3-D Printing Hazards

Literature Review & Preliminary Hazard Assessment

By Tim Ryan and Daniel Hubbard

With 3-D printing stories seemingly appearing weekly, one could get the impression that it is a recent technological advance. Indeed, the increase in personal 3-D printers alone reportedly averaged almost 350% per year from 2008 to 2011 (Wohlers Associates, 2013). However, the essential technique, also known as additive manufacturing (AM), has existed for several decades. It is only because of recent advances in CAD/CAM software, in conjunction with important lapsed patents, that the technology has seen such intensive attention and explosive growth (IPO, 2013).

OSH professionals encounter AM in the aerospace, architecture, automotive, medical and dental fabrication, defense, and commercial and consumer product manufacturing industries (Stratasys, 2016). Key areas of interest for newer or emerging development are biomedical applications, electrodes and circuits, but the technology has potential uses in a nearly limitless number of applications. A sampling of these include medical prosthetics (Photo 1), miniature Li-ion microbatteries only 200 µm long (Sun, Wei, Ahn, et al., 2013), embedded inventory control tags and shoes. In an amusing case of life imitating art, NASA has even demonstrated an interest in 3-D printing to create food for astronauts while in flight, much like the food replicators of the Starship *Enterprise* in the 1966 television show *Star Trek* (NASA, 2013).

As it is most often seen commercially, 3-D printing, or AM, employs the use of premixed resins sold in proprietary cartridge containers for use in a manufacturer's printer carcass. Two major categories of materials are utilized: inks and supports. Inks are most often plastic monomers thin-layered atop each other to create an object, and support materials are simultaneously layered in and around the inks to provide structure during the build-up (i.e., printing) process. A vendor-supplied makeup for representative types of such inks and supports is shown in Tables 1 and 2 (p. 58), respectively. When exposed to UV light, these organic polymers polymerize, or cure, to a solid, finished state. During the jetting process of the inks and support materials, and/or under the UV polymerization step, hazardous airborne decomposition materials may be produced (CMU).

The literature has reported the generation of large numbers of nano-sized, ultrafine particulates (UFP) (i.e., 1~100 nm) in 3-D printing utilizing the thermoplastics acrylonitrile butadiene styrene (ABS) or polyactic acid (PLA) in association with polytetrafluoroethylene (PTFE)-related gases, raising the prospects of adverse health effects from such exposures. Work by Stephens, Azimi, El Orch, et al. (2013), estimates that UFP concentrations from desktop 3-D printers employing a molten polymer deposition process could be extremely high, ranging from about 1.9×10^{10} per minute to 2.0×10^{11} per minute. Both the ABS and PLA feedstocks used in the Stephens, et al. (2013), study differ substantively from the UV cured resins the authors examined. Nevertheless, because of their findings and the

