An exposure assessment of desktop 3D printing

A preliminary hazard analysis of 3D printing included process monitoring in two working environments; a small well ventilated materials development laboratory with a Makerbot printer (polylactic acid filament) and a poorly ventilated lab, home-like in terms of room size and ventilation with a Da Vinci XYZ printer (acrylonitrile-butadiene-styrene). Particle number, size and mass concentration were measured within the printer enclosures, breathing zone, and room simultaneously. Number concentrations were elevated above background typically in the 10^3 - 10^5 particles/cm³ range. During printing >99% of the aerosol number concentration was within the ultrafine particulate (UFP) and nanoscale size range. Condensed aerosol emissions from the Da Vinci XYZ printer was examined by Fourier infra-red spectroscopy and suggested isocyanic acid and n-decane as two possible chemical components. Light microscopy and transmission electron microscopy with energy dispersive analysis by X-ray identified individual and aggregated particles highly suggestive of combustion, accompanied by a variety of metallic elements. Adverse health effects associated with 3D printing related to chemical vapor off-gassing in well ventilated space appears to be low. At this point the significance of ultrafine particle emission is under growing suspicion in its relationship to inflammatory, pulmonary, and cardiovascular effects. Preliminary recommendations for particulate control developed from this analysis are based on good industrial hygiene practice rather than compelling adverse health effects.

By Tracy L. Zontek, Burton R. Ogle, John T. Jankovic, Scott M. Hollenbeck

INTRODUCTION

The availability of low cost desktop size three dimensional (3D) printers has increased due to easy availability and their ability to customize object printing to exact specifications based on CAD drawings. This availability for use in non-industrial settings (offices and homes) may create an environment where poor ventilation and limited health and safety controls exist; thus, there may be an increased risk for adverse health effects, particularly if the user is in close proximity to emissions, the zone of highest exposure. While 3D printers are becoming more accessible and widely used in professional and personal applications, studies depicting the potential health effects and indoor air quality implications are still emerging.

When reviewing regulatory limits on particle exposure, the United States Occupational Safety & Health Administration (OSHA) defines nuisance dust, Particulates Not Otherwise Regulated (PNOR), into two categories: total dust (Permissible Exposure Limit (PEL),

Tracy L. Zontek, PhD is affiliated with the School of Health Sciences, Western Carolina University, Cullowhee, NC 28723, United States (Tel.: 828 227 2146; *e-mail: zontek@email.wcu.edu*).

Burton R. Ogle, PhD is affiliated with the Western Carolina University, Cullowhee, NC 28723, United States.

John T. Jankovic, MSPH is affiliated with the Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States.

Scott M. Hollenbeck, *MSPH is affiliated with the Oak Ridge National Laboratory*, *Oak Ridge, TN 37831, United States.*

15 mg/m³ as 8-hour TWA) and respirable dust (50% cut point of 4 μ m) (PEL 5 mg/m³ as 8-hour TWA).¹ These classifications are mass based and apply to particulates that do not have a specific OSHA regulation. The United States Environmental Protection Agency has promulgated the National Ambient Air Quality Standards for PM_{2.5} (35 μ g/m³ of particulate matter less than 2.5 μ m, measured as a 24 hour average).²

Initial studies of 3D printers classified particulate emissions primarily in the ultrafine range.^{3–5} Ultrafine particles (UFD) are defined as those with a diameter less than 0.1 μ m. Ultrafine particles contribute negligibly to PM_{2.5} mass but contribute significantly to the particle number concentration.⁶ Therefore mass based measurements may not be appropriate to measure exposure, and subsequent exposure assessment to 3D printer emissions.

Ultrafine particulate air pollution is associated with a variety of adverse health effects in the scientific literature.^{7,8} Ultrafine particles cause more respiratory system inflammation than larger particles in rodent studies and UFP surface properties greatly influence toxicity.⁸ Mass based measurements do not consider number count or surface properties of particulates. Further, epidemiological studies have associated increased particulate exposure and adverse health effects on those people with pre-existing respiratory and cardiovascular diseases.⁸ Due to the primary particulate emission of 3D printers in the UFP range with the increasingly associated health effects, this size range is significant to characterize in desktop 3D printers.

The printers used in this study use additive manufacturing where a filament of acrylonitrile-butadiene-styrene (ABS) or polylactic acid (PLA) is fed at a constant rate. extruded at a set temperature, and builds the selected object layer by layer, on a heated plate. Thermal oxidative degradation of filament material during heating and extrusion are known to release a variety of irritants and systemic toxins in low amounts.⁹ It is not clear what physical form these low level combustion degradation products may take. One study noted that emissions consisted of volatile droplets with little solid matter.⁴

The purpose of this study was to characterize particle emissions from two widely used 3D printers whose price point makes them attractive to businesses and consumers.

