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Laser and 3-Dimensional Printers:

Characterizing Emissions and Occupational Exposures

Alyson R. Johnson

Dissertation submitted to the School of Public Health at West Virginia University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in Public Health Science

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Abstract

Laser and 3-Dimensional Printers: Characterizing Emissions and Occupational Exposures

Alyson R. Johnson

Introduction: Toxicology and epidemiology studies have observed an association between ultrafine particles (UFPs) and respiratory, cardiovascular, and neurological health effects. While there is a paucity of data in the literature on the potential toxicity and health effects from indoor UFP exposure, more exposure assessment studies and research evaluating the efficacy of controls is merited. An increased demand for efficiency, productivity, and manufacturing has led to conception of laser and 3-dimmensional (3-D) printers in various indoor workplaces. The indoor environment is one of the most important determinants of personal exposure. Introducing laser and 3-D printers to indoor workplaces, introduces a potential indoor source of UFP emissions. Given the current knowledge on the potential health effects from exposure to UFPs, Further research is needed to fully characterize occupational exposures to printer emissions and evaluate factors influencing exposures to better guide control strategies.

Methods: The source-receptor model was used to identify relevant factors that may affect emissions and worker exposure. Mixed-effects regression modeling was used to identify sources of variability in exposure to laser printer emissions. UFP and co-pollutant emissions from laser printers were measured in a laboratory chamber to test the hypothesis that device-specific factors (e.g. make-model, technology, print speed, voltage) influence printer emission profiles. Results are described in **Chapter 2**. Real-time air samples for UFPs were collected at a laser printing facility. Emission rates for laboratory and real-world exposures were calculated using a one-box model and compared to emission rates calculated using the test method for hard copy devices to determine if results were significantly different. Results are described in **Chapter 3**. Real-time and time-integrated personal and area air sampling was performed to characterize indoor UFP and co-pollutant exposures to 3-D printer emissions during industrial printing. Personal and area air levels were characterized during industrial 3-D printing and post-processing tasks to determine if exposures were above occupational exposure limits. Results are described in **Chapter 4**.

Conclusions: Device-specific factors such as, copy rate and printer voltage affect exposure. Laser printers evaluated in this study had higher between-device variance. Control strategies should focus on device-specific factors (e.g. copy rate). Future research will focus on other factors potentially influencing exposure (e.g. toner type, paper type). The test method for hard copy devices emission rates differed significantly differed from the one-box model emission rates. Continued research will use exposure and dose modeling to provide estimates and distributions that are meaningful or comparable to previously published data. Occupational exposures to metals and organic vapors during industrial 3-D printing were below respective occupational exposure limits. Further research is needed to fully characterize exposure and understand determinants (e.g. materials, tasks) of higher or lower exposure.

DEDICATION

I dedicate this dissertation to my friends and family.

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Chapter 1:

Introduction

Overview of Ultrafine Particles

Ultrafine particles (UFPs) are a class of nanoscale particles with a diameter less than 100 nanometers (nm) or <0.1 micrometers (µm). UFPs exist naturally in the environment (e.g. sand dust) or as emissions from specific processes and combustion reactions, such as laser printers and fossil fuels. Most research has focused on the effects of UFPs in the outdoor environment; however, there are many sources of indoor UFP emissions [1]. Changes in industrial processes and the application of UFPs in industry has increased occupational exposure potential. Because of their nanoscale size, UFPs have the ability to penetrate into the lower airways, and to some extent, can be absorbed into the bloodstream leading to risk for respiratory and cardiovascular disease [2, 3]. The health risks associated with UFPs are believed to have greater implications than regulated, larger particulate matter (PM) size classes PM₁₀ and PM_{2.5} [1]. Recommended exposure limits for specific UFPs, such as titanium dioxide, exist, but in general, no regulations for UFPs currently exist [4].

UFP physiochemical properties and inhalation exposure

Inhalation is the primary route of exposure to UFP emissions. Associated health risks of particulate matter inhalation depend on the physiochemical properties of the particle (e.g. size, surface area, composition), the respiratory region of deposition (Figure 1-1), and the clearance mechanisms of the respective region. UFPs have high lung penetration efficiency leading to deposition in the lower airways. Once deposited into the lower airways, insoluble particles may accumulate or soluble particles may be absorbed into the bloodstream inducing localized and systemic health effects [2, 3].



Figure 1-1. Deposition of inhaled particles in the human respiratory tract during mouth breathing. Source: Kreyling et al. 2006a, Figure 2, reprinted with permission from Springer Science+Business Media.

The small size and large surface area of UFPs is a significant determinant of their toxicity potential [5]. In addition to large surface area, UFPs have a high particle number count per unit mass [6] (Table 1-1). The large surface area increases surface reactivity enabling UFPs to act as carriers for co-pollutants such as, ozone and/or organic vapors [7]. Due to the large surface area and high number count per unit mass, even low toxicity, low solubility UFPs may induce inflammatory responses in the human lung [8].

Table 1-1. Particle number and particle surface area per 10 µg/m3 airborne particles.

Particle diameter	Particle no.	Particle surface
(µm)	(cm_°)	area (µm²/cm²)
5	153,000,000	12,000
20	2,400,000	3,016
250	1,200	240
5,000	0.15	12

Source: Oberdörster et al. 2005, Table 2, reproduced with permissions from Environmental Health Perspectives.

Systemic health effects in the liver, spleen, kidneys, heart, brain, and reproductive organs following inhalation exposure to UFPs has been reported in experimental studies [9-15]. These studies have provided evidence of an association between short-term and long-term exposure to UFPs and adverse respiratory, cardiovascular, and neurological health effects. The dissolution and translocation of soluble UFPs deposited into the lower airways leads to increased risk for pulmonary and systemic health effects (summarized in Figure 2-1). Most literature on UFP exposure-response relationship comes from experimental toxicology studies. While informative, major limitations exists with toxicology studies. Determining the significance of toxicology study findings for human health is often problematic. In addition, it is often difficult to replicate real-world exposure scenarios.



Figure 2-1. Hypothesized pathways for deposition of UFPs into the respiratory tract and potential effects on respiratory, cardiovascular, and neurological systems. Source: Reprinted from HEI Perspectives 3 (2013), Understanding the Health Effects of Ambient Ultrafine Particles.

UFP Health Effects: Toxicology and Epidemiology

A number of toxicology and epidemiology studies report a positive association between short-term and long-term exposure to ambient UFPs and oxidative stress, mitochondrial damage, increased allergic response, progression of atherosclerosis, and increased markers of inflammation in the brain [9, 16-19]. However, some lab-based studies report have not seen a significant association between UFP exposure and health effects. Lab-generated particles used in these studies are not representative of real-world exposures, and therefore, studies observing no health effects are likely not representative of the relationship between real-world exposure to UFP emissions and adverse health outcomes [2]. **Table 2-1:** Particulate matter exposure and health effects.

Health Effect	Measured Exposure	Findings
Oxidative stress [16]	Size and composition of coarse (2.5–10 µm), fine (< 2.5 µm), and ultrafine (< 0.1 µm) particulate matter, PAHs	UFPs were most potent toward inducing cellular heme oxygenase-1 (HO-1) expression
Mitochondrial damage [16]	Size and composition of coarse (2.5–10 µm), fine (< 2.5 µm), and ultrafine (< 0.1 µm) particulate matter, PAHs	UFPs and fine particles, localized in mitochondria inducing celluar damage
Particles in lung tissue [9]	6-hr exposure to 133 mg Ag particles	1.7 mg Ag found in lungs immediately after the end of exposure
Reactive oxygen species stimulation and damage to neurons [18]	Ultrafine titanium dioxide aggregated in physiologic buffer; 2.5 to 120 ppm	Prolonged release of ROS and oxidative stress following exposure
Damage to neurons [18]	Ultrafine titanium dioxide aggregated in physiologic buffer; 2.5 to 120 ppm	Neuronal apoptosis observed after 6-hr exposure to 5 ppm
Systemic effects [9]	6-hr exposure to 133 mg Ag particles	Liver, kidney, spleen, brain, and heart, low concentrations of Ag were observed after exposure
Alveolar inflammation [21]	Human exposure to PM ₁₀ , PM _{2.5} , and UFPs. Median UFP number concentration 15,600 particles	Strongest health effects observed for particles in the UFP size range
Increased asthma medication use [22]	Asthmatics exposed to a mean number concentration of 17,300 UFPs	Reporting of asthma symptoms and increased asthma medication use associated with exposure
Cardiovascular	Human subject with coronary heart disease exposed to mean number concentration of 14,890 UFPs	Increased ST-segment depressions associated with UFP exposure (OR 3.14, 95%, CI: 1.56 to 6.32)
	Elderly subjects with coronary heart disease exposed mean number concentration of 17,309 UFPs	UFP associated with avoidance of activities (OR 1.09, 95%, CI: 1.01 to 1.19)
Decreased peak expiratory flow [23]	Children exposed to mean number concentration of 15,200 UFPs	Exposures were associated with declines in peak expiratory flow, 2.32 percent decline

*PAH = polycyclic aromatic hydrocarbon; ppm = parts per million, UFP = ultrafine particle; OR = odds ratio; CI = confidence interval; Ag = silver.

Toxicology studies

Toxicology studies have provided a critical link between exposure to UFPs and a biologically relevant endpoint. The observed health effects are of particle size classes similar to emissions from laser and 3-D printers (diameters <100 nm) and in the presence of significant co-pollutants, such as polycyclic aromatic hydrocarbons (PAHs). UFP exposure concentrations for laser and 3-D printers may exceed emission rates of 1 million to 1 billion particles per minute [26, 27]. Laser and 3-D printer UFP emission rates are much higher than exposure concentrations in toxicology studies between UFP exposure and health effects.

Li et al. performed a study to determine whether differences in the size and composition of coarse (2.5 to 10 μ m), fine (<2.5 μ m), and ultrafine (<0.1 μ m) particles are related to their uptake in macrophages and epithelial cells and their ability to induce oxidative stress. UFPs were the most biologically potent particle size range, induced oxidative stress, and penetrated cell tissue. UFPs were localized in the mitochondria, which lead to structural cell damage. UFPs and redox-active compounds, often present in particulate matter, contribute to reactive oxygen species and oxidative stress in macrophages and epithelial cells [16]. The effect of different particle size classes on cardiovascular outcomes was compared using exposed Apo E knockout mice (mice developing atherosclerosis lesions more rapidly). Mice were exposed to fine (<2.5 μ m) and quasi-ultrafine (<0.180 μ m) particles. Increased surface area and reactivity of the quasi-ultrafine particles was associated with development of larger atherosclerotic lesions Apo E knockout mice [28]. Reactive oxygen species were stimulated in brain cultures of mouse microglia, rat dopaminergic neurons, and primary cultures of

embryonic rat striatum to ultrafine titanium dioxide particles. The ultrafine titanium dioxide at low concentrations rapidly damaged neurons [18].

Epidemiology studies

Several human health studies have observed averse respiratory and cardiovascular health effects associated with ambient particulate exposure [20-25, 29-36]. Excess mortality in epidemiologic studies of adult asthmatics was observed when adults were exposed to high UFP particle concentrations (median particle number concentration ~15,000). High UFP number exposures, not mass exposures, were significant and negatively associated with peak expiratory flow measurements [21]. UFP number concentrations (mean number concentration ~17,000) over a 14-day exposure period were associated with increased asthma medication use [20]. Human health studies are often limited to short-term exposure measurement of ambient UFP emissions. This inhibits the ability to understand potentially chronic health effects and characterize UFP exposure-response relationships in unique microenvironments (e.g., workplace, home, indoor).

DNA damage has been associated with personal UFP number concentration exposures measured in 15 healthy nonsmoking subjects. Cumulative outdoor and indoor UFP exposures were independent and significant predictors of purine oxidation in DNA. Indoor exposure to UFPs contributed more to oxidative DNA damage because of the greater amount of time study subjects spent indoors. The study results indicated that modest UFP exposures induce oxidative DNA damage in human study subjects and peak UFP exposures coincided with presence of indoor UFP emission sources such as, cooking or burning candles [20].

The respiratory health status of 57 adult asthmatics was assessed with daily expiratory flow measurements and symptom and medication diaries for 6 months, while exposure monitoring for ambient particulates was simultaneously collected. Number concentration was the metric for particulate exposure versus mass concentration measurements. Daily mean number concentrations were negatively associated with peak expiratory flow measurements, with the strongest effects observed for the UFP size range. However, the study could not differentiate the effect of ultrafine particles from co-pollutants (e.g. nitrogen dioxide, carbon monoxide) correlated with ambient UFP exposure [21].

The effect of air pollution on blood pressure was investigated by measuring blood pressure and heart rate in healthy individuals during controlled exposure to fine particulate air pollution (<2.5 µm) plus ozone [25]. Measurements for diastolic blood pressure were taken every 30-minutes for exposure and non-exposed study subjects. Exposure subjects were observed to have a significant increase in diastolic blood pressure 2-hours post exposure (p = 0.013). A strong association was observed between the 2-hour increase in diastolic blood pressure and mean arterial pressure and the concentration of the organic carbon fraction of particulate matter (*r* = 0.53, p < 0.01; *r* = 0.56, p < 0.01, respectively). The findings suggest that exposure to ambient concentrations of fine particulate matter and ozone rapidly increases blood pressure [25], and this increase in diastolic blood pressure is likely through an autonomic nervous system response [37].

The ultrafine and quasi-ultrafine particle size classes in toxicology and human health studies had the strong associations with the observed health outcomes providing

strong support for the role of ultrafine particles in respiratory, cardiovascular, and neurological human health effects. The particle number concentrations in experimental and human health studies observing health effects are reporting effects at exposure concentrations less than 10,000 particles, which is much lower than reported number concentrations from laser and 3-D printers. The presence of co-pollutants, such as PAHs, increased the significance of observed health effects. Particulate concentrations and size distributions in the toxicology and epidemiology literature are representative of particulate exposures and co-pollutants emitted from laser and 3-D printers. At present, there is little research directly assessing exposure to laser and 3-D printer emissions and human health effects despite the obvious parallels in toxicology and epidemiology studies of UFPs.

Indoor Sources of UFPs: Laser and 3-D Printers

In the 1970s, dry-process laser printers were introduced to office workplaces and over the decades have evolved into one of the most popular printing technologies [38]. According to 2016 laser printer sales research, 106 million printers were sold globally with sales totaling 30 billion USD [39]. Market research has observed major growth in the laser printer market attributable to technical advancements and increasing demand in industry verticals. Laser printers are cost-effective and generate high-speed, high-quality prints improving workplace productivity and efficiency. The global laser printer market growth between 2017 and 2023 is anticipated to grow at a compound annual growth rate of approximately 16 percent. North America is estimated to account for the largest share of the laser printer market [40]. Occupational sectors utilizing laser printers include business and financial operations, healthcare, sales and public relations,

education, manufacturing, and office and administrative support. Across all occupations, U.S. employment for printing and related support activities is estimated at 451,480 workers [41].

The invention of 3-dimensional (3-D) printers was not far behind laser printers. This additive manufacturing (AM) technology was developed in the 1980s, and today, 3-D printing is transforming the workplace. In 2015, more than 278,000 desktop 3-D printers were sold globally. The additive manufacturing industry compound annual growth rate grew 25.9 percent to 5.165 billion USD in 2015 [42, 43]. Reports have projected 3-D printer market growth to total more than 21 billion USD by 2020 [44]. Along with desktop 3-D printers, 62 manufactures sold industrial-grade 3-D printers in 2015, compared to 49 industrial-grade 3-D printer manufactures in 2014. Similar to laser printers, advances in technology and increasing vertical market demands have attributed to 3-D printer market growth. Desktop 3-D printers are cost-effective and yield high-speed prototypes and products. Industrial-scale 3-D printers are capable of manufacturing large-scale, high-quality products and increasing production output. The cost-effectiveness, rapid production, and vertical market demand has attributed to the 3-D printer market growth. Consumer and industrial goods, services, healthcare, electronic, education, automotive, and aeronautic and aerospace are industries now using desktop and/or industrial-scale 3-D printers [45]. U.S. employment for manufacturing, a major occupational sector for 3-D printing, is estimated at 573,370 production workers and machinist [46].

Emissions and exposures from laser and 3-D printers

The constituents of toner powder and 3-D printer consumables do not directly

reflect the characteristics of printer-emitted particles (PEPs). Laboratory emission

studies and workplace exposure assessments have presented data on UFP, volatile

organic compound (VOC), and ozone emissions from laser and 3-D printers

(Summarized in Tables 3-1 and 4-1) [27, 47-51].

Table 3-1.	Quantified	emissions fr	om laser,	, ink-jet ar	d 3-D	printers	and p	hotocopie	rs in	laborato	ry
emission s	studies.										

Device	Pollutants detected
Laser printer	Fine and ultrafine particulate matter, VOCs (styrene, xylenes, toluene*), SVOCs,
	ozone, transition metals, PAHs
Photocopier	Fine and ultrafine particulate matter, SVOCs, ozone, transition metals
Ink-jet printer	Fine and ultrafine particles, VOCs (styrene, xylenes [*]), ozone
3-D printer	Fine and ultrafine particles, VOCs (toluene, styrene, xylenes*)
*0	

*Specific VOCs identified in studies that are relevant for respiratory health. VOC = volatile organic chemical, SVOC = semi-volatile organic chemical, PAH = polycyclic aromatic hydrocarbon. References: [26, 47, 50, 52-92]

 Table 4-1. Quantified emissions from laser, ink-jet and 3-D printers and photocopiers during workplace exposure assessments.

 Device
 Bollytants Detected

Device	Pollutants Detected
Laser printer	Ultrafine particles, VOCs (styrene, formaldehyde, xylenes*), ozone, transition metals
Photocopier	Fine and ultrafine particulates, VOCs (toluene, formaldehyde, styrene *), ozone

*Specific VOCs identified in studies that are relevant for respiratory health. VOC = volatile organic chemical. References: [64, 68, 72, 76, 93, 94]

Photocopiers and ink-jet printers are functionally comparable to laser prints, and

therefore, emission studies summarized below have included emissions data from these

devices. Emission rates of UFPs from laser printers (Table 4-1) reported in the

literature [27] and 3-D printers [26] are at number concentrations (10⁸ to 10¹² particles

per minute) much higher than ambient air pollution UFPs exposure levels and

associated adverse health effects.

Manufacturer	Model	ER, N (part./min)	Mode (nm)
Brother	HL-1212W	6.97×10 ¹¹	19.10
Brother	MFC-9120CN	1.73×10 ¹⁰	19.10
Canon	LBP 7210 Cdn	4.07×10 ¹¹	34.00
Canon	i-SENSYS MF 4270	4.22×10 ¹⁰	29.40
Epson	Aculaser C2900N	2.00×10 ¹¹	29.40
HP	P4014	4.73×10 ¹¹	34.00
Lexmark	X264nd	1.65×10 ⁹	39.20
Lexmark	MX410de	1.96×10 ⁹	45.30
Samsung	Xpress M2675F	7.42×10 ¹⁰	34.00
Samsung	Xpress M2875FD	2.82×10 ¹⁰	34.00
Xerox	Workcentre 6505DN	4.14×10 ¹¹	34.00

 Table 5-1. Condensed listing of laser printers analysed, emission rates, and particle modes.

Reference: [27]

Emissions from laser and 3-D printers significantly contribute to increased exposure to UFPs in indoor environments (e.g., workplaces, schools) [26, 27, 55, 59]. Exposure to UFPs, particularly in the presence of transition metals, organic vapors, and ozone, is an important determinant of respiratory, cardiovascular, and neurological toxicity. Given the current knowledge on the potential health effects from exposure to UFPs, understanding determinants of higher and/or lower printer emissions is critical to implementation of targeted control strategies to minimize workplace exposure to PEPs.

Laser printing: A brief operational overview

A laser printer transfers an image to paper products using static electricity. The main component of this system is the photoconductive drum. Data are transmitted from a computer or other electronic device to the laser printer's image processor. The

photoconductive drum is positively charged by a corona-wire or a charged-roller. Corona-wire technology was the original charging mechanism for laser printers. Coronawire technology generally requires a higher voltage to charge the photoconductive drum resulting in greater ozone production. Charged-roller technology was developed later in an effort to reduce the voltage needed to charge the photoconductive drum and in theory reduce ozone production [95].



Figure 3-1. (a) A charged-roller toner cartridge when removed from the printing machine and (b) a corona-wire toner cartridge when removed from the printing machine.

As the drum revolves, a laser beam imparts a negative charge onto sections of the drum. The negatively charged sections of the drum create the image that is to be printed. Positively charged toner is attracted to the negatively charged sections of the photoconductive drum. The toner affixes to the paper, which is imparted with a negative charge, as it is passed along the revolving drum. The paper is then passed through the fuser assembly where temperatures up to 200° Celsius and pressure are used to bind the toner permanently [95]. Printer technology (e.g., corona-wire, charged-roller), voltage, fuser temperature, and output capacity of laser printers are device-specific characteristics and differences in these factors across printing devices may influence emission profiles.

