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보건학석사 학위논문

**Characterization of Particulate Matter and
Gaseous Material Emission at 3D Printer Operation**

3D printer 에서 발생하는 입자상물질과 가스상물질의
발생특성평가

2015 년 2 월

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2014 년 10 월

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ABSTRACT

Characterization of Particulate Matter and Gaseous Material Emission at 3D Printer Operation

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Objective Three-dimensional (3D) printers are used for various purposes, including education, production of vehicle and aircraft parts, and in medical science. The most popular 3D printers use the fused deposition modeling (FDM) printing method. FDM printing uses a plastic filament cartridge that contains acrylonitrile-butadiene-styrene (ABS) or polylactic acid (PLA). The objective of this study was to evaluate the emission characteristics of the particulate matter and gaseous material released during 3D printing.

Methods Particulate and gaseous materials were measured before, during, and after FDM 3D printing in a test chamber. One ABS and two PLA (PLA1 and 2; i.e., different brands) printer cartridges were tested three times.

Both on-line (real time) and off-line monitoring was conducted. For particulate on-line monitoring, a scanning mobility particle sizer (SMPS), condensation particle counter (CPC) and DustTrak with a polyvinyl chloride (PVC) filter (for the mass correction factor) was used. For total volatile organic compounds (TVOC), a ppbRAE monitor was used. For off-line monitoring of the particulate mass concentration, a polycarbonate (PC) filter was placed in an open-faced three-piece cassette. For phthalates, aldehydes, and VOCs, XAD-2 tubes, 2,4-dinitrophenylhydrazine (2,4-DNPH) cartridges, and charcoal tubes, respectively, were connected to low flow rate sampling pumps. Outdoor air was also measured during the testing period.

Results The particle concentration during 3D printing was much higher than before and after the printing period and the ABS cartridge emitted more particles than the PLA cartridges. The number concentration measured with the SMPS during ABS cartridge printing ($1,731,578 \text{ \#/cm}^3$) was 345 times higher than before printing ($5,021 \text{ \#/cm}^3$) and 272 times higher than after printing ($6,373 \text{ \#/cm}^3$). Three-dimensional printing using ABS material was found to emit 33 – 38 times more particles than when PLA materials were used ($1,731,578 \text{ \#/cm}^3$ vs. $52,252 \text{ \#/cm}^3$ (PLA1) or $45,690 \text{ \#/cm}^3$ (PLA2)). Most particles were nanosize ($<100 \text{ nm}$) during ABS cartridge use (96%), but particle size varied widely when PLA was used (98% were nanosize for PLA1, but only 12% were nanosize for PLA2). Aldehydes including formaldehyde, acetaldehyde, and isovalderaldehyde were emitted when

both ABS and PLA cartridges were used. Formaldehyde, a suspected human carcinogen, was measured at concentrations of $80 \mu\text{g}/\text{m}^3$, $72 \mu\text{g}/\text{m}^3$, $203 \mu\text{g}/\text{m}^3$ when using ABS, PLA1 and PLA2 cartridges, respectively. TVOC was also emitted when the ABS cartridge was used (GM; 155 ppb, GSD; 3.4), but not when the PLA cartridge was used. Benzene was not detected but toluene, ethyl benzene, and xylene were detected at ppb levels.

Conclusions In this study, we found that hazardous agents including nanoparticles, VOCs, and aldehydes were emitted during 3D printing, depending on the filler material used. More particles were emitted when the ABS cartridge was used compared to the PLA cartridges, and aldehydes and VOCs were emitted by both the ABS and PLA cartridges. These results suggest that caution should be implemented during FDM 3D printer use and emission control measures may be required.

Keywords: FDM 3D printing, ABS, PLA, nanoparticle, aldehydes

Student Number: 2013-21819

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1. Introduction

Three-dimensional (3D) printers are used in various industrial sectors, including electronics, automotive, aerospace, medical science, and education (Kim, 2014).

Several 3D printing techniques are available, including fused deposition modeling (FDM), selective laser sintering (SLS), and stereo lithographic apparatus (SLA).

In SLS printing, a laser beam strikes the heated powder and uses continuously laminated molding to make a product. Metal powder, ceramic powder, and thermoplastic powder have been used as cartridges (Kwak et al., 2013).

