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Exposure hazards of particles and volatile organic compounds emitted from material extrusion 3D printing: Consolidation of chamber study data

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ABSTRACT

Ultrafine particles and volatile organic compounds (VOCs) have been detected from material extrusion 3D printing, which is widely used in non-industrial environments. This study consolidates data of 447 particle emission and 58 VOC emission evaluations from a chamber study using a standardized testing method with various 3D printing scenarios. The interquartile ranges of the observed emission rates were 10^9–10^{11} #/h for particles and 0.2–1.0 mg/h for total VOC. Print material contributed largely to the variations of particle and total VOC emissions and determined the most abundantly emitted VOCs. Printing conditions and filament specifications, included printer brand, print temperature and speed, build plate heating setup, filament brand, color and composite, also affected emissions and resulted in large variations observed in emission profiles. Multiple regression showed that particle emissions were more impacted by various print conditions than VOC emissions. According to indoor exposure modeling, personal and residential exposure scenarios were more likely to result in high exposure levels, often exceeding recommended exposure limits. Hazardous VOCs commonly emitted from 3D printing included aromatics, aldehydes, alcohols, ketones, esters and siloxanes, among which were various carcinogens, irritants and developmental and reproductive toxins. Therefore, 3D printing emits a complex mixture of ultrafine particles and various hazardous chemicals, exposure to which may exceed recommended exposure limits and potentially induce acute, chronic, or developmental health effects for users depending on exposure scenarios.

1. Introduction

Material extrusion fused filament fabrication (FFF) three-dimensional (3D) printing heats and extrudes a filament shaped material, usually thermoplastics, through an extruder nozzle and deposits on a build plate to form a 3D object. Consequently, contaminants such as particles and volatile organic compounds (VOCs) are released during the printing process. Previous studies have reported high levels of ultrafine particles (UFPs, smaller than 100 nm in size) and numerous VOCs emitted from FFF 3D printing with various filament materials (Yi et al., 2016; Zhang et al., 2017; Davis et al., 2019; Gu et al., 2019; Sittichompoo et al., 2020; Azimi et al., 2016; Vance et al., 2017; Youn et al., 2019; Steinle, 2016). Reported particle emission rates ranged from nominally 10^7–10^{12} particles/min, with particle mean or mode sizes mainly in the ultrafine range (Yi et al., 2016; Zhang et al., 2017; Sittichompoo et al., 2020; Azimi et al., 2016; Vance et al., 2017; Steinle, 2016; Floyd et al., 2017; Chýlek et al., 2021; Mendes et al., 2017). Over 200 different VOCs have been reported being detected from FFF 3D printing, with commonly detected VOCs including lactide, styrene, and caprolactam (Davis et al., 2019; Gu et al., 2019; Azimi et al., 2016; Youn et al., 2019). These VOC and particle emission characterizations were found to be associated with print conditions, such as printer extruder temperature, printer and filament brands, filament type (i.e., chemical makeup) and color (Yi et al., 2016; Zhang et al., 2017; Davis et al., 2019; Chýlek et al., 2021; Zhang et al., 2018; Jeon et al., 2020; Stabile et al., 2017). Consistent findings show that ABS (acrylonitrile butadiene styrene) and nylon materials tend to have higher particle and VOC emissions than PLA (polylactic acid), and higher extrusion temperature tends to associate with higher emissions (Zhang et al., 2017; Davis et al., 2019; Sittichompoo et al., 2020; Chýlek et al., 2021; Jeon et al., 2020; Stabile et al., 2017; Hill et al., 2022), while the impacts of printer brand, filament additives and color, and build plate temperature are inconclusive (Zhang et al., 2017; Davis et al., 2019; Azimi et al., 2016; Hill et al., 2022; Potter et al., 2019). The relationship of emissions and print conditions is complex and interrelated. Large variations in print conditions, experimental setups and measurement methods make it difficult to

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achieve a general consistency from different studies.

FFF 3D printers are widely used in manufacturing and consumer settings. Their use in non-industrial environments such as offices, libraries, homes, and educational spaces has led to a public health concern related to their chemical and particle emissions and potential health impacts. 3D printer users have reported headaches, irritation and respiratory symptoms (House et al., 2017; Chan et al., 2017; Karwasz et al., 2022). Some VOCs detected from FFF 3D printing are irritants, carcinogens, odorants, and reproductive and developmental toxins (Davis et al., 2019; Azimi et al., 2016; Youn et al., 2019; Kim et al., 2015). In vivo and in vitro assays have shown that particles emitted from ABS, PLA and nylon materials induce inflammatory responses, cell deaths, and oxidative stress, which indicate potential adverse health impacts after inhalation exposure (Zhang et al., 2019). Other studies showed that exposure to ABS emissions induced inflammatory responses with minimal cytotoxicity (Farcas et al., 2022,2020). This indicates that toxicity is affected by differences in materials, printing conditions, and assessing methods, and that health outcomes are associated with the intrinsic properties of emissions, including particle size, particle chemical compositions, types of VOCs, and the magnitude and duration of exposure to each type of contaminant. Therefore, assessing exposure hazards is complex given large variations and uncertain relationships between emission characterizations and print conditions, in addition to the variations of exposure scenarios. Field studies have assessed the exposure hazards in laboratories and workplaces. The findings are difficult to translate to other exposure scenarios due to differences in ventilation rates, room volumes, and other human activities (Zontek et al., 2017; Stefaniak et al., 2019; Leso et al., 2021; Stefaniak et al., 2021).

This study summarizes particle and VOC emission results, which includes 447 particle emission and 58 VOC emission characterizations from various 3D printing conditions, obtained using an established standard testing method (ANSI, 2019) and validated exposure chamber protocols. Statistical analysis was used to evaluate the relationships of particle and VOC emission factors with various print conditions, including printer designs, print condition setups, and filament materials and properties. Exposure concentrations for both particles and VOCs with health concern were predicted using an indoor exposure model (ANSI, 2019) for different exposure scenarios. Furthermore, potential health hazards were discussed with reference to regulations and recommended indoor exposure limits.

2. Methods and materials

2.1. Print materials and conditions

This study involved 14 different printers from 6 unique manufacturers (brand *A* to *F*) and 45 filaments of different materials and colors from 13 manufacturers (brand *a* to *m*). The studied materials included 8 commonly available pure polymeric materials, namely ABS (acrylonitrile butadiene styrene), PLA (polylactic acid), nylon, HIPS (high impact polystyrene), PVA (polyvinyl alcohol), PETG (polyethylene terephthalate glycol), ASA (acrylonitrile styrene acrylate), and TPU (thermoplastic polyurethane). The studied composite materials included polycarbonate (PC), flame retardant (FR), bronze powder, chopped carbon fiber (CF), and glass fiber (GF), which were blended with ABS, PLA and nylon polymers. In addition, metal composite filaments, which are metal (or alloy) powder mixed with polymer binders, were studied. Print extrusion temperature was mainly determined by base material type and varied per printer and filament brand. In this study, PVA had the lowest extrusion temperature, followed by PLA and metal filaments; HIPS, PETG, ASA and TPU had moderate extrusion temperature; ABS and nylon filaments could have high extrusion temperature. Table A.1 lists the details of each print condition.

2.2. Emission characterizations and exposure estimations

Particle and VOC emissions were measured using stainless steel exposure chambers according to a standard testing method, ANSI/CAN/UL 2904 (ANSI, 2019). The chamber specifications and setups, validation protocols, and sampling setups have been described previously (Zhang et al., 2017; Davis et al., 2019; ANSI, 2019; Zhang et al., 2022). Also see Appendix B for details.

