Proceedings of the Safety Science of 3D Printing Summit

February 22 – 23 , 2017 • Atlanta, GA

SAFETY CONVERGENCE
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1ST ANNUAL SAFETY SCIENCE OF 3D PRINTING SUMMIT

February 22 – 23, 2017 • Atlanta, GA

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INTRODUCTION

With gratitude, we acknowledge the esteemed members of the 3D Print Advisory Board for their engaging, passionate and professional commitment to achieving a successful 2017 Summit on the Safety Science of 3D Printing. We also recognize the expert faculty for sharing their knowledge and encouraging discussion on 3D printing, testing measures, policy and regulations, and human health relative to chemical and particle exposure.

We also acknowledge the general participants who contributed their knowledge and interests as key stakeholders in this open and engaging dialogue.

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PREFACE

The following proceedings provide a summary of technical information exchange from the Safety Science of 3D Printing Summit held in Atlanta, Georgia, February 22 – 23, 2017. The summary is not intended to provide an accurate or complete transcription of each speaker's presentation.

These proceedings are provided to share summaries of the presentations and technical discussions among all stakeholders. We hope this exchange of information will enable more collaborative discussions, research, innovation, informed policy advancement, and science-based initiatives leading to the safe of use 3D printers.

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WELCOME

A LEADERSHIP SUMMIT ADDRESSING CHEMICAL AND PARTICLE EMISSIONS FROM 3D PRINTING PROCESSES

Underwriters Laboratories Inc. and our Not for Profit Safety Science Initiative, along with our co-conveners, Emory University and Georgia Institute of Technology, welcomed diverse stakeholders in Atlanta for the first Leadership Summit on 3D Printing and its potential impact on human health.

Three dimensional or 3D printers have gained momentum in the marketplace for rapid prototyping and manufacturing especially in consumer, industrial, educational, healthcare, and military environments. While there are traditional electrical and physical safety hazard considerations for the application and use of 3D printers and additive manufacturing processes, this technology also presents a human health concern from the potential release of volatile chemicals and particles into the air during operation. These pollutant releases may affect the indoor air and expose people to unexpected pollutants leading to adverse acute and chronic health concerns. Few scientific studies have been done to characterize and evaluate this potential health risk and to develop management strategies for consumer and occupational environments.

The 3D Print Summit brought together academic, government, industry, and user experts for a review of current and future additive manufacturing techniques and to hear about ongoing scientific research on pollutant releases and their potential impact on human health. UL, along with researchers from Emory University and Georgia Institute of Technology, presented data from their multi-year research initiatives on the measurement and characterization of particles and chemicals released from fused deposition modeling (FDM™) printers. This research addressed the development of controlled measurement methodologies; determination and measurement of aerosol particles – their content, size distributions, formation processes, and air levels; release of volatile organic compounds (VOCs) and calculation of exposure levels; toxicity evaluations of the aerosols; and approaches for conducting consumer, student, and office worker exposure assessments.

The Summit's goals were to enable key stakeholders to have an open, honest, and respectful dialogue on 3D printing and its potential health impacts. In a collaborative environment, we shared science, reviewed research data and agreed on a path forward to develop a standardized method for measuring and assessing the emissions released during printing. This will allow for consistent and comparative data to be obtained from laboratories, machine manufacturers, and suppliers of filaments. UL standards will initiate the development of an ANSI consensus standard and will make a call for third party participants. In addition, research will be continued to gather more toxicity information and additional emissions data on a range of filament types.

Based on the shared information, emissions from 3D printing can be a source of ultrafine particles in the nanoparticle size range as well as a source of certain VOCs, some of which are odorants, irritants, and chronic or acute hazards. These exposure levels are generally low and complete risk assessments have not been conducted, but a precautionary approach of providing good building ventilation with outdoor air exchange and local ventilation in areas where 3D printing is occurring would be prudent.

We appreciate your commitment and interest in this important topic, and your willingness to work with us to develop scientific processes for enabling safe living, learning, and working environments.

Marilyn Black, Ph.D.

VP & Senior Technical Advisor, Underwriters Laboratories Inc.

Founder GREENGUARD

Additive Manufacturing and its Applications to Three-Dimensional Bioprinting

SPEAKER

Dr. Yong Huang, University of Florida

Abstract: A general overview of additive manufacturing including bioprinting.

Dr. Huang presented an introduction and overview of additive manufacturing technologies and their significant advantages including the emerging field of bioprinting. He has coauthored two very important workshop reports on additive manufacturing research and the environmental health impacts as noted in the additional references.

Additional References:

Rejeski D and Huang Y, Environmental and Health Impacts of Additive Manufacturing, An NSF Workshop Report, October, 2014, <https://www.wilsoncenter.org/sites/nsfamenv/index.html>.

Huang Y and Leu M, Frontiers of Additive Manufacturing Research and Education, An NSF Additive Manufacturing Workshop, July, 2013, <http://nsfam.mae.ufl.edu/>.

Evaluation and Control of Human Exposures to Emitted Ultrafine Particles and Volatile Organic Compounds from Desktop 3D Printers

SPEAKER

Dr. Parham Azimi, Illinois Institute of Technology

Abstract: Illinois Institute of Technology's (IIT) research on emissions released from desktop 3D printers.