In SLA printing, an ultraviolet laser strikes the liquid material cartridge, containing the photopolymer resin, to make a product. Two cartridges are required; one for the product and another for the support material (Joe et al., 2014; Kwan and Park, 2013).

The FDM printer is popular because it is inexpensive and easy to use compared to the SLS and SLA printers. In FDM printing, a thermoplastic material, supplied as a wire, is heated at the extrusion nozzle head and hardened immediately to form successive layers as designed. The FDM method is similar to thermoplastic extrusion, which can emit various hazardous compounds depending on the types of plastic used (Forrest et al., 1995). Most FDM 3D printers use acrylonitrile-butadiene-styrene (ABS) and polylactic acid (PLA) as filler material (Huh, 2013). The major ABS breakdown products are acrylonitrile, 1,3-butadiene, and styrene at 160°C to 180°C (John et al., 2013). Acrylonitrile is toxic by inhalation and is classified as Group 2B (possibly carcinogenic to humans) by the International

Agency for Research on Cancer (IARC). 1, 3-Butadiene is classified as Group 1 (confirmed human carcinogen) by the IARC and may cause heritable genetic damage. Styrene is known to be irritating to the skin and eyes (HSE, 2010). PLA cartridges contain lactic acid, which is known to be an environmentally friendly material, but further information is required regarding the health hazard following exposure by inhalation.

All 3D printing systems (FDM, SLS, SLA, or others) are expected to be used more extensively in the near future. When considering the energy (heat, laser beam etc.) and raw materials (metal powder, thermoplastics etc.) used, hazardous agents could be emitted into the air. To our knowledge, only one technical report on nanoparticle emissions during 3D printing has been published (Stephens et al., 2013). There are also no published data for gaseous emissions during 3D printing.

The objective of this study was to evaluate the emission of particulate matter and gaseous materials during FDM 3D printing.

2. Materials and Methods

2.1. Study design

2.1.1. 3D printers and cartridges

Two FDM 3D printers were used. The printers had a similar principle of operation but were produced by different manufacturers. Different cartridges were recommended for use in the models. The brand A 3D printer (Cube, 3D systems, USA) was tested using both an ABS cartridge and PLA cartridge (PLA1). The brand B 3D printer (3DISON plus, Rokit, Korea) was tested with its own PLA cartridge (PLA2). The extrusion temperatures of ABS and PLA cartridges were 250°C and 220°C.

2.2. Sampling and Analysis

Particulate matter and gaseous materials emitted during 3D printing were measured in a test chamber. The test chamber (1 m x 1 m x 1 m) was constructed from acryl. A ventilation hole was located in the lower side of each wall and air was filtered into the chamber through a high efficiency particulate arrestor (HEPA) filter and a charcoal absorbent bed.

TVOC and particulate concentrations were measured inside the test chamber and the particulate level was demonstrated to be below that outdoors (about 4,000 particles/cm³). The TVOC concentration was close to zero.

The measurement period was divided into three sections; before (1 h), during, and after the printing period. The 3D printers were operated under the conditions recommended by the manufacturer to produce a mock-up bobbin (5 cm x 5 cm x 3 cm). The operating time varied according to the cartridge type (2 h 30 min, 1 h 55

min, and 2 h 50 min for the ABS, PLA1, and PLA2 cartridges, respectively), although the printed products were of identical size. The sampling duration was equal to the printer operating time and each cartridge was tested three times (Figure 1).

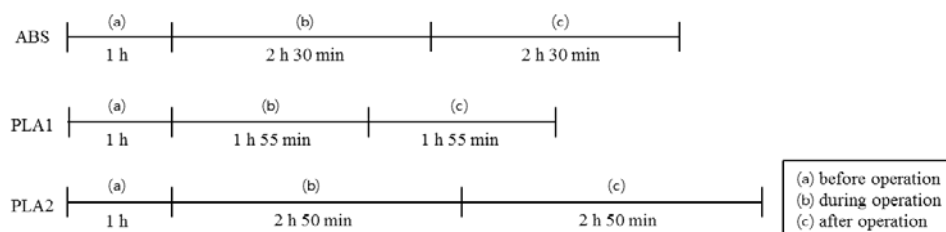


Figure 1. The measurement period divided into three sections (before, during, and after printer operation).