Number distributions of particles with electrical mobility diameters from 7 to 300 nm were measured with a scanning mobility particle sizer (SMPS) spectrometer (TSI models 3081, 3082, 3785, 3789). Particle number distributions of fine and coarse particles with diameters larger than 0.3 μm were measured by an optical particle counter (OPC, TSI model 9306, upper size 25 μm) or an optical particle sizer (OPS, TSI model 3330, upper size 10 μm). Particle measurement interval was 2 min per scan for both SMPS and OPC/OPS. Particle mass concentration was calculated from the measured number concentration assuming particles were spherical with unit density (1 g/cm^3) (Zhang et al., 2017,2019). Previous studies have shown that particles are likely formed from low volatility vapors emitted from heating of the polymers, which results in potentially different particle chemical compositions than the raw filament materials. Therefore, the bulk filament density may not apply to the emitted particles and thus it is assumed unit density (Zhang et al., 2018,2019,2023). Particle monitoring protocol and emission rate (ER) calculation have been described previously (Zhang et al., 2017; ANSI, 2019; Zhang et al., 2023).

VOCs were collected onto Tenax® TA sorption tubes and then thermally desorbed (Perkin Elmer TurboMatrix 650) into the gas chromatograph-mass spectrometry (GC–MS, Agilent 8890 GC, Agilent 5977B mass selective detector). The analytical methodology followed US EPA Compendium Method TO-17 and ASTM D 6196 and was generally applicable to organic compounds with boiling points ranging from 35−250 °C. Individual VOCs were identified using a mass spectral database and quantitated using multipoint calibration standards, if available. Total VOC (TVOC) was the sum of individual VOC responses in the C_6–C_{16} range obtained by the mass spectrometer and calibrated relative to toluene. Sorbent cartridges with DNPH (2,4-dinitrophenylhydrazine) were used to collect low-molecular-weight carbonyl compounds and were analyzed by high performance liquid chromatography (HPLC, Agilent 1260 Infinity) following ASTM D 5197 and US EPA Method TO-11A. The combined data from Tenax® tubes and DNPH cartridges are referred to as VOC data in this study unless specifically differentiated. Note that low-molecular-weight compounds (typically below C_6) like formaldehyde and acetaldehyde are also often referred to as very volatile organic compounds (VVOCs) (AgBB, 2021). VOC sampling protocol and emission calculation have also been described previously (Davis et al., 2019; ANSI, 2019; Zhang et al., 2022).

Furthermore, emission rates were applied to an indoor exposure model to predict exposure concentrations according to ANSI/CAN/UL 2904 (ANSI, 2019). The model was based on a steady state mass balance that defined different exposure scenarios. Personal exposure represented a worst-case scenario where a person is within a distance of 1 m from an operating FFF 3D printer, assuming the air is well mixed with an outdoor ACH (air changes per hour) of 0.23 h^{-1} (Zhang et al., 2022). Three typical non-industrial environments representing home, office and school conditions were applied assuming that the printer was the only emission source. The school scenario had three printers in a 231 m^3 room with 0.82 ACH; the office and home scenarios had one printer in a 30.6 m^3 room with 0.68 ACH and 28.2 m^3 with 0.23 ACH, respectively (Davis et al., 2019; Zhang et al., 2019; ANSI, 2019).

2.3. Statistical analyses

The dataset included a total of 447 print runs for particle emissions with calculated emission factors for particle number and mass distributions and 58 print runs for chemical emissions with emission factors

for TVOC and each detected individual VOCs. Kernel density estimation was used to calculate the probability density function in violin plots to provide additional understanding of the distribution of data. (Chen, 2017) Linear regression was used to investigate the association between two continuous variables, with the Pearson correlation coefficient (r) indicating the strength of the linear correlation. The Wilcoxon singed-rank test was used to determine if two groups are different. The one-way analysis of variance (ANOVA) was used to determine if the means of three or more groups are different, as well as used to estimate the association between categorical and continuous variables. The Pearson's chi-squared test was used to determine whether two categorical variables are independent. Multiple regression was used to investigate the relationship between a dependent variable and multiple predictor variables that included both continuous and categorical variables using Eq.1.

$$y = \beta_0 + \beta_1 x_{1,1} + \beta_2 x_{1,2} + \cdots + \beta_k x_{i,j} \quad (1)$$

where y is the dependent variable, i.e., emission factor; x is the predictor variable, i.e., print condition; β is the regression coefficient; β_0 is the intercept or baseline where each predictor variable equals 0 (or false) and each nominal categorical variable takes the first value as default; k is the number of regression coefficients; i is the number of predictor variables; j is the number of dummy variables of a categorical predictor variable. The studied predictor variables included three nominal variables, namely printer brand (*A* through *F*), filament brand (*a* through *m*), and filament color (black, blue, bronze, gray, green, natural, orange, red, white, yellow), two binary variables, namely filament composite (true or false), and build plate heating (true or false), and two continuous variables, namely extrusion temperature (209–270 °C) and print speed (0.9–32 cm^3/h). Print speed was calculated as $\frac{\text{print object mass (g)}}{\text{print time (h)} \times \text{filament density (g/cm}^3\text{)}}$. The dependent variable was fitted based on the least squares criterion estimation method. Note that the actual print conditions were not an exhaustive combination of the listed variable values but were subjected to availability and applicability, see Table A.1 for the studied print conditions. The p-value for statistical significance of all statistical analyses was 0.05. Statistical analysis was calculated using R (ver. 4.2.2).

3. Results and discussion

3.1. Overview of emission data

Studies have shown that particle emission characterizations vary during the printing process, which are also subject to experimental conditions like chamber setups and measurement instruments (Yi et al., 2016; Zhang et al., 2017; Gu et al., 2019; Azimi et al., 2016; Floyd et al., 2017; Jeon et al., 2020; Kim et al., 2015; Zhang et al., 2022). Therefore, the integrated particle emission factors (e.g., emission rate) that are associated with print conditions were used for data analysis and comparison among studies. The statistics of particle number and mass emission rates (NER and MER) from all experiments (n = 447) are summarized in Fig. 1A and B. Particle NERs in this study ranged from 3.80×10^6 to 5.73×10^{12} particles/h, which are comparable or lower than those observed from laser printers, (He et al., 2007) and particle MERs ranged from below quantification levels to 1.46×10^3 μg/h. Data obtained in this study extended up to 7 orders of magnitude due to the variations of materials and printing conditions. Similarly, a large deviation was reported from other chamber studies, whereas the majority of the NER data were in the range of 10^9–10^{12} #/h (Yi et al., 2016; Azimi et al., 2016; Steinle, 2016; Floyd et al., 2017; Mendes et al., 2017; Jeon et al., 2020; Kim et al., 2015; Chýlek et al., 2019; Kwon et al., 2017). The distribution of particle MER was positively skewed, with a median of 65.0 μg/h and 75% of the data below 300 μg/h. This is likely associated with the fact that emitted particles were mainly UFPs, which have limited contribution to particle mass emissions. The median of the geometric mean diameter (GMD) in this study was 50.7 nm and 85% of the measured GMD were less than 100 nm. Other chamber studies also have shown the small sizes of particles emitted from FFF 3D printing. (Azimi et al., 2016; Youn et al., 2019; Floyd et al., 2017; Kim et al., 2015; Kwon et al., 2017; Bernatikova et al., 2021) Overall, the large variation of UFP emissions was associated with print conditions, which could affect the release of low volatility vapors during the printing process that condense and form new particles (Zhang et al., 2017; Vance et al., 2017; Chýlek et al., 2021; Zhang et al., 2018; Jeon et al., 2020; Stabile et al., 2017; Hill et al., 2022).