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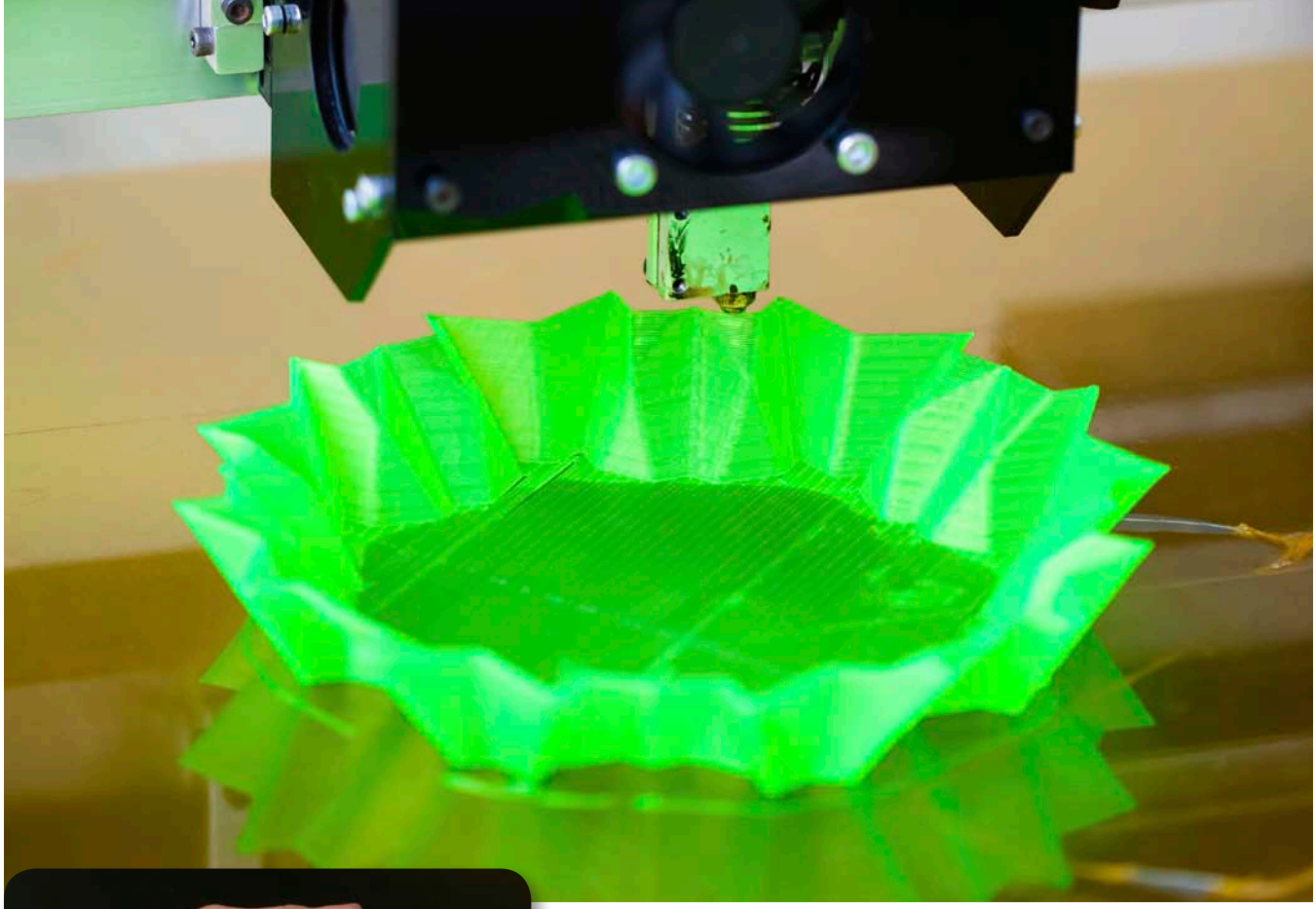

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Photo 1: The manufacture of medical prosthetics is one application for additive manufacturing, also known as 3-D printing.

dearth of information presently known about 3-D printing hazards, particulate concentrations were included in the research reported here. Furthermore, the baseline particulate data collected in this study might prove useful in future studies in which 3-D-printer-generated particulates are questioned as negative influences on ambient air quality.

The printer measured in this study (Stratasys Objet350 Connex 3-D printer) uses a technology called photopolymerization, in which liquid plastic is jetted out then exposed to a laser beam of ultraviolet light, rapidly converting the liquid into a solid (Stratasys, 2015). Because the jetting process may create aerosols, as well as the possibility for the creation of particulate-bound hazardous decomposition products created by the photopolymerization process, particulates (and UFPs especially) are of interest in this printing process.

The work herein was undertaken as a preliminary hazard assessment of the process and chemicals associated with a commercial grade photopolymerization 3-D printer. The unit studied was a new acquisition to the organization, and in the absence of detailed guidance concerning the hazards of such machines, this project was developed.

To date, only limited air sampling data has been published. To quantitatively characterize selected decomposition materials, sampling was conducted inside the 3-D printer housing during printing. A commonplace, validated ambient air sampling method, TO-15 (EPA, 1999), was utilized to obtain a base listing of volatile organic compounds (VOCs) produced from three specific polymeric feedstocks. In addition, particulate matter in the 1.0, 2.5 and 10 µm size ranges are reported. The use of a corrosive cleaning agent (sodium hydroxide) and noise were also assessed. The authors decided that should any category of area sampling reveal elevated exposure potential, future personal sampling studies of VOC, inhalation or noise exposures could be designed to more accurately delineate such hazards.