Toner particles consist of a polyester thermoplastic resin containing a colorant such as carbon black or an organic pigment to create colored toners. Historically, toner particles were created by pulverization, which resulted in coarse (greater than 10 μ m) irregular shaped particles with low respirability [96-98]. Polymerized emulsion aggregation (EA) toner, an advancement used today to improve toner adhesion, yields smaller (less than 10 μ m), spherical toner particles [97]. These modern toner particles are often coated with engineered nanomaterials (ENMs), such as silica dioxide or titanium dioxide.



Figure 4-1. The internal components of the laser printing process.

3-D printing: A brief operational overview

3-D printers manufacture products by depositing material layer-upon-layer. Objects are designed in computer-aided design (CAD) software to generate a digital image [99]. The digital image is sent to the 3-D printer, which then prints the 3-D object. Fused filament fabrication (FFF) is a type of material extrusion 3-D printing. During the FFF process, polymer filament is heated above 200° Celsius as it is extruded through a nozzle onto a build plate to create an object [100].



Figure 5-1. Fused filament fabrication (FFF) material heating and extrusion process and components.

Parallel to laser printer toner, 3-D printer consumables (e.g., filaments) contain thermoplastics, colorants, metals, and/or ENMs. The most common 3-D printer consumables are thermoplastic filaments, polylactic acid (PLA), derived from lactic acid, and acrylonitrile butadiene styrene (ABS), derived from acrylonitrile, butadiene, and styrene. Research on the constituents of 3-D printer materials is limited, specifically; minimal research is available on the constituents of resin materials and emissions from 3-D material jetting printers. As 3-D printing capabilities continue to expand, filaments with additives such as carbon nanotubes and graphene are becoming commercially available [101]. Printer technology (e.g., FFF), nozzle temperature, number of nozzle heads present, and consumable used (e.g. filament) are 3-D printing device-specific characteristics and differences in these factors across printing devices may influence emission profiles.

Laser and 3-D printers emit UFPs and co-pollutants, which pollute indoor environments and have the potential to negatively affect the health of thousands of U.S. workers [41]. Given the prevalence of these printing devices in various workplaces, it is likely the potential burden of their emissions on worker health is underestimated. They are ubiquitous in modern indoor and occupational environments and printer markets are projected to continue to increase in the future [40, 43]. The expected market growth and ubiquity of laser and 3-D printers in modern indoor and occupational environments highlights the significance of the research herein.

Conceptual Models of Factors Affecting Exposure

A major challenge in occupational exposure assessment is the inability to measure each exposure scenario. Source-receptor models establish a quantitative relationship between exposure scenarios and personal exposures and their determinants [102]. Exposure modeling is a critical component of exposure assessment and should be a high priority when designing exposure assessment studies [103]. Laser and 3-D printing includes thermal processes involving the vaporization of materials have the potential to generate significant UFP number concentration [104, 105]. While research directly assessing the relationship between UFP exposure from laser and 3-D printers is lacking conceptual models identifying potential determinates of higher or lower exposure are critical to future exposure assessment studies.

Figure 6-1. Conceptual model for inhalation exposure including sources, compartments, and receptor and transport between these components.



Source: Tielemans et al. (2008) Ann. Occ. Hyg., Conceptual Model for Assessment of Inhalation Exposure: Defining Modifying Factors

Conceptual models (Figure 6-1) and identification of determinants of exposure and the magnitude of effect these factors have on exposures is informative to exposure assessment studies and control strategies to reduce exposures to laser and 3-D printer emissions. Using conceptual models and statistical tools to explore associations with exposure levels may lead to the discovery of previously unidentified emission and/or workplace factors and the magnitude of effect these factors have on exposure levels [106]. Source-receptor models can schematically describe inhalation exposure to help better understand the process leading to inhalation of hazardous substances. These models are constructed by identifying the source, various transmission compartments, and the receptor, describing the emission and pattern of transport [102].

These factors should be evaluated and defined in a stepwise fashion to appropriately model exposure potential. To identify the source-receptor pathways, the emission source or activity generating exposure needs to be defined. If necessary, the source may be broken down further into sub-classes, emission potential, or mechanism of emission generation [102, 107]. Once the source and potential modifying factors have been defined, transmission compartments such as local exhaust ventilation, being nearfield or far-field from the source, and/or enclosures need to be identified. Finally, the transport pathway from the source via the identified compartments will need defined to appropriately assess inhalation exposure [102]. In Chapter 2 of this study, we will identify modifying factors related to the source of the emission (laser printer). We will evaluate the effect of voltage and copy rate on laser printer emissions. Identifying printer-specific factors influencing printer emissions is the first step in the sourcereceptor pathway. This information can be used in conjunction with information on ventilation, enclosures, personal protective equipment, and other engineering controls to appropriately define the transport pathway to inhalation exposure [102, 107].

The first step for laser and 3-D printers will involve identifying modifying factors such as, voltage or temperature that potentially affect emissions at the source. Understanding of these factors may require groupings into sub-classes based factors such as thermal degradation of printer consumables. The source-receptor pathway will continue with identification of printer enclosures, ventilation, and personal, near-field, and far-field exposures in an effort to begin to understand the process leading to inhalation of laser and 3-D printer emissions. Understanding of the source-receptor pathway for laser printers is critical for systematic data collection during exposure

assessment and epidemiology studies. This information can then be applied to studies attempting to directly assess the relationship between laser and 3-D printing, and printing-related tasks, and health effects.

Mixed-effects regression model to identify exposure determinants

A mixed-effects regression model is a statistical tool containing random and fixed effects variables. This statistical modeling describes the relationship between a response variable (continuous) and covariates. In mixed-effects regression models, at least one of the covariates is a categorical covariate representing experimental units in the data set and all the covariates in the data set are observed at a set of discrete levels. The fixed effects are the parameters that are selected by a nonrandom process and consist of the entire population of possible levels. For the fixed effects, inferences should only be made for the levels included in the study. The random effects represent a random sample of parameters from a population of possible levels. For the random effects are called variance components. For the random effects, inferences associated with random effects are called variance components. For the subset of levels included in the study [108].

A mixed-effects regression model test whether fixed effects have a significant effect on a response variable and whether the variance components associated with random effects equal zero. These models are commonly used to analyze repeated measures data. To determine percent of variability explained by fixed effects, the variance components from the random effects only model are compared to the variance components of the mixed effects model. The types of factors included in mixed models are between-subject factors and within-subject factors. The between-subject factors are

the factors that separate the experimental subjects into groups (e.g., printer makemodel). The within-subject factors are those in which the response is measured on the same subject several times (e.g. printer serial number) [109]. When study designs are unbalanced, the restricted maximum likelihood (REML) method of estimating variance components is favorable. REML constructs the likelihood function in two parts (1) involving the fixed effects and (2) free of the fixed effects. This obtains maximum likelihood estimates of the variance components from the portion of the model that is free of fixed effects [108, 110].

$$y = \mathbf{X}\beta + \mathbf{Z}\gamma + \varepsilon$$

where,

y is the vector of observed response data values **X** is the design matrix for the fixed effects β is the vector of unknown fixed effect parameters **Z** is the known design matrix for the random effects γ is the vector of the unknown random effects parameter ϵ is the vector of random errors

assume that γ and ε are independently and normally distributed with, $\mathbf{u} \sim N(0, G)$ $\varepsilon \sim N(0, R)$ variance-covariance matrix of the errors and Cov [\mathbf{u}, ε] where, G variance-covariance matrix of \mathbf{u} R variance-covariance matrix of the errors $E\begin{bmatrix} \gamma\\ \varepsilon\end{bmatrix} = 0 \text{ and } Var = \begin{bmatrix} \gamma\\ \varepsilon\end{bmatrix} = \begin{bmatrix} G & 0\\ 0 & R \end{bmatrix}$

Conceptual models of factors affecting exposure and regression modeling will predict variability, identify determinants of exposure, and guide control strategies. Similar statistical regression modeling has been applied to environmental UFP monitoring data with land-use regression models [2]. These studies identified determinants of exposure, such as temporal or spatial factors and predicted pollutant concentrations using relationships with land-use features such as traffic intensity, building density, industrial development, and green space. A study by Hoek et al. modeled particle number exposure data with land-use regression modeling and was able to explain 67% of the variability in measured particle number concentration. When the land-use variables were removed only 44% of the particle number concentration variability was explained [111]. Applying a similar identification of factors affecting exposure and using mixed-effects modeling will identify factors affecting laser and 3-D printer exposure.

While no specific regulatory occupational exposure limits for UFPs exists, a number of studies have highlighted the importance for the risk characterization of UFPs to reduce indoor UFP emissions and protect workers from exposure [112-115]. The relationship between indoor UFP exposure, specifically printer UFP exposure, and health effects continues to develop in the epidemiology literature, prediction of exposure determinants to determine factors of exposure and for hazard control is imperative. For identification of control strategies, the significance of the fixed effects and the magnitude of the effect are considered important for evaluating the usefulness of the models. Previous printer emission studies have also reported a high level of variability in UFP emissions from laser printers. The model variance components can be used to inform control strategies. If the within printer variance is higher will indicate that control efforts should focus on characteristics common to all printer types (e.g. ventilation). If the between printer variance is higher between printers then efforts should be focused on printer specific characteristics (e.g. printer technology) [110].

Comparison of Emission Rate Calculations

Test method for the determination of emissions from hardcopy devices

This method is a standardized protocol developed to identify emissions from photocopiers and laser printers. This equation provides a time-resolved measurement of the particle emissions homogeneously distributed in a test chamber. The emission rate calculation requires that the data be smoothed over a 31-second time interval.

Particle Loss Coefficient β :

$$\beta = \frac{\ln(c_1/c_2)}{t_2 - t_1}$$

The value pairs c_1 , t_1 and c_2 , t_2 should be read from the smoothed timedependent curve of particle number concentration as accurately as possible or determined by means of a cursor. On a logarithmic scale, t_1 should be chosen within the linear descending range at least 5 minutes after the end of the print phase and t_2 at least 25 minutes after t_1 .

Calculation:

$$TP = V_c \left(\frac{\Delta C_p}{t_{stop} - t_{start}} + \beta \cdot C_{av}\right) (t_{stop} - t_{start})$$

t_{stop} – t_{start}: emission time [s]

Modified one-box model

The one-box model equation can be used for cyclic and irregular processes and can be applied to scenarios where worker exposures generally occur away from the emission source. In the case of laser printing, most workers may periodically spend time next to the printer but workstations may be far field from the printer. This method calculates the area under the curve for a repeating task involving concentration rise and decay curves. It is also possible to generate task-specific emission rates for a cyclic process or the effective emission rate for a fixed pattern of different tasks using the one-box model.

Calculation:

$$C = \frac{\gamma G}{Q}$$

C: concentration in the room

y: the fraction of time that the substance is emitted

Q: the room ventilation rate

G: estimate of average emission rate for the concentration rise phase of a cyclic process

The main components of the test method for hard copy emissions include (1) particle loss coefficient, (2) room volume, and (3) the average particle concentration and difference in particle concentration during the emission time for a single emission profile. The main components of the one-box model include (1) the average particle concentration, (2) the percent emission time, and (3) the ventilation rate for a single or multiple emission profiles. The fundamental difference in the two equations is the one-

box model calculates the area under the curve for a repeating task involving concentration rise and decay curves, whereas, the test method for hard copy devices calculates the emission rate for a single concentration rise and decay curves. Calculation of a single rise and decay curve is appropriate for evaluating laser printers in a test chamber but may misrepresent workplaces exposures where printing is occurring as a cyclic, irregular process over the duration of the workday. The emission rate determined from the test method for hard copy devices must be regarded as device-specific emission behaviors. However, emission rates calculated using the onebox model may be regarded as task-specific emission behaviors.

Lung Deposition Modeling

Dose modeling can provide an experimental determination of particle deposition in the human respiratory tract and characterize the exposure-dose relationship [116]. Characterization of exposure and dose is an essential component of managing occupational health risks. UFPs contribute very little to particulate mass but have high lung penetration efficiency and are capable of translocating via the bloodstream. Therefore, current mass-based dosimetry models may not fully account for differences in the clearance and translocation of UFPs. However, research comparing observed versus model-predicted lung burdens have reported that dosimetry models are capable of predicting lung burdens for fine and ultrafine particles reasonably well [117].Exposure assessment of UFP emissions alone cannot fully characterize the potential health risk. Lung deposition modeling can characterize risk by establishing a connection between measured exposure levels and inhaled dose. Due to their physiochemical properties

and ability to act as a carrier for co-pollutants, UFPs are suggested to be hazardous to human health when inhaled [3].

Lung physiology and clearance mechanisms

The respiratory system exists as three major regions and several anatomical units. Regions of the respiratory system differ in structure, airflow patterns, function, retention time, and sensitivity to deposited particles. The three regions of the respiratory system include the extrathoracic region (nose, mouth, pharynx, larynx), tracheobronchial region (trachea to terminal bronchioles), alveolar region (beyond the terminal bronchioles; gas exchange) [3, 118]. Dose and location of particle deposition is dependent on particle size, density, and shape, and individual breathing patterns [3]. Deposition of inhaled particles in the regions of the respiratory system follows the action of the five deposition mechanisms (1) interception, (2) inertial impaction, (3) diffusion, (4) gravitational settling, and (5) electrostatic attraction. UFPs are deposited into the lower airways by diffusion and can translocate into the bloodstream [118].

Respiratory deposition occurs in a physiologic system of changing structure and flow. Due to the complexity of the respiratory system, prediction of deposition from basic theory is challenging. Thus, prediction of deposition is reliant upon experimental data and empirically derived equations [118, 119]. Once particles are deposited in the respiratory system they are retained in the lung for varying times. The retention and clearance times for deposited particles are dependent on physiochemical properties of the particles, the respiratory region of deposition and the clearance mechanisms of the respective region. Before particles deposit into the respiratory system, they must first be inhaled. The average human breaths approximately 10 to 25 m³ per day [3, 118, 119]

with an approximate total gas exchange surface area of 75 m². The nose and mouth have an aspiration efficiency and the inhalable fraction defines this curve as a function of particle size [118-120].

Clearance mechanisms differ for the three regions of the respiratory system. The extrathoracic and tracheobronchial regions clear deposited particles via mucociliary mechanisms. These mechanisms utilize the cilia and mucosa membranes of the respiratory system to eliminate deposited particles via entrapment in the mucus layers and ciliary action movement. This clearance mechanism is present starting at the bronchioles and extending up through the trachea to the nasal-oral region [3, 119].

Within the alveolar region of the respiratory system no such clearance mechanism exists. Insoluble particles deposited within the alveolar region are slowly cleared over long periods. Soluble particles deposited within the alveolar region solicit an immune response resulting in activation of macrophages which engulf and dissolve deposited particles or transport deposited particles to the lymphatic system for clearance from the body [3]. UFPs have been observed to have deleterious effects on macrophages, induce markers of inflammation, and translocate from the respiratory system generating a hazard for human health.

Lung deposition models for particles

There are many lung deposition models and tools available for exposure risk

characterization. The method chosen for a particular study is dependent on the

contaminant information and the biological endpoint of interest (e.g. animal, human).

Table 6-1. Available	Tools and	Resources for	or Dosimetry	Modelina.
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Tool or Resource	Description
Multiple-path	Deposition, clearance, and retention estimation of inhaled particles in the
particle dosimetry	respiratory tract of the human, rat, and mouse
model (MPPD)	
Respiratory tract	Deposited dose estimation of inhaled particles or vapors
region deposited	Interspecies dosimetric adjustments.
dose equations	Derivation of reference concentrations
Human respiratory	Deposition, clearance, and retention estimation of inhaled particles
tract model	(including non-radioactive) in the human respiratory tract
PBPK modeling	Guidance on principles of characterizing and applying physiologically
guidance	based pharmacokinetic (PBPK models) in risk assessment
Human reference	Anatomical and physiological parameters (reference values) in humans
values	Inter-individual variability by age and gender
	Parameters for PBPK models
Interspecies	Physiological parameters for dose normalization or PBPK modeling
reference values	Application to Biological Exposure Indices
Particle size	Criteria for airborne sampling of particle size fractions by probability of
definitions	deposition in human respiratory tract regions

PBPK = physiologically based pharmacokinetic model Source: Reproduced with permissions from Taylor & Francis, Journal of Occupational and Environmental Hygiene, Kuempel et al. (2015), Advances in Inhalation Dosimetry Models and Methods for Occupational Risk Assessment and Exposure Limit Derivation.



Figure 7-1. Regional lung deposition (percent) as determined by particle size. ET, extra thoracic region, BB, bronchial region (generations 0–7); bb, bronchiolar region (generations 8–15); AI, alveolar region (generations 16–23). Reprinted from the International Labor Office, Encyclopedia of Occupational Health and Safety (Fourth Edition), Respiratory System [121].

Multiple Path Particle Dosimetry (MPPD) is a commonly used and freely availably dosimetry software [122]. MPPD includes deposition modeling for both human and rat respiratory tract models and accounts for the clearance and retention of spherical particles. Additionally, MPPD models total, regional, and airway-specific lung doses as a function of particle properties and breathing parameters. The deposition of UFPs into the human respiratory tract is reasonably well understood. UFPs are known to have a high lung penetration efficiency. Once deposited into the lungs, due to their size and physiochemical properties, UFPs are reactive and have the ability for uptake into other cells and translocation into the bloodstream. Moreover, nasally inhaled UFPs have been observed to translocate to the brain via the olfactory nerve in rats. Because MPPD evaluates total, regional, and lobular deposition, accounts for clearance and retention, and accounts for nasal-oral breathing patterns, MPPD is the most appropriate lung dosimetry methods to characterize exposure risk from laser and 3-D printer UFP emissions [3, 119, 122].

Lung deposition modeling, exposure, and health effects

Understanding the potential risk associated with inhalation of UFP-related hazards is dependent on the understanding the deposition of the UFPs into an exposed persons airway [123]. Methods of lung deposition modeling can help extrapolate observed animal health effects and measured human exposure to associate those exposures with health effects. Furthermore, UFPs may contribute to health effects of particulate matter in humans. Human subjects research evaluating particle number deposition following inhalation of UFP carbon particles with a count median diameter of 23 nm noted that number deposited fraction increased with decreasing particle size, and

efficient respiratory deposition of UFPs increased further in subjects with asthma [124]. Suggesting that exposure to UFPs leads to increased particle number deposition, with potential to induce adverse health outcomes, particularly in susceptible populations such as asthmatics. Lung deposition modeling can be used to compare exposure to determine if exposure to different exposure profiles to identify potential differences in pulmonary hazard [125]. In the absence of health data, deposition modeling unites that relationship between the emission source, inhalation, deposition and clearance, and potential health effects.

UFP Particle Number Concentration Exposure Limit

Currently, exposure limits for UFP number concentration do not exist; however, number concentration is one of the more reliable metrics for quantifying UFP emissions. The derivation of the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for methylene chloride is an example involving dosimetry modeling to derive an occupational exposure limit. Using number concentration and size distribution exposure data and workplace factors (e.g. duration of time exposure is occurring, nasal-oral breathing parameters) is an initial step in determining an appropriate UFP number concentration occupational exposure limit [122]. Literature assessing the relationship between UFP exposure and health effects has reported health effects associated with ambient UFP number concentrations between 10,000 to 20,000 particles per cubic centimeter (Table 2-1). In the case of benzene, the Environmental Protection Agency (EPA), Integrated Risk Information System (IRIS) has a benzene general public exposure limit of 0.009 parts per million (ppm), while the OSHA and NIOSH time-weighted average (TWA) occupational exposure limits (OEL) are 1 ppm and 0.1 ppm, respectively [126]. Experimental and
human health studies evaluating the harmful effects of particulate matter have supported the claim that UFPs number, not mass, concentration contributes more UFP toxicity potential. Adverse health effects in ambient UFP studies have observed health effects at number concentrations between 10,000 to 17,000 particles/cm³. Based on the current body of literature evaluating the relationship between ambient UFP number exposure and adverse health effects, it is reasonable to suggest an UFP number 8-hour TWA OEL between 100,000 to 200,000 particles/cm³.

Research Objective and Hypotheses

The **long-term** goal of the research herein is to reduce morbidity and mortality associated with indoor UFP exposures. The research objective is to understand factors influencing laser and 3D printer UFP emission profiles. The **central hypothesis** for the proposed research is that factors significantly influencing (p < 0.05) printer emissions can be predicted with statistical and mathematical modeling to inform control strategies and reduce work-related respiratory and cardiovascular disease. The rationale underlying the proposed research is that effective prediction of factors influencing printer emissions will systematize control strategy development and mitigate occupational exposure to UFP printer emissions. Current literature has been devoted to quantifying emissions in laboratory studies (laser and 3-D printers) and in workplace assessments (laser printers) to inform toxicology and epidemiology studies. The proposed research addresses: (1) use of laboratory and real-world emission data for laser and 3-D printers to characterize exposures and identify determinants of exposure to inform control strategies and (2) workplace exposure assessment for 3-D printer emissions. This work will have an **impact** on efforts to reduce indoor UFP exposure.