An overview of the total volatile organic compound (TVOC) emission rate in this study (n = 58) is shown in Fig. 1C. Overall, 75% of TVOC emission rates were below 1 mg/h, with a few outliers having emission rates over 2.5 mg/h. This is comparable to the literature showing that

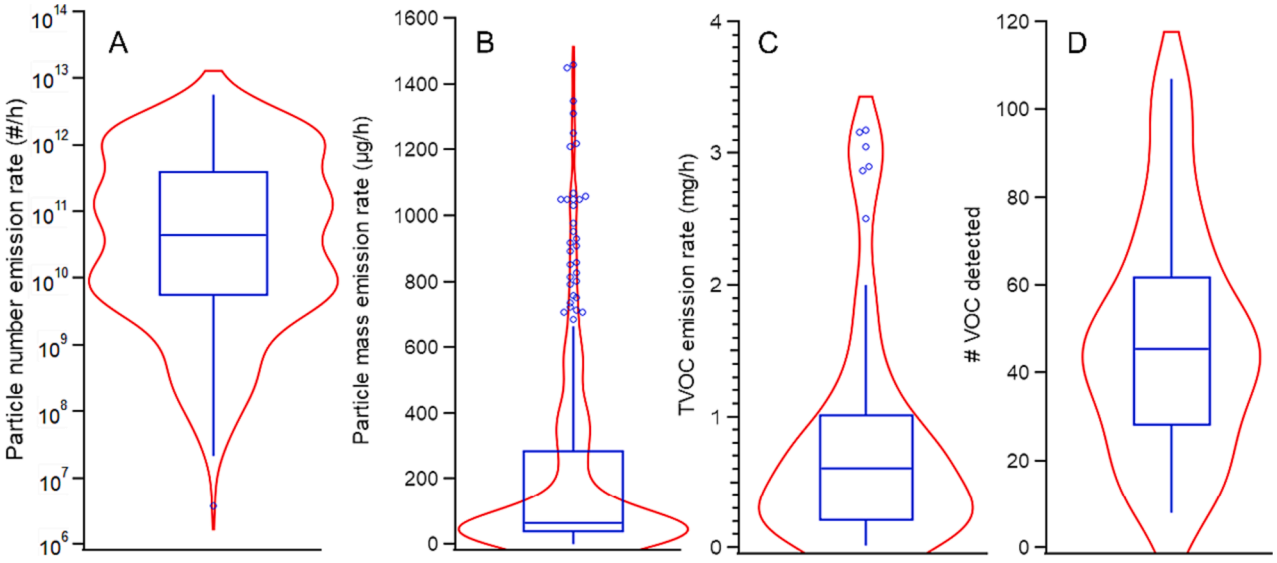

Fig. 1. Overview of emission dataset for particle number emission rate (A), particle mass emission rate (B), total volatile organic compound (TVOC) emission rate (C) and number of VOCs detected (D). Boxplot shows the central tendency, quartiles, and range of the dataset and violin plot shows the probability density of the dataset using kernel density estimation.

TVOC emission rates ranging from nominally 0.01 to 3.5 mg/h for ABS, PLA, nylon and other materials (Gu et al., 2019; Azimi et al., 2016; Stefaniak et al., 2017). There are additional studies reporting higher TVOC emission rates (up to over 10 mg/h) from various filament materials (Azimi et al., 2016; Floyd et al., 2017). Similar to particle emissions, VOC emissions are affected by various print conditions and sampling and analysis methods. Regarding individual VOC emissions, there were up to 107 VOCs detected from an individual print run, with a median of 46 (Fig. 1D). The detected VOCs were associated with a wide range of functional groups, such as aliphatic and aromatic hydrocarbons, aldehydes, esters, ketones, acids, alcohols, and siloxanes, which were also reported from other studies (Davis et al., 2019; Gu et al., 2019; Azimi et al., 2016; Potter et al., 2019; Stefaniak et al., 2017; Wojnowski, 2022). Some of the VOCs like benzene, xylene, and toluene are also commonly found in indoor environments (Jia et al., 2008; Arata et al., 2021; Idris et al., 2020), while some are specifically associated with filament materials and additives.

Based on the 58 print runs with both particle and VOC emission measurements, correlation coefficients between particle and VOC characteristics were calculated. Although both particle and chemical emissions were found to be influenced by the print conditions (Zhang et al., 2017; Davis et al., 2019; Gu et al., 2019; Azimi et al., 2016; Chýlek et al., 2021; Mendes et al., 2017; Jeon et al., 2020), overall, there was low to no correlation between these data, potentially resulting from the large variations of print conditions. When grouped by filament materials, there were cases when strong correlation was found, see Table A.2 for coefficients. Metal composite filaments had the highest correlation coefficients, which was likely associated with the less variations in print conditions since they were from the same manufacturer and used the same printer and similar setups. It should be noted that the previously reported correlation coefficients were relatively higher for ABS and PLA (Davis et al., 2019), however, the coefficients decreased as more variations were included. The lack in correlation among emission factors indicated the association between particle and VOC emissions, if any, was impaired by the variations in print conditions, although they could be concurrently affected by the same print condition to different extents. Therefore, emission factors of particles generally cannot be used to predict that of VOCs or vice versa, especially with large variations in print conditions.

3.2. Effects of print conditions on emissions

3.2.1. Filament material type

Among the various print conditions, different filament materials have different properties that require varying optimal printing setups, making filament material a major influencing factor. Filament material specific particle emissions are shown in Fig. 2. ABS, nylon and HIPS filaments had the highest NER medians (in the order of 10^{11} #/h), followed by metal (10^{10} #/h), and then PLA, PETG and PVA filaments (10^{9} #/h). Although large ranges in NER were observed for PLA and ABS materials with $n > 100$, the interquartile range (IQR) for each material was about one order of magnitude. It is noted that PLA filaments had the largest range, and the highest observed NERs in this study were from a composite PLA filament. The NERs of ASA and TPU were comparable to the medians of PETG and PVA materials. The medians of GMD for PLA, ABS, nylon, PETG and ASA materials were smaller than 100 nm, and those of HIPS and PVA materials were slightly over 100 nm. Metal composite filaments had the largest mean particle sizes with a GMD of over 400 nm and thus relatively higher particle MERs (up to 1451 μg/h). This is likely associated with the different emission behavior of metal composite filaments and pure polymer filaments depending on the mass fraction of volatile components. It is also noted that metals were found in the particles emitted during printing from both pure polymer and metal composite filaments, which potentially increase the health concern of exposure (Zhang et al., 2023). PLA material had low median MER (1.42 μg/h) and 13% of the MER data were below the quantification criterion, however, its highest MER reached 438 μg/h. Therefore, it should be noted that even the IQR of the particle emission data for a specific material was within in a certain range, the overall distribution could extend much wider. Factors that potentially result in the wide range and outliers will be discussed in later section.

Total VOC emission rate is summarized for each material in Fig. 3. High TVOC emitting cases included ASA, PETG, and some ABS and nylon filaments, with the highest TVOC ERs reached over 3 mg/h, while the median was 1.02 mg/h for ABS and 0.61 mg/h for nylon. PLA filaments showed a narrower range for TVOC ER with a median of 0.23 mg/h, which was comparable to metal and PVA materials. The low TVOC emissions from metal composite filaments could be associated with that approximately 90% (w/w%) of the filaments was metal powder that is unlikely to generate VOCs during printing. Note that TVOC is used for general comparison of emission among different conditions, it does not represent the significance of emissions or health-related exposure implications (Salthammer, 2022).