METHODS

The 3D printers chosen were based on availability at Oak Ridge National Laboratory. Multiple research groups use various 3D printers: the Maker Bot and Da Vinci XYZ were chosen according to their common use, price point, and availability for testing purposes. Current literature depiction of 3D printer emissions in the UFP and nanoscale range led investigators to use the U.S. Department of Energy (DOE) Approach to Nanomaterial ES&H industrial hygiene sampling protocol.¹⁰ The investigators of this study developed the initial DOE industrial hygiene sampling protocol and have made multiple revisions (not yet available to public) based on new air sampling equipment that is better able to resolve UFP and nanoscale materials. The DOE protocol focuses on collecting size and number concentration of particulates to characterize the aerosol exposure as well as microscopy to provide morphology and elemental analysis. NIOSH identified tools for exposure assessment that are similar to the DOE protocol; however air sampling equipment to measure UFP and nanoscale aerosols have improved tremendously since these protocols were published.¹¹ NIOSH also has a protocol for carbon nanotubes and carbon nanofibers that is mass based; however, it does not cover other nanoscale materials.¹² The methodology used in this study was based on these protocols and new aerosol monitoring equipment.

Two different 3D printers were used in testing. The Makerbot Replicator 2X printer was run at 180–230 °C, feed rate of 40 mm/s with a polylactic acid (PLA) filament. This singular run, approximately 60 min, printed multiple objects. The Makerbot data was included as the pilot study to refine a sampling strategy and protocol. Makerbot data is included for reference, particularly to demonstrate the concentration maps in a well ventilated space.

The primary "test" printer was a Da Vinci XYZ model 1.03D. Initially the printer was run with different objects and run times to identify a standard object that could be printed consistently (keychain was chosen). The test printer was operated at a printing temperature of 213 °C using an acrylonitrile-butadiene-styrene (ABS) filament. These are fixed parameters for this particular printer. The resolution was set at best quality (Fine 0.1 mm) resulting in the longest printing times. Filament feed rate is a variable function of the part being printed, as is the amount of filament used. The test printer did not provide the precise amount of filament used. Therefore, the same part was printed for all of the trial measurements (n = 10), thereby keeping filament quantity and print time constant.

Instrumentation used to characterize particle count and size in this study included condensation particle counters (CPC) (measured #/cc at various locations for Makerbot and test printer); a TSI scanning mobility particle sizer (SMPS) 3080 equipped with either a long differential mobility analyzer (DMA) (TSI 3081) or nano DMA (TSI 3085) (measured #/cc and μ g/m³ from 2 nm to 300 nm at various locations for test printer only): a TSI optical particle sizer (OPS) (measured #/cc and $\mu g/m^3$ from 300 nm to 10 μm at various locations for test printer only); and the TSI Mim2 software to merge data from the SMPS and OPS. In order to characterize particulate emissions from 3D printers, instrument data was used to develop the following: particle size and concentration comparisons during the heating and printing process and concentration maps. Figure 1 provides an overview of equipment, data and subsequent analysis. Since no single method of analysis is competent to evaluation UFP and nanoscale materials, microscopy was also used.¹³

Particle characteristics and mapping

Particle concentration measurements (#/cc) were performed with three TSI model 3007 condensation particle counters (CPC) for both the MakerBot and test printer. Time series measurements were collected inside and outside the test printer enclosure. The monitoring position outside the enclosure was located at a point representative of the breathing zone (BZ) of a person sitting at the table where the printer was located. Background particulate concentrations were determined prior to filament heating and extrusion. Room concentration maps during printing (based on initial testing that this produced highest number concentration) using 3DField mapping freeware¹⁴ and a handheld CPC were developed.

For the test printer runs only, particle number and mass concentration by size was determined using a combination of scanning mobility particle analyzer, including a TSI SMPS 3080 equipped with either a long differential mobility analyzer (DMA) (TSI 3081) or nano DMA (TSI 3085). The long DMA and nano DMA were alternated in order to obtain particle sizes from 2 nm to 300 nm. A TSI optical particle sizer (OPS) was simultaneously run to measure particle size information from 300 nm to 10 µm. TSI's merging software (Mim2) was used to combine the small fraction mobility diameters with the large fraction optical diameters into one normalized particle size distribution as either $\Delta N / \Delta \log d_{\rm p}$ or $\Delta M /$ $\Delta \log d_{\rm p}$. These instruments also



Figure 1. Summary of equipment, data collection, and analysis results.

provided corresponding number and mass concentrations using TSI algorithms provided in their internal Mim2 software. These instruments were run inside and outside the test printer enclosure (n = 10) and reported data averaged.

