PP, or PET-based polymers such as T-lyne.

Impacts of Waste Generation and Recycling. FFF 3-D printing may generate significant amounts of waste polymer, and this problem is especially apparent in college Makerspaces where inexperienced users have access to printers.[23] One study reported that 34% of ABS polymer used in a college Makerspace ended up as waste.[23] One means to reduce the environmental impact of FFF 3-D printing is to use a filament made from recycled polymer; however, it is unknown whether recycled and virgin polymer filaments will have the same emission characteristics. It is important to note that the properties of recycled filaments will depend, in part, on how well the waste plastic is sorted.[23]

Student Knowledge of Printer Settings. Open-access educational settings give students the opportunity to manually adjust any number of printer settings, including extruder nozzle and/or build platform temperatures. Generally, the FFF 3-D printer temperature settings are unique to a specific type of polymer filament. Allowing users to manually adjust the extruder nozzle temperature presents the opportunity to print at a temperature higher than recommended by the filament manufacturer. Studies with ABS, PLA, and several other polymers have shown that particle and/or TVOC emission rates (ERs) increase with increasing printer nozzle temperature.[11,13,16,18,24−28] Additionally, the exposure potential for subsequent print jobs would remain elevated if the nozzle temperature is not reset.

Research Questions. There are many knowledge gaps on the safer use of FFF 3-D printers in educational settings. Therefore, to test the hypothesis that FFF 3-D printing in educational settings can alter indoor air quality, we (1)

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characterized and compared ERs during FFF 3-D printing using recycled and virgin 3-D printer filaments and (2) determined how simulated FFF 3-D printing with a filament at a temperature higher than that recommended by the manufacture influenced emissions. All printing and contaminant measurements were performed in a university FFF 3-D printing teaching laboratory.

MATERIALS AND METHODS

Ten different filaments were printed at the polymer manufacturer's recommended FFF 3-D printer nozzle temperature ("normal") and at a temperature higher than recommended ("hot") to simulate the scenario of printing on a machine with a changed setting. The normal temperatures were chosen to be within the range recommended for each polymer, and the hot temperatures were chosen to be at least 20 °C higher, which based on a prior study,[27] could yield a measurable difference in emissions. All filaments were made in-house at Robert Morris University from recycled (r) or virgin (v) polymer material using a commercially available filament extruder (Table 1).[29] Briefly, granulated waste PLA or ABS and virgin polymers purchased in pellet form were fed into the extruder hopper, melted, extruded as a softened filament, pulled across cooling fans to bring back to a hardened state, and then wound onto a spool. The rPLA (gray and green) and rABS (tan) filaments were made from granulated waste polymer composed of previously 3-D printed parts made by students as part of their coursework. The vPLA and vABS were purchased from manufacturer A. The vHDPE, vLDPE, vHIPS, and vPP pellets were all from manufacturer B, and the vT-lyne pellets were from manufacturer C. All filaments had a 2.85 mm (mm) diameter except vT-lyne, which had a 1.75 mm diameter. Previously, Byrley et al. reported that particles and organic chemicals were released during filament extrusion.[30] To avoid bias from extrusion emissions, FFF 3-D printing was performed at different times and/or days.

Table 1. Filaments and FFF 3-D Printer Conditions[a]

	normal			hot		
filament	T_{nozzle} (°C)	$T_{platform}$ (°C)	time (min)	T_{nozzle} (°C)	$T_{platform}$ (°C)	time (min)
rPLA (green)	210	60	35.2	265	65	27.8
rPLA (gray)	210	60	33.0	265	65	28.0
vPLA	212	60	41.0	265	65	28.0
rABS	245	105	26.0	265	110	10.0
vABS	245	105	35.0	265	110	28.0
vHDPE	220	100	9.0	270	100	10.0
vLDPE	230	100	17.0	270	100	11.0
vHIPS	230	100	11.0	265	110	29.0
vPP	235	100	13.0	[b]	[b]	[b]
vT-lyne	225	60	45.0	[b]	[b]	[b]

[a] r = recycled polymer, v = virgin polymer, T_{nozzle} = temperature of the extruder nozzle, $T_{platform}$ = temperature of the build platform. [b] Not determined because of difficulty with printing using this filament.

Table 1 summarizes the FFF 3-D printer conditions for all tests. Printing was performed in a 278 m^3 teaching laboratory with an air exchange rate of 9.3/h, as determined using sulfur hexafluoride (SF_6) tracer gas.[31] The same object, a dog bone for tensile testing, was printed for each filament using FFF 3-D printer A with a 0.5 mm diameter brass nozzle, except for the narrower vT-lyne filament, which was printed using FFF 3-D printer B with a 0.4 mm brass nozzle. These 3-D printers represent widely available commercial machines typical for educational settings. For the vHDPE and vHIPS prints only, glue (Elmer's Extra Strength, Columbus, OH) was used to help adhere the dogbone to the build platform. To avoid cross-contamination (and associated effects on emissions), the printer nozzle was purged using the next filament for printing before any monitoring or the actual print test was performed.

Quantification of Contaminants Released during 3-D Printing. For all polymers, an aerodynamic particle sizer (APS, Model 3321, TSI Inc., Shoreview, MN) was used to determine the particle number concentration and size distribution (range: 0.5−20 μm). Particle emissions from FFF 3-D printers are dominated by UFP.[12] As such, a condensation particle counter (CPC, P-Trak Model 8525, TSI Inc.) was used to determine the particle number concentration in the size range 20−1000 nm, and on select site visits, a fast mobility particle sizer (FMPS, Model 3091, TSI Inc.) was used to determine the particle number concentration and size distribution in the size range 5.6−560 nm. The purpose of using the FMPS was to determine if some particle emissions had sizes smaller than 20 nm, the lower cutoff of the CPC. During all print jobs, a photoionization detector (PID) with a 10.6 eV lamp (Ion Science Inc., Stafford, TX) was used to monitor TVOC levels. All instruments were calibrated by their manufacturer and their performances verified before use.

Time-integrated air samples were collected using calibrated sampling pumps (AirChek XR5000, SKC Inc., Eighty Four, PA), except for evacuated canister samples, which use a flow controller. Airborne particles were collected onto 37 mm track-etched polycarbonate filters (TEPC, 3.0 μm pore size, cat. TSTP03700, Millipore, Burlington, MA) housed in open-faced cassette samplers at 4.0 L/min followed by analysis using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Tokyo, Japan) to determine particle morphology and size. An energy dispersive X-ray (EDX, Quantax, Bruker Scientific Instruments, Berlin, Germany) analyzer attached to the FE-SEM was used to determine the elemental composition of individual particles. Air was drawn through 37 mm mixed cellulose ester filters (MCE, 0.45 μm, cat. 225−1914, SKC Inc.) housed in close-faced cassette samplers at 3.0 L/min followed by an analysis of elements using inductively coupled plasma−optical emission spectrometry (ICP−OES) in accordance with National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods (NMAM) 7303.[32] FFF 3-D printing with ABS polymer is reported to release particulate bisphenol A (BPA).[18] During printing with rABS and vABS, airborne particles were collected on 25 mm quartz fiber filters (QFF; cat. 225-401, SKC Inc.) housed in close-faced cassette samplers by drawing air at 3.0 L/min followed by analysis for BPA using quadrupole liquid chromatography−mass spectrometry (Waters Corp., Bedford, MA) as described previously.[33] FFF 3-D printing with ABS polymer can also release caprolactam in the particle[10] and gas phases.[18] Total caprolactam (particles and gas) was sampled using Occupational Safety and Health Administration (OSHA) versatile sampler (OVS-7) tubes (cat. 226-57, SKC Inc.) at 2.0 L/min and analyzed by high-performance liquid chromatography with an ultraviolet detector (HPLC-UV) in accordance with OSHA method PV2012.[34] To quantify specific VOCs, 450 mL Silonite-coated evacuated canister air samplers (Model 29-MC450SQT, Entech Instruments Inc., Simi Valley, CA) with 3 h flow