The 3D printer was located at the center of the test chamber. Sampling tubes or the on-line monitoring instruments were located in the upper part of the test chamber. Both on-line (real time) and off-line (integrated sampling) monitoring was used to measure particulate and gaseous materials (Figure 2).

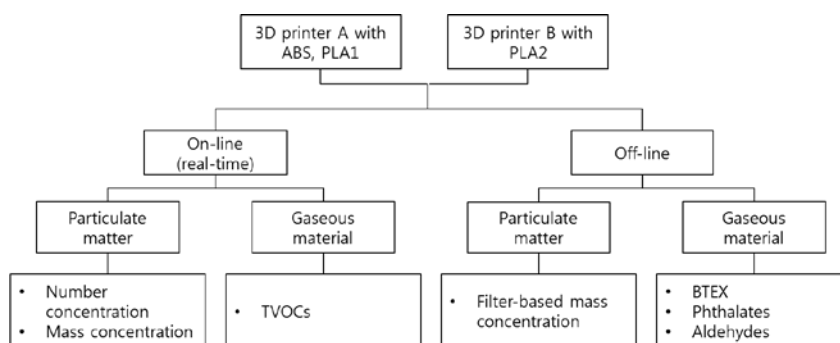


Figure 2. Outline of the sampling design.

Three samples were collected for each cartridge by off-line and on-line sampling. On-line (real-time) samples were collected at 1 min intervals during the sampling period.

To measure the particulate concentration in air with the on-line method, three instruments were used to collect data at 1 min intervals. A scanning mobility particle sizer (SMPS, Model 3910, TSI Inc., USA) with a detectable size range of 10 nm to 420 nm, was used to investigate the particle size distribution and number concentrations. A condensation particle counter (P-Trak Model 8525, TSI Inc., USA) was used to measure the total particle number concentration, with a range from 20 nm to 1,000 nm and an upper limit of 500,000 particles/cm³. All real-time instruments were calibrated by the manufacturers, and a zero calibration using a HEPA filter was performed before and after sampling.

A DustTrak (DRX aerosol monitor model 8533, TSI Inc., USA) with a size range of 0.1 µm to 15 µm was used to measure the mass concentration. The mass concentration was recalculated using the C-factor. The C-factor was calculated using a polyvinyl chloride (PVC) filter placed at the exit point of the instrument (Park, 2009).

Particle mass concentration was measured by off-line monitoring using a polycarbonate (PC) filter (37 mm, 0.4 µm, SKC Inc., USA) in an open-face three piece cassette using a high volume pump (Escort ELF, MSA, USA) at a constant flow rate of 2.0 L/min. After sampling, the cassettes were sealed using silicon tape and kept in a desiccator in a weighing room (Temp 20°C ± 1°C, RH 50% ± 5%). A microbalance (XP6 microbalance, Mettler-Toledo, Switzerland), with a sensitivity of 1 µg, was used for gravimetric analysis.

To measure the total volatile organic compounds (TVOCs), a ppbRAE monitor (ppbRAE 3000, RAE systems Inc., USA) was used for on-line sampling. Before sampling, the ppbRAE was calibrated using 10 ppm isobutene standard gas (CALGAZ Inc., USA), and zeroed with an adsorbent tube attachment.

Airborne aldehydes were measured using the National Institute for Occupational Safety and Health (NIOSH) method 2016. Aldehydes were sampled using a 2,4-dinitrophenylhydrazine cartridge (2,4-DNPH, Supelco, USA), with an ozone scrubber (WAT054420, Waters Sep-Pak, USA) using a low-volume pump (Gillian LFS-114, USA), with a constant flow rate of about 0.2 L/min (NIOSH method 2016, 2003). After sampling, all samples were sealed using aluminum foil to protect against light exposure and kept at a temperature of less than 4 °C until desorption.

