

# **Proceedings/Presentation**

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### **Fine Particulate and Chemical Emissions from Consumer 3D printers**

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#### **SUMMARY**

Fused deposition modeling printers, most common type of desktop 3D printers, emit volatile gases and particulates that may deteriorate indoor air quality. The developed method for characterizing and quantifying emissions from an operating 3D printer measures ultra-fine particulates (UFP) and volatile organic compound (VOC) concentrations over time using an environment controlled testing chamber.

All tested printers emitted UFPs. Approximately 70% of the particulates emitted were less than 50 nm in diameter. Chemical compositions of the released gases varied depending on the filament. Volatile chemicals such as styrene and ethylbenzene were released from acrylonitrile butadiene styrene (ABS), caprolactam from nylon, and methyl methacrylate from polylactic acid (PLA). The extrusion nozzle temperature on the printer had the greatest effect on both particles and VOC emissions; the emissions increased as the temperature of the nozzle increased. Depending on the source of the filaments, the total particle number emissions varied by a factor of 20.

#### **PRACTICAL IMPLICATIONS**

This study brings characterization data on chemical and particle emissions released from desktop 3D printers during operation. The results will provide guidance to safely operate printers as well as shed light on potential health concerns for manufactures to consider.

#### **KEYWORDS**

Desktop 3D printer, ultrafine particles, VOCs, PLA, ABS

#### **1 INTRODUCTION**

3D printers are used in various applications, by designers and students for their inventions, as well as industrial, medical, and residential purposes. Fused deposition modeling (FDM) works by heating a coil of thermoplastic filament and extruding the filament from a nozzle onto a moving platform, building the object layer by layer. Heating of thermoplastics typically range between 180°C and 270°C but can be as high as 320°C. Printers typically have small motors and fans, but only some printers are enclosed. Numerous filaments available for FDM are usually a blend of thermoplastic (e.g., polylactic acid (PLA), acrylonitrile butadiene styrene

(ABS), thermoplastic polyurethane (TPU), nylon and polycarbonate) with coloring dye, metal, wood, plant, and other additives.

3D printers emit volatile gases and particulates that deteriorate indoor air quality (Stienle 2015; Stephens et al. 2013). These emissions can occur over a long period of time since the printers are typically operated indoors for hours. Ultrafine particulates (UFP) present a hazard to human health since they are capable of penetrating through lungs and into the bloodstream. Gaseous emissions are complex and contain a mixture of low level volatile organic compounds which may include odorants, irritants and carcinogens. Currently, little research has been done on desktop 3D printer emissions. Previous studies did not investigate in depth on key parameters that affect 3D printer emissions.

We have developed a methodology for characterizing and quantifying UFP and VOC emissions from operating 3D printers that involves operation inside a controlled environmental chamber. To capture the wide range of 3D printer emissions, various combinations of printers and thermoplastic filaments were tested. The following printer parameters and their effects on particle and VOC emissions were studied: filament color, filament brand, extrusion nozzle temperature, and printer brand.

## 2 MATERIALS/METHODS

### 3D Printer and Filaments

Three commercially available desktop 3D printers from different manufactures were purchased for this study (Table 1). Printer A processes ABS, PLA, and nylon filaments, and its nozzle temperature can be adjusted from 215 to 270°C. There is no enclosure around printer A, and the platform was heated above 85°C before extrusion. Printer B was designed for PLA filament only. All settings are predetermined by the manufacturer, and the nozzle temperature is constant at 215°C. The printer has a door to access to the platform and only the top is open to ambient. Printer C processes ABS and PLA at 260°C and 230°C respectively. Printer C has 4 out of 6 sides of the printer covered with its casing. Printer B and C do not have heated platforms but instead require tape and/or glue to mount the extruded layers. ABS, PLA, and nylon filaments with 1.75 mm diameter were obtained from 6 different filament distributors for different colors, for a total of 24 different filaments.