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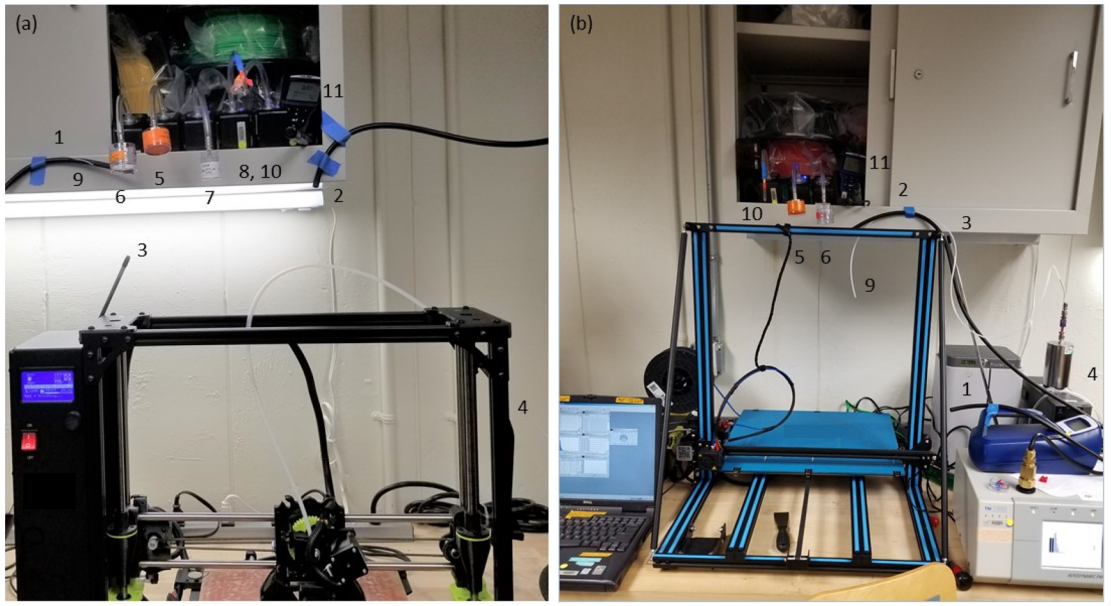

Figure 2. Positioning of sampling equipment during FFF 3-D printing: (a) printer A and (b) printer B. Key: 1 = APS inlet, 2 = FMPS inlet, 3 = P-Trak inlet, 4 = PID inlet (positioned just outside of the photo to the right), 5 = TEPC filter sampler, 6 = MCE filter sampler, 7 = QFF sampler (ABS on printer A only), 8 = OVS-7 sampler (ABS on printer A), 9 = canister sampler inlet, 10 = DNPH sampler, 11 = ambient monitor.

controllers were collected and analyzed in-house to quantify 14 target compounds (acetaldehyde, acetone, benzene, D-limonene, ethanol, ethylbenzene, *n*-hexane, methyl methacrylate, methylene chloride, styrene, toluene, α-pinene, *m*,*p*-xylene, and *o*-xylene) using gas chromatography−mass spectrometry in accordance with NMAM 3900.[35] Typical canister sampling volumes were on the order of 0.02−0.4 L. Samples for airborne aldehydes were collected using cartridges that contained silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) (cat. 226-119, SKC Inc.) at 1.5 L/min and analyzed for formaldehyde in accordance with NMAM 2016,[36] or for 10 aldehydes (acetaldehyde, acrolein, benzaldehyde, crotonaldehyde, formaldehyde, hexaldehyde, isovaleraldehyde, *o*,*m*,*p*-tolulaldehyde, valeraldehyde, and propionaldehyde) in accordance with Environmental Protection Agency (EPA) method TO-11A,[37] using HPLC-UV. At this flow rate, carbonyl sample volumes ranged from 0.022 to 0.13 m^3. Figure 2 illustrates the placement of the sampling equipment. The height of the sampler inlets was at the breathing zone (around the face) if the user was standing at the printer. The sampler inlets were positioned to minimize the potential for sampling bias.

Background samples (FFF 3-D printer A or B powered on but not operating) were collected for at least 15 min at the same location as the printers prior to each print test. When multiple print tests were monitored on the same day, the room was allowed to air out for approximately 20−30 min (approximately 3−5 air changes) between tests. Background samples collected prior to each print test were subtracted from the sampling results of the ensuing print test to ensure that background corrections were spatially and temporally related and accounted for in the reported concentrations and emission rates. With the exception of 1 day, there were no other activities occurring in the room during printing and air monitoring. During one visit, an FFF 3-D printer was extruding the PLA filament approximately 5 m from FFF 3-D printers A and B for a short time. Note that, on this specific day, if there were any fluctuations in emissions from this printer running PLA during emissions monitoring of a test at printer A or B, the background samples collected prior to the print test would not account for this variability. However, in addition to sampling at printer A or B, samples were also collected at far field locations in the room (data not shown); the instruments closest to the printer that was already running PLA did not show any large fluctuations, and concentration values were very low compared with the instruments at printer A or B, which indicated that there was no confounding of sampling results.

Emission Rate Calculations. Average particle ERs in units of no. per minute (min) were calculated as described by He et al.[38] and used to describe emissions from FFF 3-D printers in real-world settings.[27,39] ERs were calculated separately for the CPC and FMPS to determine whether a fraction of the UFP were below the lower size cutoff of the CPC.

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

Here, V = the volume of the teaching laboratory (278 m^3), C_{peak} = the instantaneous peak particle number concentration during FFF 3-D printing in units of no. per cubic centimeter of air (no./cm^3), C_{bkgd} = the average background concentration of particles indoors during the few minutes preceding the start of printing, Δt = the time difference between C_{peak} and C_{bkgd}, AER = the air exchange rate in the room as determined by the measurement of SF_6 decay (9.3/h), $\overline{\mathrm{AER} + k}$ = the average total removal rate of particulate (AER plus k, the rate of contaminant loss due to deposition onto surfaces) calculated from a plot of particle concentration decay versus time, and $\overline{C}_{\mathrm{in}}$ = the average particle number concentration (no./cm^3) during active printing. C_{in} and C_{bkgd} are functions of other factors and can vary in time.[37] Hence, to estimate the average emission rate, the equation is simplified by using average C_{in} and C_{bkgd} values instead of functions and by ignoring the effects of particle dynamics (i.e., condensation, evaporation, and coagulation), which are considered to be minor.[37] Total print times varied depending on the polymer; however, nearly all values of Δt

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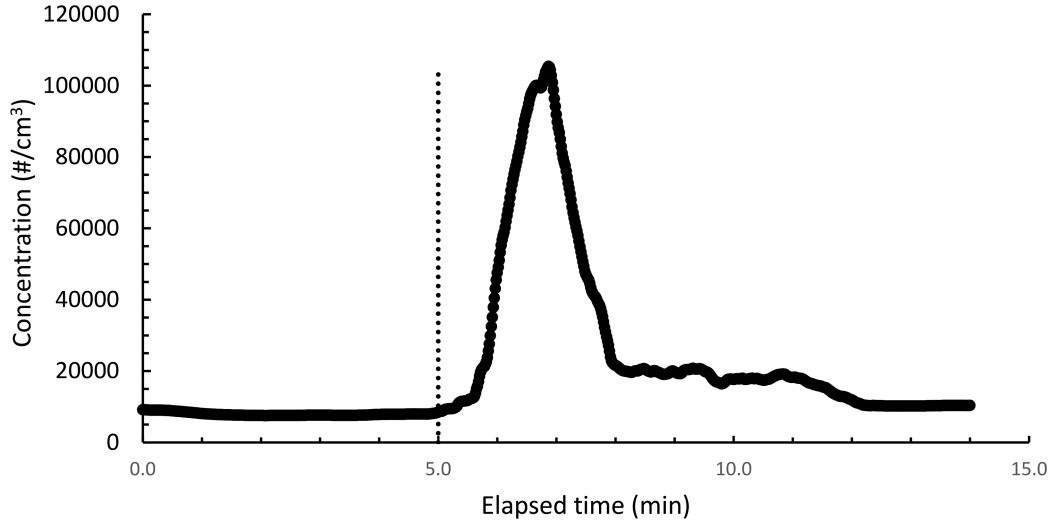

Figure 3. Example time-series plot of particle concentration for an HDPE (normal temperature) print test illustrating the rapid burst in concentration followed by decay over the remaining print time. Dotted vertical line = start of printing.

Table 2. Particle Number and TVOC Emissions during FFF 3-D Printing

		APS		FMPS				P-Trak		PID
filament[a]	print	median (nm)	95th % (nm)	median (nm)	% < 100 nm[b]	ER (no./min)	TP (no.)	ER (no./min)	TP (no.)	ER (mg TVOC/min)
rPLA (green)	normal	594 (585–600)	598	n/a[c]	n/a	n/a	n/a	–[d]	–	2.39
	hot	620 (613–626)	624	16.9	99.9	2.35×10^{14}	6.83×10^{15}	9.93×10^{12}	2.88×10^{14}	1.35
rPLA (gray)	normal	652 (642–662)	660	49.2	90.7	1.17×10^{11}	3.85×10^{12}	–	–	0.94
	hot	638 (631–646)	643	16.4	99.9	1.80×10^{14}	5.03×10^{15}	2.37×10^{13}	6.63×10^{14}	1.72
vPLA	normal	651 (631–810)	665	45.7	96.4	–	–	–	–	1.81
	hot	621 (614–626)	626	16.3	99.9	1.29×10^{14}	3.61×10^{15}	1.13×10^{13}	3.15×10^{14}	2.28
rABS	normal	658 (647–849)	675	26.7	99.0	4.09×10^{12}	1.06×10^{14}	2.36×10^{12}	6.12×10^{13}	2.08
	hot	617 (613–621)	621	19.9	99.9	3.21×10^{14}	3.21×10^{15}	1.87×10^{13}	1.87×10^{14}	0.74
vABS	normal	657 (638–877)	675	38.0	96.8	3.59×10^{12}	1.26×10^{14}	6.10×10^{11}	2.14×10^{13}	4.67
	hot	614 (606–620)	619	18.5	99.9	2.65×10^{14}	7.42×10^{15}	2.99×10^{13}	8.37×10^{14}	1.59
vHDPE[e]	normal	594 (591–598)	597	n/a	n/a	n/a	n/a	1.42×10^{13}	1.27×10^{14}	2.03
	hot	594 (590–596)	596	n/a	n/a	n/a	n/a	2.18×10^{14}	2.18×10^{15}	5.22
vLDPE	normal	593 (591–595)	595	n/a	n/a	n/a	n/a	3.92×10^{12}	6.67×10^{13}	1.69
	hot	590 (585–594)	593	n/a	n/a	n/a	n/a	8.16×10^{13}	8.98×10^{14}	2.12
vHIPS[e]	normal	590 (584–681)	641	n/a	n/a	n/a	n/a	1.30×10^{13}	1.43×10^{14}	3.44
	hot	650 (615–677)	675	32.8	99.4	1.19×10^{14}	3.45×10^{15}	2.05×10^{13}	5.95×10^{14}	0.34
vPP	normal	591 (588–598)	593	n/a	n/a	n/a	n/a	1.12×10^{13}	1.45×10^{14}	0.44
	hot	[f]	[f]	[f]	[f]	[f]	[f]	[f]	[f]	[f]
vT-lyne	normal	631 (620–644)	638	84.2	76.8	–	–	–	–	2.25
	hot	[f]	[f]	[f]	[f]	[f]	[f]	[f]	[f]	[f]