In summary, the CPC concentrations were used to develop number concentration data to establish exposure assessment. The measurements from the SMPS and OPS were used to develop size selective number and mass concentration data for exposure assessment (e.g. breathing zone, inside vs. outside test printer enclosure).

Microscopy and chemical analysis

Methods to characterize the morphology and nature of the particles emitted from the printing process followed Department of Energy and NIOSH guidelines.^{10,11,13} Large particles were collected on glass coverslips using a single stage inertial impactor¹⁴ and examined under a light microscope at 40, 100, and $400 \times$ to view physical characteristics such as size, shape, and liquidity. These particles were also examined by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) with a Bruker Vertex 70/OPUS spectral library for tentative substance identification; additional analysis was not performed at this time to confirm substance identification. Aerosol was also collected on transmission electron microscope (TEM) grids (nickel mesh with carbon film) using a thermophoretic sampler, inside the printer enclosure, developed by RJ Lee, to obtain high resolution images of the smaller particles, and determine elemental composition by energy dispersive analysis of X-rays (EDAX) as part of the particulate characterization process.¹⁵

A direct reading photoionization detector (PID) with a particulate filter was located inside the printer enclosure to detect any gaseous emissions during printing with test printer (detection limit nominally 0.01 ppm as isobutylene). A direct reading nondispersive infra-red analyzer with particulate filter (Foxboro Sapphire) was also used to probe the test printer enclosure during printing.

RESULTS

Particle characteristics and mapping

The Makerbot pilot study used the CPCs to measure particle number concentration throughout the printing process (Figure 2). During the time depicted, several different "runs"

occurred due to filament issues. Spikes represent initial heating and printing of different items. In Figure 2a, a time study of all monitoring using CPCs is expressed such that the process CPC was placed inside the MakerBot enclosure during printing; the computer CPC represents the breathing zone, and the *cart* CPC represents conditions in lab away from MakerBot printer. In Figure 2a, the number concentration in the breathing zone and lab conditions is difficult to discern due to high concentration inside the printer enclosure. For better resolution, Figure 2b only represents the breathing zone and lab conditions. During filament heating, particle concentration exceeded 250,000 #/cc inside the enclosure and 4.000 #/cc outside the enclosure (breathing zone and lab). Higher printing temperatures resulted in higher number particle concentrations. The TSI CPC 3007 measured everything from 10 nm to $>1 \,\mu$ m but there is no size distribution available with these instruments.

Particle number concentration maps were developed for each printer during the *print phase*. The number of air changes/hour (AC/hr) was calculated for each room to demonstrate "poor" and "good" ventilation.¹⁶ While the number of air changes/hour is







Figure 3. Makerbot printing, good ventilation.

considered a poor basis for industrial ventilation due to its limited impact on contaminant control, it can be used as an easy method of comparison, especially for non-industrial or indoor air quality.¹⁷

Breathing zone number concentration maps from a well-ventilated laboratory ($10 \text{ m} \times 10 \text{ m} \times 6 \text{ m}$, 20 AC/hr) during a routine Makerbot printer operation using polylactic acid filament (PLA), printer top removed, were developed during the background (before printer was turned on) and printing stages (Figure 3). Air concentrations reached a nominal 3,000 #/cc close to the printer, but fell off rapidly with distance from the printer. Approximately 3/4 of the room maintained particle concentrations at or near background levels.

The test printer was located in a poorly ventilated storage room $(3 \text{ m} \times 9 \text{ m} \times 6 \text{ m}, 1.8 \text{ AC/hr})$, and used acrylonitrile-butadiene-styrene filament (ABS) with printer fully closed (as manufacturer designed), but not air tight. Rapidly, particles built up in the breathing zone near the printer to 10^4 #/cc (Figure 4). With increased printing time (middle to end of the 60 min printing cycle), the surrounding room concentration reached 10^4 particles/cc as well.

The remaining results apply to the Da Vinci XYZ test printer. Particle size and concentration numerical data is presented in Table 1 depicting use of test printer (ABS) in a poorly ventilated space.

Table 1 depicts the specific aerosol parameters obtained from the SMPS inside and outside the test printer enclosure, providing an enclosure reduction factor. During heating and printing, the highest number and mass concentration, the enclosure (keeping 3D printer door closed) provided approximately 95% reduction in the number and mass concentration, thus reducing exposure to individual using the printer and others in the area.

Figure 5 graphically depicts the number concentration over a variety of printing conditions (warm-up, initial printing, continued printing, and cool-down). Each line represents a different run of all printing conditions (n = 10). Figure 5 depicts size variation



Figure 4. Test printer, poor ventilation.