The central hypothesis and overall objective of this proposed research will be accomplished by three sub-hypotheses:

- (i) Copy rate and voltage will significantly influence (p < 0.05) ultrafine particle, total volatile organic compound, and ozone emissions from eight make-models of laser printers tested in an environmental chamber. Results will be described in Chapter 2.
- (ii) Emission rates for laboratory and real-world exposures will be calculated using a one-box model and compared to emission rates calculated using the test method for hard copy devices to determine if emission rates are significantly different (p < 0.05). Results will be described in **Chapter 3.**
- (iii) Personal exposures to metals, acetone, and chloroform collected during industrial 3-D printing and post-processing tasks will be above the respective occupational exposure limits. Results will be described in Chapter 4.

In **Chapter 5**, the overall conclusions of this research project and future research plans will be discussed. **Chapter 6** is a related publication from this research project. The co-authored publication characterizes chemical contaminants from 3-D printers in an environmental chamber and compares the quantified emissions to laser printer emissions.

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Chapter 2:

Determinants of Higher or Lower Ultrafine Particle, Volatile Organic Compound, and Ozone Emissions from Laser Printers

Abstract

Objective: Laser printers are globally present in modern indoor and occupational environments. Laboratory emission studies have reported ultrafine particle (UFP) (less than 100 nm), volatile organic compound (VOC), and ozone emissions from laser printers. Laser printer emissions pollute indoor environments and occupational exposure to printer emissions may lead to work-related respiratory and cardiovascular disease. This study quantifies UFP, total VOC and ozone emissions from laser printers in an environmental chamber and applies statistical models to identify factors influencing laser printer emissions.

Methods: Ozone, total VOC, and UFP size distribution and number concentration were measured in an environmental chamber for eight printer make-models. The sourcereceptor model was used to identify relevant factors that may affect emissions and worker exposure. Mixed-effects regression modeling was used to identify sources of variability in exposure to laser printer emissions. The effects of printer technology, voltage, and copy rate were evaluated in the mixed effects models for UFP and total VOC emission rates (ERs); UFP, total VOC, and ozone concentration during printing; and UFP, total VOC, and ozone concentration post-printing.

Results: The fixed effect of copy rate significantly affected UFP number emission rate, and the between-device variance by 23% (reduction from 1.04 to 0.80). The fixed effect of voltage significantly affected total VOC emission rate, and the between-device variance by 44% (reduction from 0.88 to 0.51). Within-device variance components were unaffected in the models. A significant trend (p < 0.003) of increasing UFP size was observed from the print phase to the post-print phase.

Conclusion: Understanding factors influencing UFP, total VOC, and ozone emissions from laser printers, and the magnitude of their effect, informs control strategy efforts focused on reducing indoor contaminants emitted by laser printers.

Key words: Laser printing, mixed regression modeling, determinants of exposure, ultrafine particles, volatile organic compounds

Introduction

Laser printers are ubiquitous in modern indoor and occupational environments, and laboratory studies have reported emissions of polycyclic aromatic hydrocarbons (PAHs), formaldehyde, styrene, ultrafine particles (UFP), and ozone from these devices [1-18]. Laser printers transfer toner powder from the toner cartridge onto paper. Historically, toner particles were created by pulverization, which resulted in coarse (>10 µm) irregular shaped particles with low respirability. Polymerized emulsion aggregation (EA) toner, an advancement used today to improve toner adhesion, yields smaller (<10 µm), spherical toner particles [19, 20]. These modern toner particles are often coated with engineered nanomaterials (ENMs), such as silica dioxide or titanium dioxide [21]. Toxicological and epidemiologic studies have provided evidence suggestive of an association between exposure to these printer-emitted particles (PEPs) and adverse respiratory and cardiovascular health outcomes [22-25].

With the ubiquity of laser printers in modern indoor and occupational environments, understanding factors that modify PEP emissions is critical to reducing exposure, which will ultimately lead to reduction in morbidity and mortality associated with occupational particle and organic vapor exposure. Certain factors have been reported in the literature to influence emissions from laser and inkjet printers and photocopiers (Table 1-2) [4, 10, 26-29]. These factors, such as temperature, voltage, copy rate, and paper and toner type can be identified through statistical and mathematical models. The models can be used to inform strategies to mitigate occupational exposure to printer emissions and reduce work-related respiratory and cardiovascular disease. The aims of this study were to (1) characterize UFP, total VOC, and ozone emissions from laser printers in an environmental chamber and (2) use

mixed effect models to identify factors influencing laser printer emission and the

magnitude of their effect.

	Em	ission Type		
Factor	Particulate	Chemical	Ozone	Affect
Inter-machine	+	+	+	Emissions of VOCs and ozone were higher from laser printers compared to ink jet printers [3]. Emission levels of >7 nm and >0.1 um particles varied among hardcopy devices [4]. 62 printers categorized as non-emitters or low, med, high emitters of submicron particles [17].
Technology	+	+	+	Laser printers with traditional corona discharge technology emitted more ozone and formaldehyde than non-corona machines [14].
Temperature	+	+	±	Fluctuations in heating of fuser unit influences generation of ultrafine particles (high vs low emitters) [4]. Particle number emission concentration but not PM _{2.5} or ozone followed the cycle of fuser roller temperature variation [6].
Copy rate	+	+	±	Increase in emission concentrations dependent on printing speed [16]. Linear relationship between particle emissions and print jobs of different number of pages [10].
Voltage	±	±	±	Not evaluated in the current literature.

Table 1-2. Factors influencing emissions from office equipment.

+ = factor reported to influence emissions; \pm = influence of factor on emissions unclear.

Materials and Methods

Environmental chamber design

Laboratory laser printer emissions evaluation trials were performed in a

temperature- and humidity- controlled 13.85 cubic meter stainless steel chamber

(Figure 1-2), meeting the international requirements (ASTM 6670 and ISO/IEC 28360)

for office equipment emissions testing. Air mixing was assessed using sulfur

hexafluoride as a tracer gas. The calculated mixing level was 92 percent (a level of 80

percent is considered satisfactory). The leak rate was 0.024 air changes per hour

(ACH), which is negligible. The chamber air change rate was one ACH. Air entering the chamber passed through a carbon filter and high efficiency particulate air (HEPA) filter.



Figure 1-2. Laboratory chamber laser printer experimental and data acquisition design.

Instrumentation

A summary of real-time and time-integrated sampling instruments is provided in Table 2-2. Emission sampling was conducted for ozone, TVOCs, and particle size distribution and number concentration. Ozone emissions were quantified using a realtime gas sensitive semiconductor sensor (Ozone Solutions, Inc., Hull, IA) with a lowrange sensing head (model EOZ). A real-time total organic compound (TVOC) photoionization detector (9.8eV, RAE Systems, San Jose, USA) was used to monitor TVOC emissions. A condensation nuclei counter (CNC) (P-Trak Model 8525, TSI Inc., Shoreview, MN) was used to determine real-time particle number concentration. Particle size distribution and total number concentration was measured using a direct-reading Scanning Mobility Particle Sizer (SMPS, Model 3080) and Condensation Particle Counter (CPC, Model 3775) (TSI Inc., Shoreview, MN). All real-time instruments were factory calibrated prior to use. Time-integrated samples for specific VOCs were collected using 6-L Silontie[®] evacuated canisters (Entech Instruments Inc., Simi Valley, CA) equipped with an instantaneous flow controller (< 1 minute sample) and analyzed by gas chromatograph-mass spectrometer (GC-MS) [30].

Table 2-2. Real-time and air monitoring instruments.

Instrument	Parameters
Ozone monitor	Ozone concentration 0.01 to 10 ppm
TVOC photoionization detector	Total organic chemicals 10 to 99 ppm
Condensation nuclei counter (CNC)	Number of particles from 20 to 1000 nm
Scanning mobility particle sizer	Number and size of particles from 10 to 1000 nm

Study design

Eight printer make-models were evaluated in N=67 trials; seven printer makemodels that were run in triplicate for three devices of each make-model (N=63 trials) and a single device make-model which was run in quadruplicate (N=4 trials). Print jobs were monochrome, one-sided prints with 10% page coverage. The number of pages printed ranged from 100 to 500 pages depending on the printing device's print speed and output tray capacity. Sampling times included a pre-print, printing, and post print phase. A 30-minute background sample was collected during the pre-print phase. Postprint data collection continued for two ACH following the time recorded for the last page printed.

Data analysis

To identify factors influencing laser printer emissions and assess between- and within-device variance, a null random effect and two mixed effect models were performed. Outcome variables for the models included: UFP and TVOC emission rate; UFP, TVOC, and ozone concentration during printing; and UFP, TVOC, and ozone concentration post-printing. The null random effect model included the random effect of printer serial number and make-model (8 make-models). Two-way table analysis was performed to determine whether significant relationship existed among covariates. Technology and voltage were mutually exclusive in two-way table analysis. Therefore, the fixed effect models included only the fixed factors of copy rate (high, low) and voltage (high, low). A significance level of α =0.05 was used for all comparisons. Statistics were computed using JMP software (version 13, SAS Institute Inc., Cary, NC).

Results

Emission profiles

Particle number concentration (Figures 2-2 (a) and (b)) would rise sharply at the start of the print and then quickly decay once the print had completed. The HPM451dn printer had a unique particle emission profile where the same immediate rise and decay in particle number concentration was not observed. For this printer, a small burst of particle number concentration was observed at the start of the print and then quickly diminished. TVOC emission profiles (Figures 2-2 (c) and (d)) were observed to either rise sharply at the start of the print and then immediately begin to decay or rise sharply at the start of the print and plateau throughout the decay period. Four of eight evaluated printer make-models had TVOC emission profiles similar to Figure 2-2 (c)

(RicohSP311dnw, Brother6200w, Brother HL3170cdw, BrotherHL2240). Full emission

profile data from all printer make-models is presented in Appendix D.





Figures 3-2 (a) and 3-2 (b) plots of particle size distribution and particle concentration over time demonstrate that when the print job begins there is an initial burst of ultrafine particles and over time particle size begins to increase as the particle concentrations being to either decay or plateau.





Descriptive statistics

Characterization of emissions from laser printers is presented by descriptive means and standard deviations by printer make-model to show the range of exposures quantified in the study. Standard deviations are quite large which is likely attributable to within device variability. Results are presented in Table 3-2.

 Table 3-2.
 Summary statistics for particle number and total VOC emission rates, ozone concentration, and average particle geometric mean size.
 Means ± standard deviations.

Make-Model	UFP ER (#/min)	TVOC ER (μg/min)	Ozone (µg/m³)	Avg. GM (nm)
Brother6200dw	$3.21e^{10} \pm 2.76e^{10}$	7.23e ⁵ ± 1.03e ⁵	6.67 ± 0.94	81 ± 14
BrotherHL2240	3.64e ¹¹ ± 1.95e ¹¹	$3.26e^5 \pm 8.15e^4$	8.89 ± 0.05	43 ± 12
BrotherHL3170cdw	7.89e ¹¹ ± 3.58e ¹¹	5.24e ⁵ ± 2.34e ⁵	6.29 ± 2.50	67 ± 15
BrotherHL8350	$3.96e^{11} \pm 4.30e^{11}$	$1.47e^{5} \pm 2.51e^{4}$	8.93 ± 0.04	47 ± 11
HPM451dn	$1.26e^{11} \pm 2.98e^{10}$	$9.49e^4 \pm 4.76e^4$	8.93 ± 0.01	65 ± 17
LexmarkMS810	1.24e ¹¹ ± 1.84e ¹¹	$5.30e3 \pm 2.09e^4$	8.95 ± 0.05	69 ± 14
RicohSP311DNW	5.51e ¹¹ ± 5.89e ¹¹	$3.02e^5 \pm 5.86e^4$	8.90 ± 0.05	51 ± 7
SamsungMX2020	3.90e ¹¹ ± 1.78e ¹¹	3.63e ⁴ ± 9.81e ³	2.97 ± 0.00	52 ± 8

UFP = ultrafine particle, TVOC = total volatile organic compound, GM = geometric mean, ER = emission rate.

Several specific VOCs were quantified from evacuated canisters during the study. Isopropyl alcohol, benzene, ethylbenzene, styrene, ethanol, and acetaldehyde were present during operation of the eight make-models evaluated. Toluene was not detected in any environmental chamber assessments of the Brother HL2240 printer. m,p-Xylene was not detected in any environmental chamber assessments of the Brother HL2240 printer. Brother 6200dw printer. Qualitative specific VOC results are presented in Table 4-2.

 Table 4-2. Qualitative list of specific VOCs by percent presence in each emission test by make-model.

 Specific VOCs (% present)

Analyte	Brother6200dw	BrotherHL2240	BrotherHL3170cdw	BrotherL8350	HPM451dn	LexmarkMS810	RicohSP311DNW	SamsungMX2020
Isopropyl Alcohol	89	100	67	44	67	56	44	25
Benzene	89	33	22	78	33	11	22	50
Toluene	78	0	100	78	78	11	22	100
Ethylbenzene	67	11	100	78	67	89	56	25
m,p-Xylene	0	11	78	44	56	89	44	50
Styrene	89	67	100	78	89	89	78	100
Ethanol	78	44	89	67	89	67	44	75
Acetaldehyde	56	56	100	89	78	44	67	75

Contingency analysis of copy rate and voltage

To classify printers as "high emitters" or "low emitters" the average UFP and TVOC emission rates by copy rate and voltage were reviewed. High particulate emitters were defined as devices with high copy rate (\geq 25 pages per minute). High TVOC emitters were defined as devices with low voltage (>15 mA). The data presented below suggest that there is an interaction between copy rate and voltage; however, we do not have enough data to further assess the potential interaction.



Figure 4-2. Contingency analysis of copy rate and voltage with mean UFP and TVOC emissions rates.

	Copy Rate							
	Count	Low	High	Total				
	Total %							
	Col %							
	Row %							
đ	Low	13	18	31				
'oltag€		19.40	26.87	46.27				
		41.94	50.00					
^		41.94	58.06					
	High	18	18	36				
		26.87	26.87	53.73				
		58.06	50.00					
		50.00	50.00					
	Total	31	36	67				
		46.27	53.73					

Mixed model output

The fixed effect of copy rate was significant for UFP ER and UFP concentration during printing. The total variance for the fixed effect of copy rate was 13% and 17% for UFP ER and UFP concentration during printing, respectively. The between-device percent variance for UFP ER and UFP concentration during printing was 23% and 38%, respectively. The within-device variance was not affected by copy rate (Table 5-2).

The fixed-effect of voltage was significant for UFP concentration post-print, TVOC ER, TVOC concentration during printing, TVOC concentration post-printing, and ozone concentration post-printing. The total variance for the fixed effect of voltage was 23% for UFP concentration post-printing. The between-device variance for UFP concentration post-printing was 29%. The total variance for the fixed effect of voltage was 30%, 9%, and 28% for TVOC ER, TVOC concentration during printing, and TVOC concentration post-printing, respectively. The between-device variance was 44%, 22%, and 47% for TVOC ER, TVOC concentration during printing, and TVOC concentration post-printing, respectively. The total variance for the fixed effect of voltage was 24% for ozone concentration post-printing and the between-device variance was 33% for ozone concentration post-printing. The within-device variance was not affected by voltage (Table 5-2).

Table 5-2. Intercepts, parameter estimates, variance components, and percent of total, between-device, and within-device variance for the fixed effects of Copy Rate and Voltage.

Copy Rate	UFP	UFP	UFP	TVOC	TVOC	TVOC	O ₃
	ER	Print	Post	ER	Print	Post	Post
Intercept	25.89	20.98	22.55	12.13	5.60	6.11	2.19
Parameter Est.	0.52	0.46	0.26	-0.09	0.03	-0.05	0.02
Between-Device	0.80	0.33	1.58	0.93	0.49	0.47	0.03
Within-Device	0.72	0.59	0.45	0.37	0.50	0.36	0.006
Variance explained by f	ixed effe	cts	1	1		1	1
Total Variance (%)	13	17					
Between-Device (%)	23	38					
Within-Device (%)	0	0					
Voltage	UFP ER	UFP Print	UFP Post	TVOC ER	TVOC Print	TVOC Post	O₃ Post
Intercept	25.89	20.98	22.55	12.13	5.60	6.11	2.19
Parameter Est.	-0.07	-0.17	-0.71	-0.63	-0.34	-0.47	0.09
Between-Device	1.10	0.54	1.11	0.51	0.36	0.23	0.02
Within-Device	0.72	0.59	0.45	0.37	0.50	0.36	0.006
Variance explained by fixed effects							
Total Variance (%)			23	30	9	28	24
Between-Device (%)			29	44	22	47	33
Within-Device (%)			0	0	0	0	0

*Significant effects are **bold** in the table. ER = emission rate; Print = during the print phase; Post = during the post-print phase; UFP = ultrafine particle; TVOC = total volatile organic compound; O_3 = ozone.

Ultrafine particle size distribution during post-print

Average geometric mean sizes during printer operation ranged from 43 nm (Brother HL2240) to 81 nm (Brother 6200dw). Average geometric mean sizes during post-printing phase ranged from 30 nm (Brother HL2240) to 70 nm (HP M451dn). Figure 5-2 visualizes the significant trend (p < 0.0045) of increasing geometric mean size over post-print time for all printers. Figure 6-2 visualizes the significant trend of increasing geometric mean size over post-print time for all printers. The nonparametric test for significant trend determined whether particle size post-print consistently increases across 30 minutes to 120 minutes post-print.





Note. Nonparametric test for increasing GM size over post-print time trend p < 0.0045.



Figure 6-2. Nonparametric test for significant trend of increasing geometric mean size between each time point during the post-print phase by make-model.

Discussion and Conclusions

Copy rate significantly influenced (p < 0.05) UFP ERs and UFP concentration during printing. Copy rate parameter estimates were positive and significant (p < 0.05) for UFP ERs and UFP number concentrations during printing. The positive parameter estimates indicate that as copy rate increases the UFP ERs and UFP number concentrations during printing will increase. A linear relationship between particle emissions and print jobs of different number of pages was has been observed in previous work [10]. However, another study evaluating the effect of copy rate on UFP emissions noted higher copy rate output printers had lower UFP emissions rates due to faster fixation of toner; therefore, resulting in rapider evaporation of toner/fuser materials and lower UFP ERs [27].

Voltage significantly influenced (p < 0.05) TVOC ERs, TVOC concentration during printing, TVOC concentration post-printing, and ozone concentration postprinting. Voltage parameter estimates were negative and significant (p < 0.05) for UFP concentrations post-print, TVOC ERs, TVOC concentrations during printing and TVOC concentrations post-printing. The negative parameter estimates indicate that as voltage increases, UFP concentrations post-print, TVOC ERs, TVOC concentrations during printing, and TVOC concentrations post-printing decrease. The findings for voltage are contrary to expected results that higher voltage would lead to higher operating temperature leading to greater thermoplastic degradation of toner material and a subsequent increase in TVOC emissions. Voltage parameter estimates were positive and significant (p < 0.05) for ozone concentrations post-printing. The positive parameter estimates indicate that as voltage increases the ozone concentrations post-printing will increase.

Laser printers emit UFPs, VOCs, and ozone during operation, which contributes to indoor air pollution and has the potential to pose a serious health hazard to the human respiratory system. Because regulations for UFPs do not exist yet, reducing worker exposure to UFP emissions from laser printers is a priority while UFP health effects research and UFP particle regulations continue to develop. Many laboratory studies and workplace exposure assessments have quantified UFP emissions form laser printers. A number of studies have called for the risk characterization of UFPs to reduce indoor UFP emissions and protect workers from exposure [28-30]. Scungio et al. [31] assessed particle emissions from 110 laser printers. Emission rates were between 10⁹ and 10¹² for particle number concentration and mode particle diameters were <124.10 nm [31]. These findings are consistent with UFP ERs and size distributions reported in this study. UFP and TVOC ERs calculated in this study had large standard deviations. Future work would benefit from increased repeated measures for each printing device in attempt to decrease the standard deviations. Copy rate and voltage significantly influence the UFP, TVOC, and ozone emissions at the source. These factors should be considered in studies evaluating emissions from laser printers.

Understanding factors influencing UFP, total VOC, and ozone emissions from laser printers, and the magnitude of their effect, informs control strategy efforts focused on reducing indoor contaminants emitted by laser printers. To better understand determinants of higher or lower emissions from laser printers, it is critical to understand device-specific factors (e.g. copy rate, voltage). Using statistical models to explore associations with exposure levels may lead to the discovery of previously unidentified emission factors and the magnitude of effect these factors have on exposure levels.

