EPA Public Access

Author manuscript

Sci Total Environ. Author manuscript; available in PMC 2021 September 20.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Sci Total Environ. 2020 September 20; 736: 139604. doi:10.1016/j.scitotenv.2020.139604.

Particle and Volatile Organic Compound Emissions from a 3D Printer Filament Extruder

Peter Byrley¹, M. Ariel Geer Wallace², William K. Boyes³, Kim Rogers⁴

¹Health and Environmental Effects Assessment Division, Center for Public Health and Environmental Assessment, USEPA, RTP, NC 27711

²Air Methods and Characterization Division, Center for Environmental Measurement and Modeling, USEPA, RTP, NC 27711

³Public Health and Integrated Toxicology Division, Center for Public Health and Environmental Assessment, USEPA, RTP, NC 27711

⁴Watershed and Ecosystem Characterization Division, Center for Environmental Measurement and Modeling, USEPA, RTP, NC 27711

Abstract

Fused Deposition Modeling (FDM®), also known as Fused Filament Fabrication (FFF), 3D printers have been shown in numerous studies to emit ultrafine particles and volatile organic compounds (VOCs). Filament extruders, designed to create feedstocks for 3D printers, have recently come onto the consumer market for at-home hobbyists as an alternative to buying 3D printer filaments. These instruments allow for the creation of 3D printer filaments from raw plastic pellets. Given the similarity in processes and materials used by 3D printers and filament extruders, we hypothesized that filament extruders may also release ultrafine particle emissions and VOCs. An off-the-shelf filament extruder was operated in a 2 m³ chamber using three separate feedstocks: acrylonitrile butadiene styrene (ABS) pellets, pulverized poly-lactic acid (PLA), and PLA pellets. Ultrafine particle emissions were measured in real-time using a scanning mobility particle sizer and thermal desorption tubes were used for both non-targeted and targeted analysis of VOCs present in emissions. Ultrafine particle number emission rates were comparable to those found in 3D printer studies with the greatest to least emission rates from ABS pellets, pulverized PLA, and PLA pellets, respectively. In addition, the majority of particles released were found to be ultrafine (1–100 nm), similar to 3D printer studies. A variety of VOCs were identified using the ABS feedstock, including styrene and ethylbenzene, and PLA feedstock. Styrene average mass

CRedit authorship contribution statement

Peter Byrley: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **M. Ariel Geer Wallace:** Methodology, Investigation, Formal analysis, Resources, Writing - original draft, Writing - review & editing. **William K. Boyes:** Conceptualization, Methodology, Writing - review & editing, Resources, Supervision, Project administration, Funding acquisition. **Kim Rogers:** Conceptualization, Methodology, Writing - review & editing, Resources, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors have no conflict of interest.

Appendix A. Supplementary data

Conflict of Interest

The authors have no conflict of interest.

concentration amounts were found to be near the EPA Integrated Risk Information System Reference Concentration for Inhalation Exposure for 3 min and 5 min samples. Further studies will be needed to determine the impact on emissions of environmental volume, air exchange rate, and extruder settings such as extrusion speed and temperature. The results support the hypothesis that use of a filament extruder may present an additional exposure risk to 3D printer hobbyists.

Graphical Abstract

Keywords

Extruder; Plastics; VOCs; 3D printer; Ultrafine particles; Emissions

1. Introduction

Emissions in Fused Deposition Modeling (FDM®) 3D printers have been recorded in studies since 2013 (Byrley et al., 2019; Stephens et al., 2013; Vance et al., 2017). These emissions consist of both particles and volatile organic compounds (VOCs) that are released from the heated feedstock material as it is pushed through the printer's nozzle to create a 3D object. The majority of these particles have been consistently found to be ultrafine in size (less than 100 nm in physical diameter) and released on the order of millions to billions of particles per min (Vance et al., 2017; Yi et al., 2016; Zhang et al., 2017). Emitted VOCs have been found to be a mix of different compounds depending on the filament used (Gu et al., 2019). Available filament materials include acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), nylon, high impact polystyrene (HIPs), polyvinyl alcohol (PVA) and others (Azimi et al., 2016). VOCs, and their associated filaments, that have been recorded include styrene (ABS), ethylbenzene (ABS, HIPs), benzaldehyde (ABS, PLA), acetaldehyde (ABS, PLA), caprolactam (PLA, nylon, HIPs), acetone (ABS, PLA), lactide (PLA) and many others (Azimi et al., 2016; Davis et al., 2019; Gu et al., 2019; Potter et al., 2019).

There has been concern that the emissions from use of FDM® 3D printers may present an exposure risk. Inhalation of ultrafine particles (UFPs) from sources other than 3D printers has been associated with oxidative stress and cytotoxicity in the lungs and translocation to

other organs causing extrapulmonary effects. In addition, inhalation of UFPs has been linked to systemic and pulmonary inflammation, and increased morbidity and mortality (Oberdorster et al., 2005; Poh et al., 2018; Schmid et al., 2009). UFPs have been shown to have greater deposition efficiency in the deep lung than larger particles (Daigle et al., 2003). Inhalation of some VOCs has been linked to adverse effects, including irritation of the respiratory system, sensory effects, and cancer formation (Dehghani et al., 2018; He et al., 2015; Wolkoff, 2013). In particular, styrene and ethylbenzene are labeled as “probably carcinogenic to humans” (Group 2A) and “possibly carcinogenic to humans” (Group 2B), respectively by the International Agency for Research on Cancer (IARC) (IARC, 2000, IARC, 2019). 3D printer emissions stimulated adverse cardiovascular responses in Sprague-Dawley rats (Stefaniak et al., 2017a). Also, a recent study found that 3D printer emissions induced toxicological effects in human small airway epithelial cells (Farcas et al., 2019).

To reduce the filament cost and customize compositions, 3D printer filament extruders are being used in residential and small business settings to create filaments for 3D printers. Creation of filament using raw plastic pellets can be cheaper than buying fabricated filament and give the consumer the option of recycling used plastic. To date, most commercially available 3D printer filament extruders use a screw extrusion process to create base polymer filaments such as PLA and ABS or composite filaments that incorporate a filler material into the polymer matrix (Fig. 1). These composite filaments are varied and may include carbon nanotubes, graphene, metal particles, wood, and other additives.

Emissions from FDM® 3D printers have been recorded for operating temperatures from 180 °C to 280 °C with higher temperatures producing higher levels of both particulates and VOC emissions (Byrley et al., 2019; Deng et al., 2016; Potter et al., 2019; Zhang et al., 2017). In addition, a wide variety of filament materials have been shown to release emissions, including ABS and PLA (Azimi et al., 2016; Davis et al., 2019; Vance et al., 2017). Although the operating temperature recommended for extruders (both ABS and PLA feed stocks) are typically lower (e.g. 180 °C), the increased metal heating contact areas for the screw and extrusion nozzle are likely to result in particulate and VOC emissions comparable to 3D printers. A study in 2008 found that a large, industrial sized, twin-screw extruder produced airborne particles when using nano-aluminum oxide additive and polymethyl methacrylate (PMMA) or ABS as feedstocks (Tsai et al., 2008). A study in 2002 looking at extrusion of polycarbonate (PC) and a PC/ABS blend from a large, industrial sized, single-screw extruder found that, while overall emissions were low, the PC/ABS blend had the highest emissions of particulates and VOCs (Rhodes et al., 2002). A study in 2015 found that extrusion of ABS plastic solid waste using an industrial extruder released styrene, ethylbenzene, xylene, toluene, and i-propylbenzene (He et al., 2015). These studies suggest that smaller, hobbyist filament extruders may also release emissions. However, to our knowledge, emissions from at-home filament extruders have not been previously reported.