[a]r = recycled, v = virgin. [b]Particles with size 5.6–107 nm (size bin with upper cutoff closest to 100 nm) [c]n/a = not applicable (FMPS not available on day of sampling) [d]– = ER could not be calculated from data. [e]Glue (Elmer's Extra Strength) applied to build platform. [f]Not determined because of difficulty with printing using this filament.

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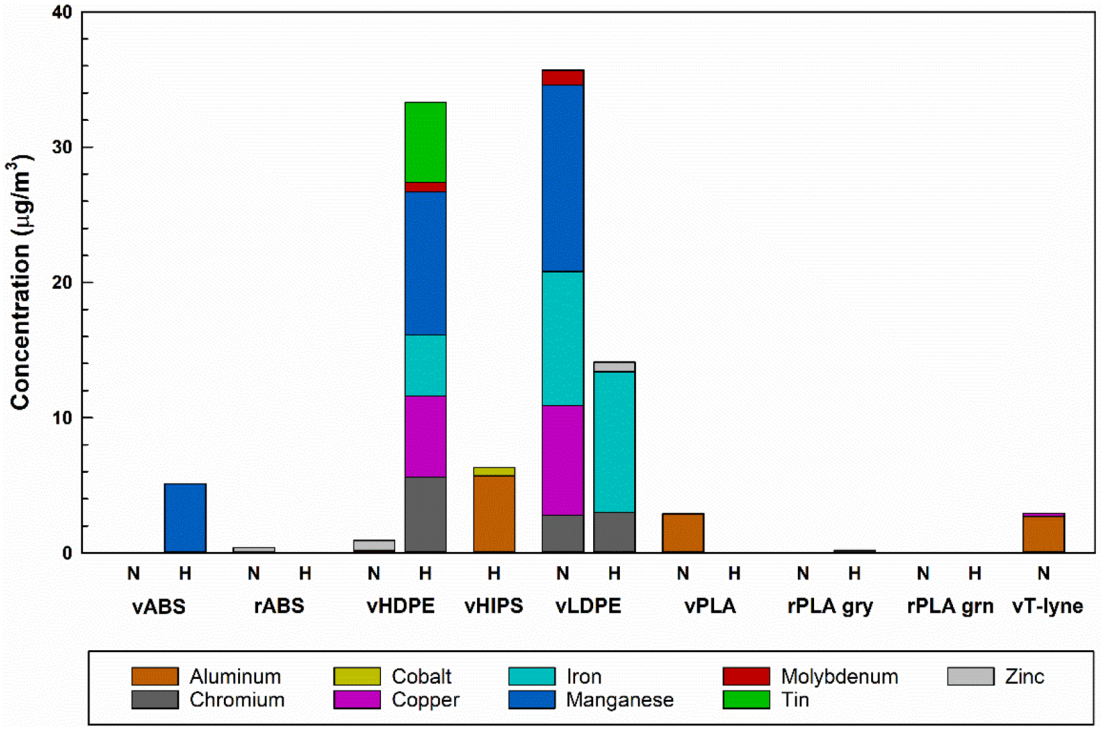

Figure 4. Concentrations of elements released during print tests.

ranged from <1 to 6 min; i.e., the peak concentration occurred near the start of a print test (see example in Figure 3). This emission profile of an "initial burst" followed by rapid decay in particle concentration during FFF 3-D printing has been observed by others.[24,28] The emission profile shown in Figure 3 indicated that, in this study, under the unique conditions of printer, filament, and print duration, particle release was dominated by an initial burst. It is important to note that not all emission profiles follow this pattern. For example, Zhang et al. reported that, for some FFF 3-D printing tests, the particle concentration rose and then plateaued and remained steady for the duration of the printing.[28] The total number of particles (TP) emitted during a print job was calculated as the CPC or FMPS ER × Δt. The second-by-second particle number concentration measurement data were smoothed by using a 1 min moving average for calculations.

Average TVOC ERs were calculated using a model that was previously applied to gas-phase emissions from a binder jetting AM machine assuming that all TVOC losses were from air exchange in the workspace:[40]

$$\mathrm{ER} = (C_{\mathrm{TVOC},t} - C_{\mathrm{bkgd}}) \times V \times \mathrm{AER} \quad (2)$$

Here, $C_{\mathrm{TVOC},t}$ is the instantaneous TVOC concentration at an elapsed time, t; and C_{bkgd} is the average background TVOC concentration indoors during the few minutes preceding the start of FFF 3-D printing.

Statistical Analysis. Statistics were computed in JMP (version 13, SAS Institute Inc., Cary, NC). Paired t tests were used to evaluate the null hypotheses that median particle sizes; number and TVOC ERs; proportion of UFP, C_{peak}, and TP; and summed concentrations of individual VOCs measured using canister samplers ($\sum \mathrm{VOC}_i$), individual aldehydes measured using DNPH samplers ($\sum \mathrm{Ald}_i$), and individual elements measured using MCE filter samplers ($\sum \mathrm{Elem}_i$) were equal between the normal- and hot-temperature prints and between recycled and virgin filaments (significance level of $\alpha = 0.05$).

RESULTS

Influence of Temperature on Particle Size, Number-Based ERs, and TVOC ERs. Table 2 summarizes the emissions during normal- and hot-temperature printing. The median diameter of particles (APS data) ranged from approximately 590 to 660 nm; a paired t test failed to reject the null hypothesis that sizes were equal between the hot- and normal-temperature prints ($p = 0.66$). Average particle concentrations measured using an APS were low, and number-based particle ERs were incalculable. From the FMPS data, the median diameter of airborne particles ranged from 16 nm (all PLA, hot prints) to 84 nm (vT-lyne, normal print), and for 7 out of 11 polymers, the proportion of particles that were UFP exceeded 99%. Particle number-based ER values ranged from 1.17×10^{11} no./min (rPLA: gray, normal) to 3.21×10^{14} no./min (rABS, hot). Paired t tests rejected the null hypotheses that median FMPS particle sizes, proportion of UFPs, and average particle number-based ERs were equal between the hot- and normal-temperature prints (all p-values <0.05). P-Trak particle concentration data for vPLA and rPLA prints at the normal temperature were equivalent to the background, so number-based ERs were incalculable. For all other prints, ER values (P-Trak data) ranged from 6.10×10^{11} no./min (vABS, normal) to 2.18×10^{14} no./min (vHDPE, hot); a paired t test failed to reject the null hypothesis that ERs were equal between the hot- and normal-temperature prints ($p = 0.14$). Looking individually at TP values calculated from the FMPS and CPC data, TP appeared higher for the hot-temperature prints compared with normal-temperature prints. For example, TP calculated from FMPS data for the hot rPLA (gray) print test was 1.80×10^{14} particles, and for the normal-temperature print test, TP was 1.17×10^{11} particles. However, when data for all print jobs were pooled, there were no statistical