Since 3D printing processes involve high temperatures, melting, and sintering, it is likely that they emit various pollutants. Most desktop 3D printers use a process called molten polymer deposition or fused deposition modeling (FDM™). This involves a thermoplastic filament being melted through an extruder and dropped through the nozzle onto the print bed. Research has shown that using a 3D printer might have a health effect. Previous studies have shown that gases and particles can be emitted during industrial thermoplastic processing; that decomposition products from acrylonitrile butadiene styrene (ABS) thermal processing can

have toxic effects in rats and mice; and exposure to ultrafine particles (UFPs) from other sources have been linked to a variety of adverse health effects.

As part of the IIT's initial research studies, unenclosed printers were tested with polylactic acid (PLA) and ABS filaments in a closed 45 m^3 office environment for ultrafine particles. From an ABS printer, the total ultrafine particle emission rate was 1.9×10^{11} particles/minute, and for a PLA printer, the total ultrafine particle emission rate was 2.0×10^{10} particles/minute.

Additional chamber studies were done to look at a variety of printers, filaments, and exposure scenarios for UFPs and volatile organics. Based on this research, ultrafine particle concentrations reached an approximate steady state towards the end of the print period, and about 50 speciated volatile organic compounds (VOCs) were identified from chamber samples. Based on the estimated emission rates, the top three emitted VOCs were styrene, caprolactam, and lactide. The total volatile organic compound (TVOC) emission rate of 3D printers was estimated between ~1 and ~200 μg/min for nGen (Next-generation polymer from ColorFabb) and nylon filaments, respectively.

Some potential control strategies for 3D printer emissions include: upgrading central HVAC filtration with a higher efficiency filter impregnated with activated carbon; operating a portable, stand-alone air-cleaner in near-distance zones with a clean air delivery rate of 100 or 300 m^3/hr; installing spot ventilation systems in near-distance zones; and creating custom-made enclosures. Human exposure models were created to measure the magnitude of exposure to emitted pollutants that would be present in a one-story office building with multi-zone airflow and a contaminate transport analysis modeling software (CONTAM). The simulation results demonstrate that high-efficient spot ventilation systems and custom-made enclosures have the highest impacts on reducing the human exposures to emitted pollutants from 3D printers in near, adjacent, and far distances from the printer.

Additional References:

For more information, please visit the following resources on the Built Environment Research Group website:

The Built Environment Research Group, VOC & Particle Emissions from 3D Printers, <http://built-envi.com/portfolio/ultrafine-particle-emissions-from-3d-printers/>.

The Built Environment Research Group, Publications, <http://built-envi.com/pubs/>.

NIOSH Efforts that Support Responsible and Rapid Development in Advanced Materials and Manufacturing

SPEAKER

LCDR Kevin Dunn, MS, CIH, National Institute for Occupational Safety and Health

Abstract: An overview of research by NIOSH and their Nanotechnology Research Center was presented.

The National Institute for Occupational Safety and Health (NIOSH) is a part of the U.S. Department of Health and Human Services and is federally funded for occupational health and safety research. It has no regulatory authority. Its primary goal is to generate new knowledge in the field of occupational safety and health and to transfer that research knowledge into practice and guidance.

The five goals for the NIOSH Nanotechnology Research Center (NTRC) include:

- Increasing understanding of new hazards and related health risks to advance materials and manufacturing
- Expanding the understanding of the initial hazard findings of engineered nanomaterials, advanced materials, and additive manufacturing
- Supporting the creation of guidance materials to inform workers, employers, health professionals, regulatory agencies, and decision-makers about hazards, risks, and risk management approaches
- Supporting epidemiologic studies for nanomaterial workers, including medical, cross-sectional, prospective cohort, and exposure studies
- Assessing and promoting national and international adherence with risk management guidance

The NTRC Field Team, also called the Advanced Materials and Manufacturing Technologies Team, performs on-site assessments to gain real world insight on potential exposures, develop mitigation strategies, as well as develop and share best practice guidance for safe development and commercialization. The Field Team is currently studying Fused Deposition Modeling (FDM™), Selective Laser Sintering (SLS), Stereolithography (SLA), and Polyjet printing along with key partners.

The NIOSH working definition of advanced materials is: "advanced materials refers to all new materials and modifications to existing materials that are specifically engineered to exhibit novel or enhanced properties that result in superior performance in one or more characteristics, relative to conventional materials, that are critical for the application under consideration."

Testing methods are a combination of traditional industrial hygiene processes and newer sampling techniques. Personal and area air were sampled for total particulate and respirable particulate data, as well as volatile organic compounds (VOCs). There are six instruments that are commonly used for direct reading of particle counts, sizing, and classification – Condensation Particle Counter (CPC), Optical Particle Sizer (OPS), Aerosol Photometer, Nano Scan Scanning Mobility Particle Sizer (SMPS) Spectrometer, Fast Mobility Particle Sizer (FMPS) Spectrometer, and Electric Low-Pressure Impactor (EPLI). The Thermophoretic Sampler, designed by RJ Lee Group, Inc. and Colorado State University, looked at particle deposition based on a heat differential or gradient transfer. For this method, no sample preparation was needed and size is selective for 300 nm or lower. It was sampled directly onto an Electron Microscopy (EM) grid. The Real-time Aerosol Multi-elemental Spectrometer is a NIOSH device that takes a direct reading of aerosols, has low detection limits and can analyze samples on-site. There were also lab based and portable test chambers used for the studies. Each includes high-efficiency particulate arresting (HEPA) filter, sampling probes, and air handling unit, and can be configured in multiple sizes.