Methods

A 1.4-L TO-15 canister was placed directly adjacent to the 3-D printer, with a short (1 ft) piece of Tygon tubing fixed to the inlet of the canister extending into the 3-D printer point of operation, underneath the hinged, unventilated and interlocked guard. The canister was under negative pressure (~ -30″ Hg) and its sampling

IN BRIEF

- **Printing in three dimensions (3-D printing) constitutes an emergent technology for producing objects made of metals, biologicals and polymers. Already used in several industries, the process holds promise for larger-scale commercialization and, thereby, elevated worker exposures to process hazards. This article examines some of those hazards specifically.**
- **This article frames the present state of 3-D printing and examines the literature about related hazards.**
- **The authors also report original findings from a preliminary hazard assessment of the process and chemicals associated with a commercial-grade photopolymerization 3-D printer. Exposures to organic polymers, particulate matter, the corrosive cleaning agent sodium hydroxide and noise were assessed.**

Table 1
Representative 3-D Printer Ink

Chemical name	CAS no.	Concentration (%)
Isobornyl acrylate	5888-33-5	15 to 30
Acrylic monomer	*	15 to 30
Urethane acrylate	*	15 to 30
Epoxy acrylate	*	5 to 15
Acrylic oligomer	*	5 to 15
Photo initiator	*	0.1 to 2.0

Note. *Data for Objet VeroWhitePlus RGD835. *Claimed as proprietary by manufacturer.*

Table 2
Representative 3-D Printer Support

Ingredient	CAS no. EINECS/ELINCS no.	Concentration (%)
Propane-1,2-diol	57-55-6 200-338-0	20 to 40
Polyethylene glycol 400	25322-68-3 203-473-3	20 to 40
Glycerol	56-81-5 200-289-5	5 to 20

Note. *Data for Polymerized Fullcure 705.*

rate determined by a precision flow regulator. Air was collected in a single sampling run during an approximately 8-hour period, during which time the 3-D printer operated continuously. Due to expense, laboratory air on a nonprinting day was not sampled. Upon sampling completion, the canister was returned for analysis to an Industrial Hygiene Laboratory Accreditation Program (IHLAP)-accredited laboratory (AIHA, 2016).

Particulate matter was sampled by the use of three simultaneously operated environmental particulate air monitors (EPAM) (HazDust EPAM-5000, Environmental Devices Corp., Plaistow, NH). The monitors are highly sensitive to preselected sizes of particles and were configured to measure the specific cutpoint diameters of 1.0, 2.5 and 10 µm for this project, as the authors could find no reports of $PM_{1.0}$, $PM_{2.5}$ or PM_{10} from the 3-D printing process reported in the literature.

Concentrations were sampled every minute, data were logged and average hourly concentrations were calculated. Total suspended particulate (TSP) measurements are also possible with the EPAM units but data were not collected for TSP in this project given the specificity available for the three size ranges stated.

While it must be acknowledged that the TSP concentrations could potentially include unrecognized harmful elements, adverse upper respiratory effects associated with such larger particle fractions

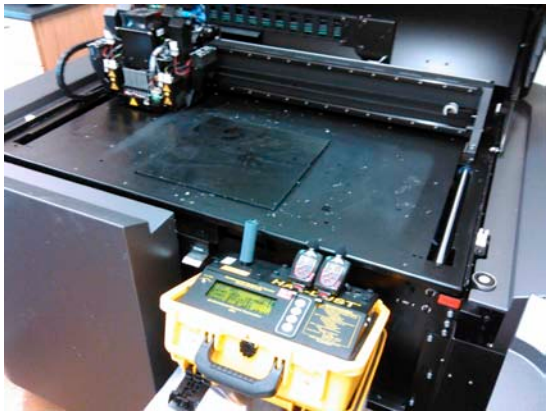


Photo 2: A 3-D printer being configured for printing, with one of the three HazDust units in place, as well as dual noise dosimeters in place for monitoring.

from 3-D printers have yet to be reported in the literature and were not evident within the facility studied. UFPs were not assessed as work on that size has previously been reported (Stephens, et al., 2013). The three PM monitors were colocated by the TO-15 inlet and operated contemporaneously with the TO-15 units for 8 hours, with their isokinetic inlets inserted into the gap between the printer guard and base.