The objective for this study was to test both particle and VOC emissions from a commercially available filament extruder. We hypothesized, based on the similarity between the materials and processes of 3D printing and filament extrusion, that filament extruders may also release particles and VOCs. To simulate the use of a filament extruder by an at-home hobbyist and limit the amount of testing variables, we tested one common extruder

brand and used three different plastic feedstock types under the same conditions. These three feedstocks, ABS pellets, PLA pellets, and pulverized PLA are plastics that make popular filaments in FDM® 3D printing and their filaments have been analyzed for emissions frequently in the literature (Byrley et al., 2019; Zhang et al., 2017).

2. Methods

2.1. Chamber experiment setup

A commercially available twin-screw 3D printer filament extruder was placed inside a Hazelton (Lab Products, Seaford, DE) 2000 liter (2 m^3) chamber and operated according to manufacturer instructions. Particle emissions and VOCs were measured from the extrusion process while using the chamber as secondary containment for particles and VOCs. The overall methodology for measuring emissions was based on the “ANSI/CAN/UL 2904 Standard for Measuring Particle and Chemical Emissions from 3D Printers” (Underwriter Laboratories, 2019). The chamber had an air exchange rate of one exchange (2 m^3) per hour. Particle number concentrations were initially measured using a P-TRAK Ultrafine Particle Counter Model 8525 (TSI, Shoreview, MN) at several points in the chamber to ensure that particles were well-mixed within the chamber. The average coefficient of variation of particles within the chamber was found during extrusion to be 1.3% (see Supplementary Section 1). Air entered the chamber from the top and was filtered using a high-efficiency particulate air (HEPA) and activated carbon filter to create a clean, positive pressure environment. A diffuser plate was located at the top of the chamber and a small fan with an airflow of 26 cubic feet per min (cfm) was placed near the bottom of the chamber to increase mixing efficiency (McClellan and Henderson, 1995). The entire chamber was grounded to prevent excess surface charge.

2.2. Particle measurements

The filament extruder was run at a setting of 180°C for three different feedstock types: ABS pellets, PLA pellets, and pulverized PLA pellets, in order to normalize temperature as a variable (Filabot, Barre, VT). The manufacturer recommended extrusion temperatures were $180\text{--}200^\circ\text{C}$ for PLA feedstocks and $180\text{--}190^\circ\text{C}$ for the ABS feedstock. ABS pellets were rectangular and 3 by 4 by 2 mm in size. PLA pellets were spherical with an approximate diameter of 4 mm. Pulverized PLA pellets varied in diameter from approximately 2 mm and below (see Supplementary Section 2). The hopper of the extruder was completely filled with feedstock before each extrusion to maximize run time, with approximately 240 g of ABS or PLA pellets, and approximately 200 g of pulverized PLA.

Particle sampling was performed using a Scanning Mobility Particle Sizer (SMPS) Model 3936 (TSI, Shoreview, MN) and P-TRAK Ultrafine Particle Counter Model 8525. The SMPS has a lower size limit of particle measurement (15.1 nm) than the P-TRAK (20 nm) and the P-TRAK has been found to underestimate UFP counts compared to SMPS instruments (Zhu et al., 2006). Thus, the P-TRAK was only used for redundancy to ensure that fluctuations in particle number concentration were similar across instruments. Sampling lines were located 20 cm from the chamber wall and 20 cm from the extruder head. Electrostatic dissipative lines were used to prevent attraction to line sidewalls.

The chamber was sampled at 2 min intervals for 8 min prior to extrusion to provide four background measurements using the SMPS 3936 and was sampled at 1 min intervals for eight background measurements using the P-TRAK. The SMPS 3936 sampled at a flow rate of 0.3 l per min (lpm) and the P-TRAK sampled at a flow rate of 0.1 lpm. The extruder heating element, previously set to reach 180 °C, was then manually turned on by inserting a small rod through a port in the chamber sidewall. After 6 min of heating, the extruder reached 180 °C and a rod was then again inserted through the chamber sidewall to turn on extrusion. Data were recorded using both the SMPS 3936 and P-TRAK during extrusion and continuing for an hour after extrusion had been terminated to observe the decay in particle number concentration within the chamber. Twelve runs of each plastic type were performed. The first six runs were completed to purge the system of previous plastic material. The last six runs were completed to collect particle data. Total extrusion time varied by feedstock type and from run to run, with the average run time for the last six runs being 51 min for ABS pellets and PLA pellets and 40 min for pulverized PLA feedstock.

To evaluate particle morphology, particles were captured on carbon film 200 mesh nickel grids (catalog no. 1840-F, Ted Pella, Redding, CA) using a TPS100 Nanoparticle Sampler (RJ Lee Group, Monroeville, PA). These experiments used 40 g of each feedstock material which allowed the extruder to run for a total of 7 min. The TPS100 was operated for 27 min at a flow rate of 5 ml/min to capture particles during the 7 min of extrusion and 20 min afterward. The sampler was placed next to the extrusion head to ensure the capture of particles. After sampling, the grids were secured to metal stubs and imaged using a Zeiss Sigma EVO Scanning Electron Microscope (Carl Zeiss Microscopy LLC, White Plains, NY).

2.3. Particle data analysis

The particle number concentration data from the last six runs of each plastic type were analyzed. Concentration data measured by the SMPS were averaged for each plastic type and a standard deviation at each point was calculated. Size distribution data were extracted for each run and a representative set was published in the results for the eleventh run. Particle mass concentrations were calculated using the equation (TSI, 2010):

$$dM = dN \left(\frac{\pi}{6} \right) D_p^3 \rho \quad [\text{Eqn. 1}]$$

where dM is mass concentration, dN is the number concentration, D_p is the geometric midpoint of the particle size channel and ρ is the density input for those particles. Mass concentration data were internally calculated within the SMPS instrument using an input bulk polymer density for ABS and PLA, 1.05 and 1.24 g/cc, respectively. Particle number emission rates were calculated using the following equation in the ANSI/CAN/UL 2904 standard (Underwriter Laboratories, 2019):

$$PER(t) = V_c^* \frac{C_p(t) - C_p(t - \Delta t) \exp(-\beta \Delta t)}{\Delta t \exp(-\beta \Delta t)} \quad [\text{Eqn. 2}]$$

where V_c is the volume of the chamber, C_p is the measured number concentration, and Δt is the change in time from one sampling point to the next. In addition, a loss factor, β , was calculated using the concentration values recorded between 15 min after termination of extrusion until the end of the recorded data for each individual run, as recommended in the ANSI/CAN/UL 2904 standard (Underwriter Laboratories, 2019). The loss factor considers particles lost through flow out of the chamber from continuous air exchange and sampling lines along with wall losses (Underwriter Laboratories, 2019). All emission rates were calculated from the raw data from each run and, as explained in Section 3.4, averaged over the last six runs.

Any negative emission rate values in individual runs were set to zero, similar to 3D printer studies (Azimi et al., 2016; Vance et al., 2017). Negative emission rates resulted from factors not considered by the emission rate equation including particle-size dependent losses or variations in particle loss rates from moment to moment, because the particle loss coefficient is an average, which can lower the overall count of particles (Azimi et al., 2016; Underwriter Laboratories, 2019; Vance et al., 2017). In addition, calculated emission rate values that were negative were set to zero because a negative extruder emission rate would indicate the extruder is removing more particles than it is generating, which does not make physical sense (Byrley et al., 2019).