Current field studies are designed to:

1. Identify and quantify emission sources and emission rates
2. Characterize task-based exposures by direct-reading instruments and filter-based sampling
3. Assess plant ventilation and its effect on the potential exposures
4. Assess or design engineering controls

To create control measures for 3D printers, data is being collected to measure worker exposures and emission rates. Using direct-reading instruments allows for the identification of potential exposure sources in real time. A collection of air filter samples will give more detailed information about the materials, such as morphology and chemical characteristics. Plant ventilation is also being evaluated to ensure that the design is appropriate for the application.

Additional References:

Centers for Disease Control and Prevention, The National Institute for Occupational Safety and Health (NIOSH), Workplace Safety & Health Topics, Nanotechnology, <https://www.cdc.gov/niosh/topics/nanotech/>.

Centers for Disease Control and Prevention, The National Institute for Occupational Safety and Health (NIOSH), Workplace Safety & Health Topics, Nanotechnology, Field Studies Effort, <https://www.cdc.gov/niosh/topics/nanotech/field.html>.

Chemical Emissions from a Desktop 3D Printer

SPEAKER

Dr. Aleksandr Stefaniak (Presented by Alyson Johnson), National Institute for Occupational Safety and Health

Abstract: NIOSH's research on emissions released from desktop 3D printers.

Fused deposition modeling (FDM™) printers extrude thermoplastic filament through a heated nozzle. The heating of the polymer leads to its breakdown and release of chemical emissions. There are many printer and consumable factors that can influence emissions. These include printer design and operating temperature, as well as additives, colorants, and composition of filaments used. For NIOSH (National Institute for Occupational Safety and Health) testing, FDM™ 3D printers were tested in a 0.5 m^3 stainless steel chamber and the print job was a 100 mm x 33 mm x 3mm comb. The filaments used were acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA), with four colors for each filament type. The research looked at the identification and quantification of volatile organic compounds (VOCs), with real-time monitors and time-integrated sampling and off-line analysis. Four ABS colors were analyzed – natural, blue, red, and black. Four PLA colors were analyzed as well – ocean blue, transparent blue, true red, and army green. All of the following total volatile organic compound (TVOC) emission values were from printers with their covers on and with replicate prints of a comb.

Thermoplastic	**Average TVOC ± Standard Deviation (µg/hr)**
ABS Natural	3552 ± 549 µg/hr
ABS Blue	2385 ± 82 µg/hr
ABS Red	2383 ± 357 µg/hr
ABS Black	1085 ± 217 µg/hr
PLA Ocean Blue	ND µg/hr
PLA Transparent Blue	131 ± 37 µg/hr
PLA True Red	ND – 49 µg/hr
PLA Army Green	ND – 51 µg/hr

These printers were also tested with a cover on versus cover off, which showed no effect. There was one run of data which consisted of a printer malfunction, which had very high emissions, but its full effect is unknown.

All ABS and PLA filaments emitted acetaldehyde, ethanol, acetone, and isopropanol. ABS only emitted ethylbenzene, xylenes, and styrene. There were no emissions unique to PLA from the list of measured chemicals. Emissions were generally influenced by filament type and color. They were not controlled with the use of a printer cover.

There were also ozone reaction products measured during the print runs. These included 4-oxopentanal, glyoxal, and o,m,p-tolualdehyde.

Exposure to the emissions from printing with ABS filament have shown increased mean arterial pressure, increased arteriolar tone, and decreased endothelium-dependent arteriolar dilation in mice.

Ongoing research will include continued in vivo studies of cardiovascular health; additional chamber testing and comparisons between FDM™ and vat polymerization processes as well as comparisons of filaments containing engineered nanomaterials; and workplace exposure evaluations in facilities using FDM™ and selective laser sintering (SLS) printers.

Additional References:

Yi J, LeBouf RF, Duling MG, Nurkiewicz T, Chen BT, Schwegler-Berry D, Virji MA, Stefaniak AB: Emission of particulate matter from a desktop three-dimensional (3-D) printer. J. Toxicol. Environ. Health Part A. 79:453-465 (2016), <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4917922/>.

Stefaniak AB, LeBouf RF, Yi J, Ham J, Nurkewicz T, Schwegler-Berry DE, Chen BT, Wells JR, Duling MG, Lawrence RB, Martin Jr. SB, Johnson AR, Virji MA: Characterization of chemical contaminants generated by a desktop fused deposition modeling 3-dimensional printer. J. Occup. Environ. Hygiene. (Accepted).

Lessons Learned from 4 Years of Laser Printer Particle Emission Testing

SPEAKER

Dr. Stefan Seeger & Dr. Olaf Wilke, Bundesanstalt für Materialforschung und -prüfung (BAM), (Federal Institute for Materials Research and Testing), Germany

Abstract: Historical experiences testing particle emissions from laser printers and comparison to 3D printer emissions is discussed.

Laser printers and 3D FDM™ printers show similarities in fine and ultrafine particle emissions.

Laser printer particle emissions are already dealt with in the internationally recognized German Blue Angel Ecolabel Program since 2012. The Blue Angel acknowledges more than 12,000 environmentally friendly products that have been tested and shown to meet specific ecological and quality award criteria. Because only 20 – 30 % of all products are able to meet the requirements, the Blue Angel is an effective market conformity instrument of environmental policy that works on a voluntary basis. The final decision on test guidelines and award criteria is always made by the independent 'Blue Angel Environmental Label' Jury, following the precautionary principle. The driving policy is reducing possible harm to the environment and health risks.