The researchers believed that since there were no existing complaints related to ambient air quality at the facility, and since low concentrations of fine particulates are generally imperceptible by building occupants, baseline air quality data should be collected for comparison to air quality while the printer was in operation. Reference control data was collected utilizing the three PM monitors in the printing room on a different day during which no printing took place. Photo 2 shows the printer while it is being configured for printing, with one of the three EPAM units in place, as well as dual noise dosimeters in place for monitoring.

Noise data were also collected during the operation of the printer, both inside the printing head area and in the printer lab, as a preliminary characterization of any potential noise hazards present during printer operation. Area samples (only) were obtained; no personal sampling was performed. Two calibrated 3M Eg5 personal dosimeters (3M, St. Paul, MN) were used for integrated, contemporaneous sampling runs of approximately 30 minutes each. Results were compiled using 3M Detection Management Software (DMS) version 2.7.152.0.

For the assessment of the cleaning process used at the end of production, the printer technician/operator was interviewed about his practices. Other printed resources were also examined (CMU), but no air monitoring was conducted.

Results

Volatile Organic Compound Sampling

Air within the 3-D printer enclosure yielded low but detectable concentrations of seven compounds: acetone, n-butane, 2-butanone, 1,4-diox-

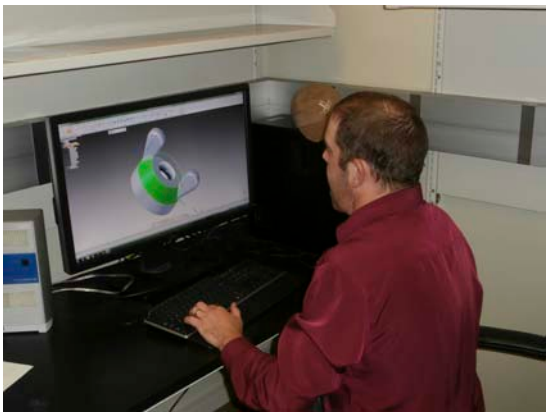


Photo 3: Computer-aided design/computer-aided manufacturing (CAD/CAM) is used to design and prototype parts prior to printing.

ane, ethanol, isopropyl alcohol (2-propanol) and toluene (Table 3, p. 61). All of the chemicals quantified were significantly under current regulatory limits, typically present at only one to two orders of magnitude lower concentrations than permitted. Notably, the compound present at the highest concentration (dioxane, 27 ppb) is also "reasonably anticipated to be a human carcinogen" according to the latest report on that chemical from National Toxicology Program (2014).

Particulate Matter Sampling

PM concentrations are displayed in Figures 1-3. Figures 1a and 1b (p. 60) display the average $PM_{1.0}$ concentrations per hour inside the printer head enclosure and in the printer room while no printing was taking place (control), respectively. Figures 2 (p. 61) and 3 (p. 62) similarly depict the $PM_{2.5}$ and PM_{10} concentrations. Examining all three PM cut-points as a whole, values ranged from a low of about 0.003 mg/m^3 (PM_{10} and $PM_{2.5}$ controls) to a tenfold higher value of 0.030 mg/m^3 for $PM_{1.0}$ concentration inside the printer. For all three inside-printer versus control comparisons, the measured range of values was similar for each, although $PM_{1.0}$ values were noticeably higher (> 0.010 mg/m^3) on average than either $PM_{2.5}$ or PM10 data (~0.006 mg/m^3, both). As can be seen in the PM plots, $PM_{1.0}$ concentrations began high (0.015 mg/m^3) and fell throughout the printer run, while just the opposite occurred for $PM_{2.5}$, beginning at 0.004 mg/m^3 and gradually leveling out at approximately 0.007 mg/m^3.

Noise Sampling

Noise levels measured in the vicinity of the 3-D printer while it was engaged were OSHA compliant, with average sound pressure levels of ~78 dBA. Sound inside the printer's guarded enclosure was approximately double that in the room per se (~83 dBA), but still below the OSHA action limit of 85 dBA for implementation of a hearing conservation program.

Cleaning Hazard Assessment

Cleaning of the finished article presents the most obvious, well-recognized hazard associated with 3-D printing: corrosives exposure. Upon the completion of the printing process, the printed support material (e.g., Table 2, polymerized Fullcure 705) must be removed from around and inside of the intended object. This is done using concentrated, highly corrosive (pH = 13.0) sodium hydroxide. Typically the intended object is submersed in a bath of the corrosive and allowed to soak for a short interval to permit liquid penetration to all void areas. Physical removal tools such as brushes, picks or pins are then employed to free the waste support material from the intended object as far as possible. Repeated soaking/physical removal cycles may be utilized depending on the object's size or geometry.