2.4. VOC measurements

VOC samples were collected using Carbograph 2TD/1TD dual bed sorbent tubes (catalog no. C2-AXXX-5126, Markes International, Gold River, CA). Sorbent tubes were conditioned at 380 °C for 2 h while purging with 75 ml/min of research grade helium gas (99.9999%, Airgas, Morrisville, NC, USA) using a TC-20 tube conditioner (Markes International). Sorbent tubes were blanked by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) and conditioned again at 380 °C for 2 h prior to sample collection.

Samples were collected for non-targeted analysis of the three plastic types and additionally, samples were collected for ABS pellets as a targeted analysis to quantify priority compounds, including styrene and ethylbenzene. Overall guidance on how to perform VOC measurements was taken from EPA Method TO-17 (EPA, 1999). Sampling was performed for non-targeted analysis in a set of four samples for ABS pellets and three samples for pulverized PLA and PLA pellets. Non-targeted VOC samples used a full hopper of feedstock material and samples were taken 23 min after extrusion began, as this was the average time when particle emissions were found to be at their peak. VOC measurements were taken for 10 min at 100 ml/min for a total of 1 l of air. The vacuum line used for the VOC measurements was calibrated before each run using a DryCal DC-1 flow calibrator (Mesa Labs, Butler, NJ).

Samples collected for targeted analysis of ABS pellet emissions were collected using 70 g of ABS pellets for each run. Samples were collected at a flow rate of 50 ml/min in two sets: 3 min and 5 min samples. Five min samples were taken immediately after 3 min samples for each extrusion. Sample blanks of chamber air were collected without extruder operation using the same temporal schedule. Three independent samples were collected for targeted

analysis of ABS pellets. ABS was reported in the 3D printing literature to have the greatest types and amounts of VOCs released, so these were investigated in more depth than the other plastic feedstocks (Davis et al., 2019; Stefaniak et al., 2017b).

VOC calibration standards were prepared by diluting a TO14 calibration standard mixture with humidified air and varying the volume of standard gas that was added to each tube to achieve the desired concentration. The gaseous TO14 43 component standard mixture at 1 parts per million (ppm) in nitrogen was supplied by Linde Electronics & Specialty Gases (Stewartsville, NJ, USA). Tylan mass flow controllers (Coastal Instruments, Burgaw, NC) were used to control the flow rates, and all flow rates were verified prior to calibration loading. An EASY-VOC syringe was used to load the calibration gas onto each sorbent tube. For the 0.50 parts per billion by volume (ppbv) calibration level, 50 ml of diluted calibration gas was loaded; for 1.0 ppbv, 100 ml was loaded; for 2.0 ppbv, 200 ml was loaded; for 4.0 ppbv, 400 ml was loaded; for 10.0 ppbv, 1000 ml was loaded, and for 20.0 ppbv, 2000 ml was loaded. All standards were loaded in duplicate at 18.7 °C and a relative humidity of 48.8%. Calibration standards were stored at 4 °C until instrumental analysis.

The TD-GC/MS was calibrated by analyzing two sorbent tubes as helium blanks and then a conditioned Carbograph 2TD/1TD sorbent tube as a laboratory blank. Standards were analyzed from low to high concentration, with two sorbent tubes per concentration. A calibration check sample (2.0 ppbv) was included before and after the sample sequence to assess instrument drift.

2.5. TD-GC/MS analysis

Samples and standards were analyzed using a Markes International TD-100xR thermal desorption system coupled to an Agilent Technologies 7890B GC/5977B MSD (Santa Clara, CA, USA). Thermal desorption was achieved using a standby split of 20 ml/min and a dry purge of 50 ml/min for 5 min. Sorbent tubes were desorbed for 10 min at 375 °C with a 100 ml/min trap flow. The trap was purged for 2 min at 50 ml/min. The trap was heated from 30 °C to 385 °C at 40 °C/s, and the trap was desorbed for 3 min. The flow path temperature was set to 120 °C. For targeted analyses only, a 20 ml/min outlet split was employed.

Compounds were separated using a 30 m Rtx-VMS column with 0.25 mm ID and 1.4 µm film thickness (Restek Corporation, Bellefonte, PA). Research-grade helium carrier gas was used with a column flow rate of 2 ml/min. The oven temperature was held at 30 °C for 3 min, ramped to 150 °C at 8 °C/min, and ramped to 240 °C at 36 °C/min and held at 240 °C for 5 min. The MS source and quadrupole temperatures were held at 230 °C and 150 °C, respectively. For non-targeted analyses, ions were monitored from 35 to 300 *m/z* (mass/charge number) using scan mode. For targeted analyses, ions were monitored from 35 to 300 *m/z* using SIM/scan mode. Target and qualifier ions for benzene, toluene, ethylbenzene, and styrene were monitored in SIM mode.

2.6. VOC data analysis

Non-targeted data were analyzed using Unknowns Analysis software version B.09.00 (Agilent Technologies). Features were identified by deconvolution, excluding ions 28 and 207 with an area filter of greater than 15,000 counts. Three window size factors were

allowed: 50, 100, and 200. Ions were extracted from 0.3 to 0.7 m/z and the base peak shape was used with a 25% sharpness threshold. Spectra were searched using the NIST14 library with a normal pre-search, adjustable score, and a pure weight factor of 0.3 (where zero is reverse search and one is forward search). A maximum hit of five compounds was allowed with a minimum match score of 75 to screen a large number of initial identifications. The match score reflects how closely the sample spectrum and reference spectrum compare, and is calculated using an internal algorithm (Agilent Technologies, 2017). Blank filtration was performed within a 5x full-width half-maximum (FWHM) retention time window if the component area in the sample was less than or equal to 100% of the blank. Chamber blanks were paired with the corresponding samples for Unknowns analysis.

All non-targeted compounds with a match score below 85 were then excluded from the final data to remove identifications that were less reliable. These compounds were then ordered by base peak area from largest to smallest and the top 10 compounds from each sample were combined into a master list for each plastic type. The top 10 hits for each blank and sample (based on base peak area) were assessed for accuracy according to NIST library search identifications. A confidence level in determination was made using the guidance from published criteria (Schymanski et al., 2014). Decision criteria for identifying compounds, including retention time, mass/charge ratio and identified qualifier ions are presented in supplementary tables (see Supplementary Section 6).

Targeted data were analyzed using Enhanced ChemStation version F.01.03 (Agilent Technologies). Base peak ions for target compounds (benzene, toluene, ethylbenzene, and styrene) were integrated, and peak areas were exported into Excel along with retention times and qualifier ion ratios. M- and p-xylene co-eluted and were therefore integrated as one peak. Six-point calibration curves were constructed in Excel at levels of approximately 0.50, 1.0, 2.0, 4.0, 10.0, and 20.0 ppbv based on benzene equivalency. Exact concentrations of each target compound (based on -mass (or amount) loaded on each tube according to the TO-14A standard) were used for construction of calibration curves. Calibration curves were background corrected by subtracting out the average value of the laboratory blanks from each calibration point. This was performed to account for any background contaminants remaining on sorbent tubes prior to sampling. Calibration curves were fit to second-order polynomial regression equations, which were used to calculate VOC concentrations in the samples. The calculated concentrations were corrected for instrument drift using the weighted average of the 2.0 ppbv calibration check standard that was analyzed before and after the sample sequence. Sample concentrations were then corrected for tube background by subtracting out the average value of the conditioned sorbent tube blanks analyzed in the calibration and sample sequence.