Risks associated with laser printer emissions are seen to be at level with other indoor air pollution sources and the Blue Angel is considered appropriate for reducing consumer exposure.

Blue Angel testing of laser printers includes emission limits for certain volatile organic compounds (VOCs), total particle mass, ozone, and number of fine/ultrafine particles. The device under test is placed in the middle of an environmental test chamber and the total particle number concentrations before, during, and after printing is measured along with gaseous emissions. The test requires a standard print job of 10 minutes.

Factors that can influence the measurement include:

- Chamber volume
- Particle losses and air exchange
- Aerosol measuring device performance
- Particle emission characteristics, e.g. size range
- Duration of printing operation

The derived objectifiable test quantity (i.e. independent of chamber volume, losses, air exchange rate a.s.o.) is the averaged particle emission rate (PER10) that is the number of particles released during a 10-minute standard print job. PER10 is only measured once per test in order to reduce costs and effort. In order to apply the Blue Angel RAL 205 pass-fail criterion of 3.5×10^{11} emitted particles during 10 minutes printing, an estimate of the typical measurement uncertainty is considered which has been obtained from round robin testing.

Currently, there are 17 laboratories that participate in the standard test measurement and qualification process for laser printers. These laboratories have to show competence in the operation of test equipment; performance of the complete test method; and interpretation of raw data and calculation of final results. Based on more than 300 tests, only 3% of the reports were considered not valid due to major deficiencies. The high quality of testing is maintained by round robin testing on a regular basis.

Applying the laser printer test design to FDM™ 3D printers and filament testing requires reconsidering of several aspects, such as the emissions source and particle formation mechanism, the duration of print jobs and characteristics of emissions and the definition of appropriate measurands.

Selecting suitable instrumentation is crucial insofar as devices may not cover the full-size range of emitted particles or may not provide sufficient time resolution and detection efficiency.

In conclusion:

- Positive experiences with Blue Angel testing encourages designing of emission tests for FDM™ 3D printers and filaments
- Number of variables and influencing factors should be kept small, simple models and criteria should be applied
- Following the Blue Angel test design quality and accuracy of FDM™ 3D printer/filament testing are expected to be sufficient for comparison of particle emissions
- Careful selection of appropriate measuring equipment (particle size range, time resolution, and combination of instruments) and primary measurands are crucial

Additional references:

The Blue Angel, Environmental Label Jury, Office Equipment with Printing Function, printers and Multifunction Devices, RAL-UZ 205:2017, <https://www.blauer-engel.de/en>.

Karrasch, S, Simon, B., Herbig, B., Seeger, S. et al: Health effects of laser printer emissions: a controlled exposure stud, Indoor Air (2017), <http://onlinelibrary.wiley.com/doi/10.1111/ina.12366/full>.

Barthel, M. Seeger, S. et al: Measurement of Fine and Ultrafine Particles from Office Devices during Printing in order to Develop a Test Method for the Blue Angel Ecolabel for Office-Based Printing Devices, Umweltbundesamt, Germany, UBA-Texte 75 (2013), <https://www.umweltbundesamt.de/en/publikationen/measurement-of-fine-ultrafine-particles-from-office>.

Nanoparticle – Cell Interactions: TiO_2 Nanoparticles and Corona – Induced Oxidative Stress

SPEAKER

Dr. Christine Payne, Georgia Institute of Technology

Abstract: Research on nanoparticle and cell interactions was presented.

Metal oxide nanoparticles are widely used in paint, food, sunscreens, cosmetics, plastics, ceramics, and as anti-bacterial agents. Titanium dioxide (TiO2) nanoparticles are of particular importance as the most common metal oxide nanoparticle, used as photocatalysts, as well as the white pigment in foods, sunscreens, cosmetics, paints, and coatings. The high levels of use of these nanoparticles have raised the question of the effects of long-term exposure and subtle cellular effects. We have recently found that incubation of cells with low, non-cytotoxic, concentrations of TiO2 nanoparticles, in the absence of UV light, produces a unique oxidative stress response. We used a PCR array to screen 84 oxidative, stress-related genes following the incubation of cells with TiO2 nanoparticles. At the concentrations used, standard measures of cell viability (MTT, LDH, and PI assays) showed no decrease in cell health. However, the PCR array showed that four members of the peroxiredoxin family of anti-oxidant enzymes were altered by ~50%. These enzymes, responsible for the clearance of peroxides from the cellular milieu, are essential to the oxidative stress response of cells. The changes observed for the peroxiredoxins were specific to TiO2 nanoparticles: experiments with polystyrene nanoparticles showed no change in the peroxiredoxins. Current research is aimed at determining the chemical and biological relationship between metal oxide nanoparticles and cellular oxidative stress in the absence of UV light.

Additional References:

Runa S, Khanal D, Kemp ML, Payne CK (2016) TiO2 nanoparticles alter the expression of peroxiredoxin anti-oxidant genes. J Phys Chem C 120(37):20736–20742

Fleischer C.; Payne C. Nanoparticle–Cell Interactions: Molecular Structure of the Protein Corona and Cellular Outcomes. Acc. Chem. Res. 2014, 47, 2651–2659. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4139184/>

UL Recognition of 3D Printed Plastics

SPEAKER

Dr. Thomas Fabian, UL LLC

Summary: A review of research on the impact of 3D printing on printed polymer material properties and performance is presented.