Additional device-specific factors and consumables may influence laser printer emissions (e.g., temperature, toner type, paper type). These factors were not evaluated in this phase of the study. For phase two of the study, three printers have been selected (1) low UFP/VOC emitting printer (2) high UFP emitting printer and (3) high VOC emitting printer. In this phase, we will evaluate the effect of after-market and bio-based toner and recycled paper content on printer emissions.

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Chapter 3:

Comparison of Quantified Laboratory and Real-world Laser Printer Emission

Abstract

Objective: This study aims to (1) characterize indoor ultrafine (UFP) exposures during laser printing in a copy center, (2) calculate emission rates for real-world UFP exposure data using a one-box model, and (3) compare laboratory and real-world laser printer emission rates.

Methods: Real-world exposures were measured using a real-time particle number counter (0.02 to 1 μ m, CNC) and optical particle counter (0.30 to 20 μ m, GRIMM Technologies). Emission rates were calculated using a steady state one-box model, augmented to account for percent time print activity occurred. A T-test was performed to determine is laboratory and real-world emission rates were significantly different (α = 0.05). Polycarbonate track-etched open-face cassette samples were collected at the copy center and analyzed by scanning electron microscopy (SEM) to determine UFP morphology and elemental composition.

Results: Laboratory emission rates calculated using a standard emission rate equation and one-box model were significantly different (p < 0.0445). Real-world particle number emission rates ranged from 1.86e+03 #/minute to 2.08e+06 #/minute. Real-world particle concentrations were highest in the >0.30 µm size particle size class. SEM analysis identified titanium (Ti), sulfur (S), calcium (Ca), aluminum (AI), zinc (Zn), and silicon (Si).

Conclusion: This study is limited to six real-world UFP exposure samples. Further research is needed to understand factors contributing to the observed significant difference between BAM and TEAS calculated emission rates.

Key words: laser printers, copy center, ultrafine particles, one box-model, emission rate

Introduction

Toxicology and epidemiology studies have observed an association between ultrafine particles (UFPs) and respiratory, cardiovascular, and neurological health effects. Between work, school, and home-life people spend 80 to 90 percent of their time indoors. Laser printers are ubiquitous in the indoor environment and UFP emissions from laser printers have been quantified in laboratory chambers and workplaces (1-10). The relationship between ambient UFP exposure and health effects has been well studied; however, very few have examined the relationship between indoor UFP exposure and health effects. Characterization of indoor UFP exposures is important to develop effective control strategies to reduce indoor UFP exposure [1-3].

To date, only a small number of studies have performed workplace assessments to characterize indoor exposure to UFPs emitted from laser printers [9-14]. This study aims to characterize workplace UFP exposure from laser printers at a copy center. Realworld emission rates calculated using a one-box model will be compared to laboratory emission rates (data collected in previous study) calculated using the test method for hard copy devices and the one-box models. A Student's t-test will be used to determine if the three emission rate groups (1) real-world one-box model, (2) laboratory one-box model, and (3) laboratory test method for hard copy devices are significantly different.

Materials and Methods

Copy Center

Emissions were assessed from laser printers located in an office copy center. The copy center prints, copies, binds, and distributes workplace print orders and is located on the basement level of the office building. The space is a 343 cubic meter

room with three laser image press machines (Cannon c850 (one unit) and Xerox D136 (two units) and three laser printers (HP LaserJet Enterprise 600 Printer M603). Sampling Location 1 and Location 2 were near-field to the emission source and sampling Location 3 was far-field from the emission sources and representative of where employees spent most of their workday.



Figure 1-3. Copy Center floorplan with printing equipment and sampling locations designated.

Note. Image is not draw to scale. Sampling locations: (1) on table near-field to two laser pritners and two laser image press machines, (2) near-field of single laser image press machine, (3) centrally located in the employee worksations.

A recirculating air unit was located on the back wall of the copy center. General ventilation existed for occupant comfort with a ventilation rate of two air changes per hour (ACH). The room was staffed full-time by three employees and staffed by two additional employees. The copy center was under negative pressure from the hallway. Copy center doors were closed throughout the workday.

Ultrafine Particle Measurement

Air sampling was conducted over the course of two consecutive workdays. A condensation nuclei counter (CNC) (P-Trak Model 8525, TSI Inc., Shoreview, MN) was used to measure particle number concentration. An optical particle counter (OPC) (Model 1.108, GRIMM, Aerosol Technik GmbH & Co. Ainring, Germany) was used to measure particle number concentration and size distribution. Airborne particles were collected on polycarbonate track-etched filters for off-line analysis using scanning electron microscopy with an energy dispersive x-ray detector to identify elemental constituents. Lung deposition measurements were calculated using particle size in MPPD (v3.04).

Emission Rates

Emission rates for previously collected laboratory chamber data and real-world exposure data were calculated (Table 1-3) using a constant emission one-box model (Figure 2-3) (TEAS, Exposure Assessment Solutions, Inc., Morgantown, USA). Input parameters included percent activity time, room volume, ventilation rate, and average concentration during the total sample time.

Figure 2-3. Standard one box model (Model 100 and 101) used to calculate generation rates using measured particle number concentration, room volume, ventilation rate, and fraction of time printing occurred during sampling.



Source: Hewett and Ganser, JOEH (2017).

Laboratory and real-world emission rates calculated using the one-box model were compared to emission rates calculated in a laboratory chamber study using the test method for hard copy devices (Blue Angel Method, RAL-UZ-171). To determine if calculated emission rates were significantly different, emission rates were compared using a Student's t-test (JMP software, version 13, SAS Institute Inc., Cary, NC).

Results

Characterization of Ultrafine Particle Exposure

Particle size distribution and number concentration results are presented in Figure 3-3. Measured particles were smaller than 0.80 μ m, with the highest number concentration measured in the > 0.03 μ m size class. Throughout the day UFP number concentrations (Figure 4-3) would rise sharply at the beginning of a print task and exponentially decay at the completion of the print. Particle concentrations on average ranged from 994 #/cm³ to 3,189 #/cm³ over the course of the workday.





Note. Particle number concentration (#/cm³).


Figure 4-3. UFP number concentration plots (#/cm³) over the duration of the workday by sampling location. The start of a print job is denoted by black arrows.

Location 1: (a) day 1 (b) day 2; Location 2: (c) day 1 (d) day 2; Location 3: (e) day 1 (f) day 2.

Regional Lung Deposition

Mean total UFP deposited number ranged from ~90 to ~2500 particles for sampling Locations 1, 2, and 3. The higher deposited number was estimated for sampling Locations 1 and 2, which are near-field samples located directly beside the printing equipment. Maximum total UFP deposited number for sampling Locations 1, 2, and 3 ranged from ~7,800 to ~9,600 particles.



Figure 5-3. Estimated particle number depositon by lung region for each sampling location.

UFP Elemental Composition

High magnification pictures of particles collected on filters in the copy center illustrate the small size of airborne particles released during laser printing. The collected particles are clusters of many small particles. The inorganic components and elements identified during analysis included titanium (Ti), sulfur (S), calcium (Ca), aluminum (AI),

zinc (Zn), and silicon (Si).

Figure 6-3. High magnification of images of particles (denoted by yellow arrows) emitted from a laser printer while printing with stock toner. Figures (a) and (b) were collected from employee workstations and Figures (c) and (d) were collected nearfield of the printing equipment.



Comparison of Calculated Emission Rates

Laboratory emission rates calculated using the BAM equation were significantly different (p < 0.0445) from laboratory and real-world emission rates calculated using the TEAS equations. The groups were two times as different from each other as they were

within each other (t score = 2.14). However, laboratory and real-world emission rates calculated using the TEAS equation were not significantly different.

Particle Number Concentration Emission Rates (#/minute)							
Sample	Laboratory ER BAM	Laboratory ER TEAS	Real-world ER TEAS				
	Calculated	Calculated	Calculated				
1	8.26E+10	5.63E+03	1.60E+04				
2	2.46E+11	8.47E+04	9.89E+04				
3	1.50E+12	3.51E+04	2.00E+06				
4	1.94E+11	8.50E+04	3.25E+04				
5	1.26E+11	5.20E+03	4.17E+04				
6	7.26E+11	1.40E+05	9.48E+05				

 Table 1-3. Particle number concentration generation rates by sampling location.

ER = emission rate; BAM = Blue Angel Method; TEAS = Task Exposure Assessment Simulator

Discussion and Conclusions

Because laser printers at the copy center were not the same make-model of printers used in the laboratory chamber study direct comparison of laboratory and realworld emission rates provides little insight to difference between laboratory and realworld emission rates. Comparing laboratory emission rates calculated using the test method for hardcopy devices and the one-box model resulted in significantly different emission rates. One major difference in the two methods that may contribute to the significantly difference emission rates is that one-box model has been augmented to account for the percent time activity is occurring during the entire sample time and the ventilation rate for the space. Imminent next steps in this research would be to distinguish differences in the test method for hard copy devices and one-box model equations to identify which factors may be causative significantly different emission rate values. This study is limited to only six UFP exposure measures collected at the copy center. Further data collection is needed to determine the accuracy of study findings.

The main components of the test method for hard copy emissions include (1) particle loss coefficient, (2) room volume, and (3) the average particle concentration and difference in particle concentration during the emission time for a single emission profile. The main components of the one-box model include (1) the average particle concentration, (2) the percent emission time, and (3) the ventilation rate for a single or multiple emission profiles. The fundamental difference in the two equations is the onebox model calculates the area under the curve for a repeating task involving concentration rise and decay curves, whereas, the test method for hard copy devices calculates the emission rate for a single concentration rise and decay curves. Calculation of a single rise and decay curve is appropriate for evaluating laser printers in a test chamber but may misrepresent workplaces exposures where printing is occurring as a cyclic, irregular process over the duration of the workday. The emission rate determined from the test method for hard copy devices must be regarded as device-specific emission behaviors. However, emission rates calculated using the onebox model may be regarded as task-specific emission behaviors.

Exposure assessment of UFP emissions alone cannot fully characterize the potential health risk. Research has shown that laser printers are noteworthy sources of indoor UFP emissions comprised of elemental, inorganic, and organic components [11, 13, 20-23]. Laser printers emit high concentrations of UFPs with known toxicological properties, such as small particle size and large surface area which have a high particle

number count per unit mass [16, 17]. The large surface area increases surface reactivity and enables UFPs to act as a carrier for co-pollutants such as ozone and/or organic vapors also emitted from laser printers [18]. This suggest that even low toxicity, low solubility UFPs induce may induce an inflammatory response in the lungs [19].

A study by Salthammer et al. [15] performed a risk characterization assessment on laser printers and toasters emitting UFPs indoors. To characterize exposure to indoor airborne particles, particle intake and deposition in the human respiratory tract from measured particle number concentrations was calculated following the model of the International Commission on Radiological Protection. A similar approach will be used in the next phase of this research to determine if modeled exposures and estimated dose are meaningful or comparable to previously published data.

The TEAS program will be used to model worker exposure by combining collected activity and task exposures and their duration and frequency. The exposure simulator in the TEAS program will be used to estimate modeled exposure distributions for the copy center workers. The modeled distributions will then be compared to other studies that have measured workplace laser printer exposure data. Because studies evaluating the directly relationship between printer emissions and health effects are limited. A similar approach will be used in lung deposition modeling to link exposure to a biologically relevant endpoint. For each observed printing activity, geometric mean, standard deviation, and size distribution will be modeled to predict dose. The data will be summarized by the distribution of dose and determine whether certain activities resulted in larger or smaller doses.

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Chapter 4:

Exposures during Industrial 3-D Printing and Post-processing Tasks

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Abstract

Objective: This study aims to assess whether exposures occur during 3-dimmensional (3-D) printing and post-processing tasks in an industrial workplace.

Methods: Emissions were assessed using real-time particle number (0.007 to 1 µm) and total volatile organic compound (TVOC) monitors and thermal desorption tubes during various tasks at a manufacturing facility using FDM[™] 3-D printers. Personal exposures were measured for two workers using nanoparticle respiratory deposition samplers for metals and passive badges for specific VOCs.

Results: Opening industrial-scale FDM[™] 3-D printer doors after printing, removing desktop FDM[™] 3-D printer covers during printing, acetone vapor polishing (AVP), and chloroform vapor polishing (CVP) tasks all resulted in transient increases in emissions of submicrometer-scale particles and/or organic vapors, a portion of which enter the workers' breathing zone, resulting in exposure. Personal exposure to quantifiable levels of metals in particles <300 nm were ≤0.02 mg/m³ for aluminum, chromium, copper, iron and titanium during FDM[™] 3-D printing. Personal exposures were 0.38 to 6.47 mg/m³ for acentone during AVP and 0.18 mg/m³ for chloroform during CVP.

Conclusions: Characterization of tasks provided insights on factors that influenced emissions, and in turn exposures to various particles, metals < 300 nm and organic vapors. These emissions and exposure factors data are useful for identifying tasks and work processes to consider for implementation of new or improved control technologies to mitigate exposures in manufacturing facilities using FDM[™] 3-D printers.

Key words: 3-D printing, ultrafine particles, volatile organic compounds, additive manufacturing, post-processing

Introduction

Additive manufacturing (AM) is the process of joining materials to make objects, usually layer-by-layer [1]. Several AM technologies exist, including fused deposition modeling (FDMTM), a form of material extrusion 3-D printing. During the FDMTM process, polymer filament is heated and extruded through a nozzle onto a build plate creating an object. Numerous types of filaments with different properties are commercially available for FDMTM 3-D printing. One group of filament types are those that are extruded in desktop model FDMTM 3-D printers under relatively low build chamber temperatures such as acrylonitrile butadiene styrene (ABS) and poly lactic acid (PLA). Another group of filament types are extruded in industrial-scale 3-D printers under much higher build chamber temperatures such as polycarbonate (PC) and ultem (polyetherimide).

The heating of thermoplastic filaments results in breakdown of the filament polymer and release of organic vapors and particles which could have health significance if inhaled [2, 3, 4]. Exposures to volatile organic compounds (VOCs) is of concern for workers because some of these chemicals are respiratory and mucous membrane irritants [5, 6] or allergic asthmagens [7, 8]. Ultrafine particles (UFP, defined in the environmental, safety and health community as those having diameter < 100 nm) have known toxicological properties. Numerous studies have confirmed that UFPs penetrate into the alveolar (gas exchange) region of the lungs where it is difficult for the body to clear them and cause inflammatory responses [9] or may be translocated and cause cardiovascular effects [10, 11].

Despite early recognition of environmental, health and safety issues in AM and post-processing tasks [5], existing literature is limited to emission studies of desktop FDM[™] printers in test chambers or small rooms [12-19]. In the absence of real-world data, these studies have provided valuable insights on emission characteristics from desktop FDM[™] 3-D devices and indicate that both VOCs and UFP are emitted during printing. Some VOCs that are emitted may react with ozone to form oxygenated compounds that have chemical structures relevant for asthma [19]. The types and levels of VOCs are known to differ between ABS and PLA filaments [14, 20]; however, there is no data available for PC and ultern filaments. Emission rates of UFP may exceed 1 billion particles per minute during printing. Some of these emitted particles contain transition metals such as chromium from thermoplastic additives. Transition metals are important in generation or reactive oxygen species, which are involved in development of lung inflammation [17]. Given the results of these chamber and room studies, it is clear that there is a need to evaluate whether exposures occur in real-world occupational settings; however, such data is currently lacking.

Herein, we report on emissions and personal exposures from 3-D printers at a manufacturing facility. Our results indicate that exposures to both VOCs and UFP occur in workplace settings and are influenced by the scale of 3-D printing (desktop versus industrial) and that post-processing tasks also result in exposure. Further, task-based exposure assessment provided important insights on variability in exposure.

Materials and Methods

Emissions (release of contaminants) were assessed from FDM[™] 3-D printers located in two different rooms at a manufacturing facility. The first room (66 m3)

contained three industrial-scale FDM[™] printers (Stratasys, Inc., Eden Prairie, USA) using ABS, PC, and ultem filaments, respectively. No local exhaust ventilation (LEV) designed to remove emissions directly from the printer source or general ventilation (open windows, etc.) existed in the room. The room was intermittently staffed by one employee. The second room, an office and prototyping space (40 m3), contained 10 desktop FDM[™] printers (3D Printing Systems, Rustenburg, SA) using either ABS or PLA filaments. This room was primarily staffed by one employee. No LEV existed for the desktop printers. The room had a recirculating air conditioning unit but no general ventilation.

The doors of the industrial-scale FDMTM printers remained sealed during printing. In contrast, the covers to the desktop printers in the office were frequently removed by the operator during printing to check on the build. Once built, an object is removed from a printer and may be subjected to post-processing tasks such as polishing to enhance appearance. Acetone vapor polishing (AVP) of ABS objects was conducted in the 40 m3 room at a station equipped with a crude LEV system that consisted of a flex duct connected to a wall-mounted fan with flex duct on the downstream side that exhausted outdoors. Objects subjected to AVP were placed into a small custom made rectangular chamber (15 cm x 12 cm x 12 cm, W x L x H) for treatment with acetone. Chloroform vapor polishing (CVP) of PLA objects was performed outdoors. AVP and CVP tasks were performed by the same employee who wore a half-mask air purifying respirator with organic vapor cartridges and nitrile gloves during these tasks.

A condensation nuclei counter (CNC) (P-Trak, TSI Inc., Shoreview, USA) was used to characterize particle number concentration from 0.007 to 1 µm when opening

doors of the industrial-scale printers and when removing covers on the desktop printers. A real-time total organic vapor (TVOC) photoionization detector (RAE Systems, San Jose, USA) was used to monitor vapor emissions when opening doors to the industrialscale printers and during AVP and CVP. Soil vapor intrusion thermal desorption (TD) tubes (Perkin Elmer, Waltham, MA) were used to specifically measure acetone concentrations in room air during AVP. All sampler inlets were positioned at locations representative of where the worker normally occupied to understand worker exposure potential.

Personal air sampling is effective to determine a person's exposure to contaminants in the air throughout his or her routine work day. Two types of personal air sampling techniques were used. Personal air sampling pumps with nanoparticle respiratory deposition (NRD) samplers and passive diffusion badges. The nanoparticle respiratory deposition NRD samplers [21] were used to measure personal exposure to particles with diameters <300 nm in the breathing zone (defined as the air around the worker's head). The NRD sampler consists of a respirable cyclone to remove large particles followed by an impactor and a diffusion stage containing mesh screens. The diffusion stage screens collect particles smaller than 300 nm with an efficiency that matches their deposition efficiency in the human respiratory tract. Following collection, the mesh substrates were analyzed for metals content using inductively coupled plasma-mass spectrometry. Passive diffusion badges (TraceAir® 521, Assay Technology, Livermore, CA) were used to measure personal exposure to vapors in the breathing zone. These badges are lightweight and were worn on the collars of workers, and operated by means of diffusion exposure.

Badges were analyzed using gas chromatography-mass spectrometry (GC-MS) using NIOSH Methods 1500, 1501, and 2500. TD tubes were analyzed using a thermal desorption unit (ATD650, Perkin Elmer) connected to a GC-MS. All real-time instruments were factory calibrated and sampling pumps were calibrated to 2.5 L/min and 0.050 L/min for the NRD and TD tubes, respectively.

Results

Concentrations of VOCs and UFP in air were monitored during industrial-scale and desktop FDM[™] 3-D printing and post-processing tasks over the employees' work shifts and during specific tasks on two consecutive days. Results of sampling are presented in Figure 1-4,Table 1-4 and Table 2-4.

Each industrial-scale 3-D printer contained a large build chamber with a door that was sealed closed during printing. The temperature inside the build chambers was too high to place our air sampling instruments inside during printing without risk of damage. Instead, the hand-held CNC was moved to various locations less than 10 cm from the printer (near the door seams, rear panel, side, exhaust fans, etc.) and there was no appreciable change in particle number concentration (data not shown). These results indicated that these models of industrial-scale 3-D printers were effective in containing emissions during printing. Given this containment, we assessed whether the task of opening the industrial-scale 3-D printer doors after printing would result in exposure. Data from the CNC indicated that particle number concentrations were relatively low when doors of the industrial 3-D printers were opened (Figure 1-4a). In contrast, a burst in TVOC concentration was evident when doors were opened, with levels increasing

well above background to 17.7, 1.6, and 3.6 mg/m³ for ABS, PC, and ultem, respectively (Figure 1-4b).

In contrast to these industrial-scale FDM[™] 3-D printers, the desktop printers could be operated with the doors open or covers removed. In our experience, we often observe that desktop FDM[™] 3-D printers are operated with the doors open and/or covers removed and this workplace was no exception. When covers were removed from the desktop 3-D printers, particle number concentrations at the interface of the printer and room air were elevated relative to background and exhibited a strong dependence on filament color and/or type (Figure 1-4c). Particle emissions exceeded 200,000 particles per cm³ of air (#/cm³) when the cover was removed from the machine printing with black ABS, followed by the machine printing with red PLA, which emitted about 50,000 #/cm³. Removal of covers from the machines using the other filaments (green PLA, blue ABS, and light blue PLA) yielded emissions <50,000 #/cm³.