Table 1. Studied 3D Printers and Filaments

Printer brand	Material	Filament brand	Color
A	ABS	d	Yellow, blue, green, red, white
	ABS	a	Red, white
	Nylon	e	White
B	PLA	b	Red, white, yellow, blue
C	ABS	c	Red, white, yellow, blue
	PLA	c	Red, white, yellow, blue, black
-	ABS	f	Red, white
-	PLA	f	Red, white

### Environmental Chamber

Each 3D printer was tested in an environmental chamber 1 m<sup>3</sup> in volume specially designed for quantifying emissions in a well-mixed clean environment. Chamber operation and control measures used in this study complied with the GREENGUARD Method and Laboratory Quality Requirements (UL 2013) and ASTM Standard D 6670 (ASTM 2013). The chamber is made of stainless steel to minimize contaminant adsorption. Air flow through the chamber enters and

exits through an aerodynamically designed air distribution manifold also manufactured of stainless steel. Supply air to the chamber is stripped of formaldehyde, VOCs, and other contaminants, including particulates, so that any contaminant backgrounds present in the empty chamber fall below strict levels ( $< 10 \mu\text{g}/\text{m}^3$  total VOC (TVOC),  $< 10 \mu\text{g}/\text{m}^3$  total particles,  $< 2 \mu\text{g}/\text{m}^3$  formaldehyde,  $< 2 \mu\text{g}/\text{m}^3$  for any individual VOC). Air supply to the chamber was maintained at a temperature of  $23^\circ\text{C} \pm 1^\circ\text{C}$  and relative humidity at  $3\% \pm 1\%$ . The air exchange rate was  $1 \pm 0.05$  air change/hour (ACH).

Gaseous emissions from only the filaments were tested in a smaller chamber  $0.1 \text{ m}^3$  in volume with a similar manifold setup as the  $1 \text{ m}^3$  chamber, all constructed with stainless steel. The lid on the top of the chamber has a built-in IR temperature sensor that detected the temperature of the filaments. The filaments were placed on top of a microscopic glass at the bottom of a chamber, and this was heated to  $230^\circ\text{C}$  by a heating element that was placed directly underneath the chamber. Air supply to the chamber was maintained at a temperature of  $23^\circ\text{C} \pm 1^\circ\text{C}$  and relative humidity at  $50\% \pm 5\%$ . The air exchange rate was  $1 \pm 0.05$  air change/hour (ACH).

### Emission Measurement

Particle emissions were measured by online particle counters. A condensation particle counter (CPC, model 3022, TSI Inc.) was used to measure total particle number concentration over time for particles greater than 3 nm in diameter. A scanning mobility particle sizer (Classifer model 3080, DMA model 3081, CPC model 3785, TSI Inc.) was used to obtain particle size distribution for particle size ranging from 7 to 300 nm, and optical particle counter (AeroTrak model 9306, TSI Inc.) for particles larger than 300 nm. Particle mass and surface area were calculated based on the assumption that particle is spherical with its density as  $1 \text{ g}/\text{cm}^3$ .

Particle measurements were continuous for pre, during, and post printing. Printer-loaded background chamber concentration was measured before printing for at least 10 minutes. As soon as a print job was submitted, the printer started printing in a few minutes. Measurements were taken for 4 ACH after the print ended or until the concentration decreased to background level. Particle emission rate and total particle number emitted were calculated from the same equations used for RAL-UZ 122 printer testing procedure for the German “Blue Angel” certification, which are:

$$PER(t) = V_C \left( \frac{C_P(t) - C_P(t-\Delta t)e^{-\beta \cdot \Delta t}}{\Delta t \cdot e^{-\beta \cdot \Delta t}} \right) \quad (1)$$

$$TP = V_C \left( \frac{\Delta C_P}{t_{stop} - t_{start}} + \beta \cdot C_{av} \right) (t_{stop} - t_{start}) \quad (2)$$

where  $PER$  is particle emission rate,  $C_P$  is particle concentration at time  $t$ ,  $\Delta t$  is sampling time interval,  $V_C$  is volume of the chamber,  $\beta$  is particle loss coefficient,  $TP$  is total particles emitted, and  $C_{av}$  is arithmetic average concentration. Emission yields (total mass or number emission/g printed object) were used to compare particle and VOC emissions data.