The top 5 most abundant VOCs emitted from each material with average emission rates are also shown in Fig. 3, which were selected from those with the highest detection frequency (i.e., # of times detected/# of experiments) and then with the highest ER. Among the 25 VOCs listed, there were 6 aldehydes, 6 aromatics, 5 cyclic methyl siloxanes (D*n* with *n* indicating the number of chain units), 3 alcohols, and others. These VOCs could be products from desorption, degradation and reaction of the monomers and polymers of the raw materials (Potter et al., 2019). Therefore, typically the most abundant VOCs emitted were

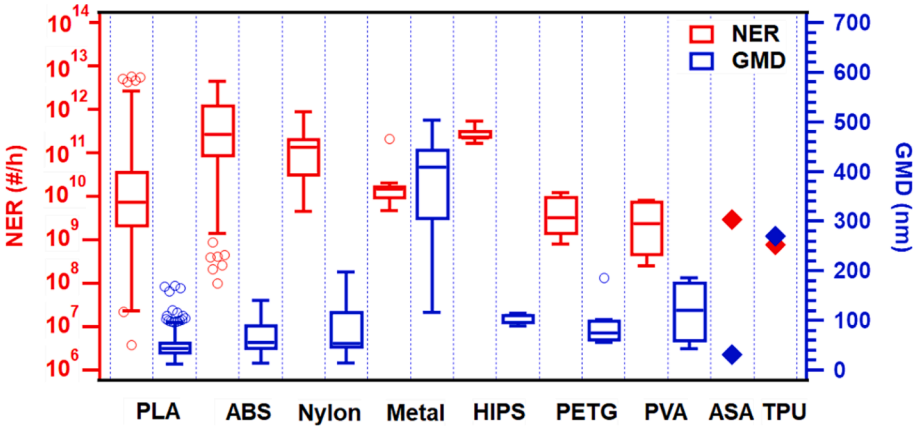

Fig. 2. Particle number emission rate (NER) and geometric mean diameter (GMD) for each filament material type. Boxplot shows the range, quartiles, and central tendency of the dataset; diamond marker shows data from one experiment.

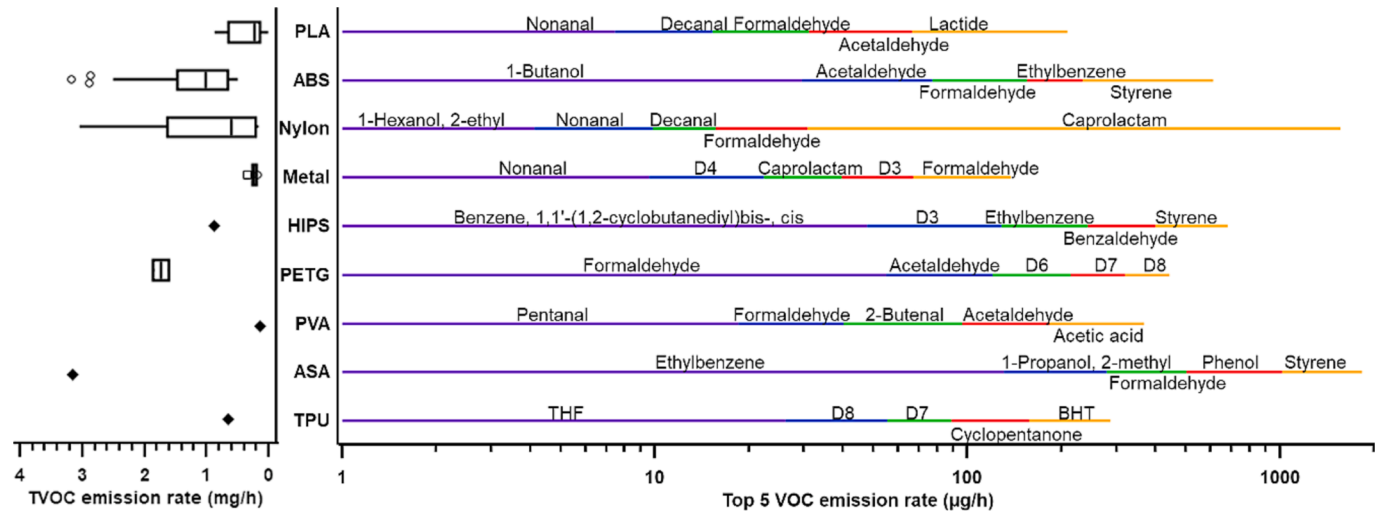

Fig. 3. Total VOC emission rate (left) and the top 5 most abundant VOC emission rate (right) for each filament material type. The top 5 VOC emission rate is descended from right to left; note its axis is logarithmic. D3 = hexamethylcyclotrisiloxane; D4 = octamethylcyclotetrasiloxane; D6 = dodecamethylcyclohexasiloxane; D7 = tetradecamethyl-cycloheptasiloxane; D8 = hexadecamethylcyclooctasiloxane; BHT = 2,6-di-*tert*-butyl-4-methylphenol; THF = tetrahydrofuran.

associated with the main polymer material of the filament (Davis et al., 2019; Azimi et al., 2016). Specifically, they are lactide from PLA, styrene from ABS, HIPS, and ASA, caprolactam from nylon, and acetic acid from PVA. In addition, tetrahydrofuran (THF) stabilized with butylated hydroxytoluene (BHT) can be used to produce ether based soft segments (e.g., polytetrahydrofurans) in TPU synthesis (Wölfel et al., 2020). The most abundant VOC from metal filaments, namely formaldehyde, could be associated with the polymer binders (or adhesives) in the filaments (Hodgson et al., 2000; Sands et al., 2001). In addition, formaldehyde was among the top 5 most abundant VOCs for 7 out of 9 materials studied; following that were some other aldehydes and aromatics. PETG, TPU and metal materials each had two siloxanes as abundantly emitted VOCs. Additional frequently emitted VOCs with over 50% of detection frequency included D5 (decamethylcyclopentasiloxane), acetophenone, xylenes, toluene, hexadecane, tetradecane, and TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate).

The sum of the top 5 emitted VOCs typically accounted for about 30% up to over 90% of the sum of VOC ERs. However, there were

Table 1
Summary of multiple regression coefficients.