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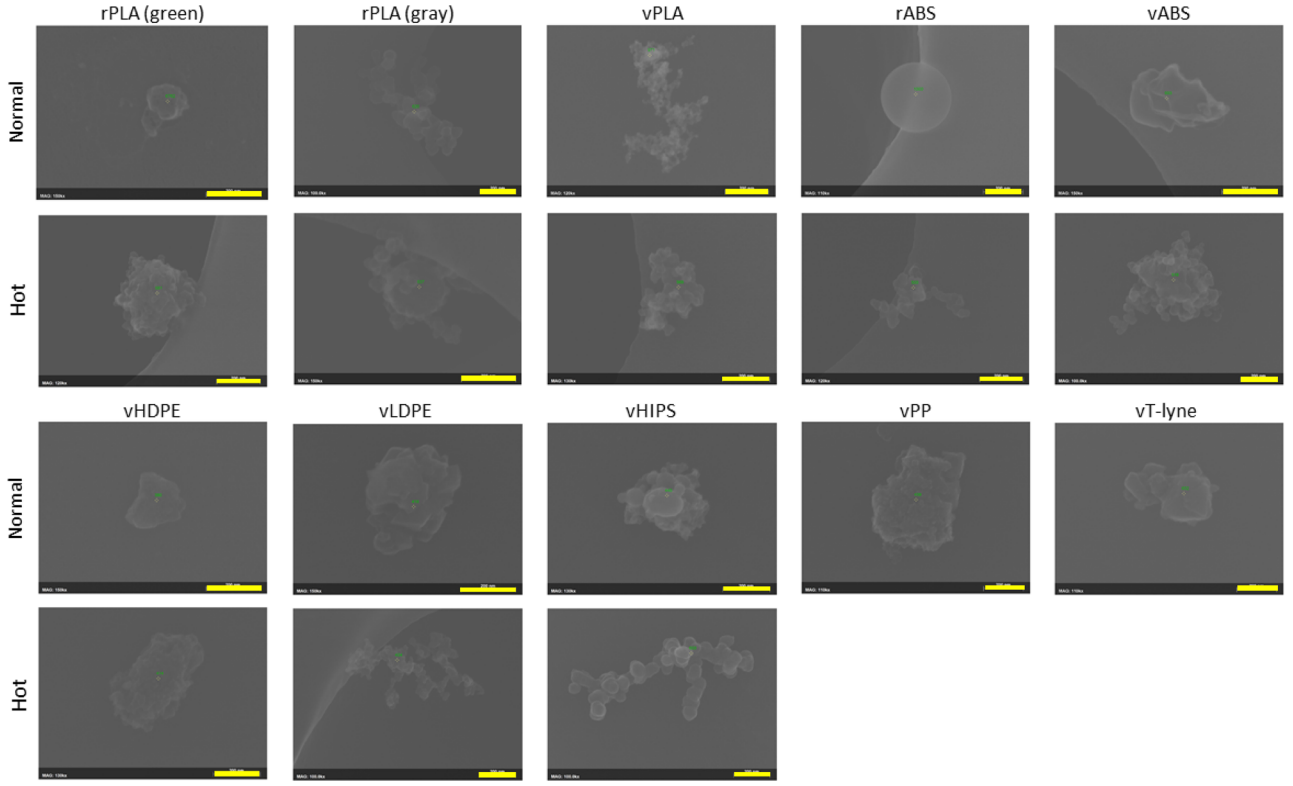

Figure 5. FE-SEM images showing examples of particles released during FFF 3-D printing with rPLA, vPLA, rABS, vABS, vHDPE, vLDPE, vHIPS, vPP, and vT-lyne filaments for normal- and hot-temperature print tests (vPP and vT-lyne polymers were not evaluated at the hot temperature because of difficulties with printing). Scale bar = 200 nm on all images.

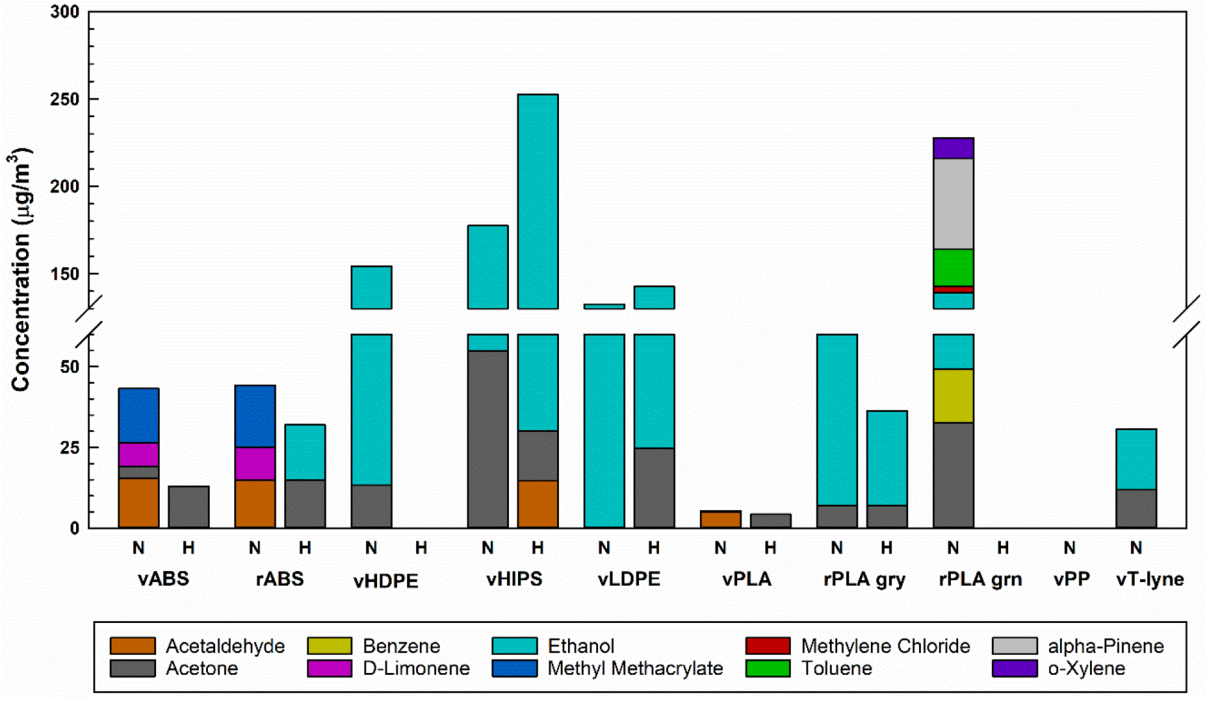

Figure 6. Concentrations of individual VOCs released during normal- and hot-temperature FFF 3-D print tests.

differences in TP values between normal- and hot-temperature prints that were calculated from the P-Trak data (p = 0.06) or from the FMPS data (p = 0.05). Values of C_{peak} (not presented in Table 2) from P-Trak and FMPS measurements were not different between the hot- and normal-temperature prints (p = 0.49 and p = 0.24, respectively).

TVOC ER values varied by a factor of 15 among polymers. The lowest calculated ER was for vHIPS (hot print), and the highest ER value was for vHDPE (hot print). There were no statistical

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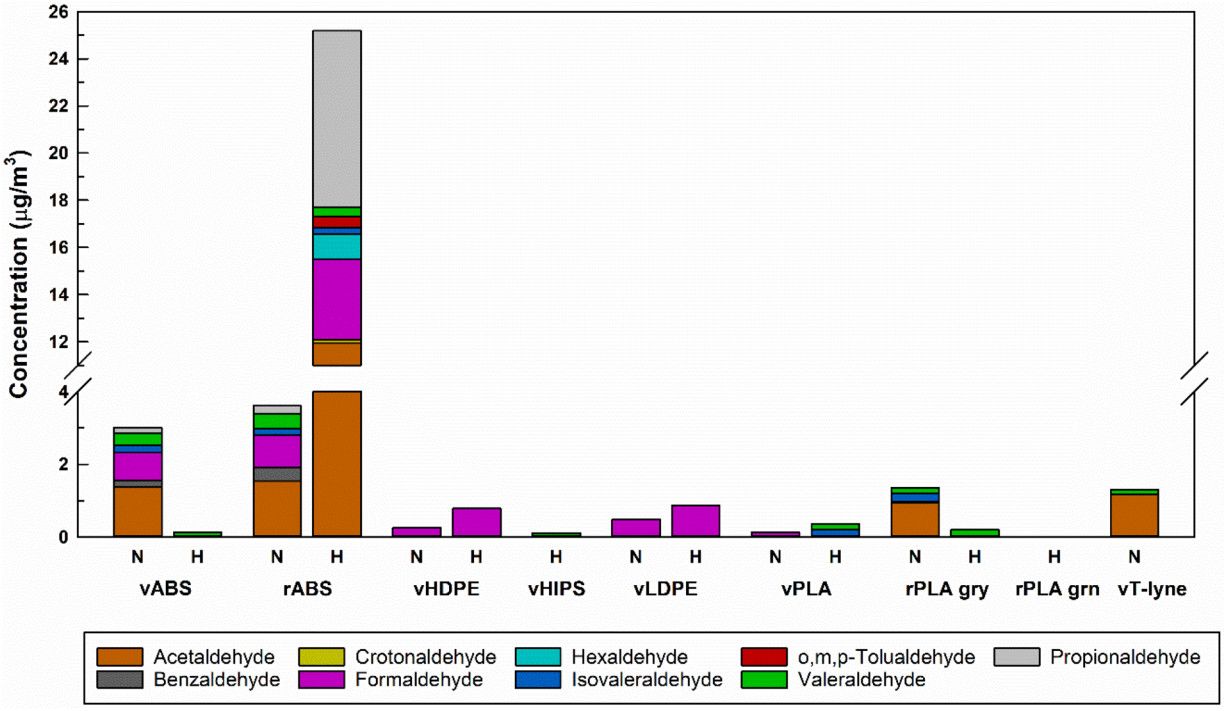

Figure 7. Concentrations of individual aldehydes during normal- and hot-temperature FFF 3-D print tests.

differences in average TVOC ER and C_{peak} (not presented in Table 2) values between the hot- and normal-temperature prints ($p = 0.56$ and $p = 0.29$, respectively).