3. Results and discussion

3.1. Particle number concentration

Average particle number concentrations for each feedstock material over the extrusion time are displayed in Fig. 2. These averages were calculated from the last six runs of the filament extruder for each plastic type. ABS was shown to have the highest particle number concentration, followed by pulverized PLA and finally PLA pellets. This is similar to 3D

printing studies which show that ABS produced greater emissions than did PLA (Byrley et al., 2019). The temporal pattern of particle number concentration was different from 3D printers, however, in that 3D printer emission studies typically show a large peak of particles in the beginning of the run followed by an exponential decay of particle number concentration (Zhang et al., 2017). This is theorized to be because of overheating of the 3D printer filament in the 3D printer nozzle at the start of printing (Simon et al., 2018). The filament extruder was started immediately once the temperature reached 180 °C preventing overheating from occurring. It was observed that particle number concentrations from the extrusion of pulverized PLA were found to be much higher than when PLA pellets were used. This is hypothesized to be due to the increased surface area per volume ratio of pulverized PLA versus PLA pellets which aided in the evolution of particles and vapors, though the difference in surface area per volume was not quantified between the pulverized PLA and PLA pellets. Typically, when degradation of a polymer occurs, mass loss is proportional to the surface area (Chamas et al., 2020). The difference in particle concentrations is also hypothesized to be due to impurities present in pulverized PLA that were different from those found in PLA pellets. Table 2, Table 3 show that different volatile compounds were identified between emissions from the extrusion of pulverized PLA or PLA pellets.

3.2. Particle number concentration size distributions

Fig. 3 shows particle number concentration size distributions over time for the 11th run using ABS pellets, pulverized PLA, or PLA pellets. For run 11, extrusion stopped at 50, 54, and 38 min for ABS pellets, PLA pellets and pulverized PLA, respectively. The time points from 0 to 40 min for ABS pellets and PLA pellets, and time points 0–30 min for pulverized PLA occur during extrusion, at which particles and VOCs start to generate (left side of Fig. 3). The time points past these values, 50–80 min for ABS pellets and PLA pellets, and 40–70 min for pulverized PLA occur during the end of the extrusion process and after extrusion has been terminated (right side of Fig. 3). The left side of Fig. 3 shows emissions of mostly UFPs at the start of the extrusion process. The 20 min line takes place 6 min after extrusion has started. The right side of Fig. 3 shows a drop in concentration with a shifting median particle size. This indicates particles leaving the chamber and a physical phase shift from vapors to aerosols present in the atmosphere, similar to that seen in 3D printer studies (Vance et al., 2017; Zhang et al., 2017). As the amount of VOCs emitted from a 3D printer increases in a chamber environment, the rate at which new larger particles are formed increases (Zhang et al., 2017). The filament extruder showed a similar drop in concentration and shifting median particle size, similar to 3D printers.

Particle sizes were found to be overall larger for ABS and PLA pellets than pulverized PLA. This may be due in part to the difference in size between starting feedstocks. Pulverized PLA feedstock (2 mm in diameter and below) was smaller than the ABS pellets (4 by 3 by 2 mm) and PLA pellets (4 mm diameter) (see Supplementary Section 2). The effect of the filament extruder grinding and heating processes on the two PLA pellet size distributions may have contributed to the observed differences in emissions. In future studies, a wider range of starting feedstocks, including those with different sizes, will need to be studied.

Scanning electron microscope (SEM) images were also taken of particles captured during active extrusion (see Supplementary Section 5). Particles imaged were larger than the majority of the UFPs measured with the SMPS. This is in part due to limitations of the size resolution that the SEM system could not overcome. Also, it may be that vapors adsorb to the surface of these particles while on the filter causing caught particles to be larger in size. The particles identified are similar in morphology and size to those imaged using SEM in 3D printer studies (Farcas et al., 2019; Stefaniak et al., 2018).

3.3. Particle mass concentration

Fig. 4 displays particle mass concentration summed over all particle sizes and recorded over the extrusion time for each type of plastic. ABS was found to have the greatest mass emitted followed by pulverized PLA and PLA pellets. These mass concentrations were estimated for each size bin by the SMPS software assuming the particle densities of the bulk polymers were 1.04 g/cm³ for ABS and 1.25 g/cm³ for PLA, according to the manufacturer. Total particle mass concentrations were found to be above the 24-h ambient exposure limit for PM_{2.5} set by the EPA of 35 µg/m³ for both ABS pellets and pulverized PLA. The peak value for PLA pellets was found to be 34.7 µg/m³, right at the limit of the 24-h exposure limit set by EPA. This indicates that continuous operation of a filament extruder in a confined space with an air exchange rate of one or smaller may lead to inhalation of PM_{2.5} above regulatory ambient standards. However, it should be noted that because the majority of the particles measured in this study are ultrafine in size that there are additional exposure implications specifically for inhalation of UFPs that cannot be completely summarized by comparing it to the PM_{2.5} mass standard (Ohlwein et al., 2019). In this study, we use the PM_{2.5} standard as a best comparison metric.

Because the densities of the airborne particles were not measured directly, a sensitivity analysis was performed using various densities to show how mass concentration could differ based on assumed density of each plastic type (see Supplementary Section 3). The sensitivity analysis showed that calculated mass concentration could vary considerably depending on assumed density. Particle mass concentration was found to peak above the 35 µg/m³ regulatory standard for all ABS cases and for one pulverized PLA case. In future studies, density of particles could be measured to obtain more accurate results such as by the use of a tandem method that first sizes particles by electrical mobility and then by aerodynamic sizing (Maricq and Xu, 2004).

As outlined in Section 2.2, these measurements were recorded within a chamber setting at 20 cm away from the extrusion head. This being the first study of emissions from a consumer extruder, understanding exposure within a realistic setting is beyond the scope of this project. However, ultrafine particles have very long settling times in comparison to larger particles so they may travel throughout a room. Also, volatile compounds may agglomerate onto particle surfaces and be inhaled or deposit onto surfaces (McClellan and Henderson, 1995). Further studies will need to be done to understand exposure in a realistic setting.

3.4. Particle number emission rates

Particle number emission rates were calculated and are shown in Fig. 5 for the same six runs used in Fig. 2, Fig. 4. ABS had the highest emission rates followed by pulverized PLA and then PLA pellets. Average emission rates over the active extrusion time were 3.5×10^{11} particles/min, 5.6×10^{10} particles/min, and 1.7×10^9 particles/min for ABS pellets, pulverized PLA and PLA pellets respectively. ABS and PLA particle emission rates were found to be comparable in order of magnitude to those found in 3D printer emission studies using these materials, including those with similar sized test chambers (Azimi et al., 2016; Byrley et al., 2019; Mendes et al., 2017; Vance et al., 2017; Yi et al., 2016; Zhang et al., 2017). Vance et al., 2017 measured the average emission rates of various 3D printers in a chamber and in several rooms and suggested that the relative particle exposure for a 1-h print time would be similar to that for laser printers under similar conditions. As explained in Section 2.3, all negative emission rates were set to zero. All negative emission rates occurred after active extrusion and their absolute values did not exceed 5% of the maximum emission rate for that run, as per the ANSI/CAN/UL 2904 standard (Underwriter Laboratories, 2019). All plastics showed slightly higher emission rates at the beginning of extrusion than the rest of the extrusion period.