To desorb aldehydes, solvent extraction equipment (Vacuum Elution Rack, Supelco, USA) was used. They were slowly eluted with 5 mL of acetonitrile (ACN, HPLC grade, J.T.Baker, USA). All of the experimental equipment used for analysis was cleaned using acetonitrile and baked at 60 °C to 80 °C. Extracted aldehydes were analyzed using high pressure liquid chromatography (HPLC, Ultimate 3000, Thermo scientific, USA) with an ultraviolet (UV) detector (Ultimate 3000 Variable Wavelength, Dionex, Germany) and an auto-sampler (Ultimate 3000, Dionex, Germany). A C-18 column (Eclipse XDB, Agilent Inc., USA) was used for analysis, which has 4.6 m in length, 250 mm in inner diameter and 5 μ m in film thickness and the wavelength of the detector set to 360 nm. ACN (60%) and water (40%; HPLC grade, J.T. Baker, USA) was used as a carrier liquid, with the flow rate set to 1.0 mL/min. The carrier liquid was filtered before analysis. The injection

volume was 20 μ L and the column temperature was 25 $^{\circ}$ C. An aldehydes standard solution (T011/IP-6A Aldehyde/Ketone-DNPH mix, Supelco, USA) was used in the analysis. Field blank and spiked samples were analyzed simultaneously for quality control. The limit of detection (LOD) was estimated from seven replicates of the lowest standard solution. The results for the standard solution and the LOD are shown in Appendix 1.

Benzene, toluene, ethyl benzene, and m, p-xylene (BTEX) were measured according to a standard NIOSH method using an adsorbent charcoal tube (cat. no. 226-01, SKC Inc., USA) with a flow rate of 0.2 L/min (NIOSH method 1501, 2003). Before analysis, charcoal tubes were extracted with 1 mL of carbon disulfide (CS₂). 1 mL of the extraction sample was injected by auto-sampler (CombePAL, CTC analytics, Switzerland) into a gas chromatograph (HP 6890, Hewlett Packard Co., USA) - mass spectrometer (HP 5975C, Agilent Technology, USA) (GC-MS). A capillary column (DB-5ms, Agilent Technologies, USA) was used for the analysis (30 m × 0.25 mm × 0.25 μm). The GC-MS was programmed with a 1.60 min solvent delay, initial temperature of 35 °C for 3 min, rising by 10 °C/min to 100 °C. The selected ion monitoring (SIM) mode was set for m/z 78 (benzene and m, p-xylene) and 91 (toluene). Field blank and spiked samples were analyzed simultaneously for quality control and the LOD was estimated from seven replicates of the lowest standard solution.

Five phthalates were collected and analyzed according to an Occupational Safety and Health Administration (OSHA) standard method (OSHA method 104, 1994). Five substances were selected as phthalate components that can emission during 3D printer operation: (1) dimethyl phthalate (DMP), (2) diethyl phthalate (DEP), (3) dibutyl phthalate (DBP), (4) di-2-ethylhexyl phthalate (DEPH), and (5) di-n-octyl phthalate (DnOP). Phthalates were collected using XAD-2 tubes (cat. no. 226-30-06, SKC Inc., USA) with a flow rate of 1.0 L/min. Sampled phthalates were extracted with 4 mL of a hexane and acetone mixture (9:1). All of the experiment equipment used in the analysis was cleaned using ACN (HPLC grade, J.T.Baker, USA). Extracted samples were injected by the auto-sampler (CombePAL, CTC analytics, Switzerland) into the gas chromatograph (HP 6890, Hewlett Packard Co., USA) - mass spectrometry (HP 5975C, Agilent Technology, USA) (GC-MS). A capillary column (DB-5ms, Agilent Technologies, USA) was used for the analysis ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). The GC-MS was programmed with a 5 min solvent delay, an initial temperature of 60°C for 5 min, increasing by temperature heating $10^{\circ}\text{C}/\text{min}$ to 100°C , $20^{\circ}\text{C}/\text{min}$ to 220°C , and then $5^{\circ}\text{C}/\text{min}$ to 300°C for 3 min. The selected ion monitoring (SIM) was set for m/z 149 (DEP, DBP, DEPH, and DnOP), and 163 (DMP). A field blank and spiked sample were analyzed simultaneously for quality control and the LOD was estimated from seven replicates of the lowest standard solution.