Material	ABS				PLA			
Dependent	NER	MER	TVOC ER	Styrene ER	NER	MER	TVOC ER	Lactide ER
Predictor								
Intercept	$\mathbf{-7.12 \times 10^{12}}$	$\mathbf{-2.86 \times 10^{3}}$	0.64	0.48	$\mathbf{7.19 \times 10^{12}}$	$\mathbf{1.16 \times 10^{3}}$	**4.14**	0.46
Printer *B*	2.96×10^{11}	**206**	–	–	-1.25×10^{11}	**−45.5**	–	–
Printer *C*	$\mathbf{-1.27 \times 10^{12}}$	**−403**	–	–	3.46×10^{11}	27.5	–	–
Printer *D*	8.25×10^{10}	−194	–	–	$\mathbf{-6.67 \times 10^{11}}$	46.7	–	–
Composite	–	–	0.72	0.54	7.64×10^{10}	**78.6**	−0.07	−0.01
Filament *b*	$\mathbf{6.76 \times 10^{11}}$	169	/	/	/	/	/	/
Filament *c*	-3.65×10^{10}	**364**	0.42	0.28	1.08×10^{10}	−3.21	0.08	−0.06
Filament *d*	$\mathbf{1.12 \times 10^{12}}$	**320**	−0.53	−0.01	/	/	/	/
Filament *f*	4.26×10^{10}	**159**	/	/	-2.11×10^{9}	−5.11	−0.24	0.08
Filament *g*	/	/	/	/	$\mathbf{1.03 \times 10^{12}}$	2.89	0.22	**0.23**
Filament *h*	/	/	/	/	$\mathbf{1.27 \times 10^{12}}$	0.39	0.22	**0.34**
Filament *j*	/	/	/	/	$\mathbf{6.20 \times 10^{12}}$	**205**	**0.74**	**0.38**
Filament *l*	-6.12×10^{10}	51.4	−1.22	−0.37	$\mathbf{6.29 \times 10^{11}}$	−56.2	−0.16	0.03
Filament *m*	/	/	/	/	$\mathbf{1.42 \times 10^{12}}$	−10.5	/	/
Blue	$\mathbf{1.19 \times 10^{12}}$	**443**	−0.25	0.45	/	/	/	/
Bronze	/	/	/	/	–	–	–	–
Gray	/	/	/	/	–	–	–	–
Green	$\mathbf{1.04 \times 10^{12}}$	**496**	−0.69	0.20	–	–	–	–
Natural	/	/	−0.06	0.40	–	–	–	–
Orange	7.68×10^{11}	277	−0.64	0.21	–	–	–	–
Red	$\mathbf{1.16 \times 10^{12}}$	**564**	−0.76	0.11	–	–	–	–
White	$\mathbf{1.24 \times 10^{12}}$	**637**	−1.45	0.00	–	–	–	–
Yellow	$\mathbf{1.03 \times 10^{12}}$	**459**	/	/	–	–	/	/
Temperature	$\mathbf{2.41 \times 10^{10}}$	**8.52**	0.01	0.00	$\mathbf{-3.26 \times 10^{10}}$	**−5.15**	**−0.02**	0.00
Heat plate	$\mathbf{-1.22 \times 10^{12}}$	−164	–	0.93	-2.67×10^{11}	**−68.9**	0.07	**−0.10**
Speed	$\mathbf{7.79 \times 10^{10}}$	**31.6**	−0.38	−0.12	-3.51×10^{9}	0.01	0.01	0.00
Adjusted R^2	0.66	0.62	0.64	0.18	0.87	0.58	0.62	0.94
p-value	0.00	0.00	0.18	0.48	0.00	0.00	0.01	0.00
F-value	22.1	18.2	3.23	1.27	101	21.6	4.65	35.2

Note: "–" indicates the predictor variable removed due to high intercorrelation or it was the default category; "/" indicates not applicable for this condition; bold indicates p-value < 0.05.

individual VOCs with low detection frequencies that consistently showed high ERs from a specific filament. Methyl methacrylate was detected from 39% of PLA prints with typically low concentrations, while it accounted for 54.8% and 62.2% of the sum of VOC ERs for the two prints with the same filament (brand *c* red color) but different printers and extrusion temperatures. For ABS material, phenol was only detected from brand *b* filaments with various colors and composites; 2-butoxyethanol was detected in relatively high ERs only from brand *l* filaments. These indicated that manufacturer specific formula and unspecified additives may contribute to high emission of certain VOCs, despite the variations of printer brand, extrusion temperature, filament color or composite.

3.2.2. Combination of various print conditions

Multiple regression was applied to ABS and PLA materials given the large numbers of experiments, to evaluate the effects of print conditions. Furthermore, analysis was conducted separately for each material type to avoid results being biased due to the unbalanced experiment numbers. Predictor variables were particle NER and MER, TVOC ER and the ER of the most abundantly emitted VOCs. The coefficients of the optimum regressions are listed in Table 1, which explained more of the dependent variable variations using fewer predictor variables.

Particle emissions from ABS and PLA materials were found to be dependent on all of the predictor variables to different extents (Table 1). Among the 4 printer brands, only printer *C* consistently showed negative coefficients for ABS particle emissions, which indicated it being a low emitting printer brand for ABS filaments. Composites in PLA filaments showed significant association with higher MER and trended towards higher NER but the trend was not statistically significant. Among the 6 ABS filament brands, filament *a* was a relative low emitting brand. Filament *d* was a significant higher emitter for both particle number and mass; while filament *d* was a pure polymer filament, which indicated some unspecified additives could contribute to high particle emissions. Among the 8 PLA filament brands, filament *j*, a PLA composite filament with bronze powder, was a significant high emitter for particle emissions. Filament color was an important variable for particle emissions from ABS filaments, while not for PLA filaments. The black color (default in categorical variables) tended to be a low emitting color with all other colors having positive coefficients. Increase in extrusion temperature was significantly associated with increased particle emissions from ABS filaments, while interestingly, it was significantly associated with decreased particle emissions from PLA filaments. Previous studies have shown a positive association between extrusion temperature and particle emission, which was based on only changing the temperature and controlling other conditions (Zhang et al., 2017; Floyd et al., 2017; Chýlek et al., 2021; Jeon et al., 2020; Stabile et al., 2017). However, this trend could be compensated by a complex matrix of other variables, such as printer and filament brands (Azimi et al., 2016). Heating of the build plate tended to be associated with lower particle emissions. This is different from previously reported data showing that higher build plate temperature was associated with higher particle emissions (Azimi et al., 2016), which could be influenced by the effect of printer brand. Printing speed was significantly associated with an increase in particle emissions from ABS filaments, while no significant association was found for PLA.

Specified VOC emissions were less sensitive to the predictor variables (Table 1). Particularly for ABS material, no significant association was found from the predictor variables. For PLA, only filament brand, extrusion temperature and build plate can present a significant association. Specifically, filament *g* and *h* were likely to emit more lactide. Similar to particle emissions, filament *j* was a high emitter for both TVOC and lactide. Extrusion temperature and heating of the build plate had insignificant or minimal association with TVOC and the most abundant VOC ERs.

Overall, print conditions were able to explain 58% up to 94% of the variations in emission factors, except for TVOC and styrene ERs from ABS material that were insignificant. Categorical predictor variables had relatively larger coefficients than continuous predictor variables. Significant emission influential conditions were identified using multiple regression and the emissions can be affected interactively by different conditions. Regarding filament properties, brand had the most cases of significant association with emission factors, followed by color and composite. Regarding printer design, brand and extrusion temperature were more influential than build plate heating and print speed. Printer brand, filament brand and extrusion temperature were consistently significantly associated with particle emissions for both materials. In addition, filament color and print speed were significantly associated with particle emissions for ABS material. On the other hand, VOC emissions showed less associations in general.