3-D Printing Key Definitions & Terms

3-D Printing or AM. Three-dimensional printing or additive manufacturing. The creation of items using additive methods in three planes simultaneously. Print heads deposit fluidized materials according to computerized plans, allowing the buildup of various printing media without the need for forms, templates or guides. Such materials are cured with light, or naturally set up when cooled. 3-D/AM is just the opposite of removal methods used by techniques such as routers, saws or drills to form finished objects from blocks of feedstock material.

CAD/CAM. Computer-aided design/computer-aided manufacturing. The use of photos or computer-generated plans to inform a 3-D printer where to deposit which printer material. Photo 3 shows the design stage of a simple part being prototyped prior to printing.

PM. Particulate matter. A suspension of extremely small particles in air, associated with respiratory diseases because of its ability to penetrate into the deepest reaches of the human lung. $PM_{2.5}$ is frequently heard with respect to PM, and refers to a PM suspension where the average size of the particles are only 2.5 micrometers, or just slightly larger than 1/1,000,000 (one one-millionth) of a meter.

UFP. Ultra-fine particles. Particles in air almost 1,000 times smaller than the more common $PM_{2.5}$ particles. UFPs are nano-sized, or one one-billionth of a meter in average diameter, and so are in the size range of many viruses or other extraordinarily small materials.

ABS and PLA. Acrylonitrile butadiene styrene and polyactic acid are two usual 3-D printing feed stocks. ABS is a hard, somewhat brittle polymer with recognized uses such as plastic hubcaps, automobile interior parts and LEGO toy blocks. PLA is a softer polymer with a relatively low melting point, with properties similar to translucent milk cartons, biodegradable cups or landscaping fabrics, for example.

VOC. Volatile organic compound. Any of thousands of mostly solvent vapors that readily evaporate into surrounding air, causing various human responses depending on their chemical nature and concentration.

Discussion

This article presents study results of a single 3-D printer type and brand, and for some hazards (e.g., VOCs), a single sample. In addition, no background laboratory air was sampled for VOCs. Caution in interpretation is therefore warranted. Nevertheless, it is accurate to state that 1,4-dioxane was detected inside the printer workspace, albeit at a low concentration. Given the carcinogenic status of that chemical, vigilance by the OSH community with respect

Figure 1
Average $PM_{1.0}$ Concentrations

Average $PM_{1.0}$ concentrations in printer (Figure 1a) and in printer room (control) (Figure 1b).

Figure 1a

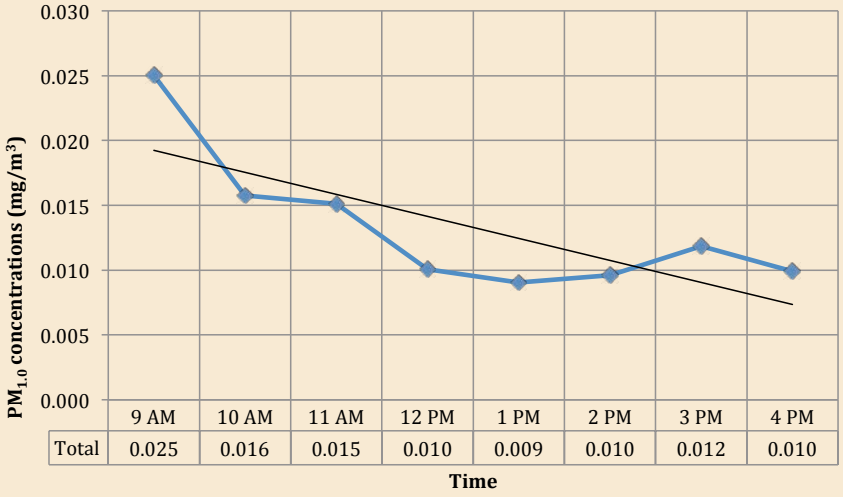
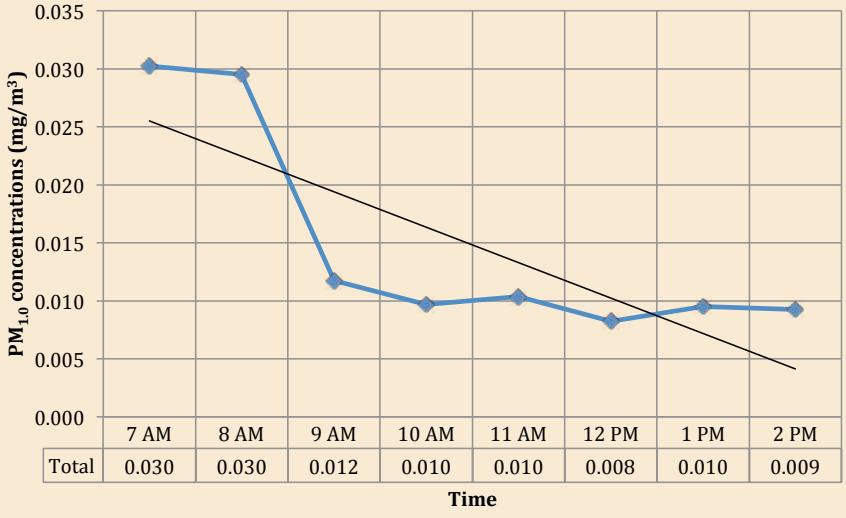