Influence of Temperature on Particle- and Gas-Phase Emission Characteristics. From Figure 4, trace levels of nine different elements were quantified by ICP−OES analysis during all print tests (excluding vPP, for which no samples were collected for metals analysis because media was not available at the time). The highest concentration detected was for manganese (14 $\mu g/m^3$) during the vLDPE normal-temperature print. Six elements (chromium, copper, iron, manganese, molybdenum, and tin) were released into the air during FFF 3-D printing with vHDPE (hot), which was a higher frequency than any other polymer type. A paired t test failed to reject the null hypothesis that $\sum Elem_i$ was equal between the normal- and hot-temperature prints ($p = 0.77$).

Figure 5 shows FE-SEM images of particles released during FFF 3-D printing. Some particles had a spherical shape (e.g., rABS, normal) while others had an irregular shape (e.g., vT-lyne, normal). Observed morphologies included compact particles (e.g., vHDPE, normal) and diffuse clusters composed of nanoscale primary particles (e.g., vHIPS, hot). Most particles were composed of carbon, though some also contained iron and/or nickel (e.g., vLDPE, normal); the source of these metals (e.g., constituents of the filament or contamination from the brass extruder nozzle) is unknown (EDX data not shown).

The concentration of BPA was 17.1 ng/m^3 during the vABS hot-temperature print, but for all other samples, it was nondetectable (<12.5 ng/m^3). All samples for total caprolactam collected during printing with the ABS and PLA filaments were below the analytical limit of detection of (6.7 $\mu g/m^3$).

Ten VOCs were quantified in the air using evacuated canister samplers (see Figure 6). A paired t test failed to reject the null hypothesis that $\sum VOC_i$ was equal between the normal- and hot-temperature prints ($p = 0.21$).

Nine of the target aldehydes (acrolein was not detected on any samples, i.e., <0.4 $\mu g/m^3$) were released into the teaching laboratory air (Figure 7). For rABS, six different aldehydes were released during the normal-temperature print, and eight aldehydes were released during the hot-temperature print, which were higher frequencies than any other polymer type. In general, concentrations of aldehydes emitted during printing with ABS filaments appeared to be higher compared with all other polymer types. No samples were collected for PP because media was not available at the time. A paired t test failed to reject the null hypothesis that $\sum Ald_i$ was equal between the normal- and hot-temperature prints ($p = 0.45$).

Comparison of Emissions between Recycled and Virgin ABS and PLA Polymer Filaments. For the ABS and PLA filaments, paired t tests failed to reject the null hypotheses that median particle sizes (APS, FMPS), proportion of particles that were UFP (FMPS), number-based ERs, C_{peak}, and TP (P-Trak, FMPS), and TVOC ERs and C_{peak} were equal between recycled and virgin polymers (all p-values ≥0.09). On a mass concentration basis, the $\sum VOC_i$ appeared to be highest for rPLA (green) at 228 $\mu g/m^3$, followed by rPLA (gray) at 74 $\mu g/m^3$ and vPLA at 4 $\mu g/m^3$; however, a paired t test failed to reject the null hypothesis that $\sum VOC_i$ was equal between recycled and virgin polymers ($p = 0.17$). Additionally, paired t tests failed to reject the null hypothesis that $\sum Elem_i$ ($p = 0.12$) and $\sum Ald_i$ ($p = 0.36$) were equal between recycled and virgin polymers.

■ DISCUSSION

Environmental test chamber evaluations of FFF 3-D printer emissions have reported that particle number-based ERs and/or TVOC ERs increased as the printer extruder nozzle temperature increased.[11,13,16,18,24−26,28] Whether nozzle temperature could influence particle and TVOC levels in large rooms (similar to the size in this study) under dynamic real-world settings is poorly understood. Stabile et al. evaluated FFF 3-D printer emissions in a 40 m^3 room (AER = 0.22/h) and reported significantly

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increased particle number-based ERs with increased nozzle temperature.[27] In the current study, particle number-based ER values (FMPS data) were significantly higher; median particle sizes were significantly smaller, and the proportion of UFPS was higher for the hot-temperature prints compared with the normal-temperature prints ($p < 0.05$) in a 278 m^3 college teaching laboratory (AER = 9.3/h). Collectively, our data and the available literature indicate that ventilation based on occupant comfort was insufficient to exhaust contaminants released from an FFF 3-D printer.[41] Interestingly, the lower particle size detection limit for the P-Trak instrument (20 nm) was greater than the median particle sizes measured using an FMPS during all hot-temperature prints except vHIPS (see Table 1), so the P-Trak did not count a high number of particles emitted during the hot-temperature prints, which translated into lower calculated ER values compared with the FMPS instrument. The release of sub-20 nm particles during FFF 3-D printing highlights the importance of air monitoring instrument choice when planning an exposure assessment.[16]

Particle number-based ERs (P-Trak data) for vHIPS ranged from 1.3 to 2.0 × 10^{13} no./min (Table 2), which were higher than the values of 10^8−10^{11} no./min reported in the literature.[10,18,22,42] The TVOC ER for HIPS calculated in the current study was 0.34−3.44 mg/min (Table 2), which was higher than the values of 0.015−0.047 mg/min reported in the literature.[10,11,21] Previous studies indicated that, during FFF 3-D printing with the HIPS filament, styrene was the major VOC emission with lesser amounts of acetic acid, acetaldehyde, acetone, benzaldehyde, ethylbenzene, formaldehyde, hexanal, methyl methacrylate, toluene, and xylenes.[10,11,18,21,22] In the current real-world study, for vHIPS, acetaldehyde and acetone were quantified using canister samplers (Figure 6); however, the concentrations of ethylbenzene were equivalent to the background, and levels of styrene were below the analytical limit of detection. The only aldehyde detected during printing with HIPS was valeraldehyde (Figure 7). Several factors may explain the differences in particle and VOC emissions between our study and the prior literature, including the source of filament (brand), printing parameters (e.g., use of glue to adhere the dog bone to the build platform), sampling strategies (e.g., placement near printer), and analytical methods employed to measure contaminant concentrations.

Particle number-based ER values (P-Trak data) for vHDPE, vLDPE, and vPP filaments ranged from 0.4 to 1.4 × 10^{13} no./min for the normal-temperature prints (Table 2). Literature values of particle ERs for ABS, PLA, nylon, polycarbonate, PETG, and several other types of filaments ranged from 10^8 to 10^{11} no./min.[10,28,43] A comparison of results in Table 2 to existing literature values indicated that the vHDPE, vLDPE, and vPP filaments emitted particles at higher number-based rates than ABS polymer. A prior study demonstrated that rats developed acute hypertension with a one-time exposure to emissions from 3-D printing with the ABS filament.[17] If vHDPE, vLDPE, and vPP emissions induce a similar effect, it would be prudent to perform FFF 3-D printing with these filaments only in a well-ventilated area. TVOC ERs for vHDPE, vLDPE, vT-lyne, and vPP in the current study range from 0.44 to 2.25 mg/min for the normal-temperature prints (Table 2), which was higher than those reported for ABS, PLA, nylon, HIPS, and PVA (0.003−0.028 mg/min).[11] Numerous reasons may explain the differences in TVOC ERs among studies, including the source of polymer feedstocks, printing parameters, and sampling and analytical methods.

HDPE, LDPE, and T-lyne are all made from polyethylene, a linear polymer of carbon and hydrogen atoms. T-lyne is a copolymer of polyethylene and Surlyn ionomer (made from ethylene/methacrylic acid copolymer and a zinc salt). During FFF 3-D printing with these polymers, several metals were quantified at concentrations above background levels in the teaching laboratory air (Figure 3). The exact source of the metals in the aerosol is unknown. Many plastics contain metal additives that are used as antioxidants, colorants, and stabilizers.[44] It is likely that the metals quantified in the air were from additives unique to the synthesis of each of these polymers. Many of the metals quantified in the air during printing with these filaments were not present when printing with ABS or PLA filaments (Figure 4), which suggested that there was not contamination from a systematic source (e.g., the brass FFF 3-D printer extruder nozzles). Though area air sampling results are not directly comparable to occupational exposure limits, for perspective, concentrations of metals were at least a factor of 80 below NIOSH recommended exposure limits.[45]

During FFF 3-D printing with vHDPE and vT-lyne filaments at the normal temperature, levels of ethanol and acetone increased in the teaching laboratory air; for vLDPE, only ethanol was quantified in the air. Formaldehyde was released during FFF 3-D printing with vHDPE and vLDPE; however, printing with vT-lyne released acetaldehyde and valeraldehyde (Figure 7). FFF 3-D printing with other polyethylenes such as PET and PETG primarily released xylene, toluene, styrene, and ethylbenzene, though none of these compounds were observed in the current study.[43,46] The literature from plastics extrusion (a process analogous to FFF 3-D printing) studies provides additional insights on possible emissions. Unwin et al. reported that formaldehyde was quantifiable in the air of workplaces that extruded polyethylene polymers.[47] Barlow et al. measured emissions during the extrusion of HDPE at 193−221 °C (lower than the FFF 3-D printing temperatures in the current study) and reported the release of acetone and formaldehyde; and measured emissions during the extrusion of LDPE at 260−315 °C (similar to the hot-temperature print in the current study) and reported the release of formaldehyde.[48]

Levels of VOCs and aldehydes in the teaching laboratory air during FFF 3-D printing with the vPP filament were below analytical detection limits for all target compounds. Purohit and Orzel reported that the thermo-oxidative combustion induced degradation of PP from 220 °C (similar to the normal-temperature print in the current study) to 280 °C released acetone, acetaldehyde, formaldehyde, and other gases.[49] Note that their data were for the combustion of PP, whereas during FFF 3-D printing, the polymer was only heated to just above its glass transition temperature.