Mechanical properties of 3D printed materials have repeatedly been demonstrated to significantly vary based on how test specimens were printed. These variations are substantially greater than for conventional injection molded samples. Furthermore, there is a lack of research on the influence of 3D printing on ignition, flammability, and electrical material properties associated with UL safety standards. Yet, thermal mass and surface roughness- which is expected to differ for 3D printed parts- are known to influence ignition and flame spread.

UL is investigating the influence of different combinations of fused filament formation (FFF, which is the same as FDM™) print parameters and build strategies on flammability, ignition, electrical and thermal distortion properties. More than 4,000 test specimens of fire retardant acrylonitrile-butadiene-styrene (frABS) and polyetherimide (Ultem™) were 3D printed to a full-factorial plus center point design of experiment plan covering the four targeted factors of build orientation, raster angle, air gap, and layer thickness. Corresponding test specimens were also injection molded from the respective chopped filaments for further comparison of FFF versus injection molded samples.

As a part of the project, an ancillary study into the consistency of test specimens printed on identical printers was conducted to determine if parts made on two different identical model printers could be used indiscriminately for testing. Twenty flame bars printed in each of the X- and Z-directions on two identical printers were assessed for thickness and UL 94 vertical flame response. Printed specimen thicknesses were not normally distributed but rather bimodally or trimodally distributed due to the differing number of discrete layers used to print the specimens. Likewise, the UL 94 afterflame burn times (t1, t2, and t1+t2) were also bimodally or trimodally distributed. Afterflame burn times did not correlate with the specimen thickness despite the similarly appearing distributions. Nonparametric tests comparing the thicknesses and afterflame burn times of the respective samples sets printed on the two units did not reveal the measured differences to be statistically significant. Variation in the thicknesses of the printed specimens was 3 – 4 times more than observed for traditional injection molded specimens.

Results from this research will provide insights on the effects of 3D printing by FFF on ignition, flammability, electrical and thermal distortion material properties relied upon by UL and product design engineers. Results are being used to guide the development of requirements to address the gap in performance between 3D printed parts and traditional injection molded parts. UL expects to introduce the “Blue Card”, a “Yellow Card” specific to materials intended for 3D printing, to facilitate qualification of 3D printed components and products as well as specific materials used in the printing process.

Characterization of Chemical and Particle Emissions from Consumer FDM™ 3D Printers

GEORGIA TECH/EMORY/UL INC. RESEARCH STUDIES

Fine Particulate Emissions from Desktop 3D Printers

SPEAKER

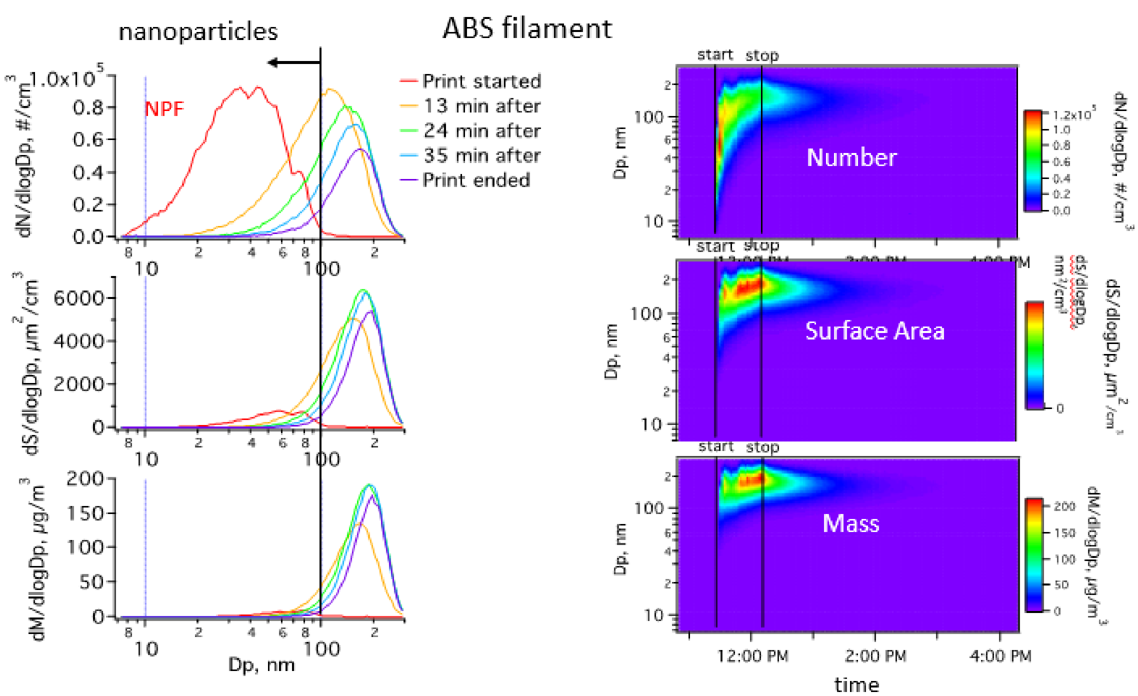
Rodney Weber, Ph.D., Georgia Institute of Technology

Abstract: Research on particulate emissions was presented.