Table 1.	Aerosol	Parameters	Measured	Inside and	l Outside	Test Printer	Enclosure	During	Printing
----------	---------	------------	----------	------------	-----------	---------------------	-----------	---------------	----------

Printer Function	Parameter	Inside Printer Enclosure					Outside Printer Enclosure in BZ				
		dp ₅₀ (nm)	Mode (nm)	GSD	#/cc	$\mu g/m^3$	dp ₅₀ (nm)	Mode (nm)	GSD	#/cc (reduction)	μg/m ³ (reduction)
Heating		24.2	16.4	20.7	522,000	83.3	14.7	9.3	1.79	1,860 (0.996) ^a	0.0237 (0.999) ^a
		3.5	2.4	0.34	582,258	70.2	2.9	2.5	0.56	640	0.0410
Printing		30.5	34.1	1.95	71,450	7.6	16.3	9.4	1.71	3,780 (0.947) ^a	0.0013 (0.999) ^a
		4.6	13.2	0.12	45,068	6.2	0.5	2.1	0.01	283	0.0019
Cooling		16.3	14.3	1.50	66,308	0.4					
		1.1	1.0	0.05	38,234	0.2					
Door open		25.6	19.2	2.17	834	0.2					
		3.3	4.7	0.21	33	0.1					

^a Values inside parentheses represents the enclosure reduction factor.

n = 10 for both sample sets.



Figure 5. Inside test printer enclosure; variability in size and cumulative frequency distributions from SMPS with Nano DMA (3–100 nm size resoultion).

over an entire run (all printing conditions) using the Nano DMA (3–100 nm size resolution). The *x*-axis depicts the mobility median diameter (dp₅₀) from 1 to 100 nm, the *y*-axis depicts particle concentration (#/cc) and cumulative percentage respectively. As depicted in Figure 5, the dp₅₀ diameter of approximately 10 nm has the highest concentration (10^7 #/cc) and particles with a dp₅₀ diameter ≤ 10 nm account for approximately 40% of particle number count. Note all particles in Figure 5 are in the respirable region and have the potential to travel to the alveolar region of the respiratory system; they also can be classified as UFP and/or nanoscale.

Figure 6 used the TSI SMPS 3080 and TSI OPS, along with Mim2 software to characterize aerosol from 1 to 10,000 nm in theoretical operator breathing zone. Figure 6 further confirms that majority of particulates, measured both as number count and mass, are in the UFP range. In Figure 6a, particle mobility diameter is almost entirely (99%) within the UFP classification. Particles collected near the printer in the theoretical breathing zone of someone monitoring the operation are also presented as a normalized number distribution (Figure 6b); the aerosol had a bimodal distribution with modes at approximately 7 and 15 nm. This was typical of BZ values for most printing runs in the early stages of extruder heating and printing. As time of printing progressed, often the particles



Figure 6. Test printer using ABS. Representative cumulative number frequency (a, b) and representative cumulative mass frequency size (c, d) in theoretical breathing zone.



Figure 7. Inside and outside test printer mass and number concentration time series (ABS).

grew in size to between 20 and 30 nm (not depicted).

Sixty-eight percent of the particle mass was present as UFP (Figure 6c). The normalized size distribution of particle mass presented as bimodal with the largest mode at about 90 nm and a second, smaller mode centered at about 230 nm (Figure 6d).

Figure 7 (test printer with ABS) demonstrated concentrations at various stages in the process, as well as

between inside and outside the printer enclosure. It also demonstrated small mass concentrations in contrast to number concentrations.

Microscopy and chemical analysis

Light microscopy at $400 \times$ was used to examine the large particulate fraction to confirm the suspected liquid nature of the aerosol (Figure 8).

Transmission electron microscopy (TEM) with energy dispersive analysis by X-ray was used to examine the smallest particles of the aerosol as well as to identify elemental composition (Figures 9 and 10). The TEM provided insight into the morphology and agglomeration of the particulates. Table 2 lists the elements identified by EDAX. In Table 2, the number 1 indicates the most abundant element and 5 the least abundant element found. EDAX depicts elements and their relative importance; in Figure 10, EDAX identified titanium (previously used in this area but not part of PLA filament.)

ABS materials identified by ATR FTIR and its reference spectral library were: cyclohexane, n-decane, ethylenepropylene-diene terpolymer, 1-decanol, and isocyanic acid (Table 3). A PID



Figure 8. ABS filament impactor particles from test printer.

inside the printer enclosure failed to detect any gaseous emissions during printing. The Foxboro Sapphire was also used to probe the enclosure during printing and also failed to detect any gaseous emissions.