3.3. Exposure modeling and health implications

3.3.1. Particle exposure estimations

Model predicted personal exposure to particle emissions showed that ABS and HIPS materials had the highest median exposure concentrations, while PLA, PETG, and PVA had relatively lower median exposure concentrations (Fig. A.1). The predicted levels are comparable or higher than typical indoor UFP levels, ranging from 10^9 to 10^{12} #/m^3 in homes, offices and schools (He, 2004; Bekö et al., 2013; Slezakova et al., 2019; Morawska et al., 2017). Particle concentrations in homes could reach over 10^{13} #/m^3 due to coal combustion (Luo et al., 2022; Zhang et al., 2012; Wang et al., 2020), which is comparable to the maximum predicted concentrations from some high emitting filaments. Reported UFP concentrations in rooms with 3D printers were at the low end or comparable to the predicted worst-case scenarios (Mendes et al., 2017; Stefaniak et al., 2022; Kangas et al., 2023). Therefore, personal exposure to 3D printing tended to be comparable to other indoor activities like cooking and combustion regarding particle numbers, while exposure levels also depend on exposure scenarios. The estimated mass concentrations for home, office and school scenarios reached 226, 70.4, and 23.2 μg/m^3 respectively. Since 3D print-emitted particles showed nanometer sized GMD and were rarely >3 μm according to chamber studies (Zhang et al., 2017; Zhang et al., 2023), $PM_{2.5}$ (fine particulate matter) was referred to for comparison. Indoor $PM_{2.5}$ concentration has been reported with a typical range of below 10 to 40 μg/m^3, with some cases above 50 μg/m^3 to over 100 μg/m^3, due to sever emission sources or poor ventilation (Morawska et al., 2017; Brehmer et al., 2020; Hassanvand et al., 2015). Considering daily $PM_{2.5}$ standard (35 μg/m^3) from US EPA national ambient air quality standards (NAAQS), school scenarios showed no exceedance; office scenarios exceeded for 13% of ABS, 43% of metal and 33% of HIPS filaments; residential scenarios exceeded for 61% of ABS and all of HIPS and metal filaments. Note that estimations in this study considered an overall exposure to particles as a bulk, chemical composition also plays an important role in exposure assessments.

Furthermore, the relationship of exposure mass concentration and model parameters is presented in Fig. 4. Estimations from the maximum emission rates of ABS and metal materials showed the highest concentrations. This indicated when operating one printer with these filaments and corresponding print conditions, the air change rate needs to be above 0.4 h^{-1} in a 100 m^3 room, so that the exposure concentration will be within 35 μg/m^3. Similarly, with the same print in a typical residential house bedroom (28 m^3), air change rate needs to be over 1.4 h^{-1} to maintain the concentrations below NAAQS. There are more chances for ABS, HIPS, and metal materials to exceed NAAQS, thus it is preferable to run in larger and better ventilated environments; while PET, TPU and ASA seemed to be able to comply with smaller and less ventilated room environments, given their lower emission rates. Normally PLA filaments tended to emit minimal particle mass, while a high emitting PLA filament could elevate the level by over 300 times. However, it should be noted that in this study, fewer experiments were conducted for some of the materials, so there may be high emitting conditions that have not been investigated in this study. In addition, the World Health

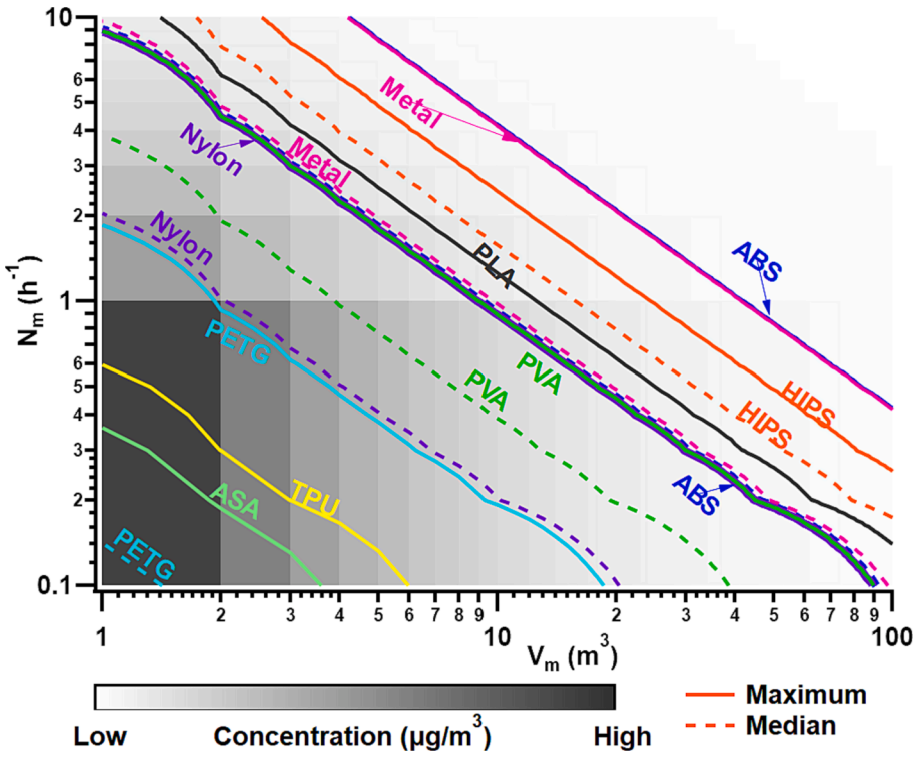

Fig. 4. Predicted particle mass concentrations under different room conditions. Image plot indicates nominal predicted concentrations; contour line marks where exposure concentrations equal NAAQS fine particulate matter daily standard (35 μg/m^3) for each material using median data (dash line) and maximum data (solid line). V_m and N_m indicate the size and the air change rate of the room respectively.

Organization (WHO) has a lower level for daily $PM_{2.5}$ (15 μg/m^3) (WHO, 2021). It should also be noted that exposure could be higher for situations such as a person is closer to the operating printer; the air-mixing inside the room is uneven with stagnant air regions; the printer malfunctions; or there are other emission sources in the room.

3.3.2. *VOC exposure estimations*

The predicted TVOC exposure concentrations for home, office and school scenarios reached 489, 153, and 17 μg/m^3 respectively. The office and school scenarios are comparable to typical indoor TVOC concentration, while the home scenario is comparable to that during heating season (Norris et al., 2019,2022). TVOC estimations showed 10% of the data were above 10^4 μg/m^3, which is more than some of the highest levels in newly built and renovated buildings (Holøs et al., 2019).

There were 111 chemicals of concern identified from FFF 3D printing in this study. Chemicals of concern refer to VOCs that impact indoor air quality and/or may cause health concerns thus are typically associated with recommended exposure concentration limits (Davis et al., 2019; Zhang et al., 2022). The references included WHO International Agency for Research on Cancer (IARC) monographs on the identification of carcinogenic hazards to humans, California (CA) Office of Environmental Health Hazard Assessment (OEHHA) Proposition 65, Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB) lowest concentration of interest (LCI), CA Specification 01350 maximum allowable concentration, and OEHHA acute (1-hour), 8-hour and chronic reference exposure levels (RELs). Fig. 5 summarizes the detection frequency of common chemicals of concern in this study for each functional group. The mainly emitted chemicals of concern included aromatic compounds, aldehydes, alcohols, ketones, esters, siloxanes, and others. Their short-term health effects include irritation to eyes, nose, and throat, headache, and dizziness, and long-term effects include increasing the risk for developing lung, oral, and gastrointestinal cancer, liver, kidney, and central nervous system damage. Among these VOCs, styrene, 2-ethylhexanol, formaldehyde, benzaldehyde, acetaldehyde, nonanal, decanal, acetophenone, D5 and D6 have been detected from all material types, although not all filaments. Formaldehyde had the highest detection frequency (98%), followed by decanal, nonanal, acetaldehyde, benzaldehyde, 2-ethylhexanol and styrene with detection frequencies over 80%. According to the IARC classification, two human carcinogens (benzene and formaldehyde), one probable carcinogen (styrene) and four possible carcinogens (ethylbenzene, cumene, acetaldehyde and tetrahydrofuran) were frequently detected. Overall, ABS material tented to emit the most chemicals of concern (72), followed by PLA (66), and then nylon (52). Thirteen less frequently detected VOCs listed with Proposition 65 are in Table A.3. It should be noted that 4-vinylcyclohexene (carcinogenic) was detected from over 88% of ABS filaments. Another thing to note is, some ototoxic chemicals, such as toluene and styrene, were also among the commonly detected VOCs. Exposure to these chemicals, or concurrently exposing to chemicals and noise, may pose increased risks of hearing loss (Hemmativaghef, 2020; Hoet and Lison, 2008).