Our initial research focused on characterizing the particle and chemical emissions from multiple FDM™ 3D printers using various filaments with different chemistries. A methodology was initially developed by operating the printers in controlled environmental chambers and monitoring total particles and characterizing their size distributions and behavior over time. For acrylonitrile butadiene styrene (ABS) filaments, particle concentrations reached up to $10^6/cm^3$

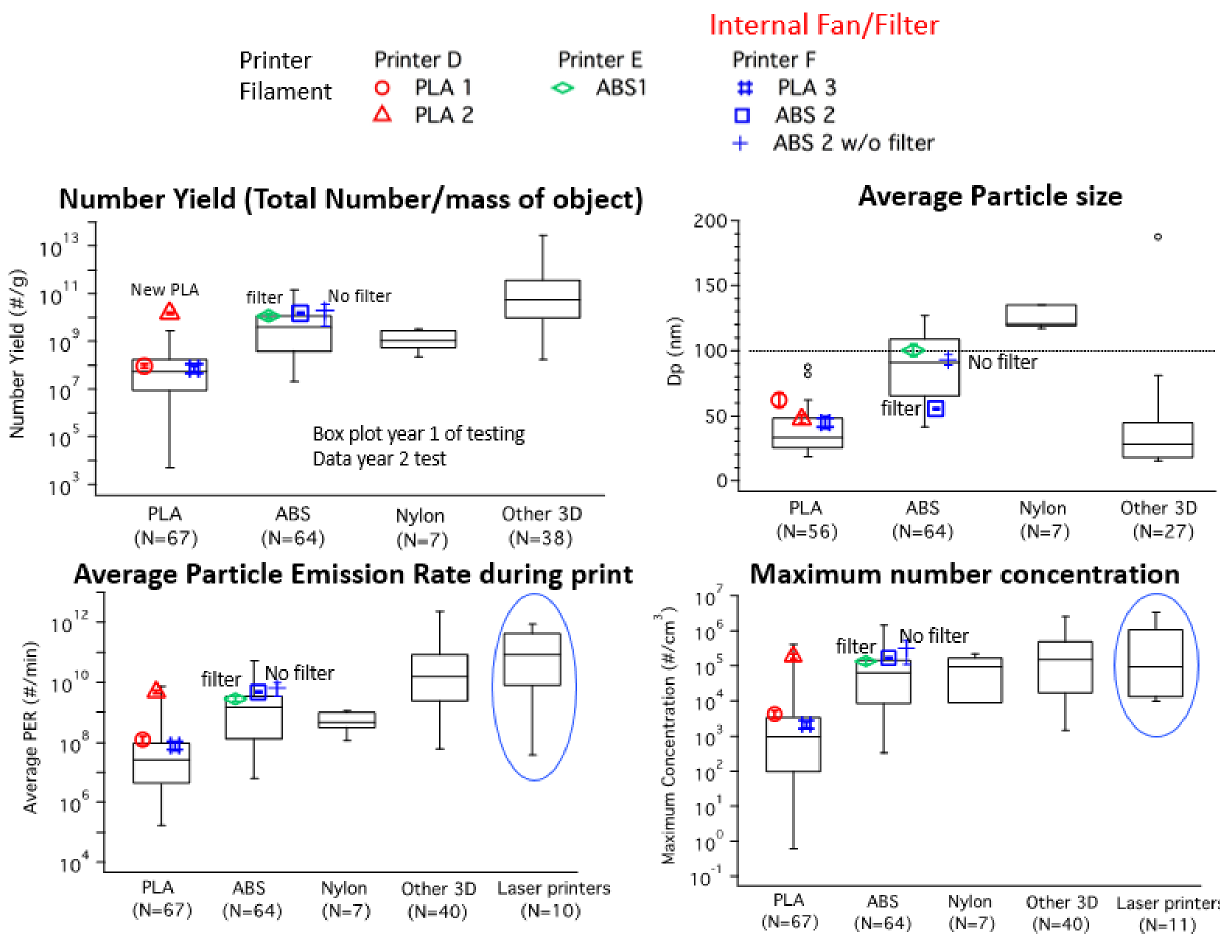
with mean particle sizes of 20 – 40 nm. During operation, particles were continually formed and size distribution evolved due to vapor condensation and particle coagulation. The number of particles emitted was dependent on the printer brand and filament type. For the various filaments tested, the average particle number ranged from 1.8 x 10^8 to 5.6 x 10^{10} per gram of filament material. Nanoparticles with diameters less than 100 nm dominated the number distributions, whereas diameters in the 200 – 500 nm range contributed the most to mass.

Additional chamber experiments were carried out in a recent round robin with additional printer and filament combinations based on the Blue Angel laser printer method, and the results showed emissions were all within the range of data obtained in the first year of research. Comparisons of overall emissions based on yield (= total particles emitted/print object mass) showed that filament material and filament brand had large effects. In general, ABS emitted more particles than polylactic acid (PLA). Unusual high emitters were found among ABS and PLA, indicating unknown additives might have large effects on emissions. Extruder temperature was driving the differences associated with printer brands and partially for filament materials. Other conditions like filament color, build plate heating, printer enclosure and internal filter had small effects. Since particles were formed from a few vapors from the filament, their chemical composition might be similar to the bulk material (PLA) or different (ABS). Measurement of particle chemical composition is required and cannot be inferred.