The emission rates for the ABS values had greater standard deviations than the rates obtained using PLA. This correlated with greater number concentration standard deviations in Fig. 2. There was greater emission rate standard deviations than number or mass concentration because the emission rate calculation is created using the derivative of the rate of change of number concentration with additional losses considered from airflow out of the chamber, losses to surfaces and losses to instrument sampling lines that are incorporated into the equation (see Eq. (2) and Supplementary Section 4) (Byrley et al., 2019; Underwriter Laboratories, 2019). These components combined create greater variability, in terms of standard deviation.

Given the size and number of UFPs emitted from the filament extruder, it is reasonable to expect that these particles may provide greater cumulative exposure when used in conjunction with a 3D printer. UFPs may penetrate deeper into the lung and have longer retention times in the pulmonary region of the lungs than larger particles (ICRP, 1994). Thus, there may be cumulative deposition in the respiratory system if used frequently with some fraction of these particles also exiting into the bloodstream. In addition, though only base polymers were investigated in this study, it is likely that at-home hobbyists will use these extruders to create composite filaments like those sold commercially. Use of ABS-carbon nanotube (CNT) composite filament in a 3D printer has been shown to release particles with approximately 1% of those containing CNTs (Stefaniak et al., 2018). The proliferation of composite filaments may also lead to exposures from other embedded materials.

In future studies, different operational temperatures will need to be tested to understand temperature's effect on particle number concentration emissions for different feedstocks in the extruder. As mentioned in Section 2.2, the extrusion temperature used in this study was chosen as 180 °C to normalize temperature as a variable. Some 3D printer studies have shown that 3D printing ABS and PLA at the same temperature results in greater particle

number concentration emissions from ABS filament (Azimi et al., 2016; Deng et al., 2016). Another study showed the opposite result with PLA having greater particle number concentration emissions than ABS at the same temperature (Mendes et al., 2017). Total degradation of ABS filament in a nitrogen atmosphere has been reported at a higher temperature than PLA, 380–430 °C and 300–400 °C, respectively (Wojtyla et al., 2017). Different operational temperatures may degrade ABS and PLA in the extruder to different extents.

3.5. VOC analysis

Table 1, Table 2, Table 3 display data from the non-targeted analysis that were processed from samples collected during extrusion of ABS pellets, pulverized PLA and PLA pellets, respectively. The top 10 tentative compound identifications based on largest base peak area for each sample were combined into one list pertaining to each feedstock. Table 1 (ABS pellets) has a total of 11 compounds showing that there was heavy overlap between the top 10 compounds for each ABS sample. Table 2 (Pulverized PLA) and Table 3 (PLA pellets) have 15 and 14 compounds, respectively showing that though there was overlap between the top 10 compounds for all samples of each feedstock, there was less overlap than the ABS pellet samples. The confidence of the tentative identification of the VOCs varied based on published criteria (Schymanski et al., 2014). Only the compounds styrene, ethylbenzene, toluene, and benzene were confirmed using a standard and were thus given a confidence rating of 1, indicating that the structure was confirmed using a reference standard with mass spectrometry and retention time matching. All other identifications assigned were either 2a or 3 meaning that an exact structure was proposed using NIST library spectrum data and the spectrum-structure match was unambiguous or evidence existed for an identified structure but that the structure was similar enough to other compounds to be ambiguous, respectively (Schymanski et al., 2014).

As outlined in Section 2.6, all top ten compounds had matching scores above 85. The data revealed that all matching scores were also above 90 except for toluene in sample 1 of the PLA pellets emissions at a match score of 87.7, toluene in sample 2 of the PLA pellets emissions at a match score of 86.4, toluene in sample 3 of the PLA pellets emissions at a match score of 85.8, benzene in sample 2 of the ABS pellets emissions at a match score of 88.8 and phthalic acid in sample 3 of the pulverized PLA emissions at a match score of 85.9. Benzene and toluene, although having scores lower than 90, were confirmed by retention time and spectra match using standards and therefore these are confident identifications. Phthalic acid was not confirmed using standards but still had a match score above 85.

Results of the non-targeted analysis show that there were a variety of chemicals present in emissions from all feedstocks tested. All of the compounds in Table 1, except for 1,4-dioxane-2,5-dione, 3,6-dimethyl- (also known as lactide) have previously been reported for 3D printer emissions that used ABS feedstocks (Davis et al., 2019; Potter et al., 2019; Stefaniak et al., 2017b). The observation of lactide in ABS samples was surprising as lactide should not be a component of the ABS copolymer pellets unless there were impurities present when the plastic was manufactured. The presence of lactide in ABS sample emissions may be a result of PLA residue from previous runs. For pulverized PLA and PLA

pellets, lactide, 1-butanol, l-lactic acid, benzene, 1-dodecanol, toluene, acetic acid, methyl methacrylate, styrene, 1-hexanol 2-ethyl, methyl methacrylate, phenol, and acetophenone have been detected in 3D printer emissions using PLA feedstocks (Davis et al., 2019; Stefaniak et al., 2017b).

Styrene and ethylbenzene were detected in the ABS pellet samples and pulverized PLA samples. Ethylbenzene has been detected in numerous 3D printer studies using ABS filaments (Davis et al., 2019; Stefaniak et al., 2017b). Styrene has been detected in both the use of ABS and PLA feedstocks in 3D printers, though more prominently with the use of ABS feedstocks (Davis et al., 2019). The EPA Integrated Risk Information System (IRIS) program sets a reference concentration for inhaled exposure (RfC) of styrene at 1 mg/m³, which indicates that daily exposure to 1 mg/m³ of styrene would likely be without deleterious effects (EPA, 1992). Targeted analysis of styrene from emissions using ABS pellets in the extruder revealed an average of 0.423 mg/m³ and 0.788 mg/m³ for 3 min and 5 min samples respectively, values that are close to the EPA IRIS RfC (Table 4).

As indicated in Table 4, 5 min sample values were found to be slightly above the standard curve meaning that they are an extrapolation and not as reliable values as the 3 min samples. Using these values to linearly extrapolate to an average run time of 37 min, the total time it would take to run a full hopper of ABS pellets, the resulting concentration would hypothetically be 5.668 mg/m³ indicating that longer collection time may indicate greater exposure. Styrene concentrations in photocopy centers have been reported to range from 1.5–30 µg/m³ (Lee et al., 2006). The herein reported styrene emission value of 5.668 mg/m³ for the standard batch extrusion cycle falls above the range of values reported for photocopy centers. The EPA IRIS program also sets a RfC for ethylbenzene at 1 mg/m³ (EPA, 1991). Average values for ethylbenzene samples, 0.0142 and 0.0282 mg/m³ for 3 min and 5 min samples, respectively are two orders of magnitude below the EPA IRIS RfC for ethylbenzene. A linearly extrapolated value to 37 min under test chamber conditions, the total time it would take to run a full hopper of ABS pellets, is 0.200 mg/m³ for ethylbenzene.

Toluene and benzene were also quantified but values were found to almost all be below calculated limits of quantification and limits of detection. Future studies will be needed to investigate the amounts of these compounds. Greater amounts of feedstock and longer collection times will need to be tested to see the impact on VOC concentration measured. In addition, different feedstocks will need to be tested to see what VOCs can be quantified in emissions from their use in a filament extruder. Other than ABS and PLA, feedstocks for at-home extruders that are on the commercial market include polyethylene terephthalate glycol, high impact polystyrene, polyetherimide, polyetheretherketone and a variety of color additives. Also, filament extruders allow for users to extrude filaments from the use of old plastic objects such as toys, once pelletized, making the number of possible feedstocks for filament extruders quite large.