There were no statistical differences in emission metrics between printing with recycled and virgin ABS and PLA polymer filaments. For rABS, the number of aldehyde compounds released during normal-temperature ($n = 6$) and hot-temperature ($n = 8$) printing was higher than for any other polymer type, though the presence of one compound, crotonaldehyde (0.14 $\mu g/m^3$, rABS hot-temperature print), could be an artifact of the DNPH sampling method.[50] A higher number of VOCs (Figure 6) and aldehydes (Figure 7) were released from the rPLA filaments compared with the vPLA filament. Additionally, $\sum VOC_i$ appeared higher for rPLA filaments compared with the vPLA filament, which suggested differences in emissions between recycled and virgin PLA filaments and warrants further

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research. It is important to note that the waste ABS and PLA parts that were granulated to make the recycled filaments were originally printed using filament from multiple manufacturers, so it was impossible to discern which waste parts were made with which manufacturer's filament. As such, it is likely that the recycled filaments represent multiple manufacturers. In contrast, the pellets used to make the virgin filaments were from a single manufacturer. Previously, Zhang et al.[28] reported that the polymer manufacturer influenced particle emissions during FFF 3-D printing; hence, it is possible that differences in the manufacturers of the recycled and virgin polymers could also contribute to the observed variability in amounts of volatile compounds released during printing. Herein, the recycled filaments were made from clean waste polymer, i.e., discarded successful and/or errant ABS and PLA parts, not food containers or product packaging. No differences were observed in emission characteristics between the recycled and virgin filaments; however, it does not mean that all recycled filaments will behave similarly to virgin polymer filaments, especially if the recycled filament is made from contaminated or soiled plastic. For example, emissions from HDPE during extrusion in the presence of detergent (to simulate household waste) demonstrated that 1,4-dioxane (throat irritant and potential occupational carcinogen[45]) was released into the air.[51]

STRENGTHS AND LIMITATIONS

Strengths of this study were (1) the use of standard industrial hygiene sampling and analytical methods to assess contaminant releases, (2) FFF 3-D printing with 10 different recycled and virgin filament materials, and (3) the fact that all monitoring was performed in an educational setting. Additionally, it is worth noting that the current study was performed in the context of a college teaching laboratory; however, the findings and conclusions also apply to the use of FFF 3-D printers in grade school, high school, and graduate educational settings as well as municipal libraries and private Makerspaces. Field evaluations that utilize multiple types of real-time and time-integrated sampling equipment are time- and resource-intensive, which limited our measurements to one print test per filament and printer nozzle temperature combination. The waste PLA and ABS parts were self-sorted by students into separate bins based on the type of feedstock. To make the recycled filaments, waste parts were taken from each presorted bin. It is possible that a printed part was mistakenly placed in the wrong bin, so to minimize this potential misclassification, waste was screened (surface appearance, color as an indicator based on knowledge of University filament inventory, and weight) prior to granulating. Emissions were only measured during FFF 3-D printing with a single printer operating, but potential exposures during teaching could be higher if multiple printers were simultaneously in use or if printers were operated in a smaller room with a lower air exchange rate. Additionally, print time varied among tests, so it is possible for some of the shorter-duration tests that the concentration of VOCs and aldehydes did not reach steady state inside the laboratory during sampling, which in turn resulted in an underestimation of concentration for some chemicals. Finally, it is important to note that measurements were collected in one location in the room (i.e., above the printer), though TVOC and particle concentrations could be different at other locations near the printer (e.g., where a user sits or stands in front of it) and locations in the room (e.g., at a distance from the printer).

IMPLICATIONS FOR EDUCATIONAL SETTINGS

The use of FFF 3-D printers in educational settings provides many unique advantages for teaching students about new technologies, serving as a support technology during teaching, and creating assistive technologies.[2,3,5,6] Previously, investigators measured particles and/or TVOCs released from FFF 3-D printers in college libraries, offices, classrooms, and dormitories and provided several recommendations for the use of these printers in college and general educational settings.[2,4] Based on the results of our study and the available literature, herein, recommendations are provided in the context of the industrial hygiene "hierarchy of controls" for the safer use of FFF 3-D printers in educational settings; i.e., elimination and substitution are preferred over engineering controls, which in turn are preferred over administrative controls. Personal protective equipment (e.g., respirators) are least preferred as their effectiveness depends on many factors such as proper selection, fit, and use.[52]

(1) Elimination/Substitution
   (a) Given the unique benefits of FFF 3-D printing in chemical education, it is unlikely that this tool will be eliminated from curricula; however, with proper training, student operators can reduce emissions and exposures via prevention through design. For example, Simon et al. demonstrated that particle emissions varied by print-phase (i.e., rapidly increased at the start of printing and remained elevated until the raft layer was completed, decreased to baseline levels while printing the sides of an object, etc.).[53] Cheng et al. demonstrated that infill height, density, and pattern all had significant impacts on emissions.[54] Hence, training on the design of parts to avoid certain build characteristics (infill amount, pattern, etc.) could be a powerful tool to help decrease emissions.
   (b) When feasible, use a filament that has lower emissions (standardized criteria are lacking for ranking filaments by their emissions, though information on various polymers can be gleaned from resources such as Table 2 in the current study).
   (c) If a higher-emitting type of polymer filament is required for a specific application (e.g., HDPE) because of its unique properties, substitute it with a lower-emitting polymer for test prints (e.g., PLA), reserving the higher-emitting polymer for printing the final part.
(2) Engineering Controls
   (a) The use of local exhaust ventilation to directly remove both particle- and gas-phase contaminants at the emission source is likely to be an effective solution to minimize exposures.[39,42,55−57] Ventilation for occupant comfort is not intended for contaminant control. Further, contaminant concentrations increase with the number of printers operating simultaneously in a room.[2,12]
   (b) Isolation of an FFF 3-D printer from students, for example, via the following:
      (i) A see-through ventilated enclosure ("vending machine approach"): the cabinet can be opened for students' access to set up the printer; then, it is closed during printing;

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after the print is completed, the student can have access to retrieve their part. With this approach, students have limited access to the printer to minimize exposures, but they still operate the machine to gain hands-on learning experience.

(ii) By placing the printer in a separate room with a real-time video broadcast for students to observe the printer operating. This control might be more suited for grade school students who do not need to operate the printer to benefit from it educationally. Ideally, the room used to isolate the printer should be well-ventilated to avoid contaminant build up and lower user exposure from a reversal of airflow when the door to the room is opened to retrieve the printed part. If ventilating the room is not feasible, sufficient time should be allowed for contaminants to dissipate before opening the door.

(3) Administrative Controls

(a) Password protect the printer settings in open-access settings to prevent intentional or errant printing at temperatures higher than recommended for a given filament polymer type.

(b) Install printers in one area of a room or away from users as far as feasible to reduce exposures if no elimination/substitute or engineering controls are available or applicable.

(c) Educate student users on the potential hazards of FFF 3-D printing, including how printing parameters influence exposures to particles and gases (current study), as well as mechanical, thermal, electrical, and ergonomic hazards.[58]

(d) Establish and require user adherence to a standard operating procedure (SOP) based on a proper risk assessment for the setup, use, and maintenance of FFF 3-D printers that includes (but is not limited to) the following practices to reduce emissions:

(i) Preheating the extruder nozzle without the filament to reduce particle emissions.[24]

(ii) Leaving the vicinity of a printer when initiating a new print job because particle concentrations are often highest at the start of printing.[59]

(iii) Only printing with a polymer filament at the lowest recommended temperature setting that yields a satisfactory print.[60]

(iv) Not immediately approaching a printer if it malfunctions because emissions increase during malfunctions.[60,61] Rather, wait for contaminants to dissipate before fixing the issue.

(v) Ensuring that the extruder nozzle and build platform surfaces are cleaned before and after each print job.[60] Ensuring that any cleaning product is used safely and is appropriate for the printer build platform.