Figure 1b



to it and 3-D printing is warranted. At the least, further statistically defensible sampling should be performed. The printer examined here had no local exhaust ventilation and, were multiple printers operating in a space served solely by general HVAC, the findings suggest that 1,4-dioxane levels might be higher, or even approach the 1 ppm REL suggested by NIOSH. Although concentrations of the other VOCs detected were also in the ppb range, depending on future production levels and the 3-D printer operating environment, VOC concentrations would reasonably be expected to move to higher levels. This is also suggested by Stephens, et al. (2013), with respect to their UFP study results.

Regarding the particulate results, several observations are notable. First, the $PM_{1.0}$ and $PM_{2.5}$ concentrations seemed to vary inversely with each other. Specifically, $PM_{1.0}$ concentrations started higher (i.e., 0.025 to 0.015 mg/m^3) and fell throughout the 8-hour printing run, while $PM_{2.5}$ values started lower (i.e., 0.004 to 0.005 mg/m^3) and rose during continuous printer operation. Interestingly, both the $PM_{1.0}$ and $PM_{2.5}$ concentrations ended up in the same general average concentration range of 0.008 to 0.010 mg/m^3 after 3 to 4 hours, by the end of the sampling run late in the day.

These results were echoed by the control room concentrations also sampled, raising the possibility that the PM concentrations sampled reflected not the printer head area air but rather the overall laboratory room air. This explanation seems plausible in that the initial flurry of activity when setting up the printer and particulate monitors could have resulted in higher initial $PM_{1.0}$ concentrations that then fell off once the printer room was closed and left free of personnel until later in the day.

The explanation for $PM_{1.0}$ values fails to describe the related rising $PM_{2.5}$ concentrations, however, and at least two plausible accounts present themselves. First, it is possible that $PM_{2.5}$ data reflect growing occupant numbers and activity at the building housing the printer. Primary evidence supporting this is the rise in values throughout the day.

Second, it is also possible that $PM_{2.5}$ concentrations actually increased as a result of 3-D printer operation. Two observations from the data support this explanation. The control room $PM_{2.5}$ data were initially much lower than those from inside the printer head area, implying that the $PM_{2.5}$ in the printer did in fact result from printer operation.

Furthermore, careful observation of the hourly averaged data in Figures 2a and 2b reveal three distinct time periods when the printer $PM_{2.5}$ values moved in opposite directions from those of the control room. If room air were infiltrating the printer housing to cause the elevated $PM_{2.5}$ concentrations, the peaks and valleys of the concentration traces should have been parallel or at least similar.

All particulate measurements were very low, with none exceeding 0.025 mg/m^3. By way of comparison, Salem, El-Haty, Al-Gunaid, et al. (2014), saw $PM_{1.0}$ (PM_{10} concentrations of 0.160) 0.20 mg/m^3 in high traffic areas such as hospital or college building entrances.