Short *et al.* (2015) recognized early that post-processing tasks were important components of the AM process. Exposure potential from post-processing tasks has not been addressed until now. We evaluated two tasks, AVP of ABS printed objects and CVP of PLA printed objects. The AVP task consisted of four steps: 1) the worker used a 5 mL syringe to withdraw 3- to 5-mL aliquots of acetone from a bottle and discharged the liquid onto the chamber walls (performed five times consecutively); 2) the ABS object was placed in the chamber and the door to the chamber closed; 3) the door to the chamber was opened after 30 minutes had elapsed; and, 4) the object was allowed to air dry in the chamber while the door was opened. As summarized in Figure 1-4d, TVOC concentration during AVP rose steeply from background to about 900 mg/m³

when the worker dispensed acetone into the chamber. It is important to note that once the chamber door was closed, TVOC concentration (presumably acetone) did not instantly return to background. Rather, about 20 minutes elapsed until TVOC concentrations decayed to near background. When the chamber door was opened after 30 minutes, TVOC concentration again rose steeply to about 900 mg/m³ and required 20 minutes thereafter to return to background. Another important observation during monitoring of AVP was that the flex duct on the LEV system for the AVP station was not properly sealed to the fan on the exhaust side. As a result, TVOC concentrations in a hallway on the downstream side of the fan were up to 330 mg/m³ (Figure 1-4e). Ostensibly, the TVOC concentration measured in the hallway was acetone. These results indicate that exposure potential was not limited to the AM machine users, but also included office staff and anyone who utilized this hallway. The CVP task consisted of two steps: 1) the worker poured chloroform from a bottle onto a paintbrush; and, 2) chloroform was brushed onto the PLA object. During CVP, TVOC concentration rose to over 240 mg/m³ when chloroform was poured onto the brush and was between 100 and 200 mg/m³ when manually brushed onto a PLA object (Figure 1-4f).

Monitoring of air in the personal breathing zone of both employees at this facility demonstrated exposures occurred to both particles (Table 1-4) and vapors (Table 2-4). Employees were exposed to particles <300 nm in diameter that contained quantifiable levels of aluminum, chromium, copper, iron and titanium; the highest time weighted average (TWA) exposure was 0.02 mg/m³ for aluminum. Personal exposure to acetone occurred during all printing and post-processing tasks. During printing, acetone exposures ranged from 0.3 to 7.2 mg/m³ and during AVP, acetone exposures ranged

from 0.38 to 6.47 mg/m³. During CVP, the chloroform concentration was 0.18 mg/m³. The acetone concentration measured with a TD tube area sample positioned 25 cm from the AVP station was 0.1 mg/m³; however, this sample only captured a portion of the task duration for employee #2.

Table 1-4. Personal exposure to metal particles with diameters <300 r	nm.
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Employee	Task description	Time (min)	Metal	Personal exposure (mg/m³)
1	ABS and PLA printing	170	AI	0.01
			Cr	< 0.01
			Cu	< 0.01
			Fe	< 0.01
			Ti	< 0.01
1	ABS and PLA printing + AVP	325	AI	0.02
			Cr	< 0.01
			Cu	< 0.01
			Fe	BDL
			Ti	< 0.01
2	ABS and PLA printing +		Al Cr Cu Fe Ti	< 0.01
	AVF			< 0.01
	ABS printing	297		< 0.01
				0.01
	printing			< 0.01
2	CVP		Al Cr Cu Fe Ti	< 0.01
		322		< 0.01
				< 0.01
				< 0.01
				< 0.01

BDL = below analytical detection limit for iron

VOC	Employee	Task description	Time (min)	Personal exposure (mg/m³)
Acetone	1	ABS and PLA printing	162	0.30
	I	ABS and PLA printing + AVP	200	6.47
Acetone	2	ABS and PLA printing + AVP	110	0.38
		ABS printing	125	7.21
		Polycarbonate printing	125	2.61
		ABS and polycarbonate printing	80	0.29
Acetone	2		100	4.05
Chloroform	2	UVF	190	0.18

Table 2-4. Personal exposure to acetone and chloroform during fused deposition modeling 3-D printing and post-processing tasks.

Discussion and Conclusions

Previous efforts to understand emissions from FDM[™] 3-D printers were conducted in test chambers or small rooms. The use of chambers or rooms was a reasonable starting point for evaluating emissions; however, task-based measurements were not evaluated in these studies nor was it clear from these data whether personal exposures would occur in real-world industrial settings where control technologies might exist. McDonnel *et al. (2017)* evaluated FDM[™] 3-D printers on a college campus and their results indicated emissions were occuring in the real-worls, and hence, personal exposures were likely to occur. In this study, task-based measurements were performed using real-time instruments and revealed that when the industrial-scale 3-D printer doors were opened, particle concentrations were only slightly above background; however, there was a notable increase in TVOC concentrations. These observations were interesting, and at first glance, could be viewed as contradictory; however, the results are easily explainable based on aerosol behavior in the build chambers. Builds were completed 16.5 (ABS), 1.75 (PC), and 23.2 (ultern) hours earlier and the printer doors had remained sealed until opened. The low levels of particles suggest that particle concentrations decayed via settling from air and/or adherence to the interior walls of the build chamber. The increase in vapor concentrations indicated that objects continued to off-gas after printing was completed and that rates were strongly dependent on the polymer properties.

The data are consistent with our previous report that ABS objects continue to offgas after printing [19]. The increase in particle number concentration when the desktop 3-D printer covers were removed is notable because up to 10 printers may operate in this room simultaneously. Usually, the cover is removed by the operator to verify that an object is printing correctly or to facilitate removal of a printed object. Collectively, these data indicate that approaches to measuring and controlling exposures from industrial- and desktop-scale FDMTM 3-D printers may need to be approached differently. During printing with the three industrial-scale printers, the build chambers remained sealed which seemed to contain both VOCs and UFPs generated during extrusion. Only during the task of opening doors did the potential for exposure exist and require monitoring (VOC concentrations were influenced by filament type). It is important to understand that we waited from about 2 to 24 hours before opening the printer doors. In practice, it is more likely that printer doors would only remain closed long enough for the temperature in the build chamber to decrease enough to safely remove the object without risk of thermal burn. Hence, potential for exposure to UFP may also exist if industrial-scale FDM[™] 3-D printer doors are opened soon after an object is built. Additionally, it should be noted that this observation may not be

generalizable to all designs of industrial-scale FDM[™] 3-D printers nor would it apply to a printer that is not functioning correctly. In contrast, operation of desktop FDM[™] 3-D printers was a source of emissions throughout the entire build process indicating fullshift sampling as well as task-based sampling (e.g., when checking on print jobs) may be necessary (in the absence of control technologies emissions were influenced by variables including the filament type and color). Previously, we determined that a loosefitting cover provided by a manufacturer for a desktop FDM[™] 3-D printer had little effectiveness in reducing UFP and vapor emissions [17, 19]. UFP are of concern because they can deposit in the pulmonary and alveolar regions of the lung and lead to inflammation [9].

During FDM[™] 3-D printing, particles <300 nm were emitted that contained aluminum, chromium, copper, iron and titanium. All concentrations were well below U.S. Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PEL) of 10, 1, 1, 10 and 15 mg/m3, respectively [22]. PELs are legallyenforceable exposure limits in the United States. The presence of these elements in workplace air supports the real-world applicability of findings from studies in chambers and a small room and lab: printing with ABS emitted UFPs that contained aluminum, chromium, copper, and nickel whereas printing with PLA emitted UFP that contained iron [16, 18,19]. Chromium is of interest as it is present in welding fume and known to generate reactive oxygen species leading to pulmonary inflammation [23].

Previously, we reported that acetone was emitted during FDM[™] 3-D printing with a desktop machine using ABS and PLA filaments in a chamber [19]. Consistent with that chamber study, personal exposures to acetone occurred in this workplace during

printing with ABS and PLA. To our knowledge, only Azimi et al. (22016) has measured PC filament emission rates in a chamber. In that study, the authors reported emission of caprolactam and styrene. McDonnell et al. (2016) evaluated PC filament emissions uring printing in a student laboratory on a college campus and also reported that caprolactam was the primary VOC emitted. Our results presented in Table 2-4 suggest that PC filaments could also be a source of acetone in workplace atmosphere. TVOC levels rose rapidly during AVP and, to a lesser degree, during CVP. Badge samples confirmed worker personal exposure to both acetone (0.38 to 6.47 mg/m3) and chloroform (0.18 mg/m3) during polishing tasks. AVP is performed one to two times per day for a total of 2 hours, indicating that the worker's TWA exposure did not exceed the OSHA PEL of 2400 mg/m3 or the National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) of 590 mg/m3. RELs are limits developed by NIOSH and are not legally enforceable and are guidance values based on available scientific data. The LEV system at the AVP station only partially removed acetone vapors (Figure 1-4d). The exhaust side of the fan the flex duct was not properly sealed to the fan resulting in up to 330 mg/m3 TVOC (presumably acetone) vapor being discharged into a hallway used by all employees (Figure 1-4e). The CVP task requires about 15 to 20 min. The OSHA PEL for chloroform, a potential carcinogen (NIOSH, 2007), is 240 mg/m3 as a ceiling (level above which exposures should not be permitted to occur) value and the NIOSH REL is 9.8 mg/m3 as a 60 minute short-term exposure limit. Though personal exposures were below the PEL and REL, the employee performed this task outside on a windy day. Hence, efforts should be made

to monitor exposures during CVP to confirm they are consistently below the acceptable exposure limits.

To our knowledge, this is the first study to report emissions from FDM[™] printers in real-world settings. Results from both task-based evaluations and full-shift personal air monitoring indicated that exposures occurred to acetone and chloroform and several metals. Use of real-time and personal sampling techniques permitted us to identify a knowledge gap in terms of the need to better understand possible exposures in realworld environments (opening printer doors and covers, during post-processing tasks, etc.). This complementary sampling approach can be used in future workplace studies to better understand exposures when performing various printing and post-processing tasks. Understanding sources and magnitudes of exposures is a pre-requisite for development of control strategies to mitigate exposures. Within the environmental, safety and health community exposure mitigation strategies are organized into a hierarchy from most to least preferred: engineering controls (isolating workers from exposure sources), administrative controls (changes in work practices), and personal protective equipment (use of respirators, etc.). Though all levels were below OSHA and NIOSH exposure limits at the time of our sampling, future changes in work (use of different printers, filaments, etc.) at this facility or conditions at other workplaces may necessitate use of controls. Based on our task characterization, some examples of possible engineering controls include: installation of a carbon filtration system inside industrial-scale 3-D printers to remove vapors thereby, mitigating emissions and potential exposure when opening doors; use of a transparent material for the cover or as a viewing port and a small light to illuminate the print space in desktop FDM[™] 3-D

printers to facilitate checking on builds during machine operation; instillation of a particle and vapor filtration system inside desktop FDM[™] 3-D printers to mitigate emissions; and instillation of a properly operating standalone fume hood with sash designed for handling organic vapors for use during AVP and CVP.

Industrial-scale and desktop FDM[™] 3-D printers emitted ultrafine particles and organic vapors into a manufacturing facility. Emissions during printing and post-printing tasks resulted in worker exposure to various metals, acetone, and chloroform. Levels observed were below legally-enforceable exposure limits; however, the results indicate that exposures occurred during manufacturing even with a LEV system in place for a post-processing task. Characterization of tasks was useful for understanding factors that influenced emissions and exposures and to identify work processes to consider for implementation of new or improved control technologies. Additional research is needed to better understand emissions and potential exposures from workplaces using other AM technologies.



Figure 1-4. Emissions during fused deposition modeling 3-D printing and post-processing tasks: (a) particle number concentrations when industrial-scale 3-D printer doors were opened; (b) increases in TVOC concentrations when industrial-scale 3-D printer doors were opened; (c) increases in particle number concentration when desktop 3-D printer covers were removed (three measurements per filament color): 1-black ABS, 2- green PLA, 3- blue ABS, 4- red PLA, 5- light blue PLA; (d) TVOC concentrations during

acetone vapor polishing task: 1- worker drew 3- to 5-mL aliquots of acetone into a syringe and discharged the liquid onto an adsorbent material lining the chamber a total of five times, 2- worker sealed the ABS object in the chamber for 30 minutes, 3- opened the chamber, and 4- allowed the object to air dry (*data gap at 40 min is for the 3 min period when TVOC monitor was moved outside of room to exhaust side of the LEV fan); (e) TVOC concentration upstream (solid circles) and downstream (open triangles) of the LEV fan at the acetone vapor polishing station indicating that duct work was not properly sealed to the fan; (f) TVOC concentration during chloroform vapor polishing outdoors: 1- worker poured chloroform onto a brush, 2- brushed solvent onto the PLA object.

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Chapter 5:

Conclusions

Conclusions

Determinants of higher or lower UFP, TVOC, and ozone emissions from laser printers

Laser printers are ubiquitous in the modern, indoor environment and known to emit ultrafine particles and total volatile organic compounds of toxicological relevance. Understanding factors influencing emissions and the magnitude of their effect informs engineering strategies to reduce indoor ultrafine particle emissions from laser printers and future occupational exposure assessment studies on factors influencing laser printer emissions. This study tested the hypothesis, that copy rate and voltage would significantly influence (p < 0.05) ultrafine particle, total volatile organic compound, and ozone emissions from eight make-models of laser printers tested in an environmental chamber. A chamber study was performed to quantify ultrafine particle number, total volatile organic compound, and ozone emissions from eight make-models of laser printers. A mixed effects regression model was performed to determine if copy rate and voltage significantly influence laser printer emissions.

Copy rate significantly influenced (p < 0.05) UFP ERs and UFP concentration during printing. Copy rate parameter estimates were positive and significant (p < 0.05) for UFP ERs and UFP number concentrations during printing. The positive parameter estimates indicate that as copy rate increases the UFP ERs and UFP number concentrations during printing will increase. Voltage significantly influenced (p < 0.05) TVOC ERs, TVOC concentration during printing, TVOC concentration post-printing, and ozone concentration post-printing. Voltage parameter estimates were negative and significant (p < 0.05) for UFP concentrations post-print, TVOC ERs, TVOC concentrations during printing and TVOC concentrations post-printing. The negative

parameter estimates indicate that as voltage increases, UFP concentrations post-print, TVOC ERs, TVOC concentrations during printing, and TVOC concentrations postprinting decrease. The findings for voltage are contrary to expected results that higher voltage would lead to higher operating temperature leading to greater thermoplastic degradation of toner material and a subsequent increase in TVOC emissions. Voltage parameter estimates were positive and significant (p < 0.05) for ozone concentrations post-printing. The positive parameter estimates indicate that as voltage increases the ozone concentrations post-printing will increase.

Copy rate and voltage significantly influence the UFP, TVOC, and ozone emissions at the source. These factors should be considered in studies evaluating emissions from laser printers. Understanding factors influencing UFP, total VOC, and ozone emissions from laser printers, and the magnitude of their effect, informs control strategy efforts focused on reducing indoor contaminants emitted by laser printers. To better understand determinants of higher or lower emissions from laser printers, it is critical to understand device-specific factors (e.g. copy rate, voltage). Using statistical models to explore associations with exposure levels may lead to the discovery of previously unidentified emission factors and the magnitude of effect these factors have on exposure levels. Additional device-specific factors and consumables may influence laser printer emissions (e.g., temperature, toner type, paper type). These factors were not evaluated in this phase of the study. For phase two of the study, three printers have been selected (1) low UFP/VOC emitting printer (2) high UFP emitting printer and (3) high VOC emitting printer. In this phase, we will evaluate the effect of after-market and bio-based toner and recycled paper content on printer emissions.

Comparison of UFP emission rates calculated using the test method for hard copy devices and a one-box model

The test method for the determination of emissions from hardcopy devices is a standardized, widely accepted method for calculating emission rates from hardcopy devices (laser printers) in an environmental chamber. Determining whether ultrafine particle emission rates calculated using a one-box model are significantly different from ultrafine particle emission rates calculated with the test method for hardcopy devices provides insight to the benefits and/or limitations to each method and their application in chamber and workplace studies. This study tested the hypothesis, ultrafine particle number emission rates, calculated using the one-box model would not be significantly different (p < 0.05) from ultrafine particle number emission rates calculated with the test method for determination of emissions from hardcopy devices. A chamber study was performed to quantify ultrafine particle number emissions from eight make-models of laser printers. Emission rates were calculated from chamber data using the test method for hardcopy devices. A workplace exposure assessment was performed at a laser printer facility on two consecutive workdays. Emission rates were calculated from workplace data using a one-box model. Laboratory emission rates calculated using the test method for hardcopy devices and the one-box model and workplace emission rates calculated with the one-box model were compared using a Student's t-test (p < 0.05).

UFP emission rates using laboratory collected data calculated with TEAS software were significantly different (p < 0.0445) from UFP emission rates calculated with the test method for hardcopy devices. Workplace emission rates calculated with the one-box model were not significantly different from laboratory emission rates calculated with the one-box model. Further research should be performed to determine why emission rates

from each of the methods were significantly different and which methods is most appropriate for application in chamber and workplace studies. Workplace ultrafine particle data was collected at three area sampling locations over two consecutive work days, ideally, future work would include workplace exposure assessment data for multiple facilities over multiple workdays.

Exposures during industrial 3-D printing and post-processing tasks

3-D printer emissions have been evaluated in laboratory chamber studies, but have not yet been evaluated in the workplace and are limited to desktop-sized 3-D printers. Evaluation of personal exposure to metals, acetone, and chloroform during industrial 3-D printing informs future exposure assessment and epidemiology studies if personal exposures to metals, acetone, and chloroform are occurring during industrial 3-D printing and post-processing and the magnitude of exposure. This study tested the hypothesis, personal exposures to metals, acetone, and chloroform collected during industrial 3-D printing and post-processing tasks were above the respective occupational exposure limits. Area and personal air samples were collected for metals, ultrafine particles, and total volatile organic compounds at an industrial 3-D printing facility to determine if exposures are occurring above occupational exposure limits. Workplace activity was observed to identify unknown post-processing tasks.

For this study, personal exposure to aluminum, iron, acetone, and chloroform were below their respective occupational exposure limits. However, personal exposure to aluminum, iron, acetone, and chloroform is occurring during industrial 3-D printing and post-processing tasks. This is the first workplace exposure assessment to quantify personal exposures during industrial 3-D printing. Although exposures were below

occupational exposure limits, there is a need to further evaluate exposures during industrial 3-D printing and post-processing tasks to conclusively determine if exposures to industrial 3-D printing are hazardous to health. Additionally, this research identified materials used in industrial 3-D printing that have yet to be assessed in 3-D printing chamber or workplace studies. Future chamber studies should included assessment of polycarbonante and ultern filaments to characterize emissions potentially hazardous to health. This study is limited to industrial 3-D printing and post-processing tasks occurring at one industrial 3-D printing facility. Future work would benefit from having exposure data from multiple industrial 3-D printing facilities.

Future Research

Future research includes continued evaluation of laser printers in an environmental test chamber to assess the effect of toner type and paper type on UFP, TVOC, and ozone emissions. Chamber testing will continue to evaluate differences in FDM[™] and vat polymerization 3-D printing. Evaluation of 3-D printing filaments with additives (e.g., carbon nanotubes, graphene) will continue in chamber studies. Workplace exposure assessment at 3-D printing facilities will continue to assess emissions from FDM[™] and selective laser sintering 3-D printers.

Chapter 6:

Characterization of Chemical Contaminants Generated by a Desktop Fused Deposition Modeling 3-dimensional Printer
Characterization of Chemical Contaminants Generated by a Desktop Fused Deposition Modeling 3-dimensional Printer

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Abstract

Printing devices are known to emit chemicals into the indoor atmosphere. Understanding factors that influence release of chemical contaminants from printers is necessary to develop effective exposure assessment and control strategies. In this study, a desktop fused deposition modeling (FDM) 3-dimensional (3D) printer using acrylonitrile butadiene styrene (ABS) or polylactic acid (PLA) filaments and two monochrome laser printers were evaluated in a 0.5m³ chamber. During printing, chamber air was monitored for vapors using a real-time photoionization detector (results expressed as isobutylene equivalents) to measure total volatile organic compound (TVOC) concentrations, evacuated canisters to identify specific VOCs by off-line gas chromatography-mass spectrometry (GC-MS) analysis, and liquid bubblers to identify carbonyl compounds by GC-MS. Airborne particles were collected on filters for off-line analysis using scanning electron microscopy with an energy dispersive x-ray detector to identify elemental constituents. For 3-D printing, TVOC emission rates were influenced by a printer malfunction, filament type, and to a lesser extent, by filament color; however, rates were not influenced by the number of printer nozzles used or the manufacturer's provided cover. TVOC emission rates were significantly lower for the 3-D printer (49–3552µgh–1) compared to the laser printers (5782–7735µgh–1). A total of 14 VOCs were identified during 3-D printing that were not present during laser printing. 3-D printed objects continued to off-gas styrene, indicating potential for continued exposure after the print job is completed. Carbonyl reaction products were likely formed from emissions of the 3-D printer, including 4-oxopentanal. Ultrafine particles generated by the 3-D printer using ABS and a laser printer contained chromium. Consideration of the factors that influenced the release of chemical contaminants (including known and

suspected asthmagens such as styrene and 4-oxopentanal) from a FDM 3-D printer should be made when designing exposure assessment and control strategies.