VOC measurements were made using gas chromatography-mass spectrometry (GC/MS). Chamber air was collected onto a solid sorbent which was then thermally desorbed into the GC/MS. Instrumentation included a sample concentrator (Perkin Elmer Model TurboMatrix ATD or TurboMatrix 650), a Hewlett-Packard/Agilent 6890 or 7890 Series Gas Chromatograph and a Hewlett-Packard/Agilent 5973 or 5975 Mass Selective Detector. The analytical methodology of the sorbent collection technique, separation, and detection have been adapted

from techniques following US EPA Compendium Method TO-17 (USEPA 1999b) and ASTM D 6196 (ASTM 2009), and is generally applicable to C<sub>6</sub> - C<sub>16</sub> organic chemicals with boiling points ranging from 35°C to 250°C.

The TVOC measurements were made by adding all individual VOC responses obtained by the mass spectrometer and calibrating the total mass relative to toluene. Individual VOCs were identified using a mass spectral database and quantitated using multipoint calibration standards, if available. Mass spectral characteristics of more than 75,000 compounds, as made available from the National Institute of Standards and Technology (NIST), the US EPA and the National Institutes of Health (NIH), were used along with a database of typical indoor air VOCs.

Emissions of selected aldehydes were measured following ASTM D 5197 (ASTM 2010) and US EPA Method TO-11A (USEPA 1999a), by high performance liquid chromatography (HPLC). Solid sorbent cartridges with DNPH (2,4-Dinitrophenylhydrazine) were used to collect formaldehyde and other low-molecular weight carbonyl compounds in chamber air. The DNPH reagent in the cartridge reacted with collected carbonyl compounds to form the stable hydrazone derivatives retained by the cartridge. The hydrazone derivatives were eluted from a cartridge with HPLC-grade acetonitrile. An aliquot of the sample was analyzed for low-molecular weight aldehyde hydrazone derivatives using reverse-phase HPLC with UV detection. The absorbances of the derivatives were measured at 360 nm. The mass responses of the resulting peaks were determined using multi-point calibration curves prepared from standard solutions of the hydrazone derivatives.

For the 1 m<sup>3</sup> chamber, air samples were consecutively collected every hour from 1 hour before printing to 4 hours (i.e. 4 ACH) after the end of printing at air volume collection of 12 L for VOCs and 30 L for aldehydes. For the filament test using a 0.1 m<sup>3</sup> chamber, the heated background concentration where only the microscope glass slide was inside the chamber was collected first. The slide was heated to the target temperature associated with the nozzle temperature, then immediately the heat source was turned off and VOCs and aldehydes were sampled for 30 minutes collecting 6 L and 15 L of background air respectively. Once the glass cooled, a measured amount of filaments were placed on top of the slide and equilibrated for 4 ACH. The filaments were then heated to the same target temperature, then immediately air samples were collected at 0.5 and 1 hour time points for 30 minutes and at 2.5 and 4 hour time points for 90 minutes.

The model measurements were made with the following assumptions: air within open areas of the building is well-mixed at the breathing level zone of the occupied space; environmental conditions are maintained at 50% relative humidity and 23°C (73°F); there are no additional sources of these pollutants; and there are no sinks or potential re-emitting sources within the space for these pollutants. The assumption is also made that the emissions are not interacting with any pre-existing air pollutants, since the chamber tests are done under clean conditions, which is not the case in the real environment.

The emission factors for gaseous emissions are calculated from the chamber concentration as:

$$EF_{m,t} = C_c(N_c/L) \quad (3)$$

Where  $EF_{m,t}$  is modeled emission factor at time  $t$  ( $\mu\text{g/g}\cdot\text{hr}$ ),  $C_c$  is chamber concentration ( $\mu\text{g}/\text{m}^3$ ) less any background concentration of chamber,  $N_c$  is chamber air change per hour ( $\text{hr}^{-1}$ ), and  $L$  is product loading ( $\text{g filament}/\text{m}^3$ ).

The predicted exposure concentrations,  $C_{p,t}$  ( $\mu\text{g}/\text{m}^3$ ) at time  $t$ , are calculated from the modeled emission factors as:

$$C_{p,t} = EF_{m,t} (A/V) (1/N) \quad (4)$$

where  $A$  is product area exposed in room (g filament),  $V$  is personal breathing space ( $\text{m}^3$ ), and  $N$  is room air change per hour ( $\text{hr}^{-1}$ ). The exposure concentrations are calculated based on average emission factors during printing.