3D Printer Particle Emissions: Size distribution evolution with printing time, evolve from small to larger particles

The conceptual mechanism of particle emissions from 3D printers is laid out as new particle formation from the semi-volatile vapors generated from the heated filament material near the extruder nozzle and from the heated plate where filament is deposited, followed by condensation of vapors onto existing particles and particle-particle coagulation. This is in addition to dilution and particle losses throughout the processes. These processes, in general, lead to a peak in particle number concentration at the beginning of the print job, and the shifting of particles to a larger size during printing. More random temporal emission patterns were observed in latest printer tests, potentially related to printer design and operating conditions. A lognormal moment aerosol model based on this theory was developed. The model results, using steady-state concentrations, were able to explain the differences of emissions observed between two different brands of ABS filament.



The toxicity of 3D printer-emitted particles was explored using *in vitro*, *in vivo* and acellular assays. Particles were collected onto filters and then extracted in DI water for the following experiments. The *in vivo* and 3 types of *in vitro* experiments all showed inflammation responses. Particles generated from PLA were found to be more toxic due to the similar level of response at much lower concentration. The *in vivo* exposure, 2′, 7′ – dichlorofluorescin diacetate (DCFDA) cellular assay, and dichloro-diphenyl-trichloroethane (DTT) acellular assay were consistent when normalized by estimated mass concentration (or surface area) of particles used in the exposures. This comparison showed that particles from PLA had an order of magnitude higher response than ABS. Based on the DTT assay, PLA particle toxicity was at the level of diesel vehicles, while that of ABS and nylon were substantially lower.

A single compartment model was used to predict particle concentrations for 1) an ordinary office room and 2) personal exposure when a person stands next to the printer with minimal ventilation. The predicted particle number and mass concentrations and oxidative potentials for case one were at the low end to significantly below exposures expected for typical ambient concentrations. For case two, concentrations could be substantial for ABS and nylon. Prudence would suggest that 3D printers should run in a well-ventilated environment and that personal time close to the printer should be minimized. A standardized method for testing and evaluating testing data for 3D printers is crucial for quantitative comparisons between different printing conditions and research groups.

Additional References:

Weber R, Zhang Q, Wong J, Davis A, Black M: Characterization of Particle Emissions from Consumer Fused Deposition Modeling of 3D Printers, Submitted to American Association of Aerosol Research, April, 2017 (Submitted).

Weber R, Zhang Q, Wong J, Davis A, Black M: Fine Particulate and Chemical Emissions from Desktop 3D Printers, Proceedings of Materials, Applications, and Processes Conference in Manchester, September, 2016.

VOC Emissions from FDM™ Desktop 3D Printers

SPEAKER

Aika Davis, Ph.D., Underwriters Laboratories Inc.

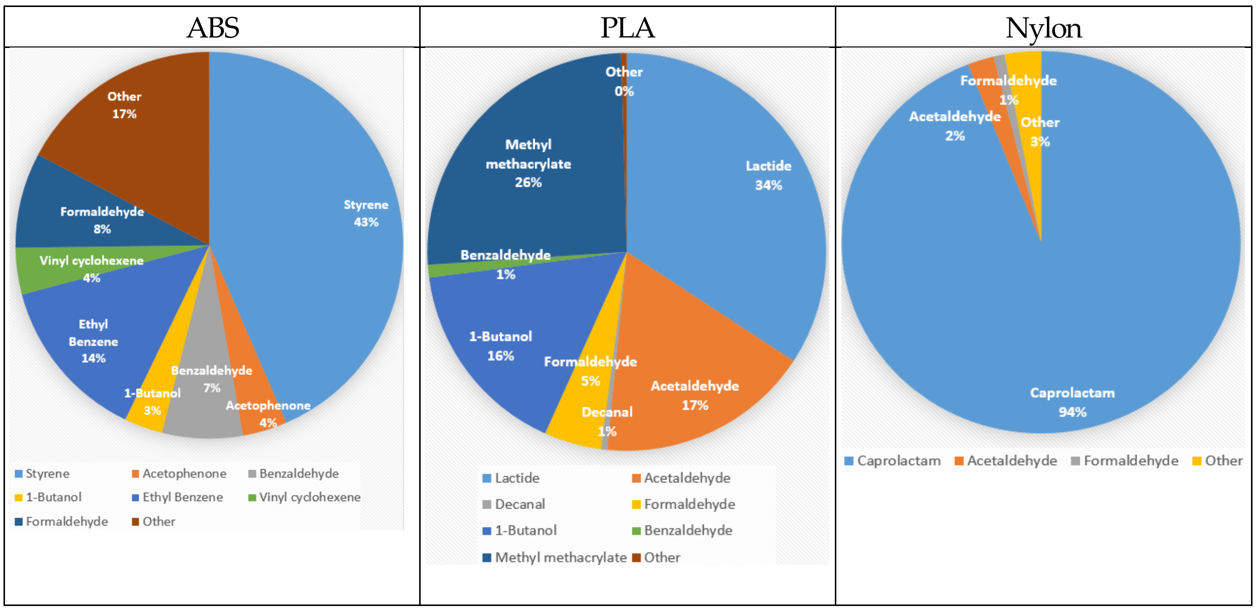
Abstract: Research on VOC emissions was presented.

Emissions of volatile organic compounds (VOCs) were simultaneously measured and patterns characterized during print operation of the various 3D printers and associated filaments. Specific VOCs were identified and quantitated using solid sorbent collection followed by thermal desorption/gas chromatography/mass spectrometry analysis. In some cases, filaments were studied independently by heating them to extruder temperatures in a controlled small chamber and identifying VOCs being emitted.