Keywords: 3-D printing; asthma; indoor air; office equipment; volatile organic compounds

Introduction

Additive manufacturing (AM) is the process of joining materials using layer-uponlayer methodologies to make objects [1]. Although AM technologies have been used for decades in industrial settings, inexpensive desktop fused deposition modeling (FDM) 3dimensional (3-D) printers are becoming common in offices, libraries, schools, universities, and the home. With increased use of desktop and small-scale 3-D printers in non-industrial settings comes the concern for user health and safety [2].

In FDM printing, a solid thermoplastic filament is forced through a heated computer-controlled nozzle which melts the filament and deposits successive layers of plastic on a baseplate to form a solid 3-D shape. Thermoplastics are composed of a polymer that is mixed with a complex blend of materials known collectively as additives. As thermoplastics are heated, they undergo physical and chemical changes which can result in emission of gases and particulates [3–5].

Exposures to volatile organic compounds (VOCs) in indoor environments is of concern for workplaces, public venues, and private homes. Some VOCs are respiratory and mucous membrane irritants [2, 6] or allergic asthmagens [7, 8]. Ozone is a lung irritant and a reactive gas that may alter indoor air chemistry by interacting with unsaturated VOCs to form secondary organic aerosols and reactive products such as carbonyl compounds [9–11]. Carbonyl compounds such as aldehydes and ketones are associated with development of asthma [12, 13].

To properly evaluate exposures from FDM 3-D printers and design control technologies, there needs to be an understanding of factors that influence emissions. Table 1-6 summarizes several factors and their influence onemissionsfromFDM3-Dprinters [14–19]. Relevant factors include those of the printer itself and the properties

of the thermoplastic filaments. Generally speaking, most emphasis has been placed on particle emissions; however, many of these same factors could also influence chemical emissions but they are not yet fully understood. Hence, the purpose of this study was to better understand factors that influence generation of airborne chemical contaminants from a desktop FDM 3-D printer. Specifically, we investigated printer- (number of nozzles, malfunction, controls) and consumable-related (filament type, color) factors to address existing knowledge gaps.

Table 1-6. Factors influencing emissions from desktop fused deposition modeling 3-D printers.

	Emiss	ion type
Factor	Particulate	Chemical
Printer design		
Model	+	+
Age	+	?
Bed temperature	+	-
Nozzle temperature	+	-
Number of nozzles	±	?
Malfunction	+	?
Control technologies	+	?
Consumables		
Filament type	+	+
Filament color	+	+

Note. + = factor reported to influence emissions; - = factor reported to not influence emissions; $\pm =$ influence of factor on emissions unclear; ? = influence of factor on emissions is unknown.

Materials and Methods

Concentrations of airborne contaminants released from the printers were evaluated in a 0.5 m³ stainless steel chamber. A two-piece high efficiency particulate filter and activated carbon filter was attached to the chamber inlet to remove particles and organic chemicals from the room air prior to entering the chamber. This chamber has multiple sampling ports on the top connected to stainless steel sampling tubes that extend into the chamber to collect air from the center of the chamber. Conductive carbon tubing and stainless steel tubing without sharp bends were used for sampling; tubing lengths were less than 1 m to minimize particle line losses [20]. The inlets of the sampling probes were placed approximately 10 cm from the printer for all trials. An upward air flow was generated through a perforated floor in the chamber, which in studies with titanium dioxide aerosols, when sampling at multiple locations in the chamber, reduced areas of stagnant air in the chamber and yielded relatively uniform contaminant concentrations, thereby minimizing bias relative to sampling positions [21]. A vacuum leak test demonstrated that the leak rate was 0.05L min–1 or~0.2% of the 25L min–1 airflow through the chamber. The total sampling air flow rate of all instruments during sampling was 25Lmin–1 which provided a chamber air change rate of 3.0h–1 which is recommended for studies of office equipment [22]. A carbon dioxide air exchange rate test was not performed because the chamber has negligible leakage, therefore the air exchange rate is equivalent to the air sampling flow rate. For more details on the experimental setup see Yi et al. [19].

Concentrations of airborne contaminants were measured while printing a hair comb (100 mm× 33 mm× 3 mm) with a desktop FDM 3-D printer (MakerBot 2x, MakerBot, Brooklyn, NY) using acrylonitrile butadiene styrene (ABS) or polylactic acid (PLA) filaments. All tests were performed with the manufacturer-provided cover on the printer except where noted. Four colors of ABS filament (natural, blue, red, and black) and four colors of PLA filament (true red, army green, ocean blue, and transparent blue) were evaluated — see Figure S1 in the Supporting Information file for images of these colors. The time to print each comb was about 14 min. Only one 3-D printer nozzle was needed to print a hair comb. To evaluate the influence of using two printer nozzles, we printed a traffic cone (40mm × 40mm × 50mm) using red and blue ABS, which took

about 34 min. The manufacturer's recommended printer settings for ABS were: extruder temperature = 230° C and baseplate temperature = 110° C; while for PLA, extruder temperature = 215° C and base plate heater was off. For comparison, we measured chamber air while printing with previously used laser printers (Laserjet P2055dn and Laserjet HP2600, Hewlett Packard, Palo Alto, CA). New manufacturer-specified toner cartridges were installed in each device prior to printing a standard 5% coverage standard pattern [22,23] on 216 mm × 279 mm white paper having weight 75 g/m2 (Office Depot, Boca Raton, FL). The print durations were 0.5– 2.4 min for 10 and 80 pages, respectively, with HP2055dn, 1.5 and 9.7 min for 10 and 80 pages, respectively, with HP20500.

Conditions inside the chamber (temperature, humidity, printer to chamber volume ratio, etc.) and our testing procedure followed RAL-UZ-171: Test Method for the Determination of Emissions from Hardcopy Devices [23]. For testing the 3-D printer, the start of the operating phase was defined as the time the print command was sent to the 3-D printer. Air inside the chamber was monitored during the pre-operating phase (~1 hr), printing phase, and post-operating phase using a suite of complementary real-time and time-integrated sampling techniques. During the pre-operating phase, the chamber was flushed with filtered air while the printer was on but not printing. During this phase, for the 3-D printer only, the nozzle and/or base plate were heated to their set temperatures (no thermoplastic was extruded). No appreciable rise in VOC or particle concentration occurred in the pre-operating phase during the nozzle and baseplate heating. For all tests, temperature inside the chamber during printing was 21.0 \pm 1.0°C and the relative humidity was 51.4 \pm 4.4%. The post-operating phase began when the

print job ended (all printers on; 3-D base plate and nozzle cooling) and lasted for three air changes.

Chamber air monitoring

Total VOC (TVOC) concentration in the chamber was measured using a realtime photo-ionization detector with 10.6 eV ultraviolet discharge lamp (Model 3000 ppbRAE, RAE Systems, San Jose, CA) during all phases to calculate units specific emission rates (SERu). This instrument was factory calibrated using isobutylene and span checked with isobutylene prior to use and is capable of measuring down to 1 ppb or 2.3 µgm –3 isobutylene equivalent. Ozone concentration was monitored using a realtime gas sensitive semiconductor sensor (Model S500, Ozone Solutions, Hull, IA) during all phases. The limit of detection for this monitor is $0.5 \mu gm - 3$. For determination of TVOC and ozone SERu, two replicate 3-D printer tests were performed and one test was performed for each laser printer. Samples for specific VOCs were collected using whole air 6 L Silonite R®-coated canisters (Entech Instruments, Inc., Simi Valley, CA) followed by off-line analysis by gas chromatography-mass spectrometry (GC-MS) as described in the Supporting Information file. Canister samples are suitable for analyzing a range of VOCs (e.g., from alcohols to terpenes) at low levels in indoor atmospheres [24]. Two canister samples were collected during each printing test, one during the preoperating phase and the other at the mid-point of the printing phase. Collection took a period of about 1–2 min per sample. Two to five replicate tests (covering both the preand post-operating phases) were performed for the 3-D and laser printers. Samples for gas-phase carbonyls were obtained by pulling air from the test chamber using a calibrated (Model 4146, TSI Inc., Shorview, MN) pump (URG 3000-02Q, Chapel Hill,

NC) at 4.0 L min⁻¹ into 25 mL of deionized water in a 60 mL Teflon bubbler (Savillex, Eden Prairie, MN) during the pre-operating phase and again during the printing and post-operating phases. Samples were derivatized and analyzed using GC-MS (see Supporting Information file). Bubbler sampling followed by derivatization is a wellestablished method for measurement of low levels of carbonyls in indoor atmospheres [25–27]. For identification of carbonyls, two tests (covering both the pre- and postoperating phases) were performed for the 3-D and laser printers.

Aerosol particles were collected on 47-mm tracketched polycarbonate filters with 2 µm pore size using a stainless-steel in line filter holder and pre-calibrated sampling pump (GilAir, Sensidyne, St. Petersburg, FL) with flow rates et to 3L min–1 during the pre-operating phase and again during the printing phase. Collection efficiency of this type of filter ranges from 20–94% for 0.10–1 µm size particles [28]. A section was cut from each filter, sputter coated with gold/palladium to enhance conductivity and imaged using field emission scanning electron microscopy (S-4800, Hitachi, Tokyo, Japan) with energy dispersive x-ray analysis (EDX, Quantax, Bruker Scientific Instruments, Berlin, Germany)to identify elemental constituents. The balance of the 25 L min–1 chamber air flow rate was accounted for by real-time particle monitors (see Supporting Information file).

Emissions from stock and printed thermoplastics

To evaluate potential for off-gassing, stock natural color ABS filament and printed 3-D combs made of natural color ABS were placed in a 375-mL glass chamber with an air exchange rate of 0.96 h-1. The glass chamber was notallowedtoequilibrate.Two450-mLfused-silicalined canisters equipped with capillary flow controllers were used to

sample the chamber effluent at 0.48mLmin-1 for 6 hr. Samples were pressurized to 1.5 times atmospheric pressure and analyzed using a pre-concentrator/GC-MS system (see Supporting Information file). Emission rates were calculated from the measured concentration, air exchange rate, and volume of the chamber.

Data analysis

Unit specific emission rates (SERu) were calculated from the TVOC and ozone data for the 3-D and laser printers in accordance with RAL-UZ-171[23] (see Supporting Information for details). Comparison of SERu between3D and laser printers is considered appropriate because: (1) both technologies use a thermoplastic feedstock (filament or toner powder); (2) both devices are used in indoor workspaces; (3) values of SERu are normalized to time which accounted for differences in printing duration among devices; and (4) in the absence of real-world data, chamber measurements, and comparison of emissions based on modeling is the method of choice for investigating factors that may influence emissions. The identities of airborne VOCs in the chamber were determined using whole-air canister samplers from 2–5 replicates tests.

One-way analysis of variance (ANOVA) models were fit in JMP (version 11.2.0, SAS Institute, Inc., Cary, NC) to investigate the impact of the fixed effects of color and filament on 3-D printer TVOC SERu and specific VOC concentration results. Tukey's test option was specified for multiple comparisons among colors within a filament type and Student's t-test was used to compare the effect of color between filament types. ANOVA F-statistics were used to note the overall differences in the means of colors within the filament types while Tukey's test was used to identify specific paired differences. For all comparisons, the significance level was set at 0.05. Note that

emission rates were not calculated for individual VOCs from the canister samples because these results are only concentration measurements at a point in time during the print phase.

Results and Discussion

TVOC Emission Rates

For the 3-D printer, the calculated TVOC SERu values were consistently higher for ABS filament compared to PLA (see Table 2-6). Azimi et al. also reported higher TVOC SERu values for ABS compared to PLA [14]. However, it is important to note that while the trend of SERu for ABS being higher than PLA is consistent between these studies, the absolute SERu values cannot be compared because we used a real-time monitor to measure TVOC concentration and Azimi et al. summed the concentrations of individual VOCs they quantified by GC-MS. In contrast to these results, Steinle, who calculated TVOC emission rates from individual GC-MS data, reported that SERu was higher for PLA compared to ABS.[17] Looking at similar colors of these filament types, the calculated TVOC SERu was significantly higher (p < 0.05) for blue ABS (2385 ± 82 µg h–1) compared to transparent blue PLA (131±37 µg h–1); TVOC levels were below the limit of detection for ocean blue PLA. SERu for red ABS (2383 ± 357 µg h–1) was significantly higher compared to true red PLA (49 µg h–1); p < 0.05.

Printer	Thermoplastic	Replicates	Cover	SERµ (µg h ⁻¹)
3-D	ABS natural	2 combs	On	3552 ± 549
3-D	ABS natural	1 comb	Off	3430
3-D	ABS natural	1 comb	Off	6454
		[malfunction]		
3-D	ABS blue	2 combs	On	2385 ± 82
3-D	ABS red	2 combs	On	2383 ± 357
3-D	ABS black	2 combs	On	1085 ± 217
3-D	PLA ocean blue	2 combs	On	ND
3-D	PLA transparent	2 combs	On	131 ± 37
	blue			
3-D	PLA true red	2 combs	On	ND - 49
3-D	PLA army green	2 combs	On	ND - 51
HP2055dn	Monochrome toner	80 pages @ 5%	N/A	5782
HP2600	Monochrome toner	80 pages @ 5%	N/A	7735

Table 2-6. Average ± st	andard deviation of	of TVOC SER	µ values for 3	-D and laser	printers

Note. N/A = not applicable for laser printers, ND = not detected using real-time TVOC instrument, ABS = acrylonitrile butadiene styrene, PLA = polylactic acid.

Within a given type of filament, color had a minor influence on TVOC SERu for ABS only, i.e., SERu for natural color ABS was significantly higher than black ABS (p < 0.05). There were no statistical difference among PLA filament colors. Kim et al. used the same type of real-time TVOC PID monitor as in our study and reported that levels were non-detectable when printing with two different PLA filaments [15]. In our study, some tests with ocean blue, army green and true red PLA yielded TVOC concentrations below the instrument limit of detection. Interestingly, in our study the laser printers that consumed powdered toner had significantly higher TVOC SERu values than the FDM 3-D printer. However, it is important to note that presently there is insufficient toxicological data available to compare 3-D and laser printers on an absolute scale, i.e., higher emission rates by one device does not necessarily imply greater hazard.

To evaluate whether printing with two nozzles vs. one nozzle influenced emissions, real-time TVOC data were used to calculate yield, which accounts for differences in the mass of filament extruded during these print jobs. When printing with two nozzles to make a traffic cone, the average yield was $328\pm41 \ \mu g \ TVOC \ g-1$ printed filament. Average yield values from printing with one nozzle to make a hair combwere: 229±64 \mu g TVOC g-1 printed filament (red comb), and $383 \pm 16 \ \mu g \ TVOC \ g-1$ printed filament (blue comb). Hence, the number of nozzles used for 3-D printing these objects with ABS filaments did not appear to influence TVOC emissions.

As summarized in Table 2-6, use of the manufacturer provided cover for the 3-D printer did not reduce TVOC SERu when we printed with natural color ABS; SERu were 3430 μ g h-1 (cover off) vs. 3552 ± 549 μ g h-1 (cover on). During a subsequent 3-D print job using natural color ABS with the cover off, there was a malfunction (object did not fully adhere to baseplate) and we continued to sample the chamber air. During thismalfunction, the calculated SERu was 6454 μ g h-1, which appears higher than when the printer was operating normally for the same type and color of filament. The printer malfunction was a random event which makes it difficult to reproduce to collect additional data and some caution is needed in generalizing our observation from this single event. Among all print jobs, the TVOC SERu followed the rank order: HP2600 (80 pages) > HP2055dn (80 pages) > 3-D printing with ABS or PLA.

Ozone emission rates

Figure 1-6 is plots of ozone concentration in the chamber for the 3-D and laser printers; for simplicity, only one representative plot is shown per 3-D printer filament type. For natural color ABS, the background ozone concentration in the chamber was steady initially but began to decrease until reaching a minimum during the printing phase before slowly returning to background (Figure 1-6a). The decrease in ozone concentration was more pronounced when the cover of the 3-D printer was taken off.

The time at which the ozone concentration began to decrease corresponded to the start of the 7-min period during which the baseplate was heated from ambient to 110°C. In contrast, for true red PLA the background ozone concentration was relatively constant throughout the pre-operating (baseplate heater off) and printing phases (Figure 1-6b).

Both laser printers generated ozone (Figures 1-6c and 1-6d). For the HP2055dn, when the print job was initiated (print command sent to device) the SERu for ozone was 0.5 μ g hr-1 but began to decay rapidly to below background during the print job (80 pages) and slowly recovered to background thereafter. For the HP2600 printer, the rise in ozone concentration (SERu = 0.2 μ g hr-1) corresponded to the output of the first page but decayed during the remainder of the 80 page print job to below background. Calculated SERu for ozone from the laser printers were quite low compared to previously published studies and may reflect improvements in technology relative to older studies [10,11,29].

Identification of carbonyl compounds

For both 3-D and laser printing, the organic compounds generated during operation may transform in the presence of ozone. Ozone can add to the carbon-carbon double bonds of airborne compounds (such as limonene) resulting in oxygenated species (i.e., aldehydes, ketones, carboxylic acids, etc.) [9–11]. These reactions can occur on a few second to few minute timescale which implies that printer generated compounds can be oxidized before they are removed by building air exchange. Several carbonyl compounds were qualitatively identified from samples collected during the print and post-print phases for all the 3-D and laser printers investigated. An example chromatogramfor 4-oxopentanal formed during 3-D printing is provided as Figure 2-6.

As seen, the signal intensity is higher than background during the printing and postprinting phases indicating that 4-oxopentanalwas formed by the printing process. An example of a mass spectrum for derivatized 4-oxopentanal is provided as Figure S2 in the Supporting Information. While the generation of these carbonyl compounds are not fully understood, they could be the result of intentional chemical reactions of the printing process and/or unintentional ozonolysis of alkene (carbon-carbon double bond) compounds from the printers (TVOC concentrations increased during all printing jobs as shown in Figure 1-6) or carbonaceous particulate matter. For the 3-D printer using ABS and PLA, regardless of color, we identified 4-oxopentanal, glyoxal, methyl glyoxal, and benzaldehyde. In addition, five other unidentified carbonyl compounds were detected when using ABS filaments. The carbonyl compounds identified during laser printing included: glyoxal, methyl glyoxal, m-tolualdehyde, and 4-oxopentanal. To our knowledge, these results are the first report of 4-oxopentanal being formed as a result of chemicals being released fromprinting systems. Exposure to 4-oxopentanal could potentially result in respiratory health effects [12,30–32]. Additional work is planned for future investigations to quantify 4-oxopentanal levels to more completely characterize oxidation reactions from printing.



Figure 1-6. Ozone concentrations for (a) 3-D printer using natural ABS with the printer cover on and off, (b) 3-D printer using true red PLA, (c) HP2055dn laser printer using monochrome toner (80 pages), and (d) HP 2600 laser printer using monochrome (80 pages) toner. Numbers for each vertical line denote 0 = begin baseplate heating (ABS only), 1 = begin print job, and 2 = end print job.



Figure 2-6. Chromatograms of the three peaks for TBOX-derivatized 4-oxopentanal **from** samples collected during background-, printing-, and post-printing phases – derivatization of non-symmetric carbonyls using TBOX typically results in multiple chromatographic peaks due to geometric isomers of the oximes.

Identification of individual VOCs

Table 3-6 summarizes the background (pre-operating phase)-corrected concentrations of individual VOCs detected in chamber air during FDM 3-D printing. Although 2–5 replicate tests (covering both the pre- and post-operating phases) were performed for the 3-D and laser printers, not all VOCs were identified in all samples. As such, when results are presented as an average in the table, the data represent at least two independent canister samples. Up to 13 different VOCs were above our analytical detection limits for ABS compared to a maximum of 9 for PLA. Four VOCs were common to both filament types: acetaldehyde, ethanol, acetone, and isopropyl alcohol. Concentrations of acetaldehyde for blue ABS were significantly higher than both blue PLA filaments and the same was true for red ABS relative to red PLA (p < 0.05). There were no differences in ethanol concentrations between filament types for blue and red colors. Acetone concentrations for blue ABS were higher than for blue PLA filaments (p < 0.05); however, the concentrations for red ABS and true red PLA were similar. Isopropyl alcohol concentrations did not differ between blue ABS and blue PLA filaments though concentrations from red ABS were significantly lower than from true red PLA (p < 0.05). Note that the data presented in Table 3-6 are for a point in time during printing and are not the same as the emission rates calculated from the real-time TVOC data. Individual VOCs may be emitted at different times throughout the print process [10]. Hence, depending on when certain VOCs are emitted during printing and the timing of the canister sample collection, the reported concentrations in Table 3-6 may or may not reflect the highest concentrations in the chamber during printing, but were recorded by the PID and accounted for in the SERu calculations.