DISCUSSION

Particle characteristics and mapping

In both the Makerbot and test printer runs, particle concentration increased in the room (Figures 3 and 4) with respect to background. During the 3D printing process particle concentration and size are seen to vary (Table 1 and Figures 2, 5–7) with the operation/time in the printing process. Note in particular the differences in the mode and dp_{50} particle sizes in Table 1. Since the mode is less affected by extremes in the size distribution, it may be a better indicator of the size of the particles produced; the geometric mean and standard deviation being relevant as an overall description of the aerosol. In either case the majority of the particles fall into the ultrafine category, an area under study for potential health effects. Note the bi-modal distributions for both number and mass (Figure 6). The test printer initially heats to 220 °C to clear the nozzle prior to printing at a nominal 213 °C. The change in number concentration between heating and printing is believed to be due to a combination of the location of the sample collection point, the rapid movement of the printer head (stirring) which is stationary until printing begins, and the intermittent nature of filament feeding



Figure 9. ABS TEM/EDAX particle examples.



Figure 10. PLA TEM/EDAX particle examples.

Element	С	0	Na	Si	S	К	Cu	Mg	Ti	Ca	Al
ABS	1	2	3	3	4	3	4	-	-	4	4
PLA	1	2	5	4	-	-	3	5	5 ^a	-	5

 Table 2. Elements Found in or as UFP Particulate by EDAX (Number 1 is Most Abundant Element; Number 5 is Least Abundant Element.).

^a Present as a contaminant from a previous specialty filament used.

Table 3. List of Liquid Aerosol Components Identified by ATR-FTIR.

Chemical Agent	Exposure Limit	Health Effects Eve irritation			
Cyclohexane	$1,050 \text{ mg/m}^3$				
·		CNS depression (high conc.)			
n-Decane	None	Eye irritation			
		Skin irritation			
		CNS depression (high conc.)			
Ethylene-propylene-diene terpolymer	None	None reported			
Low density polyethylene	None	None reported			
1-Decanol	None	Eye irritation			
		Skin irritation			
Isocyanic acid	$18 \mu \text{g/m}^3$ (Sweden)	Part of the biochemical pathway			
		linked with cataracts and inflammation			
		that can trigger cardiovascular disease			
		and rheumatoid arthritis.			
		Skin blistering (liquid contact)			

as the part is constructed. Among all the variability, a large enclosure effect seems evident and consistent over the process.

Table 1 also demonstrates the effectiveness of the enclosure reducing the particle count in the BZ. Concentrations in the BZ consistently reached 10^5 #/cc in close proximity to the test printer: while averages were somewhat lower (Figure 7 and Table 1). Particle mapping demonstrated concentration build up throughout the poorly ventilated room while staying localized around the printer in the highly ventilated laboratory (Figures 3 and 4). These demonstrated the importance of the enclosure around the 3D printer and having adequate general dilution ventilation to reduce particulate concentrations.

Microscopy and chemical analysis

A variety of materials in the aerosol particulate phase were identified (Figures 9 and 10; Table 2). The aerosol mass concentrations estimated with the SMPS and OPS, boiling points of putative chemicals, and the particulate photomicrographs collectively suggest a liquid and solid aerosol structure (Figures 8–10). As part of the exposure

assessment, possible chemical emissions in the gas phase were evaluated. In current literature, none of the chemicals released by thermal oxidative decomposition were found in measurable quantities by our techniques at printer temperatures used in experimental conditions.⁹ Direct reading survey instruments (PID and IR) monitoring of the test printing consistently found no measurable gas/vapor emissions (detection limit ~0.1 ppm).

The particles themselves contained individual and aggregated particles highly suggestive of combustion (Figures 9 and 10 and Table 2) accompanied by a variety of metallic elements. This is consistent with low level thermal degradation of carbon-based materials. Therefore, the low gas/vapor concentrations (demonstrated with PID) and high particulate loading suggest the exposure assessment for the 3D printing could focus on UFP particulates and draw on the health effects associated with UFP found primarily in indoor and outdoor air pollution studies related to combustion processes. Of the many reviewed papers, only one stipulated a no observed adverse effect level (NOAEL) of $10 \,\mu\text{g/m}^3$ for healthy non-smoking individuals; this did not include populations at risk, such as asthmatics.²⁶ The mass concentration average in the BZ while printing is lower than the stipulated NOAEL for combustion type particulate.