Exposure concentrations for the chemicals in Fig. 5 were estimated and compared to the reference levels from US and global regulations and guidance (Fig. 6). US-based references include CA Specification 01350, CA OEHHA, and ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) Standard 189.1. Global regulations were accessed via the Indoor Environmental Quality Guidelines database; specific references from Germany (DE, German Committee on Indoor Air Guide Values), Japan (JP, Committee on Sick House Syndrome), and Poland (PL, Ordinance of the Minister of Health) were selected based on their stricter requirements. (Toyinbo et al., 2022; Database - IEQ Guidelines) Among the 22 chemicals of concern with reference limits, only 8 had estimated exposure concentrations lower than the smallest reference levels. All estimated personal exposure to benzene and formaldehyde were higher than the maximum allowable concentrations listed by Specification 01350 (1.5 μg/m^3 for benzene and 9 μg/m^3 for formaldehyde). In addition, over 75% of the personal

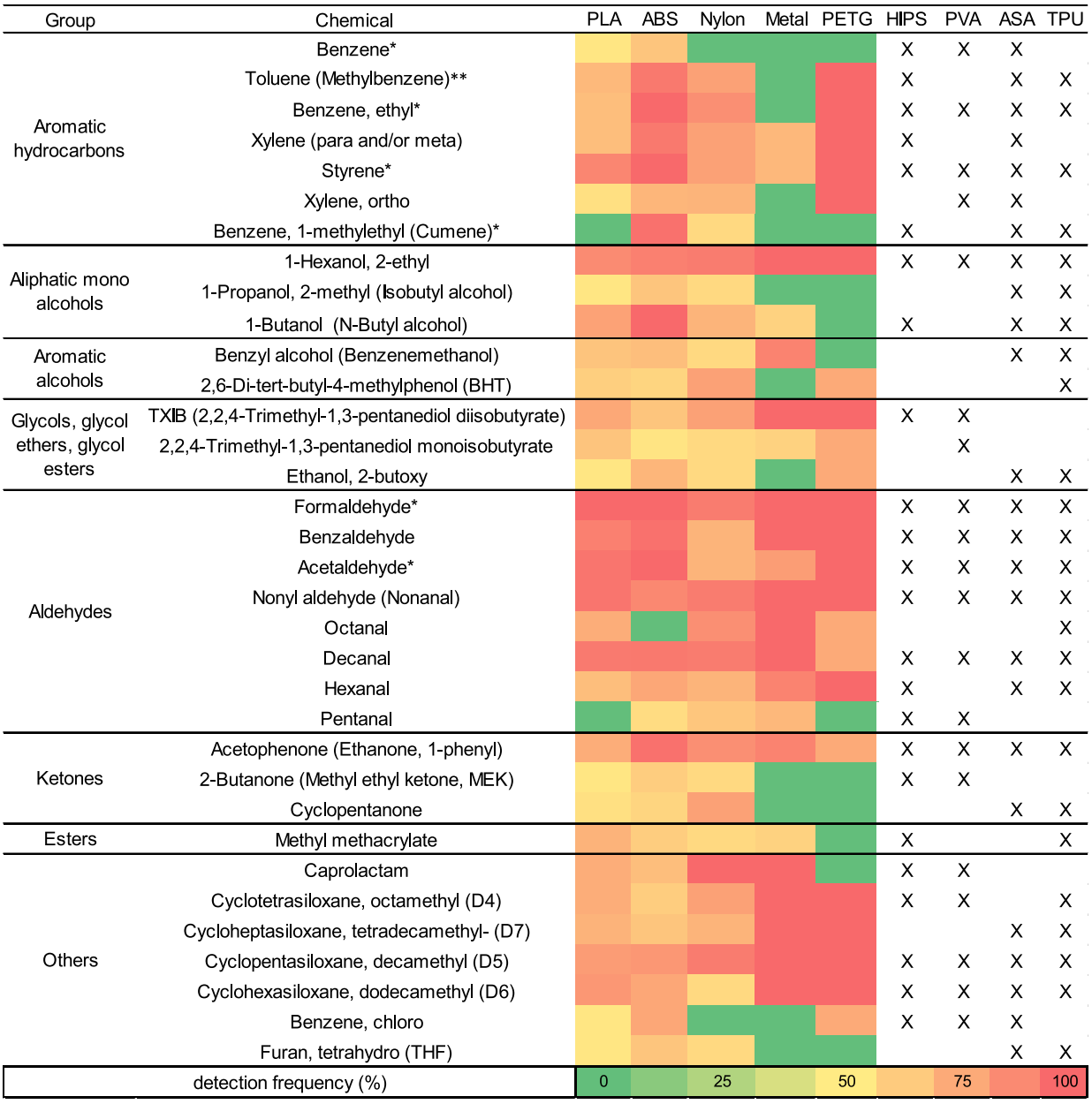

Fig. 5. Chemicals of concern detected from at least five out of nine filament materials with detection frequency (%) shown in heatmap. "*" indicates carcinogen and "**" indicates developmental toxin according to Proposition 65; "×" indicates detected from materials with one experiment.

exposure exceeded the acute REL for formaldehyde (55 μg/m^3) and all of the personal exposure exceeded the 8-hour and chronic REL for benzene (3 μg/m^3). All the personal exposure to caprolactam exceeded 8-hour REL (7 μg/m^3) and 58% were higher than the acute REL (50 μg/m^3). Exposure to nonanal and octanal both showed over 90% of exceedance according to ASHRAE 189.1. Additional 4 chemicals of concern had exceedance frequency of no less than 50%, which were acetaldehyde, styrene, benzaldehyde, and ethylbenzene. Other less frequent exceedances included chlorobenzene, 2-butoxyethanol, 2-ethylhexanol, xylene (para and/or meta), and toluene.

Specifically, all exceedances of ethylbenzene were from ABS, HIPS, and ASA filaments. In addition, personal exposure to styrene and benzaldehyde from these three filaments were all above the reference levels. These were likely associated with the styrene monomer in these filament materials. Similarly, all caprolactam from nylon materials exceeded OEHHA acute REL. Overall, ABS, HIPS and ASA materials were more likely to have personal exposure concentrations exceeding the reference levels. The print conditions with more exceedances for ABS material were associated with printer brand *B* and filament brand *b*. Among the chemicals of concern, formaldehyde, styrene, caprolactam, acetaldehyde and benzene were more likely to exceed the references for personal exposure.