### 3 RESULTS

#### Particles

With various combinations of different printers and filaments, a wide variability of particle emissions was observed. Typically, the number concentration spiked up to  $10^3$  to  $10^6$  particles/ $\text{cm}^3$ , and then gradually decreased over time until the print ended. This pattern is seen in Figure 1, which shows number concentration over time for a 7 hour print using ABS. The instantaneous increase in number concentration to  $1.4 \times 10^6$  particles/ $\text{cm}^3$  ( $1.4 \times 10^{12}$  particles/min) is enough to exceed the criteria set for laser printers by Blue Angel ( $< 3.5 \times 10^{11}/10$  min). While the number concentration starts decreasing, the mass concentration continues to increase (Figure 1), and this is due to particle growth resulting from particle coagulation and condensation of vapors. Initially, particles are in the size range of 40 to 80 nm in diameter. Over time, the particles emitted from the printer interact with particles generated earlier, and along with vapors continually being generated in the chamber by the printer, results in an increase in diameters to 100 to 250 nm (Figure 2). Despite the duration of print time, total particle emission was dominated by particles less than 50 nm, total surface area emission by particle size 50-200 nm, and total mass emission by particles size 100-300 nm.

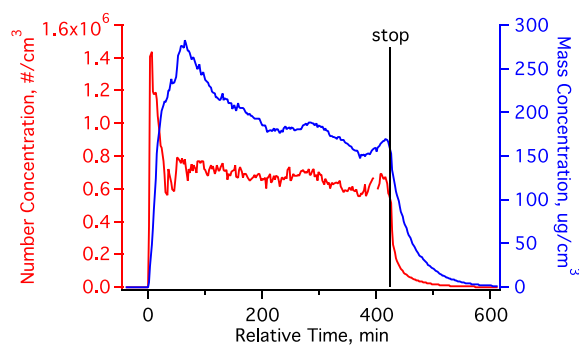


Figure 1. Particle number and mass concentrations for a 7 hr print using ABS, print start at 0 min.

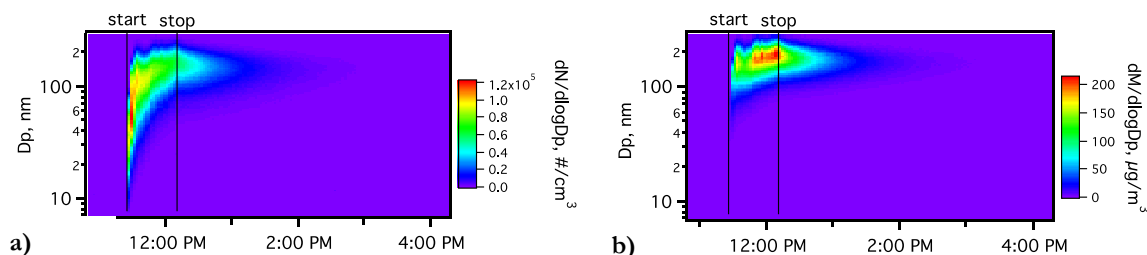


Figure 2. a) Particle number concentration per particle size over time, and b) particle mass concentration per particle size over time. Color indicates the concentration and the vertical lines

represent when the print started and ended.

One overall average particle yield for the three filament materials studied is shown in Table 2. ABS had a much higher particle number yield compared to PLA and nylon. One brand of ABS emitted much higher than other brands, thereby increasing the average. If the super emitting ABS brand is taken out from the average, the number yield decreases to  $6.3 \times 10^9$  #/g with  $2.0 \times 10^8$  to  $24.9 \times 10^9$  #/g range, which is still 4 times higher than PLA. ABS is extruded at a higher nozzle temperature, which has a large effect in particle emission.