Another study, presented by Wright, reported very low concentrations of styrene, ethylbenzene, formaldehyde, and acetaldehyde for a small printing process (255 °C) in relation to occupational exposure limits.¹⁸ Figure 11a and b contains Wright's reported concentrations for styrene and acetaldehyde on health effects graphs. In both cases possible exposures were below any adverse effect levels presented as $C_n \times T$ curves. However, several previously unreported substances were identified in the liquid phase particulate collected by impaction¹⁹ and identified by FTIR spectroscopy in this study. Of these, cyclohexane and isocyanic acid (Figure 11c and d) were selected for further hazard analysis because of their presumed toxicological relevance. Since these materials were not collected in such a way as to be quantifiable, it was assumed the total mass concentration estimate of 2 μ g/m³ determined for the printing process, was composed entirely of one substance to the exclusion of all others. These values were then



Figure 11. Health effects and reported printer emissions for styrene (a) and acetaldehyde (b), estimated for cyclohexane (c) and isocyanic acid (d).

compared with standards or other toxicological data. This is conservative since it is unlikely that any single substance composed the entire aerosol makeup. In the case of cyclohexane the potential exposure is orders of magnitude (<0.35 mg/m³ vs. OSHA $1,050 \text{ mg/m}^3$) below the occupational exposure limit established by the Occupational Safety and Health Administration. Although not enumerated here, this was also the case for the reported concentrations of styrene, formaldehyde, acetaldehyde, and ethyl benzene.¹⁸ Our finding of the possible presence of isocyanic acid is consistent with other reports of low temperature combustion byproducts.^{20,21} Isocyanic acid may be of special concern because of the low levels suggested as potentially detrimental. Exposures >1 ppb $(1.76 \,\mu g/m^3)$ isocyanic acid and cyanate ion (NCO⁻) have been associated with atherosclerosis, cataracts, and rheumatoid arthritis in humans.²¹ Isocvanic acid is also under consideration as a possible respiratory irritant and sensitizer.²² Again if the total mass printing emission estimate were due to isocyanic acid, the Swedish exposure limit of $18 \mu g/m^3$ established on the basis of di-isocyanate sensitization would not be exceeded (Figure 11b).²³ Another compound found by FTIR analysis was n-decane. Researchers experienced mild eye irritation accompanied by a chemical odor during the test printer investigation. Anecdotally these same two signs accompany most ABS filament printing operations. This effect is consistent with a finding of eye irritation bio-markers in human exposure trials with n-decane.²⁴

The limitations of this study include issues related to lack of standard protocol and toxicology information. While the purpose of this study was to develop an exposure assessment, there are no standard industrial hygiene protocols (e.g. NIOSH analytical methods) to ensure all emissions are collected in a uniform manner for easy comparison between studies. This is further exacerbated by the aerosol air monitoring equipment availability and cost. In the test printer design in this study, a TSI SMPS (mobility diameter) and TSI OPS (optical diameter) were measured and merged in the Mim2 software. The accuracy and effectiveness of the software merging process has not been experiementally tested outside of the manufacturer. Further, since particle emissions are in the UFP and nanoscale, mass is decreasingly important, number count and other properties (surface area, surface charge) become more critical to anticpiation of health effects. There is increasing data of potential health effects of UFP and nanoscale particulates, but few studies have been completed focusing on 3D printers. Further, the use of 3D printers is increasing, yet there are no guidelines on sound industrial hygiene controls. Isolation is an effective control, if printer has an enclosure and consumer uses it regularly (Table 1). General dilution ventilation can also decrease emissions if printer is used in an area with "good" ventilatilon (Figures 3 and 4); the effectiveness of ventilation is not likely known by a consumer. In this study one run was completed each day: this study does not address potential build up of aerosol if multiple objects are printed consecutively without adequate ventilation. This study did not demonstrate any exposure over regulatory limits (OSHA, EPA) or health effects (Figure 11); however, the print time and frequency was limited and may not be generalizable to other 3D printers and their subsequent use. Based on these limitations and the number of replications performed (n = 10 for test printer) in this study, the literature is ripe for additional investigations. Additional printing trials at different extrusion temperatures, feed rates, filament sizes and types would aid in providing better estimates of both mass and particle generation rates for future modeling.

When developing future studies for 3D printing, chemical exposure assessment may also be important to explore. Literature to date shows that chemical exposures do not appear to be of significant concern, with the possible exception of isocyanic acid found in this study. New information continues to emerge as the analytical methods for detection improve. Studies to confirm or reject the presence of isocyanic acid should be undertaken. If confirmed, the presence of isocyanic acid or ndecane may provide an explanation for the odor and mild eve irritation experienced during ABS filament printing. One study indicated that an indicator for ABS was styrene and an indicator for PLA was methyl-methacrylate (MMA).⁴ Further studies may test the relevance of using these chemicals as indicators, as well as conducting industrial hygiene monitoring to determine concentrations of cyclohexane and n-decane.