Higher $PM_{2.5}$ concentrations have been epidemiologically associated with elevated mortality for more than 20 years (Dockery, Pope, Xu, et al., 1993; Pope, Thun, Nambudin, et al., 1995), but a cause-effect relationship is not universally accepted (Gamble, 1998). EPA has established a primary

(i.e., protective of health) level for $PM_{2.5}$ of 0.012 mg/m³ (EPA, 2012). None of the $PM_{2.5}$ values seen here exceeded that limit, although the $PM_{2.5}$ inside the printer enclosure approached it (0.008 mg/m³). The unregulated $PM_{1.0}$ fraction showed the highest values overall, initially beginning quite high at 0.025 mg/m³, remaining above 0.012 mg/m³ for several hours before dropping to ~0.010 mg/m³ for the majority of the sampling period.

Exposure to noise from the unit studied is of little or no concern, since only under unusual circumstance might the printer be operated with the interlock defeated (e.g., during printer head alignment or calibration). The overriding impression while in the printer laboratory is not one of being in a noisy environment, and certainly not in an OSHA-regulated noise area.

The handling and use of corrosives is not unique to the AM/3-D printing process, and so requires little added discussion here. Readers are reminded that any use of corrosives with the potential for exposure require the adjacency of an emergency eye wash and/or deluge shower, per 29 CFR 1910.151(c) requirements (OSHA, 2015). Because of the potential for serious caustic burns, at a minimum the use of gauntlet nitrile rubber gloves, splash apron, face shield and splash goggles is recommended (CMU).

In summary, this was a preliminary study of VOCs and particulates from a single 3-D printer employing photopolymerization technology. Low concentrations of both were seen in the environment examined. Future studies should perform more extensive sampling not only of the $PM_{1.0}$, $PM_{2.5}$ and PM_{10} concentrations studied to date, but also of the VOCs with different inks and support materials in various printers. Because many 3-D printing processes exist, those categories should also be targeted for preliminary sampling ahead of or at least in conjunction with large-scale 3-D printing under production scenarios. **PS**

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Figure 2

Average $PM_{2.5}$ Concentrations

Average $PM_{2.5}$ concentrations in printer (Figure 2a) and in printer room (control) (Figure 2b).