4. Conclusions

This study is the first to evaluate emissions from a commercially available, personal use 3D printer filament extruder. The results show that the use of this filament extruder emits large amounts of ultrafine respirable particles and various VOCs under the conditions that we used in this study. Operation of this filament extruder may present an additional exposure to ultrafine particle and VOCs inhalation for 3D printer hobbyists who also use a 3D printer. Ultrafine particle number emission rates were found to be comparable to those found in 3D printer studies. However, the number concentration profile stayed relatively constant over extrusion as opposed to 3D printer emissions which typically peak in the beginning of the printing process. Particle number concentration size distribution varied by the type of feedstock used, but the majority of particles were found to be in the ultrafine range for all feedstocks tested. Estimated particle mass concentration, using the assumptions of bulk density and a spherical shape, showed values above the 24-h exposure limit to PM_{2.5} set by EPA for the use of ABS pellets and pulverized PLA.

Non-targeted data revealed the presence of a multitude of compounds with match scores above 85 that were released during the use of ABS pellets, PLA pellets or pulverized PLA feedstocks that were similar to previously reported 3D printer studies. Additional studies will be needed to confirm these compounds and their amounts. Most notably, styrene and ethylbenzene were found to be released from ABS pellets. Targeted analysis found that styrene mass concentrations in emissions using ABS pellets were close to the EPA IRIS RfC value for styrene.

Future studies should consider the role of how environmental conditions affect emissions. This experiment most closely represents emissions within a small space with poor ventilation. However, the air exchange rate, airflow direction and room dimensions could affect exposures for at-home hobbyists using filament extruders in more realistic environments. In addition, the impact of multiple filament extruders should be considered and extrusion parameters including extrusion speed and temperature that can be set by the user and may influence emissions, similar to how print parameters in 3D printer studies may affect emissions (Simon et al., 2018). Different plastic materials and other additive materials will need to be tested to see if the creation of composite filaments release similar particles and VOCs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

We would like to thank Dr. Mark Surrette at the EPA for imaging particles using the Zeiss SEM system. In addition, we would like to thank our technical reviewers Dr. Ian Gilmour and Dr. Mark Higuchi at the EPA for their comments and suggestions on a draft version of this manuscript. This work was supported by the intramural research program of the U.S. EPA Office of Research and Development. Funding for Dr. Byrley was provided by the EPA NSSC program.

Funding

This work was supported by the intramural research program of the U.S. EPA Office of Research and Development. Funding for Dr. Byrley was provided by the EPA NSSC program.

References

- Agilent Technologies. (2017). Agilent MassHunter Workstation Software Quantitative Analysis
- Azimi P, Zhao D, Pouzet C, Crain NE, & Stephens B. (2016). Emissions of Ultrafine Particles and Volatile Organic Compounds from Commercially Available Desktop Three-Dimensional Printers with Multiple Filaments. *Environ Sci Technol*, 50(3), 1260–1268. [PubMed: 26741485]
- Byrley P, George BJ, Boyes WK, & Rogers K. (2019). Particle emissions from fused deposition modeling 3D printers: Evaluation and meta-analysis. *Sci Total Environ*, 655, 395–407. [PubMed: 30471608]
- Chamas A, Moon H, Zheng J, Qiu Y, Tabassum T, Jang JH, Abu-Omar M, Scott SL and Suh S. (2020) Degradation Rates of Plastics in the Environment. *ACS Sustainable Chemistry & Engineering*, 8(9), 3494–3511.
- Daigle CC, Chalupa DC, Gibb FR, Morrow PE, Oberdorster G, Utell MJ, & Frampton MW (2003). Ultrafine particle deposition in humans during rest and exercise. *Inhal Toxicol*, 15(6), 539–552. [PubMed: 12692730]
- Davis AY, Zhang Q, Wong JPS, Weber RJ, & Black MS (2019). Characterization of volatile organic compound emissions from consumer level material extrusion 3D printers. *Building and Environment*, 160, 106209.
- Dehghani M, Fazlzadeh M, Sorooshian A, Tabatabaee HR, Miri M, Baghani AN, Delikhoon M, Mahvi AH, & Rashidi M. (2018). Characteristics and health effects of BTEX in a hot spot for urban pollution. *Ecotoxicol Environ Saf*, 155, 133–143. [PubMed: 29510308]
- Deng Y, Cao S-J, Chen A, & Guo Y. (2016). The impact of manufacturing parameters on submicron particle emissions from a desktop 3D printer in the perspective of emission reduction. *Building and Environment*, 104, 311–319.
- EPA. (1999). Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes
- EPA. (1991). Integrated Risk Information System; Ethylbenzene; CASRN 100–41-4
- EPA. (1992). Integrated Risk Information System; Styrene; CASRN 100–42-5
- Farcas MT, Stefaniak AB, Knepp AK, Bowers L, Mandler WK, Kashon M, Jackson SR, Stueckle TA, Sisler JD, Friend SA, Qi C, Hammond DR, Thomas TA, Matheson J, Castranova V, & Qian Y. (2019). Acrylonitrile butadiene styrene (ABS) and polycarbonate (PC) filaments three-dimensional (3-D) printer emissions-induced cell toxicity. *Toxicol Lett*, 317, 1–12. [PubMed: 31562913]
- Gu J, Wensing M, Uhde E, & Salthammer T. (2019). Characterization of particulate and gaseous pollutants emitted during operation of a desktop 3D printer. *Environ Int*, 123, 476–485. [PubMed: 30622073]
- He Z, Li G, Chen J, Huang Y, An T and Zhang C(2015) Pollution characteristics and health risk assessment of volatile organic compounds emitted from different plastic solid waste recycling workshops. *Environment international*, 77, 85–94. [PubMed: 25667057]
- IARC. (2000). IARC monographs on the evaluation of carcinogenic risks to humans: Some industrial chemicals
- IARC. (2019). IARC monographs on the evaluation of carcinogenic risks to humans: Styrene, styrene-7,8-oxide, and quinoline
- ICRP. (1994). International Commission on Radiological Protection: Human Respiratory Tract Model for Radiological Protection.
- Lee CW, Dai YT, Chien CH and Hsu DJ (2006) Characteristics and health impacts of volatile organic compounds in photocopy centers. *Environmental research*, 100(2), pp.139–149. [PubMed: 16045905]
- Maricq MM and Xu N. (2004) The effective density and fractal dimension of soot particles from premixed flames and motor vehicle exhaust. *Journal of Aerosol Science*, 35(10), 1251–1274.
- McClellan RO, & Henderson RF (1995). Concepts in Inhalation Toxicology (McClellan RO& Henderson RFEs. 2 ed.).