Table 2. Particle Count Yield for Various Filament Materials

Filament material	Number yield, $\times 10^9$ #/g	Range of yield, $\times 10^9$ #/g
ABS	62.1	0.3 - 152
PLA	1.6	0.004 - 22.5
Nylon	1.2	0.3 - 2.6

### VOCs

VOC emission factors from the filament only tests and predicted concentrations derived from  $1 \text{ m}^3$  chamber concentrations are shown in Table 3. Formaldehyde and acetaldehyde, both listed as carcinogens, were detected in all three materials. Nylon has the largest TVOC emission factor. Most of TVOC emission from nylon is caprolactam, which has an ocular and respiratory toxicity. Caprolactam has a low 8 hour chronic reference exposure level of  $7 \mu\text{g}/\text{m}^3$  (1.4 ppb) according to California's Office of Environmental Health Hazard Assessment (OEHHA), and its predicted concentrations during print with nylon are at least 14 times higher (Table 3). Methyl methacrylate, second most abundant emission from PLA, is an irritant (USEPA 1998). Lactic acid is known to be released but was not detected in our analysis since our analysis covers mostly greater than  $\text{C}_6$ . Therefore, TVOC for PLA is likely to be underestimated. ABS had the largest number of identified VOCs.

Styrene, released from ABS, is listed as a possible human carcinogen by International Agency for Research on Cancer. ABS emitted ethylbenzene, acetaldehyde, formaldehyde, and 4-vinylcyclohexene, which are recognized as carcinogens in the Safe Drinking Water and Toxic Enforcement Act of 1986, also known as California Proposition 65, and/or Candidate Chemical List by California Department of Toxic Substances Control. Maximum predicted concentration for acetaldehyde during print with ABS (Table 3) exceeds acute inhalation reference exposure level (REL) set by OEHHA ( $0.47\text{mg}/\text{m}^3$ ). For ABS, maximum predicted concentration for formaldehyde exceeds an often recommended indoor air level of 0.1 ppm or  $0.123\text{mg}/\text{m}^3$  as recognized by the World Health Organization.

### Filament Color

Coloring pigment in the filaments did show slight differences in particle and VOC emissions. For a specific brand with various colors of ABS, the particle number yield ranged from  $9.1 \times 10^{10}$  to  $11.3 \times 10^{10}$  particles/g, in increasing order, green, red, blue, yellow, and white. However, the particle mass yield is in increasing order from blue, green, red, yellow, and then white. TVOC emission by color in increasing order was white, red, green, and blue, which happens to be the opposite order of particle mass yield order.

### Filament Brand

Various ABS brand filaments were printed using a single printer. Results show that brand difference creates larger differences between particle emissions than color difference. One brand emitted about ten times higher than other ABS brands. Without the super emitter, ABS

particle yield varied between 0.3 to  $1.6 \times 10^{10}$  particles/g. The composition of the VOC emissions varied by brand as well. The percentage of emitted styrene ranged from 39 to 49% of TVOC for various ABS brands. For PLA depending on the manufacture, some included methyl methacrylate and others did not.

Table 3. Top 10 VOCs Released From Nylon, PLA, and ABS.

	Nylon				PLA				ABS		
	EF (mg/g filament)	Predicted Conc. <sub>GG</sub> (mg/m <sup>3</sup> )	Predicted Conc. <sub>Max</sub> (mg/m <sup>3</sup> )		EF (mg/g filament)	Predicted Conc. <sub>GG</sub> (mg/m <sup>3</sup> )	Predicted Conc. <sub>Max</sub> (mg/m <sup>3</sup> )		EF (mg/g filament)	Predicted Conc. <sub>GG</sub> (mg/m <sup>3</sup> )	Predicted Conc. <sub>Max</sub> (mg/m <sup>3</sup> )
TVOC	1.07	0.10	15.83	TVOC	0.177	0.004	0.538	TVOC	0.520	0.0223	4.44
Caprolactam	1.32	0.12	19.22	Lactide	0.106	0.005	0.785	Styrene	0.335	0.0126	2.53
Acetaldehyde	0.0059	0.0003	0.0522	Methyl methacrylate	0.0667			Ethylbenzene	0.0779	0.0035	0.664
Formaldehyde	0.0029	0.0001	0.0174	1-Butanol	0.0316	0.0001	0.0156	Benzaldehyde	0.0412	0.0012	0.503
Decanal	0.0011	0.0002	0.0360	1-Dodecanol	0.0104			Acetophenone	0.0237	0.0008	0.341
Nonanal		0.0002	0.0348	Acetaldehyde	0.0091	0.0006	0.0775	Phensuximide	0.0169	0.0003	0.179
Pentanal		0.0002	0.0510	Octamethyl cyclotetrasiloxane	0.0061			4-vinyl cyclohexene	0.0163	0.0012	0.249
Benzaldehyde		0.0002	0.0282	Formaldehyde	0.0029			Acetaldehyde	0.0159	0.0008	1.94
2,6-Di-tert- butyl-4- methylphenol	0.0015			Butyl acrylate	0.0018			Formaldehyde	0.0157	0.0004	0.443
tetrahydro-2H- Pyran-2-one	0.0008			Benzaldehyde	0.0018			1-methylethyl benzene	0.0120	0.0006	0.115
Diethylhexyl phthalate		0.0005	0.1333	Decamethyl cyclopentasiloxane	0.0014			Propylbenzene	0.0102	0.0005	0.111