Table 3-6. Average \pm standard deviation of background-corrected concentrations of individual VOCs measured by whole-air sampling with canisters during 3-D printing (µg m⁻³).

		A	BS			PL	A	
VOC	Natural	Blue	Red	Black	True red	Army green	Ocean blue	Trans blue
Acetaldehyde	16.3±10.1	13.7±8.5	7.7±0.4	11.1±2.2	3.6±1.4	5.5±3.7	5.0±2.0	5.0±0.6
Ethanol	57.3±32.4	67.2	39.9	63.1	103.3±5.6	85.0±79.1	55.5±22.1	73.0±77.1
Acetonitrile	0.6			2.7	5.4±1.9	0.4	0.4±0.2	1.0±1.3
Acetone	15.0±7.9	62.4±12.0	31.5	45.3±2.3	27.0±18.7	31.8±1.0	7.2±2.7	3.5±0.9
Isopropyl alc.	87.2±83.8	47.7	108.1	213.0	552.3±66.9	1582.8	278.3±3.4	99.4±44.6
n-Hexane		1.8±1.2	0.8	3.1	0.2±0.0	1.3	0.3	1.9±2.0
Chloroform		1.4	0.4	1.2	1.0	0.3	0.6	0.7±0.5
Benzene	0.2	1.5						1.8
Toluene		1.4±1.5				1.9	1.1	
Ethylbenzene	4.7	7.3±1.0	6.6±0.6					
m,p-Xylene	0.2	3.1±2.1	3.0	1.8				
Styrene	252.1±128.7	212.1±9.9	237.1±62.9	100.5±11.7				
o-Xylene		1.6±0.0		1.9				
D-I imonene								

Note. Empty cell = compound not detected or present at level less than background (pre-operating phase), ABS = acrylonitrile butadiene styrene, PLA = polylactic acid.

Of the six VOCs measured during 3-D printing with each color of ABS filaments, only acetone concentrations differed significantly (blue was higher compared to natural, red and black; p < 0.05). Seven VOCs were common to all colors of PLA filaments. The concentrations of acetone for true red and army green colors were significantly higher than either blue color (p < 0.05). Concentrations of isopropyl alcohol followed the rank order army green> true red> ocean blue> transparent blue (p < 0.05). Concentrations of acetone true red> ocean blue> transparent blue (p < 0.05). Concentrations of acetone true red> ocean blue> transparent blue (p < 0.05). Concentrations of acetone true red> ocean blue> transparent blue (p < 0.05). Concentrations of acetone true red> ocean blue> transparent blue (p < 0.05). Concentrations of acetaldehyde, ethanol, acetonitrile, hexane, and chloroform were similar. Based on the data presented in Table 3-6, filament type appears to have more influence on the identities of VOCs detected in chamber air than does color. According to the manufacturer's safety data sheet for the filaments, ABS is >98% acrylonitrile butadiene styrene co-polymer and < 0.1% styrene whereas PLA is >98% polylactide resin; however, no other specific information on ingredients is provided. Hence, the observed

difference in identified VOCs between polymer types likely reflects differences in the basic ABS and PLA ingredients used to make the polymers.

With regard to the use of the manufacturer provided cover, the same VOCs were detected while 3-D printing with natural color ABS whether the cover was on or off. Concentrations of VOCs measured with the cover on and off were generally similar, except for the following which appeared to increase (cover on vs. cover off): isopropyl alcohol (87 vs. 297 μ g m-3), ethylbenzene (5 vs. 21 μ g m-3), and styrene (250 vs. 396 μ gm-3).Hence, the loose fitting cover provided by the manufacturer did not control vapors generated during printing.

The generation of VOCs from 3-D printers is consistent with the decomposition of thermoplastic filament when it is heated by the extruder nozzle. Most of the chemical compounds detected during operation of the 3-D printer have been identified as pollutants released from various models of laser printers.[33–37] Our data is consistent with reports that 3-D printing with various ABS filaments releases toluene, ethylbenzene, styrene, and acetophenone and that printing with PLA generates low amounts of toluene [14,15,17]. We note that others have identified caprolactam, lactide, decane, cyclohexanol, methyl methacrylate, n-butanol, and other VOCs during 3-D printing with ABS or PLA filaments [14,17] although these compounds were not observed in our study. There may be several reasons for the observed differences in VOCs identified among studies such as the composition of the polymer filament, printer extrusion temperatures, and sampling methods used by investigators. Future studies would benefit from standardized emissions testing protocols.

Table 4-6 summarizes the concentrations of individual VOCs detected during laser printing. Repeat samples were collected for each combination of printer and number of printed pages; however, several VOCs were identified in only one test which precluded statistical comparison of the data. For the HP2055dn printer, concentrations of seven VOCs increased from 10 pages to 80 pages. For the HP2600 printer, concentrations of acetaldehyde, isopropyl alcohol, and d-limonene increased from 10 pages to 80 pages; however, concentrations of toluene and m, p-xylene did not increase with the number of printed pages.

Table 4-6. Average \pm standard deviation of background-corrected concentrations of individual VOCs measured by Whole-air sampling with canisters during laser printing (µg m⁻³).

	HP2055dn laser		HP2600 laser	
	10 pages	80 pages	10 pages	80 pages
VOC				
Acetaldehyde	2.0	20.5	6.8	27.2
Ethanol	24.3	38.7±45.9	53.6±15.6	
Acetonitrile	0.1	2.1	0.2	
Acetone		5.1		
Isopropyl alc.	38.6	113.2	204.6	272.1
n-Hexane	3.8	0.3	1.4±0.8	
Chloroform		0.3		3.1
Benzene		3.2±0.8	1.0	
Toluene		16.5±20.7	26.8	0.3
Ethylbenzene		87.5	4.0	
m,p-Xylene	0.3	34.7	7.9	2.5
Styrene	4.4	8.1		4.4
o-Xylene	0.3	26.9±36.5	1.3	
D-Limonene		26.6	7.1	15.5

Note. Empty cell = compound not detected or present at levels less than background (pre-operating phase).

Comparison of Tables 3-6 and 4-6 indicates that 3-D and laser printers generated numerous VOCs during operation, some of which are common to both technologies and others that are unique to one or the other. D-limonene was detected during most laser printing jobs but not with 3-D printing. In the presence of ozone, this compound may form oxidation products that are airway irritants [9]. Acetone was detected in all 3-D printing samples but in only one laser printing sample. Benzene, toluene, ethylbenzene, and xylenes were detected during most laser printing jobs but only detected in a few samples during 3-D printing with PLA filament. Variations in identities of specific VOCs among printing devices are likely due to differences in thermoplastic composition and decomposition temperatures (200-230°C for the 3-Dprinter, compared to about 170°Cfor the laser printers) as well as other factors, not all of which completely understood at this time. Combustion, injection molding, extrusion, and recycling of ABS thermoplastics is known to emit benzene, benzaldehyde, ethylbenzene, ethylmethyl benzene, toluene, styrene, acetophenone, and m, p-xylene, o-xylene, and benzaldehyde [4,38,39]. Consistent with the generation of organic chemicals from thermal degradation, we identified all of these compounds in chamber air during printing with ABS filaments. Note that some of the compounds identified in chamber air during 3-D and laser printing are associated with asthma. For example, styrene, [7] and carbonyl compounds including 4- oxopentanal are known or suspected immune-mediated asthmagens [8,12,13,30–32]. Further, ozone is known to transform styrene and unsaturated VOCs such as d-limonene into secondary organic aerosols [6,11].

Various compounds that were not in our calibration mixture were identified in chamber air during FDM 3-D and/or laser printing (Figure S3). A total of 33 different compounds were identified by spectral matching in at least two samples per tested device. Distinct differences existed between print technologies—14 compounds were identified during 3-D printing but not laser printing.

Elemental composition of airborne particulate

Particles released from the 3-D and laser printers differed in morphology and size (no particles were observed during inspection of filter samples collected during the preoperating phases). 3-D printer aerosol were generally clusters of nanoscale particles or discrete nanoscale particles (Figures S4 and S5) whereas for laser printers the particles were micron-scale (Figure S6). For ABS, the following elements were detected: Cr, Ni, Si, Cl, Ca, Mg, Na, Al, and S. In general, the relative abundance of Cr was greater than any other element for particles collected during printing with natural, blue, and red ABS colors. Particles generated during 3-D printing with PLA contained Fe. Steinle reported that a nanoscale particle collected during 3-D printing (filament type not specified) contained Fe, though the presence of transition metals was not reported in that study [17]. Particles emitted from laser printers contained Cr and/or S. Previous studies have reported that particles emitted from laser printers using monochrome toner contained all of these same elements identified in 3-D printer particles at levels less than 2% [34,37,40–43]. In those studies, the presence of Ca was attributed to CaCO3 coating on paper while Fe was attributed to iron oxide (used to make toner) and Cr, Na, Si, and S were attributed to pigments and additives [34,40,41]. Given that Fe is used tomake powdered toner, its presence in 3-D printer filaments may reflect a basic composition of thermoplastics in general. The reason for the presence of transition metals in 3-D printer emitted particles is unknown (there is no mention of these metals on the safety data sheets), though based on characterization of laser printer emissions, they could be used as pigments and additives.

The focus of the present study was on chemical contaminants generated by FDM 3-D printers; however, many types ultrafine particles (UFP, d<100 nm) can cause strong

inflammatory responses and a variety of cardiovascular effects [44–46]. We previously reported on particle emission rates (PER) for this 3-D-printer [19]. For completeness, in the present study we determined PER from the laser printers using the same methods. Table 5-6 summarizes the particle sizes and number-based PERs for the laser printers (this study) and the 3-D printer [19]. Emitted particle sizes differed significantly and followed the rank order (from largest to smallest): HP2600 (80 pages) > HP2055dn (80 pages) all colors of ABS and PLA filaments. The average number-based PER (# min-1) followed the rank order (from highest to lowest): HP2055dn (80 pages) > 3-D printer (all colors of ABS and PLA filaments) > HP2600 (80 pages); differences were significant. He et al. reported PER based on SMPS measurements for a series of laser printers [29,47]. In their first study of 3 monochrome printers, PER ranged from 4 x 107 to 7.6 x 10^{10} # min-1. In their subsequent more extensive study of 15 monochrome laser printers, all but one printer emitted more than 10¹⁰ # min-1 and were categorized as "high emitters." Comparing our data in Table 5-6 to that of He et al., the number-based PER of many laser printers can exceed those of a desktop 3-D printer. [29] Note that the elemental composition of particles that was presented in the Supporting Information file was qualitative in nature (i.e., particle number concentration was not quantified from counts of particles on filters and sample collection volumes), as such, the emission rates determined from the non-specific real-time instruments may not correspond to emission rates of some identified constituent metals. Finally, the number-based PER for particles measured using an optical particle counter (>0.65 µm) and mass-based PER values are provided in Supporting Information Table S1.

Printer	Consumable	Print job	Avg. GMª (nm)	SMPS (# < 0.66 µm min⁻¹)
HP2055dn	Monochrome toner	80 pages @ 5%	39.6	7.1±0.7 x 10 ¹⁰
HP2600	Monochrome toner	80 pages @ 5%	168.3	9.8 x 10 ⁷
3-D	ABS natural	3 combs	53.7	1.6±0.0 x 10 ¹⁰
	ABS blue	2 combs	63.1	7.5±1.0 x 10 ⁹
	ABS red	2 combs	49.9	1.4±0.3 x 10 ¹⁰
	ABS black	2 combs	45.3	1.0±0.2 x 10 ¹⁰
	PLA true red	4 combs	36.4	1.3±0.5 x 10 ¹⁰
	PLA army green	4 combs	36.1	1.3±0.2 x 10 ¹⁰
	PLA ocean blue	4 combs	36.5	1.1±0.7 x 10 ¹⁰
	PLA transparent blue	4 combs	37.7	1.6±0.2 x 10 ¹⁰

Table 5-6. Average geometric mean (GM) particle size and average \pm standard deviation particle emission rates (PER) for 3-D and laser printers.

^aMobility diameter from electrical low-pressure impactor (ELPI) measurements. ^bScanning mobility particle sizer (SMPS) data from Yi et al. (2016) ABS = acrylonitrile butadiene styrene, PLA = polylactic acid.

Implications for exposure to vapor-phase pollutants

Based on our data, exposure may occur during preprinting (e.g., handling stock filaments), printing, and post-printing (e.g., processing printed objects) tasks. From the glass chamber tests, stock ABS filament emitted 1.7 ng acetaldehyde g-1 h-1 (ng VOC per gram comb per hour) and 9.6 ng styrene g-1 h-1. ABS filament is sold in 1 kg spools; using our measured emission rates, if a 3 m3 closet without ventilation is used to store 50 spools, and a worker enters mid-shift (after 4 hours), the concentrations of acetaldehyde and styrene in the closet would be about 110 and 640 μ g m-3, respectively. During printing, TVOC SERu ranged from 1085–3550 μ g hr–1 for ABS filaments and from 50–130 μ g hr–1 for PLA filaments (Table 2-6).Hence, for an 8-hr shift, the TVOC concentrations in a 40m3 room without ventilation (typical of what we have observed in prototyping workplaces) where a single printer is operating would range from215–710 μ gm–3 (ABS) to 10–26 μ g m–3 (PLA). In our experiences, up to 10 printers have been observed to be operating simultaneously in a 40 m3 room, indicating exposures could reasonably be 7100 μ g m–3 (ABS) to 260 μ g m–3 (PLA). Once

printed, objects continue to off-gas VOCs. From the glass chamber tests, a printed ABS comb emitted 4.4–7.4 ng acetaldehyde g-1 h-1 and 5.1–5.9 ng styrene g-1 h-1.

Using the average mass of a 3-D printed ABS comb, 3.7 g from Yi et al.,[19] if a storage room (12 m3) without ventilation is used to store 1,000 combs (e.g., before packaging or shipment) and a worker enters the room mid-shift (after 4 hr), the concentrations of acetaldehyde and styrene in the room would be about 5–9 and 6–7 µg m-3, respectively. Note that these scenarios represent "worst case" situations in that we do not account for contaminant decay from air exchange or losses to walls, etc. in the rooms. Stephens et al. estimated that the combined effect of these factors may lower contaminant concentrations by 30–50%,[1] indicating exposures would occur regardless. The current Threshold Limit Value (TLV R _), a non-regulatory guidance limit, for acetaldehyde, expressed as a ceiling value (no full-shift time weighted TLV available), is 11 mg m-3. The full-shift time-weighted average TLV for styrene is 85 mg m-3 and the NIOSH Recommended Exposure Limit (REL), a non-regulatory level, is 215 mg m-3. These data indicate that low-level exposures to VOCs may occur during all steps of FDM processes (i.e., procurement/handling of feedstock, printing, and postprinting) in work environments, although the relative contributions differ among steps. Note that TLVs and RELs are not indoor air quality levels intended to protect the general public in the home environment (i.e., 24 hr per day). No standard exists for these compounds in home environments, as such, it is prudent to consider mitigating exposures when using FDM 3-D printers in the home.

Conclusions

Several printer- (number of nozzles, malfunction, controls) and consumablerelated (filament type, color) factors were evaluated to understand their influence on

chemicals generated by a desktop FDM 3-D printer. Results of our experiments indicate that TVOC emission rates from this 3-D printer were influenced by a printer malfunction, filament type, and to a lesser extent, by filament color. TVOC emission rates were not influenced by the number of printer nozzles used or the manufacturer's provided cover. Of interest is the observation that 14 different VOCs were identified during 3-D printing that were not present during laser printing. Further, carbonyl reaction products were likely formed from emissions of the 3-D printer, including 4-oxopentanal. 3-D printed objects continued to off-gas styrene, indicating potential for continued exposure after the print job is completed. Ultrafine particles generated by the 3-D printer using ABS and a laser printer contained chromium, a known toxicant. Our results indicate that both printer and consumable-related factors influenced the release of chemical contaminants from a FDM3-D printer and that understanding these factors can help to better design exposure assessment and control strategies.

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Disclaimer

Mention of a specific product or company does not constitute endorsement by the Centers for Disease Control and Prevention. The findings and conclusions in this article are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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Appendices

Appendix A: List of Abbreviations and Symbols

VOC	Volatile Organic Compound
SVOC	Semi-volatile Organic Compound
UFP	Ultrafine particle
ABS	Acrylonitrile Butadiene Styrene
PLA	Polylactic Acid
NISOH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
OEL	Occupational Exposure Limit
REL	Recommended Exposure Limit
ER	Emission Rate
PER	Particle Emission Rate
SER	Specific Emission Rate
GM	Geometric mean
PM 10	Particulate matter < 10 micrometers
PM _{2.5}	Particulate matter < 2.5 micrometers
nm	Nanometers
μm	Micrometers
μg	Micrograms

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Appendix D: Chapter 2 Supporting Information

Emission Rate Equations

Test Method for the Determination of Emissions from Hardcopy Devices within the Award of the Blue Angel Ecolabel for Equipment with Printing Function according to RAL-UZ-171

Particle Number

Particle Loss Coefficient β:

$$\beta = \frac{\ln(c_1/c_2)}{t_2 - t_1}$$

The value pairs c_1 , t_1 and c_2 , t_2 should be read from the smoothed time-dependent curve of particle number concentration as accurately as possible or determined by means of a cursor. On a logarithmic scale, t_1 should be chosen within the linear descending range at least 5 minutes after the end of the print phase and t_2 at least 25 minutes after t_1 .

TP Calculation:

$$TP = V_c \left(\frac{\Delta C_p}{t_{stop} - t_{start}} + \beta \cdot C_{av}\right) (t_{stop} - t_{start})$$

 ΔC_p : difference of $C_p(t)$ between t_{start} and t_{stop} , [cm⁻³]

 C_{av} : arithmetic average of $C_p(t)$ between t_{start} and t_{stop} , [cm⁻³]

V_c: test chamber volume [cm³]

 β : particle loss coefficient [s⁻¹]

t_{stop} – t_{start}: emission time [s]

Volatile Organic Compounds

Pre-Operating Phase:

$$SER_B = c_B * n_b * V_K$$

 $c_B = \frac{m_{VOCB}}{V_P}$

CB:	VOC concentration [µgm ⁻³] during the pre-operating phase
SER _B :	VOC emission rate [µgh-1] during the pre-operating phase
mvoc _B :	analyzed VOC mass [µg] during the pre-operating phase
NB:	air exchange [h ⁻¹] during the pre-operating phase
Vc:	chamber volume [m ³]
Vp:	sample volume [m ³] during the pre-operating phase

Print Phase:

$$SER_{DN} = \frac{\frac{m_{VOCDN}}{V_P} * n_{DN}^2 * V_K * t_G - SER_B * n_{DN} * t_G}{n_{DN} * t_D - e^{-n_{DN} * (t_G - t_D)} + e^{-n_{DN} * t_G}}$$

SER _{DN} :	VOC emission rate [µgh ⁻¹] determined from the print phase and post- operating phase
SER _B :	VOC emission rate $[\mu gh^{-1}]$ determined from the pre-operating phase
m∨oc _{DN} :	analyzed VOC mass $[\mu g]$ during the printing and post-operating phase
N _{DN} :	air exchange [h ⁻¹] during the print phase and post-operating phase
t _D :	pure printing or copying time [h]
t _G :	total sampling time [h]
Vc:	chamber volume [m ³]
Vp:	sample volume [m ³] during the print phase and post-operating phase

Ultrafine particle number concentration plots from laboratory chamber studies. Identifier = Date of emission test. Equipment = Condensation nuclei counter.

BrotherHL2240:

(a) 2016-01-26; (b) 2016-04-06; (c) 2016-04-07; (d) 2016-04-08; (e) 2016-04-11; (f) 2016-04-12; (g) 2016-04-13; (h) 2016-04-14; (i) 2016-04-15




BrotherHL3170cdw:

(a) 2016-06-20; (b) 2016-06-21; (c) 2016-06-22; (d) 2016-06-23; (e) 2016-06-24; (f) 2016-06-27; (g) 2016-06-28; (h) 2016-06-29; (i) 2016-06-30



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BrotherHL8350cdw:

(a) 2016-01-14; (b) 2016-02-22; (c) 2016-02-23; (d) 2016-02-24; (e) 2016-02-25; (f) 2016-02-26; (g) 2016-02-29; (h) 2016-03-01; (i) 2016-03-02





BrotherHL6200w:

(a) 2016-07-05; (b) 2016-07-06; (c) 2016-07-07; (d) 2016-07-08; (e) 2016-07-11; (f) 2016-07-12; (g) 2016-07-13; (h) 2016-07-14; (i) 2016-07-15





HPM451dn:

(a) 2016-01-27; (b) 2016-03-25; (c) 2016-03-29; (d) 2016-03-30; (e) 2016-03-31; (f) 2016-04-01; (g) 2016-04-04; (h) 2016-04-05





LexmarkMS810:

(a) 2015-10-30; (b) 2016-01-28; (c) 2016-01-29; (d) 2016-02-01; (e) 2016-02-03; (f) 2016-02-04; (g) 2016-02-05; (h) 2016-02-08; (i) 2016-02-10





RicohSP311dnw:

(a) 2016-01-20; (b) 2016-03-03; (c) 2016-03-04; (d) 2016-03-07; (e) 2016-03-08; (f) 2016-03-14; (g) 2016-03-18; (h) 2016-03-21; (i) 2016-03-22





SamsungMX2020:

(a) 2016-02-12; (b) 2016-02-17; (c) 2016-02-19



Ultrafine particle size distribution and number concentration plots from **laboratory chamber studies.** Identifier = Date of emission test. Equipment = Scanning mobility particle sizer and condensation particle counter.