- Mendes L, Kangas A, Kukko K, Mølgaard B, Säämänen A, Kanerva T, Flores Ituarte I, Huhtiniemi M, Stockmann-Juvala H, Partanen J, Hämeri K, Eleftheriadis K, & Viitanen A-K (2017). Characterization of Emissions from a Desktop 3D Printer. *Journal of Industrial Ecology*, 21(S1), S94–S106.
- Oberdorster G, Oberdorster E and Oberdorster J(2005) Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environmental health perspectives*, 113(7), 823–839. [PubMed: 16002369]
- Ohlwein S, Kappeler R, Kutlar Joss M, Kunzli N, & Hoffmann B. (2019). Health effects of ultrafine particles: a systematic literature review update of epidemiological evidence. *Int J Public Health*, 64(4), 547–559. [PubMed: 30790006]
- Poh TY, Ali N, Mac Aogain M, Kathawala MH, Setyawati MI, Ng KW, & Chotirmall SH (2018). Inhaled nanomaterials and the respiratory microbiome: clinical, immunological and toxicological perspectives. *Part Fibre Toxicol*, 15(1), 46. [PubMed: 30458822]
- Potter PM, Al-Abed SR, Lay D, & Lomnicki SM (2019). VOC Emissions and Formation Mechanisms from Carbon Nanotube Composites during 3D Printing. *Environ Sci Technol*, 53(8), 4364–4370. [PubMed: 30875473]
- Rhodes VL, Kriek G, Lazear N, Kasakevich J, Martinko M, Heggs RP, Holdren MW, Wisbith AS, Keigley GW, Williams JD and Chuang JC (2002) Development of emission factors for polycarbonate processing. *Journal of the Air & Waste Management Association*, 52(7): 781–788. [PubMed: 12139342]
- Schmid O, Möller W, Semmler-Behnke M, Ferron, G A, Karg E, Lipka J, Schulz H, Kreyling WG and Stoeger T. (2009) Dosimetry and toxicology of inhaled ultrafine particles. *Biomarkers*, 14(sup1), 67–73.
- Schymanski EL, Jeon J, Gulde R, Fenner K, Ruff M, Singer HP, & Hollender J. (2014). Identifying small molecules via high resolution mass spectrometry: communicating confidence. *Environ Sci Technol*, 48(4), 2097–2098. [PubMed: 24476540]
- Simon TR, Lee WJ, Spurgeon BE, Boor BE, & Zhao F. (2018). An Experimental Study on the Energy Consumption and Emission Profile of Fused Deposition Modeling Process. *Procedia Manufacturing*, 26, 920–928.
- Stefaniak AB, Bowers LN, Knepp AK, Virji MA, Birch EM, Ham JE, Wells JR, Qi C, Schwegler-Berry D, Friend S, Johnson AR, Martin SB Jr., Qian Y, LeBouf RF, Birch Q, & Hammond D. (2018). Three-dimensional printing with nano-enabled filaments releases polymer particles containing carbon nanotubes into air. *Indoor Air*, 28(6), 840–851. [PubMed: 30101413]
- Stefaniak AB, LeBouf RF, Duling MG, Yi J, Abukabda AB, McBride CR, & Nurkiewicz TR (2017a). Inhalation exposure to three-dimensional printer emissions stimulates acute hypertension and microvascular dysfunction. *Toxicol Appl Pharmacol*, 335, 1–5. [PubMed: 28942003]
- Stefaniak AB, LeBouf RF, Yi J, Ham J, Nurkiewicz T, Schwegler-Berry DE, Chen BT, Wells JR, Duling MG, Lawrence RB, Martin SB Jr., Johnson AR, & Virji MA (2017b). Characterization of chemical contaminants generated by a desktop fused deposition modeling 3-dimensional printer. *J Occup Environ Hyg*, 14(7), 540–550. [PubMed: 28440728]
- Stephens B, Azimi P, El Orch Z, & Ramos T. (2013). Ultrafine particle emissions from desktop 3D printers. *Atmospheric Environment*, 79, 334–339.
- Tsai S, Ashter A, Ada E, Mead JL, Barry CF, & Ellenbecker MJ (2008). Control of airborne nanoparticles release during compounding of polymer nanocomposites. *NANO: Brief Reports and Reviews*, 3(4), 301–309.
- TSI. (2010). Aerosol Instrument Manager® Software for Scanning Mobility Particle Sizer™ (SMPS™) Spectrometer
- Underwriter Laboratories. (2019). ANSI/CAN/UL 2904 Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers
- Vance ME, Pegues V, Van Montfrans S, Leng W, & Marr LC (2017). Aerosol emissions from fused-deposition modeling 3D printers in a chamber and in real indoor environments. *Environ Sci Technol*, 51(17), 9516–9523. [PubMed: 28789516]

- Wojtyła S, Klama P and Baran T. (2017) Is 3D printing safe? Analysis of the thermal treatment of thermoplastics: ABS, PLA, PET, and nylon. *Journal of occupational and environmental hygiene*, 14(6), D80–D85. [PubMed: 28165927]
- Wolkoff P. (2013). Indoor air pollutants in office environments: assessment of comfort, health, and performance. *Int J Hyg Environ Health*, 216(4), 371–394. [PubMed: 22954455]
- Yi J, LeBouf RF, Duling MG, Nurkiewicz T, Chen BT, Schwegler-Berry D, Virji MA, & Stefaniak AB (2016). Emission of particulate matter from a desktop three-dimensional (3D) printer. *J Toxicol Environ Health A*, 79(11), 453–465. [PubMed: 27196745]
- Zhang Q, Wong JPS, Davis AY, Black MS, & Weber RJ (2017). Characterization of particle emissions from consumer fused deposition modeling 3D printers. *Aerosol Science and Technology*, 51(11), 1275–1286.
- Zhu Y, Yu N, Kuhn T, & Hinds WC (2006). Field comparison of P-Trak and condensation particle counters. *Aerosol Science and Technology*, 40(6), 422–430.

Fig. 1. Schematic of the filament extruder. A. Feedstock is put into the hopper at the top of the extruder. B. Feedstock is then pushed by heated metal screws toward the heated extruder head. C. A continuous plastic filament is extruded to be used in a 3D printer.

Fig. 2.

Particle number concentration data recorded during extrusion for each plastic type. (Left) All plastic types are shown. (Right) Only PLA feedstocks are shown. ABS pellets, pulverized PLA, and PLA pellets are represented by dotted, dashed and solid lines, respectively. Each line represents a mean of six runs and the gray area around each line represents one standard deviation above and below each point. The three vertical lines represent the average start time of extrusion at 14 min, the average termination time of extrusion for pulverized PLA at 40 min and the average termination time of the extrusion of ABS and PLA pellets at 51 min.

Fig. 3.

Particle number concentration size distributions recorded for run eleven of each plastic type. Each curve represents a size distribution recorded at a particular time during extrusion. (Left) Time values during the start of extrusion. (Right) Time values at the end of extrusion and after extrusion was terminated and peak number concentration fell. (Top) ABS Pellets (Middle) Pulverized PLA. (Bottom) PLA Pellets.

Fig. 4.

Mass concentration data recorded over the extrusion time for each plastic type. (Left) All plastic types are shown. (Right) Only PLA feedstocks are shown. ABS pellets, pulverized PLA, and PLA pellets are represented by dotted, dashed and solid lines, respectively. Each line represents a mean of six runs and the gray area around each line represents one standard deviation above and below each point. The three vertical lines represent the average start time of extrusion at 14 min, the average termination time of extrusion for pulverized PLA at 40 min and the average termination time of the extrusion of ABS and PLA pellets at 51 min.

Fig. 5.

Emission rates calculated over the extrusion time for each plastic type. (Left) All plastic types. (Right) PLA feedstocks only. ABS pellets, pulverized PLA, and PLA pellets are represented by dotted, dashed and solid lines, respectively. Each line represents a mean of six runs and the gray area around each line represents one standard deviation above and below each point. The three vertical lines represent the average start time of extrusion at 14 min, the average termination time of extrusion for pulverized PLA at 40 min and the average termination time of the extrusion of ABS and PLA pellets at 51 min.