<sup>1</sup>Calculated using office room volume of 30.6 m<sup>3</sup> and ACH of 0.68 hr<sup>-1</sup>, parameters used for GREENGUARD offices derived from ASHRAE 62.1-2007

<sup>2</sup>Calculated using personal space of 0.833 m<sup>3</sup> (average male height × forearm to forearm breadth × (bust breadth + 30.5 cm + printer depth)) and ACH of 0.2 hr<sup>-1</sup> (USEPA 2011)



## **Extrusion Nozzle Temperature**

Printer differences had up to an order of magnitude difference in particle number yield. One of the reasons for this large difference may be due to the differences in nozzle temperatures. The same ABS filament was printed at various nozzle temperatures ranging from 220°C to 270°C. Total particle number emission increased exponentially with temperature, and TVOC and styrene emission increased linearly with increasing temperature.

## **4 CONCLUSIONS**

Elevated levels of UFP, up to  $1.4 \times 10^{12}$  particles/min, were generated from a desktop 3D printer. Chemicals unique to thermoplastics are released while operating a 3D printer. Some are known or suspected irritants and carcinogens; therefore exposure to 3D printer emissions should be minimized. Nozzle temperature, filament type, filament and printer brand, and filament color all affect particle and VOC emissions. Nozzle temperature, one parameter that users may have control over, could be set at a lower end of the suggested temperature range for a filament material to minimize direct emission exposure from 3D printers. 3D printers could also be used with caution in a well-ventilated area to increase dilution and removal of emissions.

The particle and VOC emission test method used in this study will continue to be performed on additional printers and filaments. Toxicity study on UFP from 3D printers will also be studied. With a better understanding of the emission levels from currently available consumer level 3D printers, this study provides insight into evaluating potential health concerns and defining processes for minimizing emission exposure in collaboration with manufacturers and other research organizations.

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## **5 REFERENCES**

- ASTM. 2009. ASTM D6196-03, Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air. West Conshohocken, PA: American Society for Testing and Materials International.
- ASTM. 2006. ASTM D5116-06, Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions From Indoor Materials/Products. West Conshohocken, PA: American Society for Testing and Materials International.
- ASTM. 2013. ASTM D6670-13, Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products. West Conshohocken, PA: American Society for Testing and Materials International.
- Steinle, P. 2015. Characterization of emissions from a desktop 3D printer and indoor air measurements in office settings. *Journal of occupational and environmental hygiene*: (just-accepted) 1-36.
- Stephens, B.,P. Azimi, Z. El Orch, and T. Ramos. 2013. Ultrafine particle emissions from desktop 3D printers. *Atmospheric Environment*, 79: 334-339.
- UL. 2013. UL 2821, GREENGUARD Certification Program Method for Measuring and Evaluating Chemical Emissions From Building Materials, Finishes and Furnishings Using Dynamic Environmental Chambers. Marietta, GA: UL.
- USEPA (U.S. Environmental Protection Agency). 1998. Toxicological Review of Methyl Methacrylate (CAS No. 80-62-6) in Support of Summary Information on the Integrated Risk

Information System (IRIS). National Center for Environmental Assessment, Office of Research and Development, Research Triangle Park, NC.

USEPA (U.S. Environmental Protection Agency). 1999a. Compendium method TO-11A, Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC) [active sampling methodology].

USEPA (U.S. Environmental Protection Agency). 1999b. Compendium Method TO-17 determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes. U.S. EPA Technical Assistance Document. EPA/625/R-96/010b.

USEPA (U.S. Environmental Protection Agency). 2011. Exposure Factors Handbook: 2011 Edition. Washington, D.C.: Office of Research and Development.