There were over 70 different VOCs identified in acrylonitrile butadiene styrene (ABS) filament emissions with primary contributions from styrene, ethylbenzene, benzaldehyde, formaldehyde, acetophenone, and vinyl cyclohexene. Over 20 different VOCs were identified in polylactic acid (PLA) emissions with key emissions from methyl methacrylate, lactide,

acetaldehyde, butanol, and formaldehyde. Nylon filament emissions were dominated by the emission of caprolactam.

Overall, specific VOCs emissions were a function of filament composition and filament brand. The specific color had a minimal effect. Limited studies with printer enclosures and presence of internal filters also had a minimal effect on emissions and levels. For most filaments, there was a complex mixture of VOCs emitted for each type. There were some individual chemicals of concern that exceeded recommended exposure levels for indoor environments, particularly for personal exposure scenarios for operators or close observers of the machines. A more thorough analysis would be needed to evaluate risk, but the data does indicate that effective ventilation with outdoor air or local ventilation would be prudent.



Comparison of VOCs from 3D Printers by Filaments during Operation

Additional References:

Weber R, Zhang Q, Wong J, Davis A, Black M: Fine Particulate and Chemical Emissions from Desktop 3D Printers, ASHRAE Conference Proceedings, St. Louis, US, June, 2016.

Particle Exposures from 3D Printer Emissions and Implications for Health Outcomes

SPEAKER

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Abstract: Research on the health implications of particle emissions was presented.

In order to understand the impact of exposures to 3D printer emissions, we must understand elementary lung physiology. Particles inhaled follow airflow streamlines as they are suspended in moving air through the pulmonary system. As air passes through the pulmonary system, it encounters numerous bends and bifurcations. Larger particles have more momentum and thus resist changes in flow direction, for example at bifurcations, and try to continue in a straight line. Smaller particles, with less momentum, are more able to follow these streamlines. This dichotomy results in larger particles being swept out of the air stream through a number of mechanisms. As air penetrates more deeply into the lung, its flow rate diminishes and removal processes involving diffusion become more important. This is especially true of very small particles, which act almost like gases in this respect. These two competing removal mechanisms result in very small particles and very large particles being removed prior to reaching the "bottom" of the lung – the alveoli – where gas and particle exchange can occur. This leaves an intermediate size range of particles that penetration to the alveoli. These deeply penetrating particles are in the size range of about 50-1000 nm in aerodynamic diameter.

According to work done by Weber's group at Georgia Institute of Technology, 3D printers emit particles primarily in the size range of 50-700 nm, in the middle of the minimum deposition range noted above. Such particles penetrate deeply into the lung, reaching the alveoli and potentially penetrating the lung epithelium. Here they can result in irritation, respiratory effects, and changes in blood chemistry that may precipitate cardiovascular effects.

To address potential health outcomes associated with 3D printer emissions, it is necessary to understand exposures to the particles they emit. Toward this end, we developed an exposure model that estimates exposures in two compartments – a near-field volume representing the location of the 3D printer, and the remainder of the indoor setting containing the printer itself. To be an effective tool in understanding the exposures experienced, we required the model to have several characteristics. These include: 1) estimates of exposure to users of 3D Printers as well as others in the Vicinity; 2) simplicity but defensibility; 3) all relevant physics; 4) parameters for the model that are accessible to measurement and are easily modified; and, 5) speed in model calculations. We selected a two-compartment, time-dependent model for these calculations as it delivered all five criteria listed.

To study the effects of 3D printers on exposure to particles, we selected three scenarios for examination: a home hobby room with the remainder of the home as the secondary compartment; a school art room with the remainder of the school as the secondary compartment, and a high-use facility, similar to the 3D print facility at Georgia Institute of Technology, where multiple printers are used. The remainder of the building is the secondary compartment in the third case. We examined emissions associated with three different filaments: acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and Nylon and performed sensitivity analyses looking at mean emissions from each filament type across printers, as well as a maximum emission scenario. In each case, we assumed neutral, non-reacting particles.

The results from the modeling exercise suggest that emissions from 3D printers contribute to the total particle concentration in these scenarios, but that the contribution is small. In the worst case, particle concentrations increased by about 1 $\mu g/m^3$ above an expected baseline of 10 – 20 $\mu g/m^3$ with the largest increases occurring in the room containing the printer(s). Most concentration increments were substantially lower than this amount, often by 1 – 3 orders of magnitude. Concentration increases were lower in the secondary compartments in each case. Similar increases were noted for volatile organic compounds (VOCs) in the scenarios investigated. Sensitivity analyses suggest that direct emission characteristics, deposition velocity on surfaces, and internal and external air exchange most strongly affect concentrations associated with printer emissions.

Future work in this area focuses on two aspects of particle emissions. First among these is the toxicity of the particles themselves. Our work suggests that incremental concentrations of particles associated with the use of 3D printers are not likely to be of major concern. However, the particles were treated as neutral particles with no specific toxicity. Recent work in Weber's laboratory suggests an alternative view. We expect that modification of the impact of particles could be effected using a toxicity index for the particles themselves. Such work is under consideration currently.

The second aspect of future work is to consider particle surface area, rather than concentration, to be the key to understanding the health impact of exposure. Weber's group also presents their data in surface units, i.e., number count modified to account for particle surface area. We are currently carrying out such simulations using particle surface area as the relevant parameter.

Additional References:

Cohen J, Ryan B, 3D Printing: Health Effects of Ultrafine Particle Emissions, Prepared for Underwriters Laboratories Inc., August, 2015.