The cancer risk associated with printer particulate emission seems reasonably low. However, carbon agglomerates, along with some of the metals identified, suggest an aerosol capable of generating reactive oxygen species.²⁶ This is another area that should be studied further as a mechanism of producing inflammation. Risk of adverse health effects based on mass concentration levels appears to be low from 3D printing when compared to the NOAEL for ultrafine combustion particulate. The Rochester PM Center provides an excellent compilation of Source-Specific Health Effects of Ultrafine/Fine Particles; however, risk based on number concentrations remains difficult to define.^{6,27} The National Institute for Occupational Safety and Health set a recommended exposure limit carbon nanotubes and carbon nanofibers of 1 μ g/m³ as an 8hour time weighted average (TWA) measured as elemental carbon in the respirable size fraction.¹² Again, this is a mass based limit and does not account for number count, an area ripe for future study.

Initial particle size is difficult to know beyond the fact that with a nano DMA (2 nm size limit) particles in the 5-7 nm range were observed, but not with the SMPS (10 nm size limit). Even with the larger size detection limit devices; there was evidence of rapid agglomeration (Figures 9 and 10). Printers with nonair tight enclosures reduce particle emissions substantially, but do not entirely eliminate UFP emissions. Rapid agglomeration may help explain the printer enclosure effectiveness in reducing number concentrations outside the enclosure. Regardless, it is recommended that printers without enclosures be restricted to use in large, highly ventilated spaces. Before use by asthmatic or otherwise atopic individuals, consideration should be given to incorporating local exhaust ventilation to further reduce emissions. Since the UFP fraction is essentially airborne (low sedimentation and inertia) capture velocity is less important than maintaining the printer enclosure under slight negative pressure with respect to the surroundings.

Any addition to the UFP aerosol in the home or work environment from 3D printers, somewhat similar to combustion aerosols, should be undertaken only after serious consideration. Both indoor and outdoor air pollution studies of UFP consistently associate a variety of adverse health outcomes to increases in UFP.^{27,28}

The size detection limit and maximum concentration limit before significant coincidence effects become prominent in many available direct reading particle counters may lead to an underestimate of the number concentration, and further research is needed to address these conditions. However, these instruments are superior to mass measurement devices for UFP aerosols which typically have detection limits above the mass concentrations of these small size particles.

CONCLUSION

The purpose of this study was to perform an exposure assessment of consumer desktop 3D printers. The results indicate that 3D printing generates high number concentrations of particulates in the UFP and nanoscale, further; this is an area with limited standard analytical techniques, toxicological implications, and regulatory guidance. The measurement of number and mass concentration, use of microscopy and subsequent data analysis (time series graphs, concentration maps, reduction factors) are useful in exposure assessments. Future study should target the development of analytical techniques, ventilation recommendations. and establishing suitable printer locations with respect to occupied locations.

ACKNOWLEDGEMENTS

Special thanks to Shelby Clark for her assistance with data collection. This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/ doe-public-access-plan).

REFERENCES

1. United States Department of Labor, Occupational Health & Safety Administration. Salt Lake Technical Center, Chemical Sampling Information, n.d. Available at: https://www.osha.gov/dts/ chemicalsampling/toc/toc_chemsamp.html.

- United States Environmental Protection Agency. *Particulate Matter*. 2016. Available at: https://www3.epa.gov/ airquality/particlepollution/.
- 3. Stephens, B.; Azimi, P.; El Orch, Z.; Ramos, T. Ultrafine particle emissions from desktop 3D printers. *Atmos Environ*, **2013**, *79*, 334–339.
- Steinle, P. Characterization of emissions from a desktop 3D printer and indoor air measurements in office settings. J Occup Environ Hyg, 2016, 13(2), 121-132, http://dx.doi.org/ 10.1080/15459624.2015.1090957.
- Zhou, Y.; Kong, X.; Chen, A.; Cao, S. Investigation of ultrafine particle emissions of desktop 3D printers in the clean room. *Procedia Eng*, **2015**, *121*, 506–512.
- Koehler, K. A.; Peters, T. New methods for personal exposure monitoring for airborne particles. *Curr Environ Health Rep*, 2015, 2(4), 399–411, http:// dx.doi.org/10.1007/s40572-015-0070-z.
- Manufacturers of Emission Controls Association (MECA). *Health Effects* of *Particulate Air Pollution*; MECA: 2200 Wilson Boulevard, Suite 310, Arlington, VA, 2014, October 14.
- Oberdörster, G. Pulmonary effects of inhaled ultrafine particles. *Int Arch Occup Environ Health*, 2001, 74(1), 1-8.
- Rutkowski, J. V.; Levint, B. C. Acrylonitrile-butadiene-styrene copolymers (ABS): pyrolysis and combustion products and their toxicity – a review of the literature. *Fire Mater*, **1986**, *10*, 93–105.
- U.S. Department of Energy. Approach to Nanomaterial ES&H. 2008. Available at: http://science.energy.gov/~/ media/bes/pdf/doe_nsrc_approach_ to_nanomaterial_esh.pdf [accessed 20.09.15].
- 11. United States Department of Health and Human Services. *Approaches to*

Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials. DHHS (NIOSH) Publication No. 2009-125. 2009. Available at: http:// www.cdc.gov/niosh/docs/2009-125/ pdfs/2009-125.pdf.

- 12. United States Department of Health and Human Services. Current Intelligence Bulletin 65 Occupational Exposure to Carbon Nanotubes and Nanofibers, DHHS (NIOSH) Publication No. 2013-145. 2013. Available at: http://www.cdc.gov/niosh/docs/ 2013-145/pdfs/2013-145.pdf.
- Levy, B. S. Occupational and Environmental Health: Recognizing and Preventing Disease and Injury, 6th ed. Oxford University Press: USA, 2011.
- 14. Galouchko, V. 3DField. Available at: http://3dfmaps.com/ [accessed 20.09.15].
- Leith, D.; Miller-Lionberga, D.; Casuccio, G.; Lersch, T.; Lentz, H.; Marchesec, A.; Volckensac, J. Development of a transfer function for a personal, thermophoretic nanoparticle sampler. *Aerosol Sci Technol*, **2014**, 48(1), 81-89.
- Jankovic, J. T.; Ihle, R.; Vick, D. O. Occupant generated carbon dioxide as a measure of dilution ventilation efficiency. *Am Ind Hyg Assoc J*, **1996**, 57(8), 756–759.
- 17. American Conference of Governmental Industrial Hygienists (ACGIH). Industrial Ventilation, A Manual of Recommended Practice, 21st ed. AC-GIH: Cincinnati, OH, 1992.
- Jones, W.; Jankovic, J.; Baron, P. Design, construction and evaluation of a multi-stage cassette impactor. *Am Ind Hyg Assoc J*, **1983**, 44(6), 409–418.
- Wright, S. Clearing the air about 3D printing emissions: Volatile organic compound and nanoparticle emission during fused filament fabrication, 2014. Presentation at 3D Printshow, London, Sept. 4–6, 2014.

- Hansson, K. M.; Samuelsson, J.; Tullin, C.; Amand, L. E. Formation of HNCO, HCN, and NH3 from the pyrolysis of bark and nitrogen-containing model compounds. *Combust Flame*, 2004, 137(3), 265–327.
- Roberts, J. M.; Veres, P. R.; Cochran, A. K.; et al. Isocyanic acid in the atmosphere and its possible link to smoke-related health effects. *Proc Natl Acad Sci USA*, 2011, 108(22), 8966–8971.
- 22. Health and Safety Executive Working Group on Action to Control Chemicals (WATCH). Assessment of the potential for isocyanic acid and other monoisocyanates to cause respiratory irritation and sensitization. 2008. Available at: http://www.hse.gov.uk/aboutus/ meetings/iacs/acts/watch/170608/ p4ann2.pdf [accessed 20.09.15].
- 23. National Board of Occupational Safety and Health (NBOSH). *Occupational exposure limits 2000:3*; NBOSH: Stockholm, Sweden, 2000.
- Kjaergaard, S.; Molhave, L.; Pedersen, O. F. Human reactions to indoor air pollution: n-decane. *Environ Int*, **1989**, *15*(1–6), 473–482.
- 26. Nicole, A. H.; Janssen, P. H.; Fischer, G.; et al. Contrasts in oxidative potential and other particulate matter characteristics collected near major streets and background locations. *Environ Health Perspect*, **2012**, *120*(2), 185–191.
- 27. Oberdorster, G.; Beckett, W.; Cass, G.; et al. Final Report: Ultrafine Particles: Characterization, Health Effects and Pathophysiological Mechanisms. 2006. EPA grant, Available at: http://cfpub. epa.gov/ncer_abstracts/index.cfm/ fuseaction/display.abstractDetail/ abstract/1098/report/F.
- Ibald-Mulli, A.; Wichmann, H. E.; Kreyling, W.; Peters, A. Epidemiological evidence on health effects of ultrafine particles. *J Aerosol Med*, 2002, 15(2), 189–201.