Figure 2a

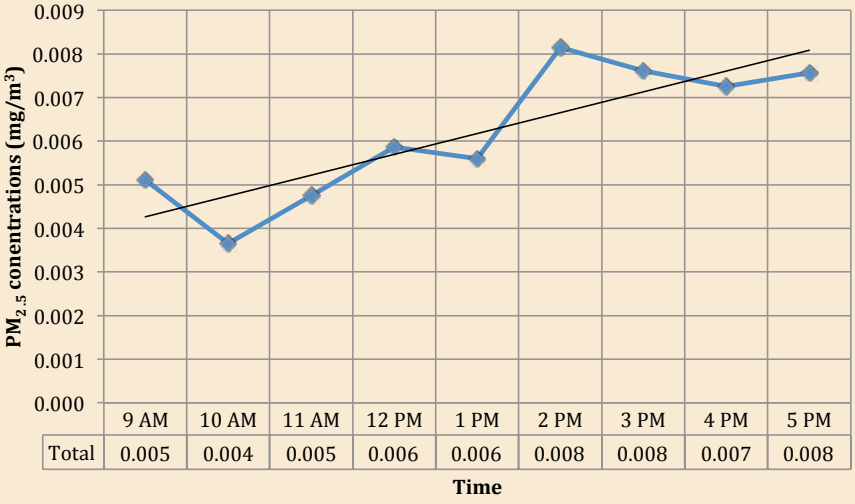


Figure 2b

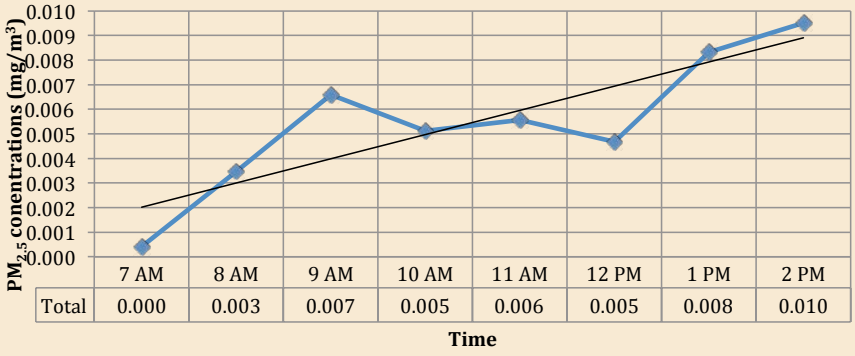


Table 3

VOCs Detected Inside Printing Jet-Cure Area & Recommended Limits

Quantitated compound	µm/m³	ppbv	NIOSH TWA-REL ppm	OSHA TWA-PEL ppm
acetone	8.3	3.5	250	1000
n-butane	2.6	0.87	800	†
2-butanone	2.4	1.0	200	200
1,4-dioxane	100	27	1 (Ca)	†100
ethanol	36	19	1000	1000
isopropyl alcohol (2-propanol)	4.8	1.9	400	400
toluene	14	3.7	100	200

Note. *†Newer or updated OSHA PEL vacated effective June 30, 1993 (NIOSH, 2016b). (Ca) NIOSH has established a 1 ppm ceiling limit and considers this substance a potential occupational carcinogen (NIOSH, 2016c).*

Figure 3
Average PM_{10} Concentrations

Average PM_{10} concentrations in printer (Figure 3a) and in printer room (control) (Figure 3b).

Figure 3a

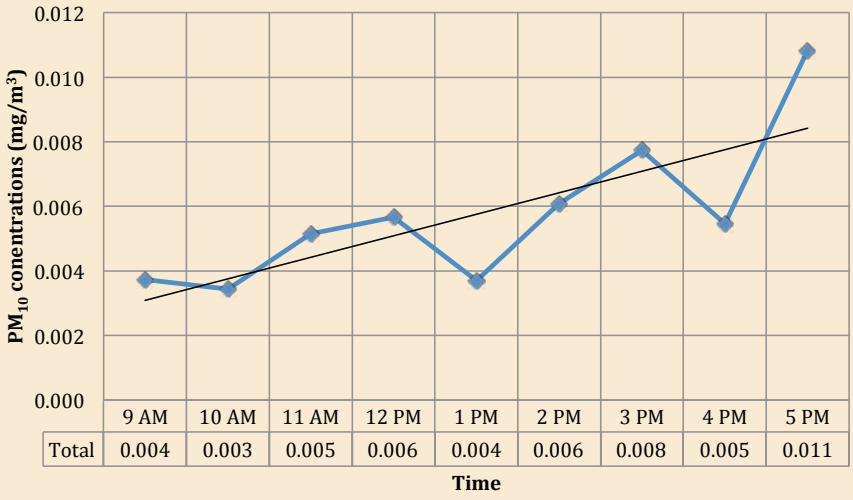
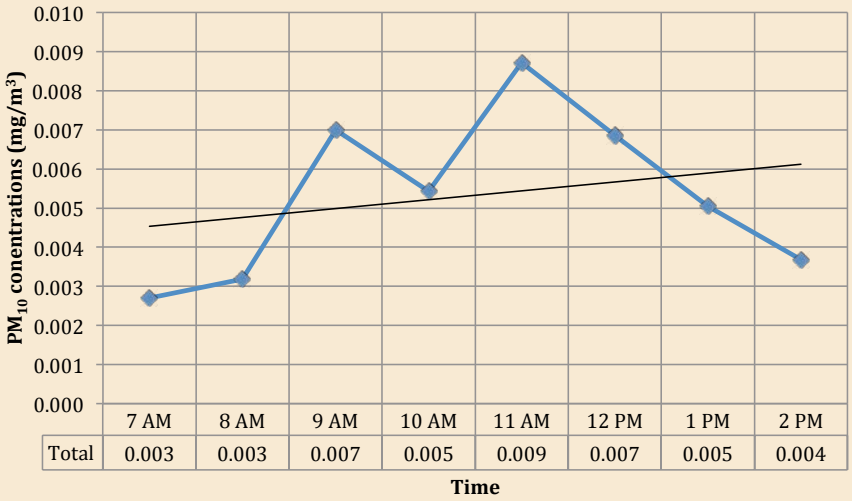


Figure 3b



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Mention of a specific brand or model does not constitute an endorsement and is solely for the purpose of the accurate interpretation of results presented.