(vi) For additional guidance that can be incorporated into an SOP, see the freely available poster "3D Printing with Filaments: Health and Safety Questions to Ask" available from NIOSH at https://www.cdc.gov/niosh/docs/2020-115/pdfs/2020-115.pdf?id=10.26616/NIOSHPUB2020115

(e) The purchase and installation of 3-D printers in educational settings should be made in consultation with qualified health and safety specialists. Free online guides are available from sources such as the United Kingdom Health and Safety Executive (http://dt.cleapss.org.uk/Resource-File/3D-printing-in-schools-and-colleges-managing-the-risks.pdf) and the University of New South Wales (https://i.unisa.edu.au/siteassets/human-resources/ptc/files/guidelines/safety-and-wellbeing/3d_printer_purchasing_safety_guidelines.pdf).

(f) Once installed, qualified health and safety specialists should conduct periodic monitoring of FFF 3-D printer emissions during use or if changes are made to the printing environment (e.g., addition of more printers to the space, changes to ventilation, or changes in feedstock materials). In the current study, several different instruments that spanned from hand-held portable instruments (P-Trak, PID) to semiportable research grade instruments (APS, FMPS) were utilized to monitor emissions. For screening purposes, hand-held instruments are suitable for most monitoring situations with FFF 3-D printers, though as shown in Table 2, because of differences in size measurement capabilities, these instruments could underestimate actual concentrations in the air. Note that these instruments are nonspecific and count any particle or measure organic gas in the environment, whether released from a 3-D printer or other source; they must be used by a qualified person.

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Notes

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■ REFERENCES

(1) *ISO/ASTM 52900: Additive Manufacturing, General Principles, Terminology*; ISO: Geneva, Switzerland, 2015.
(2) Bharti, N.; Singh, S. Three-Dimensional (3D) Printers in Libraries: Perspective and Preliminary Safety Analysis. *J. Chem. Educ.* **2017**, *94* (7), 879−885.
(3) Ford, S.; Minshall, T. Where and How 3D Printing Is Used in Teaching and Education. *Add. Manuf.* **2019**, *25*, 131−150.
(4) McDonnell, B.; Guzman, X. J.; Dolack, M.; Simpson, T. W.; Cimbala, J. M. 3D Printing in the Wild: A Preliminary Investigation of Air Quality in College Maker Spaces. In *Solid Freeform Fabrication 2016 − An Additive Manufacturing Conference*; Austin, TX, 2016.
(5) Brannon, J. P.; Ramirez, I.; Williams, D.; Barding, G. A.; Liu, Y.; McCulloch, K. M.; Chandrasekaran, P.; Stieber, S. C. E. Teaching Crystallography by Determining Small Molecule Structures and 3-D Printing: An Inorganic Chemistry Laboratory Module. *J. Chem. Educ.* **2020**, *97* (8), 2273−2279.
(6) Casas, L. Teaching Periodicity and Aperiodicity Using 3D-Printed Tiles and Polyhedra. *J. Appl. Crystallogr.* **2020**, *53*, 1583−1592.
(7) Shah, K. J.; Peterson, J. C.; Beahm, D. D.; Camarata, P. J.; Chamoun, R. B. Three-Dimensional Printed Model Used to Teach Skull Base Anatomy through a Transsphenoidal Approach for Neurosurgery Residents. *Oper. Neurosurg. (Hagerstown)* **2016**, *12* (4), 326−329.
(8) Song, M. J.; Ha, E.; Goo, S. K.; Cho, J. Design and Development of 3D Printed Teaching Aids for Architecture Education. *Int. J. Mobile Blended Learn.* **2018**, *10* (3), 58−75.
(9) Cruz Sanchez, F. A.; Boudaoud, H.; Camargo, M.; Pearce, J. M. Plastic Recycling in Additive Manufacturing: A Systematic Literature Review and Opportunities for the Circular Economy. *J. Cleaner Prod.* **2020**, *264*, 121602.
(10) Azimi, P.; Zhao, D.; Pouzet, C.; Crain, N. E.; Stephens, B. Emissions of Ultrafine Particles and Volatile Organic Compounds from Commercially Available Desktop Three-Dimensional Printers with Multiple Filaments. *Environ. Sci. Technol.* **2016**, *50* (3), 1260−1268.
(11) Davis, A. Y.; Zhang, Q.; Wong, J. P. S.; Weber, R. J.; Black, M. S. Characterization of Volatile Organic Compound Emissions from Consumer Level Material Extrusion 3D Printers. *Build. Environ.* **2019**, *160*, 106209.
(12) Stephens, B.; Azimi, P.; El Orch, Z.; Ramos, T. Ultrafine Particle Emissions from Desktop 3D Printers. *Atmos. Environ.* **2013**, *79*, 334−339.
(13) Ding, S.; Ng, B. F.; Shang, X.; Liu, H.; Lu, X.; Wan, M. P. The Characteristics and Formation Mechanisms of Emissions from Thermal Decomposition of 3D Printer Polymer Filaments. *Sci. Total Environ.* **2019**, *692*, 984−994.
(14) Vance, M. E.; Pegues, V.; Van Montfrans, S.; Leng, W.; Marr, L. C. Aerosol Emissions from Fuse-Deposition Modeling 3D Printers in a Chamber and in Real Indoor Environments. *Environ. Sci. Technol.* **2017**, *51* (17), 9516−9523.
(15) Magalhaes, S.; Baumgartner, J.; Weichenthal, S. Impacts of Exposure to Black Carbon, Elemental Carbon, and Ultrafine Particles from Indoor and Outdoor Sources on Blood Pressure in Adults: A Review of Epidemiological Evidence. *Environ. Res.* **2018**, *161*, 345−353.
(16) Poikkimäki, M.; Koljonen, V.; Leskinen, N.; Närhi, M.; Kangasniemi, O.; Kausiala, O.; Dal Maso, M. Nanocluster Aerosol Emissions of a 3D Printer. *Environ. Sci. Technol.* **2019**, *53* (23), 13618−13628.
(17) Stefaniak, A. B.; LeBouf, R. F.; Duling, M. G.; Yi, J.; Abukabda, A. B.; McBride, C. R.; Nurkiewicz, T. R. Inhalation Exposure to Three-Dimensional Printer Emissions Stimulates Acute Hypertension and Microvascular Dysfunction. *Toxicol. Appl. Pharmacol.* **2017**, *335*, 1−5.
(18) Gu, J.; Wensing, M.; Uhde, E.; Salthammer, T. Characterization of Particulate and Gaseous Pollutants Emitted During Operation of a Desktop 3D Printer. *Environ. Int.* **2019**, *123*, 476−485.
(19) Yi, J.; Duling, M. G.; Bowers, L. N.; Knepp, A. K.; LeBouf, R. F.; Nurkiewicz, T. R.; Ranpara, A.; Luxton, T.; Martin, S. B., Jr.; Burns, D. A.; Peloquin, D. M.; Baumann, E. J.; Virji, M. A.; Stefaniak, A. B. Particle and Organic Vapor Emissions from Children's 3-D Pen and 3-D Printer Toys. *Inhalation Toxicol.* **2019**, *31* (13−14), 432−445.
(20) 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 Jr, S. B.; Johnson, A. R.; Virji, M. A. Characterization of Chemical Contaminants Generated by a Desktop Fused Deposition Modeling 3-Dimensional Printer. *J. Occup. Environ. Hyg.* **2017**, *14*, 540−550.
(21) Wojtyła, S.; Klama, P.; Śpiewak, K.; Baran, T. 3D Printer as a Potential Source of Indoor Air Pollution. *Int. J. Environ. Sci. Technol.* **2020**, *17* (1), 207−218.
(22) Floyd, E. L.; Wang, J.; Regens, J. L. Fume Emissions from a Low-Cost 3-D Printer with Various Filaments. *J. Occup. Environ. Hyg.* **2017**, *14* (7), 523−533.
(23) Song, R.; Telenko, C. Material and Energy Loss Due to Human and Machine Error in Commercial FDM Printers. *J. Cleaner Prod.* **2017**, *148*, 895−904.
(24) Deng, Y.; Cao, S. J.; Chen, A.; Guo, Y. The Impact of Manufacturing Parameters on Submicron Particle Emissions from a Desktop 3D Printer in the Perspective of Emission Reduction. *Build. Environ.* **2016**, *104*, 311−319.