The minimum reference limits from regulations and guidance are typically based on long-term exposure health evaluations, which may not be the case for 3D printing use. However, these levels were referred to as conservative assessments. It should be noted that 3D printing VOC emission is a complex mixture of various chemicals that could elevate exposure health impacts due to chemical interactions. The predicted personal exposure concentrations were based on one printer operation, exposure concentrations tend to increase with more printers and other emission sources. Chemicals including aldehydes like formaldehyde, acetaldehyde, nonanal, decanal, aromatics like toluene, benzene, ethylbenzene, siloxanes and others are frequently detected in indoor environments, sourcing from building materials and furniture, consumer and

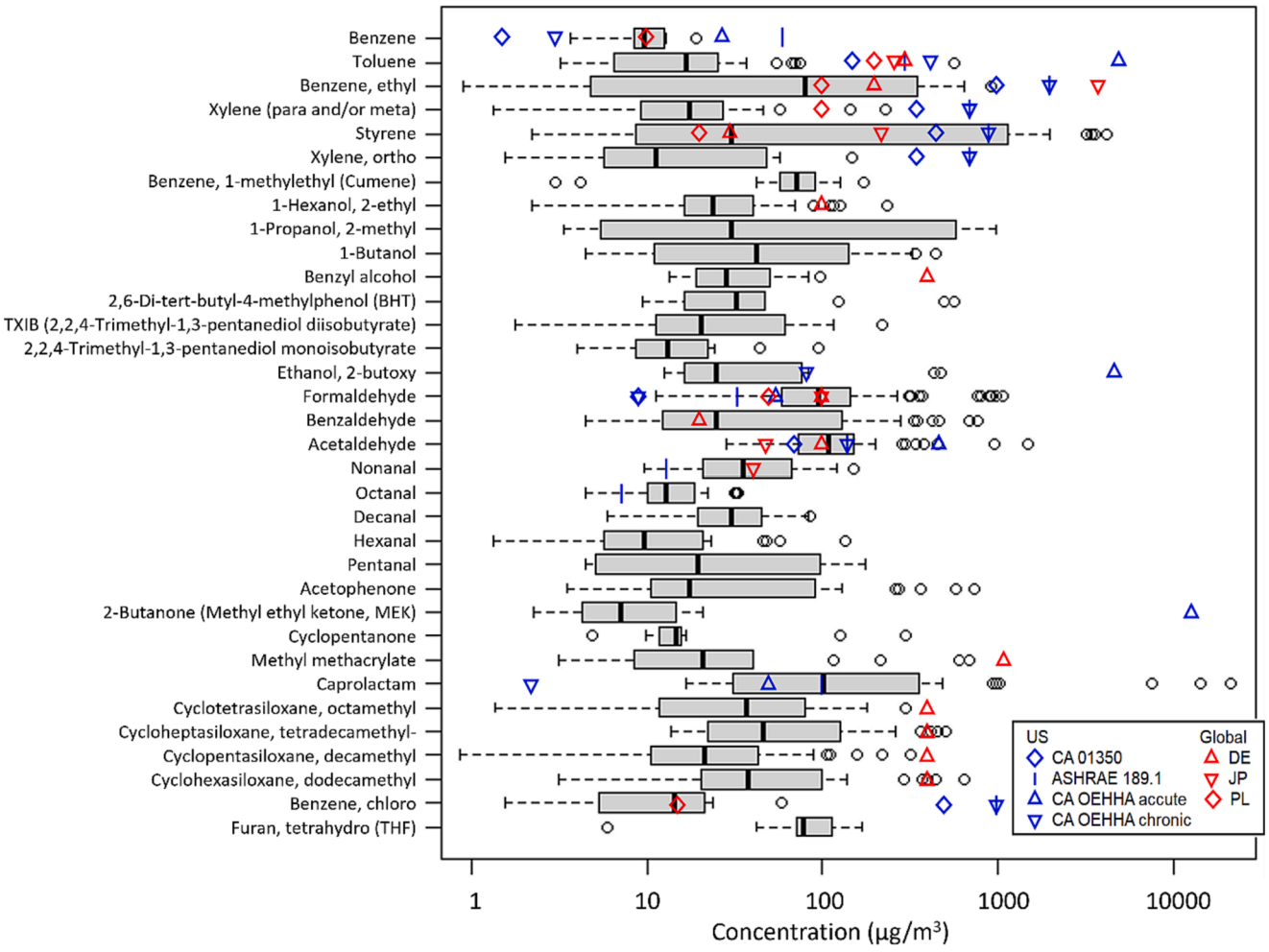

Fig. 6. Estimated personal exposure concentrations shown in boxplots for each commonly detected chemical of concern under various print conditions. Markers indicate recommended minimum indoor exposure levels from different references.

personal care products and cooking activities (Jia et al., 2008; Arata et al., 2021; Hodgson et al., 2000; Norris et al., 2019; Wakayama et al., 2019). In environments with limited ventilation, chemicals could linger for extended time or re-release from absorptive materials and objects.

4. Conclusions

In this study, a comprehensive set of 3D printing emission data obtained using a standardized chamber testing protocol, ANSI/CAN/UL 2904, was consolidated. Emission characteristics and potential health impacts of exposure were evaluated based on 447 particle emission and 58 VOC emission observations with different filament properties and print conditions. The IQR of particle emission rate ranged from approximately 10^9–10^{11} #/h with UFPs dominating the emissions, which agrees with previous publications (Azimi et al., 2016; Floyd et al., 2017; Kim et al., 2015; Kwon et al., 2017). ABS, HIPS, and nylon materials tended to emit higher particle number emissions, while metal composite material tended to emit larger particles and higher mass emissions. An extended list of VOCs was identified, which included aromatics, aldehydes, alcohols, ketones, esters and siloxanes. The most abundantly emitted VOCs were usually linked with the polymer composition, which has been previously reported for ABS, PLA, and nylon materials (Davis et al., 2019; Azimi et al., 2016). Specifically, styrene was the most abundantly emitted VOC from all three studied materials with styrene monomer. Metal composite material, on the other hand, emitted relatively lower VOCs with formaldehyde being the most abundant VOC. The association between emission characteristics and printing conditions was largely dependent on the variations of printing conditions. Printer brand, filament brand and extrusion temperature were significantly associated with particle emissions from ABS and PLA materials, while VOC emissions were less sensitive to these condition variations. In addition, no clear relationship was found between particle and VOC emission characteristics, thus the emission trend of one pollutant cannot be used to predict that of another pollutant.

Model estimated personal exposure to particles emitted from some ABS, HIPS and high emitting PLA filaments can be higher than particle levels typically measured in indoor environments. Estimated indoor exposure to $PM_{2.5}$ exceeded the NAAQS in office and residential settings. Although mass-based standards were used as references due to the lack of number-based standards, it should be noted that 3D print emitted particles are mainly ultrafine in size, which potentially pose more health concern given their high mobility and other properties associated with their small sizes. Similarly, carcinogens (including potential carcinogens) like formaldehyde, styrene, and acetaldehyde were detected from over 80% of the filaments studied. Personal exposure to chemicals of health concern showed some exceedances compared to recommended indoor exposure limits, and the most concerning VOCs were benzene, styrene, formaldehyde, benzaldehyde, acetaldehyde, and caprolactam. Overall, ABS and HIPS materials tended to have the highest concern regarding both particle and VOC exposures. Nylon presented high particle and caprolactam exposures. ASA emitted high VOCs and hazardous VOCs. Metal composite material emitted higher particle mass. PLA

showed generally low emissions although there were some outliers. Therefore, 3D printing emissions pose a health concern for users when exposed to this complex mixture of UFPs and various hazardous chemicals, which may induce acute irritation or other health effects depending on exposure scenarios. As emerging materials and technologies are becoming available, users should be aware of the potential hazards of emissions and take appropriate practices to mitigate exposure. If applicable, users can avoid using high emitting materials such as those with styrene monomer, as well as avoid operating the printer in confined spaces or with limited ventilation.

CRediT authorship contribution statement

Qian Zhang: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Marilyn S. Black:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2023.108316.

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