Table 1.

Compounds released from extrusion of ABS pellets.

Compound (tentative identification)	CAS #	Formula	Sample 1	Sample 2	Sample 3	Sample 4	Confidence
Styrene	100-42-5	C ₈ H ₈	✓	✓	✓ ^a	✓	1
Ethylbenzene	100-41-4	C ₈ H ₁₀	✓	✓	✓	✓	1
Acetophenone	98-86-2	C ₈ H ₈ O	✓	✓	✓	✓	2a
alpha-Methylstyrene	98-83-9	C ₉ H ₁₀	✓	✓	✓	✓	2a
2-Naphthalenecarbonitrile	613-46-7	C ₁₁ H ₇ N	✓	✓	✓	✓	2a
Benzene, (1-methylethyl)-	98-82-8	C ₉ H ₁₂	✓	✓	✓	✓	2a
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, cis-	7694-30-6	C ₁₆ H ₁₆	✓	✓	✓	✓	2a
Benzaldehyde	100-52-7	C ₇ H ₆ O	✓	✓	✓	✓	2a
Benzenemethanol, alpha-alpha-dimethyl-	617-94-7	C ₉ H ₁₂ O	✓	✓	✓	✓	2a
Cyclohexene, 4-ethenyl-	100-40-3	C ₈ H ₁₂	✓	✓	✓	✓	2a
1,4-Dioxane-2,5-dione, 3,6-dimethyl-	4511-42-6	C ₆ H ₈ O ₄	✓	✓	✓	✓	2a

Checkmarks indicate the compound was detected in that sample.

Confidence values are extracted from Schymanski et al. (2014) and explained in Section 3.5. Decision criteria are further explored in Supplementary Tables 2–4.

^a. Present but incorrectly identified as benzene due to poor deconvolution. Using standards, it was correctly identified as styrene.

Table 2.

Compounds released from extrusion of pulverized PLA.

Compound (tentative identification)	CAS #	Formula	Sample 1	Sample 2	Sample 3	Confidence
Benzene	71-43-2	C ₆ H ₆	✓	✓	✓ ^a	1
Styrene	100-42-5	C ₈ H ₈	✓	✓	✓	1
Toluene	108-88-3	C ₇ H ₈	✓ ^a	✓	✓ ^b	1
1,4-Dioxane-2,5-dione, 3,6-dimethyl-	95-96-5	C ₆ H ₈ O ₄	✓	✓	✓	2a
Butyl lactate	138-22-7	C ₇ H ₁₄ O ₃	✓	✓		2a
1-Butanol	71-36-3	C ₄ H ₁₀ O	✓	✓	✓	2a
Acetone	67-64-1	C ₃ H ₆ O	✓	✓	✓	2a
1-Dodecanol	112-53-8	C ₁₂ H ₂₆ O	✓	✓	✓	2a
Acetic acid	64-19-7	C ₂ H ₄ O ₂	✓	✓	✓	2a
Methyl methacrylate	80-62-6	C ₅ H ₈ O ₂	✓	✓	✓	2a
1-Hexanol, 2-ethyl-	104-76-7	C ₈ H ₁₈ O			✓	2a
1,3,5-Trifluorobenzene	372-38-3	C ₆ H ₃ F ₃	✓	✓ ^a	✓	2a
L-Lactic acid	79-33-4	C ₃ H ₆ O ₃	✓	✓	✓ ^c	3
Phthalic acid, di(6-methylhept-2-yl) ester	1000377-97-3	C ₂₄ H ₃₈ O ₄		✓ ^d	✓	3
Phenol	108-95-2	C ₆ H ₆ O	✓	✓ ^e	✓	3

Checkmarks indicate the compound was detected in that sample.

Confidence values are extracted from Schymanski et al. (2014) and explained in Section 3.5. Decision criteria are further explored in Supplementary Tables 2–4.

^a Present but at lower concentration than in blank and was filtered from the sample.

^b Present but co-eluted with another compound and not detected by Unknowns Analysis.

^c Present with same retention time and qualifier ions as L-lactic acid but was assigned as (S)-(+)-1,2,-propanediol by best hits Unknowns Analysis.

^d Present with same retention time and qualifier ions as phthalic acid, di(6-methylhept-2-yl) ester but was assigned as phthalic acid, di(cycloheptyl) ester by best hits Unknowns Analysis.

^e Present with the same retention time and qualifier ions as phenol but was assigned as 2-vinylfuran by best hits Unknowns analysis.

Table 3.

Compounds released from extrusion of PLA pellets.

Compound (tentative identification)	CAS #	Formula	Sample 1	Sample 2	Sample 3	Confidence
Benzene	71-43-2	C ₁₅ H ₂₄	✓	✓ ^a	✓	1
Toluene	108-88-3	C ₇ H ₈	✓	✓	✓	1
Diethyl Phthalate	84-66-2	C ₁₂ H ₁₄ O ₄	✓	✓ ^a	✓	2a
1,4-Dioxane-2,5-dione, 3,6-dimethyl-	95-96-5	C ₆ H ₈ O ₄	✓	✓	✓	2a
1,3,5-Trifluorobenzene	372-38-3	C ₆ H ₃ F ₃	✓	✓	✓	2a
Acetic acid	64-19-7	C ₂ H ₄ O ₂	✓	✓	✓	2a
Acetophenone	98-86-2	C ₈ H ₈ O	✓	✓	✓	2a
Acetone	67-64-1	C ₃ H ₆ O	✓	✓	✓	2a
2,5-Furandione, 3-methyl-	616-02-4	C ₅ H ₄ O ₃	✓	✓	✓	2a
Benzoic acid	65-85-0	C ₇ H ₆ O ₂	✓	✓	✓	2a
Phenylmaleic anhydride	36122-35-7	C ₁₀ H ₆ O ₃		✓		2a
1-Hexanol, 2-ethyl-	104-76-7	C ₈ H ₁₈ O	✓	✓	✓	2a
Anthrone ^b	90-44-8	C ₁₄ H ₁₀ O	✓	✓ ^c	✓ ^d	3
Phenol	108-95-2	C ₆ H ₆ O	✓	✓	✓	3

Checkmarks indicate the compound was detected in that sample.

Confidence values are extracted from Schymanski et al. (2014) and explained in Section 3.5. Decision criteria are further explored in Supplementary Tables 2–4.

^a Present but at lower concentration than in blank and was filtered from the sample.

^b Present in all three samples with same retention time and qualifier ions as anthrone but was chosen as different names by best hits Unknowns Analysis.

^c Name assigned by NIST: 2-phenanthrenol.

^d Name assigned by NIST: 3-phenanthrenol.

Table 4.

Quantification of compounds released from the extrusion of ABS pellets.

Compound	3 minute samples (mg/m ³)				5 minute samples (mg/m ³)			
	Sample 1	Sample 2	Sample 3	Average	Sample 1	Sample 2	Sample 3	Average
Styrene	0.357	0.491	0.421	0.423	0.842 ^a	0.709 ^a	0.811 ^a	0.788
Ethylbenzene	0.0128	0.0157	0.0141	0.0142	0.0299	0.0256	0.0291	0.0282

^aThese values were found to be above the standard curve for determining mass amounts in styrene samples.