(25) Jeon, H.; Park, J.; Kim, S.; Park, K.; Yoon, C. Effect of Nozzle Temperature on the Emission Rate of Ultrafine Particles During 3D Printing. *Indoor Air* **2020**, *30* (2), 306−314.
(26) 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. Characterization of Emissions from a Desktop 3D Printer. *J. Ind. Ecol.* **2017**, *21* (S1), S94−S106.
(27) Stabile, L.; Scungio, M.; Buonanno, G.; Arpino, F.; Ficco, G. Airborne Particle Emission of a Commercial 3D Printer: The Effect of Filament Material and Printing Temperature. *Indoor Air* **2017**, *27* (2), 398−408.
(28) Zhang, Q.; Wong, J. P. S.; Davis, A. Y.; Black, M. S.; Weber, R. J. Characterization of Particle Emissions from Consumer Fused Deposition Modeling 3D Printers. *Aerosol Sci. Technol.* **2017**, *51* (11), 1275−1286.
(29) Erdem, E. Robert Morris University. Personal communication, June 22, 2021.
(30) Byrley, P.; Geer Wallace, M. A.; Boyes, W. K.; Rogers, K. Particle and Volatile Organic Compound Emissions from a 3D Printer Filament Extruder. *Sci. Total Environ.* **2020**, *736*, 139604.
(31) *ASTM E741−11: Standard Test Method for Determining Air Change in a Single Zone by Means of a Tracer Gas Dilution*; ASTM: West Conshohocken, PA, 2017.
(32) NIOSH Method 7303: Elements by ICP (Hot Block/HCl/HNO3 Digestion). In *NIOSH Manual of Analytical Methods*, 4th ed.; U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Publication No. 2003−145: Cincinnati, OH, 2003.
(33) Stefaniak, A. B.; Bowers, L.; Martin, J.; Stephen; Hammond, D.; Ham, J.; Wells, R. J.; Fortner, A.; Knepp, A.; du Preez, S.; Pretty, J.; Roberts, J.; du Plessis, J.; Schmidt, A.; Duling, M.; Bader, A.; Virji, M. A. Large Format Additive Manufacturing and Machining Using High Melt Temperature Polymers. Part II: Characterization of Particles and Gases. *ACS Chem. Health Saf.* **2021**, *28*, 268.
(34) *OSHA Method Pv2012: Caprolactam*; OSHA Salt Lake Technical Center: Salt Lake City, UT, 1988.
(35) Ashley, K., O'Connor, P. F., Eds. NIOSH Method 3900: Volatile Organic Compounds, C1 to C10, Canister Method. In *NIOSH Manual of Analytical Methods*, 5th ed.; DHHS (NIOSH): Cincinnati, OH, 2018.
(36) Ashley, K., O'Connor, P. F., Eds. NIOSH Method 2016: Formaldehyde, Issue 3. In *NIOSH Manual of Analytcial Methods*, 5th ed.; DHHS (NIOSH): Cincinnati, OH, 2016.
(37) *EPA Method TO-11a: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]*; U.S. Environmental Protection Agency: Cincinnati, OH, 1999.
(38) He, C.; Morawska, L.; Hitchins, J.; Gilbert, D. Contribution from Indoor Sources to Particle Number and Mass Concentrations in Residential Houses. *Atmos. Environ.* **2004**, *38* (21), 3405−3415.
(39) Stefaniak, A. B.; Johnson, A. R.; du Preez, S.; Hammond, D. R.; Wells, J. R.; Ham, J. E.; LeBouf, R. F.; Menchaca, K. W.; Martin SB, J.; Duling, M. G.; Bowers, L. N.; Knepp, A. K.; Su, F. C.; de Beer, D. J.; JL, d. P Evaluation of Emissions and Exposures at Workplaces Using Desktop 3-Dimensional Printers. *J. Chem. Health Saf.* **2019**, *26* (2), 19−30.
(40) Afshar-Mohajer, N.; Wu, C. Y.; Ladun, T.; Rajon, D. A.; Huang, Y. Characterization of Particulate Matters and Total VOC Emissions from a Binder Jetting 3D Printer. *Build. Environ.* **2015**, *93* (P2), 293−301.
(41) Viitanen, A. K.; Kallonen, K.; Kukko, K.; Kanerva, T.; Saukko, E.; Hussein, T.; Hämeri, K.; Säämänen, A. Technical Control of Nanoparticle Emissions from Desktop 3D Printing. *Indoor Air* **2021**, *31* (3), 1061−1071.
(42) Kwon, O.; Yoon, C.; Ham, S.; Park, J.; Lee, J.; Yoo, D.; Kim, Y. Characterization and Control of Nanoparticle Emission During 3D Printing. *Environ. Sci. Technol.* **2017**, *51* (18), 10357−10368.
(43) Bernatikova, S.; Dudacec, A.; Prichystalova, R.; Klecka, V.; Kocurkova, L. Characterization of Ultrafine Particles and VOCs Emitted from a 3D Printer. *Int. J. Environ. Res. Public Health* **2021**, *18*, 929.
(44) Siddiqui, M. N.; Gondal, M. A.; Nasr, M. M. Determination of Trace Metals Using Laser Induced Breakdown Spectroscopy in Insoluble Organic Materials Obtained from Pyrolysis of Plastics Waste. *Bull. Environ. Contam. Toxicol.* **2009**, *83* (1), 141−145.
(45) *NIOSH Pocket Guide to Chemical Hazards*. http://www.cdc.gov/niosh/npg/default.html (accessed April 20, 2021).
(46) Bravi, L.; Murmura, F.; Santos, G. Additive Manufacturing: Possible Problems with Indoor Air Quality. *Proc. Manuf.* **2019**, *41*, 952−959.
(47) Unwin, J.; Coldwell, M. R.; Keen, C.; McAlinden, J. J. Airborne Emissions of Carcinogens and Respiratory Sensitizers During Thermal Processing of Plastics. *Ann. Occup. Hyg.* **2013**, *57* (3), 399−406.
(48) Barlow, A.; Contos, D. A.; Holdren, M. W.; Garrison, P. J.; Harris, L. R.; Janke, B. Development of Emission Factors for Polyethylene Processing. *J. Air Waste Manage. Assoc.* **1996**, *46* (6), 569−580.
(49) Purohit, V.; Orzel, R. A. Polypropylene: A Literature Review of the Thermal Decomposition Products and Toxicity. *J. Am. Coll. Toxicol.* **1988**, *7* (2), 221−242.
(50) Ho, S. S. H.; Ho, K. F.; Liu, W. D.; Lee, S. C.; Dai, W. T.; Cao, J. J.; Ip, H. S. S. Unsuitability of Using the DNPH-Coated Solid Sorbent Cartridge for Determination of Airborne Unsaturated Carbonyls. *Atmos. Environ.* **2011**, *45* (1), 261−265.
(51) Mylläri, V.; Hartikainen, S.; Poliakova, V.; Anderson, R.; Jönkkäri, I.; Pasanen, P.; Andersson, M.; Vuorinen, J. Detergent Impurity Effect on Recycled HDPE: Properties after Repetitive Processing. *J. Appl. Polym. Sci.* **2016**, *133*, 43766.
(52) *NIOSH Hierarchy of Controls*. https://www.cdc.gov/niosh/topics/hierarchy/default.html (accessed April 15, 2021).
(53) Simon, T. R.; Aguilera, G. A.; Zhao, F. Characterization of Particle Emission from Fuse Deposition Modeling Printers. In *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. DOI: 10.1115/MSEC2017-3007
(54) Cheng, Y. L.; Zhang, L. C.; Chen, F.; Tseng, Y. H. Particle Emissions of Material-Extrusion-Type Desktop 3D Printing: The Effects of Infill. *Int. J. Precis. Eng. Manuf. - Green Technol.* **2018**, *5* (4), 487−497.
(55) Dunn, K. L.; Hammond, D.; Menchaca, K.; Roth, G.; Dunn, K. H. Reducing Ultrafine Particulate Emission from Multiple 3D Printers in an Office Environment Using a Prototype Engineering Control. *J. Nanopart. Res.* **2020**, *22*, 112.
(56) Katz, E. F.; Goetz, J. D.; Wang, C.; Hart, J. L.; Terranova, B.; Taheri, M. L.; Waring, M. S.; DeCarlo, P. F. Chemical and Physical Characterization of 3D Printer Aerosol Emissions with and without a Filter Attachment. *Environ. Sci. Technol.* **2020**, *54* (2), 947−954.
(57) Rao, C.; Gu, F.; Zhao, P.; Sharmin, N.; Gu, H.; Fu, J. Capturing PM2.5 Emissions from 3D Printing via Nanofiber-Based Air Filter. *Sci. Rep.* **2017**, *7* (1), 103.
(58) Roth, G. A.; Geraci, C. L.; Stefaniak, A. B.; Murashov, V.; Howard, J. Potential Occupational Hazards of Additive Manufacturing. *J. Occup. Environ. Hyg.* **2019**, *16* (5), 321−328.
(59) Chýlek, R.; Kudela, L.; Pospíšil, J.; Šnajdárek, L. Fine Particle Emission During Fused Deposition Modelling and Thermogravimetric Analysis for Various Filaments. *J. Cleaner Prod.* **2019**, *237*, 117790.
(60) 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. Characterization of Emissions from a Desktop 3D Printer. *J. Ind. Ecol.* **2017**, *21*, S94−S106.
(61) Väisänen, A. J. K.; Hyttinen, M.; Ylönen, S.; Alonen, L. Occupational Exposure to Gaseous and Particulate Contaminants Originating from Additive Manufacturing of Liquid, Powdered, and Filament Plastic Materials and Related Post-Processes. *J. Occup. Environ. Hyg.* **2019**, *16* (3), 258−271.