BrotherHL2240:

(a) 2016-01-26; (b) 2016-04-06; (c) 2016-04-07; (d) 2016-04-08; (e) 2016-04-11; (f) 2016-04-12 (g) 2016-04-13; (h) 2016-04-14; (i) 2016-04-15











BrotherHL3170cdw:

(a) 2016-06-20; (b) 2016-06-21; (c) 2016-06-22; (d) 2016-06-23; (e) 2016-06-24; (f) 2016-06-27; (g) 2016-06-28; (h) 2016-06-29; (i) 2016-06-30











Brother HL8350cdw:

(a) 2016-01-14; (b) 2016-02-22; (c) 2016-02-23; (d) 2016-02-24; (e) 2016-02-25; (f) 2016-02-26; (g) 2016-03-01; (h) 2016-03-02









Brother6200w:

(a) 2016-07-05; (b) 2016-07-06; (c) 2016-07-07; (d) 2016-07-08; (e) 2016-07-11; (f) 2016-07-12; (g) 2016-07-13 (h) 2016-07-14; (i) 2016-07-15









HPM451dn:

(a) 2016-01-27; (b) 2016-03-25; (c) 2016-03-28; (d) 2016-03-29; (e) 2016-03-30; (f) 2016-03-31; (g) 2016-04-01; (h) 2016-04-04; (i) 2016-04-05











Lexmark MS810:

(a) 2016-01-28; (b) 2016-01-29; (c) 2016-02-01; (d) 2016-02-03; (e) 2016-02-04; (f) 2016-02-05; (g) 2016-02-08; (h) 2016-02-10









RicohSP311dnw:

(a) 2016-01-20; (b) 2016-03-03; (c) 2016-03-04; (d) 2016-03-07; (e) 2016-03-08; (f) 2016-03-14; (g) 2016-03-18; (h) 2016-03-21; (i) 2016-03-22









SamsungMX2020:

(a) 2016-02-12; (b) 2016-02-17; (c) 2016-02-19





Total volatile organic compound concentration plots from laboratory chamber studies. Identifier = Date of emission test. Equipment = Total VOC photoionization detector.

BrotherHL2240:

(a) 2016-01-26; (b) 2016-04-06; (c) 2016-04-07; (d) 2016-04-08; (e) 2016-04-11; (f) 2016-04-13; (g) 2016-04-14; (h) 2016-04-15





Brother HL3170cdw:

(a) 2016-06-20; (b) 2016-06-21; (c) 2016-06-22; (d) 2016-06-23; (e) 2016-06-24; (f) 2016-06-27; (g) 2016-06-28; (h) 2016-06-29; (i) 2016-06-30







Time



Time

Brother HL8350cdw:

(a) 2016-01-14; (b) 2016-02-22; (c) 2016-02-23; (d) 2016-02-24; (e) 2016-02-25; (f) 2016-02-26; (g) 2016-02-29; (h) 2016-03-01; (i) 2016-03-02





Brother6200w:

(a) 2016-07-05; (b) 2016-07-06; (c) 2016-07-07; (d) 2016-07-08; (e) 2016-07-11; (f) 2016-07-12; (g) 2016-07-13; (h) 2016-07-14; (i) 2016-07-15








Time



Time

HPM451dn:

(a) 2016-01-27; (b) 2016-03-25; (c) 2016-03-28; (d) 2016-03-29; (e) 2016-03-30; (f) 2016-03-31; (g) 2016-04-01; (h) 2016-04-04; (i) 2016-04-05







Time



Time

LexmarkMS810:

(a) 2016-01-28; (b) 2016-01-29; (c) 2016-02-01; (d) 2016-02-03; (e) 2016-02-04; (f) 2016-02-05; (g) 2016-02-08; (h) 2016-02-10





RicohSP311dnw:

(a) 2016-03-03; (b) 2016-03-04; (c) 2016-03-07; (d) 2016-03-08; (e) 2016-03-14; (f) 2016-03-18; (g) 2016-03-21; (h) 2016-03-22





Time



Samsung MX2020W:

(a) 2016-02-12; (b) 2016-02-17; (c) 2016-02-19



Appendix E: Chapter 3 Supporting Information

Scanning electron microscopy and Spectrum Images



Appendix F: Chapter 6 Supporting Information

Supporting Information

Characterization of Chemical Contaminants Generated by a Desktop Fused Deposition Modeling 3-Dimensional Printer

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Materials and Methods

Sample preparation and gas chromatography-mass spectrometry analyses

Canister samples were prepared and analysed as described previously ⁽¹⁾. Canisters were concentrated prior to analysis using an autosampler (Model 7016CA, Entech Instruments, Inc., Simi Valley, CA) with a 100 °C transfer line attached to a preconcentrator (Model 7200, Entech). The pre-concentrator was coupled with a 6890N/5973N GC-MS system (Agilent Technologies, Inc., Santa Clara, CA) with a RTX-1 capillary column 60 m long x 0.32 mm ID x 1 mm film thickness (Restek Corporation, Bellefonte, PA). Pre-concentration conditions were: modified cold trap dehydration; module 1 (empty) at -20 °C, desorbed at 10 °C, and baked at 150 °C for 7 min; module 2 (glass beads) focused at -80 °C, desorbed at 180 °C, and baked at 190 °C; and module 3 (focuser) focused at -150 °C. GC conditions were: oven temperature program set to 35 °C for 2 min, followed by 8 °C min⁻¹ ramp to 170 °C, then 20 °C min⁻¹ ramp to a final temperature of 220 °C, which was held for 3 min; injector temperature was set to 250 °C with a 20:1 split (split flow 20.2 mL/min); detector temperature was 280 °C; and column flow rate was set to 1 mL min⁻¹. Mass spectrometer analysis conditions were: scan mode 35–350 amu; threshold at 150; scan speed at 2.84 scans s⁻¹; solvent delay to 4.5 min; source temperature at 230 °C; and, guadrapole temperature at 150 °C. A one-point calibration check standard (10 ppb) and instrument blank (UHP nitrogen gas) were analyzed with each set of samples within a 24-hour period. MSD Chemstation D.02.00.275 (Agilent Technologies, Inc.) was used for data acquisition. Chromatograms were integrated and the resulting data were transferred to spreadsheets for subsequent blank correction and data handling prior to statistical analysis; final concentrations were calculated based on the response of the closest internal standard (bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5). All quantitative measurement results were background corrected for the concentration of VOCs measured inside the chamber during the pre-operating phase. Additionally, the full chromatograms were screened for tentative identification of compounds using the National Institute for Standards and Technology 2011 mass spectral database with a chemical match determined based on a 75% quality factor. A quality factor of 75% was chosen to ensure that we did not errantly dismiss compound identities based on noisy spectrum. Identified compounds were reported when their responses exceeded that of background samples.

For all carbonyl bubbler samples, after collection, the water was decanted into 40 mL vials, then derivatized with 100 mL aqueous 250 mM O-tert-butylhydroxylamine hydrochloride (TBOX, Sigma Aldrich, St. Louis, MO) and placed in a heated water bath at 70 °C for 2 hours. After removing the vial from the water bath and allowing to cool to room temperature, 0.5 mL of toluene was added to the vial. The vial was then shaken for 30 seconds and allowed to separate into a toluene layer and aqueous layer. Then

100 mL of the toluene layer was removed with a pipette and placed in a 2 mL autosampler vial with a 100 mL glass insert (Resetk, Bellefonte, PA). Then 1 mL of the TBOX-derivatized extract was analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC-MS system operated in the electron impact (EI) mode. Full-scan EI ionization spectra were collected from m/z 40-650. Compound separation was achieved by an Agilent (Santa Clara, CA) HP-5MS (0.25 mm I.D., 30 m long, 0.25 µm film thickness) column and the following GC oven parameters: 40 °C for 2 min, then 5 °C min⁻¹ to 200 °C, then 25 °C min⁻¹ to 280 °C and held for 5 min. One µL of each sample was injected in the splitless mode, and the GC injector was returned to split mode 1 min after sample injection, with the following injector temperature parameters: 130 °C for 2 min then 200 °C min⁻¹ to 300 °C and held for 10 min. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43).

Data analysis

Unit specific emission rates (SER_u) were calculated from the TVOC and ozone data for the 3-D and laser printers in accordance with RAL-UZ-171: Test Method for the Determination of Emissions from Hardcopy Devices ⁽²⁾. For TVOC, the emission rate during printing is calculated from the beginning of the print phase (from start to end of print job) until one air exchange has occurred in the post-operating phase (print job ended, printer on):

$$SER_{u} = \frac{c_{s} \cdot n_{d}^{2} \cdot v_{c} \cdot t_{g} \cdot SER_{B} \cdot n_{d} \cdot t_{g}}{n_{d} \cdot t_{d} - e^{-n_{d} \cdot (t_{g} - t_{d})} + e^{-n_{d} \cdot t_{g}}}$$

where, $c_s = TVOC$ concentration during printing and post - operating phases

 $n_d = air exchange rate (h^{-1}) during printing and post - operating phases$

 $v_c = chamber volume (m^3)$

 $t_g = total sampling time (h)$

SER_B = specific emission rate during pre - operating phase (μ g h⁻¹)

 $t_d = printing time(h)$

For ozone, the emission rate is determined from the increase in concentration during the initial printing phase (before end of print job) to minimize loss by chemical reactions with air constituents. Data points used represent the measurement interval that provided the greatest slope for the interval:

$$SER_{u} = \frac{\Delta_{c} \cdot v \cdot p \cdot 60}{\Delta t \cdot T \cdot R}$$

where, $\Delta_{c} =$ change in ozone concentration (mg m⁻³)

v = chamber volume (m³) p = air pressure in chamber (Pa) 60 = conversion factor (min to h) Δt = time interval used for calculation (min) T = absolute temperature (K) R = gas constant for ozone (339.8PaK⁻¹)

Results and Discussion

Identification of carbonyl compounds

Carbonyl compounds were formed during the print and post-print phase emissions for all the printers investigated. An example chromatogram is provided in the main text and a mass spectrum for 4-oxopentanal formed during 3-D printing with natural color ABS filament is shown as Figure S2.

Identification of individual VOCs

Various aldehydes, alkanes, alkenes, aromatics, cycloalkanes, dienes, halogenated compounds, ketones, nitriles, organic acids, organic lead, and silanes were detected during printing operations. Figure S3 shows compounds qualitatively identified by spectral matching. Note that this figure shows the presence or absence of compounds only and does not represent concentrations. No single compound was common to all printers. Silanes were frequently identified in air during 3-D and laser printing. The presence of high-boiling siloxanes is of interest because Wensing et al. hypothesize that the formation of printer UFP aerosol is significantly influenced by semi-volatile organic compounds such as siloxanes which likely originate from heating of the laser printer fuser unit ⁽³⁾; however, we cannot rule out that the silanes we observed in our samples were from GC column bleed.

Elemental composition of airborne particulate

No particles were observed during inspection of filter samples collected during the preoperating phase. Figure S4 shows electron micrographs of particles emitted while printing with different colors of ABS filament. Replicate samples were collected for each combination of filament type and color and the morphology of visualized particles was consistent among samples. For simplicity, only representative particles from the samples are shown in the figure. Particles in chamber air during printing with natural color were solid with elongated shape and diameters of ~1 to 2 µm as well as agglomerates of nanoscale particles (Figure S4a). For blue ABS, nanoparticles having smooth spherical morphology and diameters less than 200 nm were visible as clusters, some of which had a branched structure and micronscale (Figure S4b). When printing with red ABS, airborne particles had ellipsoid morphology and lengths (long axis) that were on the order of a few hundred nanometers (Figure S4c). Particles in air during printing with black ABS were discrete spherical submicron and nanoscale particles (Figure S4d). Elemental analysis revealed that captured particles from printing with natural, blue, and red color ABS contained chromium (Cr) and nickel (Ni). Other elements identified in particles, but not consistently among all filament ABS filament colors, included magnesium (Mg), silicon (Si), sodium (Na), chlorine (Cl), calcium (Ca), aluminium (AI) and sulphur (S). Figure S5 shows electron micrographs of particles emitted while printing with different colors of PLA filament. All particles were discrete spheroidal particles with nanoscale diameters. With exception of true red, all particles contained iron (Fe). Steinle also reported that a nanoscale particle collected during 3-D printing contained Fe though that study did not specify if the particle was from printing with PLA or ABS filaments ⁽⁴⁾. Previous studies have reported that particles emitted from laser printers using monochrome toner contained all of these same elements as observed for the 3-D printing ⁽⁵⁻¹⁰⁾. In those studies, Cr, Na, Si, and S were attributed to pigments and additives (5-7).

Figure S6 shows differences in morphology and composition of particles collected in chamber air during laser printing. For the HP2055dn printer, particles were elongated with micrometer-scale diameters (~3 to 5 μ m) though agglomerates of spherical nanoscale particles were also identified (see inset). Chromium and S were identified in particles collected on filters during printing with the HP2055dn. Particles collected in chamber air during printing with the HP2600 laser printer were round smooth spheres with diameters ~2 μ m.

Comparison of particulate emission rates between 3-D and laser printers

In addition to monitoring chamber air for TVOCs, individual VOCs, gas-phase carbonyls, and particulate for off-line microscopy analysis we also used real-time instruments to characterize particulate size distribution, number concentration, and mass concentration during laser printing. Briefly, particle size and number concentration were measured using complementary instruments to cover the nanoscale to the micronscale: 14.6 nm to 0.66 µm using a scanning mobility particle sizer (SMPS, Model 3910, TSI Inc., Shoreview, MN) and >0.65 to 20 µm using a GRIMM optical particle counter (Model 1.108, GRIMM Aerosol Technik GmbH & Co. Ainring, Germany). Particle size was measured over the range 24 nm to 9.38 µm using an electrical low-pressure impactor (ELPI Classic, Dekati Ltd., Tampere, Finland). Total particle mass concentration was measured using a DustTrak DRX aerosol monitor (Model 8534, TSI Inc.). The inlets of

the sampling probes were placed side-by-side and at similar locations to the probes for the gas samplers inside the chamber.

The time required to print an object using the 3-D printer differed from the time required to print a standard monochrome template using the laser printers. As such, to permit comparison between device types, we calculated real-time particle emission rates (PER) which normalize emissions to time. PER from the printers were calculated using a box-model. Details of the model derivation were given previously by Yi et al. and are only briefly summarize here. To calculate PER, we assumed the following ⁽¹¹⁾:

the particle concentration in the test chamber before printing phase is negligible compared to that of emitted particles (a vacuum leak test shows the leak rate = 0.05 L min⁻¹, ~0.2% of 25 L min⁻¹ air flow through the chamber);

the deposition of the particles on the inner surfaces of this chamber is negligible;

the particles are not broken up in the chamber and sampling tubing;

the particles do not agglomerate in the chamber and sampling tubing; and

the particle concentration is uniform in the chamber (as noted in the main text).

If we look at an incremental time period, Δt , a change in the particle number $(C(t + \Delta t) \cdot V - C(t) \cdot V)$ equates to the particles emitted by the printer $(PER \cdot \Delta t)$ minus the particles removed by the sampling air flow $(Q(t) \cdot C(\text{mean}) \cdot \Delta t)$, i.e.,

$$C(t + \Delta t) \cdot V - C(t) \cdot V = PER(t) \cdot \Delta t - Q(t) \cdot C(mean) \cdot \Delta t$$
⁽¹⁾

where, t = time, sec.

 Δt = time difference between two successive data points, sec;

 $C(t+\Delta t)$ = particle number concentration at (t+ Δt), particles cm⁻³;

C(t) = particle number concentration at (t), particles cm⁻³;

V = chamber volume, cm³;

PER(t) = real-time particle emission rate at (t), particles sec⁻¹;

C(mean) = mean particle concentration between (t) and (t + Δ t), particles cm⁻³;

Q(t) = sampling air flow rate at (t), cm³ sec⁻¹.

The air exchange rate in the chamber is given by $R = \frac{Q}{V}$. And by substitution and rearranging, PER can be calculated as:

$$PER(t) = \frac{V}{\Delta t} [C(t + \Delta t) - C(t) + R \cdot C(mean) \cdot \Delta t]$$
⁽²⁾

Equation (2) can be used to calculate PER for any real-time particle concentration data (number, mass, etc.). Yi et al. calculated PER values using their box model and the method described in RAL-UZ-171 ^(2, 11). An important difference in these methods is that the RAL calculation includes a particle loss coefficient, β , whereas Yi et al. assumed particle losses in the chamber were negligible. Values of β calculated using the RAL-UZ-171 model were on the order of 10⁻⁴, supporting the validity of our assumption and calculated PER values agreed within 8% between methods.

Table S1 summarizes PER values from the laser printers (this study) and 3-D printer ⁽¹¹⁾. In general, the laser printers had significantly higher emissions of larger particles (diameter > 0.65 µm) as measured using a GRIMM optical particle counter (from highest to lowest): HP2055dn (80 pages) > HP2600 (80 pages) > all colors of ABS and PLA filaments. Previously, we reported that UFPs emitted by a FDM 3-D printer have high probability of depositing in the lung alveoli ⁽¹¹⁾ and it is well known that UFPs and their constituents that reach this deep into the lung can cause strong inflammatory responses ⁽¹²⁾, e.g., via transition-metal-mediated reactive oxygen species generation. A detailed comparison of PER values and yield values among 3-D printer studies was given previously by Yi et al. and the reader is referred to that publication for more information ⁽¹¹⁾. On a mass basis, the PER (µg min⁻¹) were similar, i.e., HP2600 (80 pages) ≈ HP2055dn (80 pages) ≈ all colors of ABS and PLA filaments.

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FIGURE S1. (a) ABS filament colors (from left to right): natural, red, blue, and black; (b) PLA filament colors (from left to right): transparent blue, red, ocean blue, and army green.



FIGURE S2. Mass spectrum of TBOX-derivatized 4-oxopentanal.



FIGURE S3. Qualitatively identified compounds in 3-D and laser printing emissions for all combinations of device and thermoplastic tested.



FIGURE S4. Morphology and elemental composition of ultrafine particles emitted by the desktop 3-D printer using different colors of ABS filament [note that scale bars differ among images]: (a) natural, (b) blue, (c) red, and (d) black.



FIGURE S5. Morphology and elemental composition of ultrafine particles emitted by the desktop 3-D printer using different colors of PLA filament: (a) true red, (b) army green, (c) ocean blue, and (d) transparent blue.



FIGURE S6. Morphology and elemental composition of micrometer-scale particles generated by the laser printers: (a) HP2055dn, (b) HP2600 [note different scale bar between images].

			Average ± standard deviation PER	
Printer	Consumable	Print job	GRIMM	DustTrak
			(# >0.65 µm min⁻¹)	(µg min⁻¹)
HP2055d n	Monochrome toner	80 pages @ 5%	$1.2 \pm 0.1 \times 10^{10}$	11.3 ± 4.9
HP2600	Monochrome toner	80 pages @ 5%	5.6 x 10 ⁹	3.6 ± 2.5
3-D ¹	ABS natural	3 combs	7.0 x 10 ⁵	12.9 ± 7.0
	ABS blue	2 combs	$7.0 \pm 0.0 \times 10^4$	5.6 ± 0.2
	ABS red	2 combs	$3.6 \pm 0.2 \times 10^4$	2.9 ± 0.3
	ABS black	2 combs	$6.5 \pm 0.0 \times 10^4$	0.8 ± 0.2
	PLA true red	4 combs	4.7 ± 1.7 x 10 ⁵	2.7 ± 0.7
	PLA army green	4 combs	4.5 ± 1.2 x 10 ⁵	2.1 ± 0.2
	PLA ocean blue	4 combs	6.9 ± 2.3 x 10 ⁵	3.5 ± 1.1
	PLA transparent blue	4 combs	$6.6 \pm 2.4 \times 10^5$	2.5 ± 0.1

TABLE S1. Average Geometric Mean Particle Size and Particle Emission Rates (PER) for 3-D and Laser Printers

¹ Data from $^{(11)}$, ABS = acrylonitrile butadiene styrene, PLA = polylactic acid