Statistical analyses were performed using the SAS 9.13 software (SAS Institute Inc., USA). For the statistical analysis of variance we used a *post hoc* Tukey test to indicate a significant difference between the cartridges, for which we also used Excel 2010 (Microsoft Corp, USA). On-line (real-time) instrument data were presented as geometric means (GM) (geometric standard deviation (GSD)), and off-line data were collected from three samples and presented as arithmetic means (AM) (standard deviation (SD)). A graphical representation was generated using SigmaPlot 10.0 (Systat, USA).

3. Results

3.1. Particulate matter

3.1.1. Number concentration of particle

The number concentration, range of concentration, count median diameter (CMD) (unit: nm), and the fraction of nanosize particles (<100 nm) are summarized in Table 1. During 3D printer operation, the GM (GSD) number concentration for the ABS cartridge, as measured by the SMPS was 1,731,571 (1.47) particles/cm³ and for the PLA1 cartridge was 52,252 (1.98) particles/cm³. The number concentration of particles from the cartridges, as measured by the CPC, was 471,674 (1.55) particles/cm³ for the ABS, 48,447 (2.03) particles/cm³ for the PLA1, and 26,129 (2.34) particles/cm³ for the PLA2. Therefore, the ABS cartridge produced the highest number concentration.

For all cartridges, the number concentration of particles was considerably higher during 3D printing than before operation, after operation, and the outdoor concentration. When using the ABS cartridge, the GM of the number concentration during 3D printing (1,731,578 #/cm³), as measured by the SMPS, was 345 times higher than before operation (5,021 #/cm³), 273 times higher than after operation (6,373 #/cm³), and 85 times higher than that in outdoor air (20,363 #/cm³).

The same trend was found for the PLA1 and PLA2 cartridges. The GM during 3D printing is 26 times (PLA1; 52,252 #/cm³) and 21 times (PLA2; 45,690 #/cm³) higher than before printing (PLA1; 1,997 #/cm³, PLA2; 2,174 #/cm³).

The number concentration, as measured by the CPC, displayed a similar pattern. The GM of the number concentration during 3D printing was considerably higher

than before operation (ABS, 129 times; PLA1, 28 times; PLA2, 20 times), after operation (ABS, 19 times; PLA1, 41 times; PLA2, 22 times) or in the outdoor concentration (ABS, 35 times; PLA1, 11 times; PLA2, 4 times).

To confirm the outdoor concentration, SMPS and CPC results were compared. During ABS cartridge sampling, the GM (GSD) of the number concentration was 20,363 (1.63) particles/cm³ as measured by the SMPS and 13,204 (1.72) particles/cm³ as measured by the CPC. For the PLA1 cartridge the number concentration, as measured by the SMPS, was 6,222 (1.17) particles/cm³ and 4,532 (1.18) particles/cm³ as measured by the CPC.

Table 1. Particle concentrations determined by SMPS and CPC before, during, and after 3D printing

cartridge		SMPS (size range: 10 – 420 nm)				CPC (size range: 20 – 1,000 nm)			
		before operation	during operation	after operation	outdoor	before operation	during operation	after operation	outdoor
ABS ^{c)}	GM (GSD) ^{a)}	5,021 (1.46)	1,731,578 (1.47)	6,373 (2.31)	20,363 (1.63)	3,662 (1.41)	471,674 (1.55)	5,143 (2.59)	13,204 (1.72)
	range	2,447-23,993	7,661-3,395,120	2,515-1,597,471	8,447-46,616	1,785-13,938	5,811-500,000	1,950-500,000	5,078-31,746
	CMD (nm) ^{b)}	67.9 (1.18)	32.60 (1.11)	50.49 (1.07)	54.74 (1.26)	-	-	-	-
	<100 nm/total	0.655	0.957	0.887	0.768	-	-	-	-
PLA1 ^{d)}	GM (GSD)	1,997 (1.28)	52,252 (1.98)	1,374 (1.81)	6,222 (1.17)	1,724 (1.28)	48,447 (2.03)	1,193 (1.99)	4,532 (1.18)
	range	1,305-4,612	2,961-212,154	535-11,988	3,634-12,306	1,071-4,415	2,504-170,466	433-24,581	2,563-10,596
	CMD (nm)	44.46 (1.07)	27.94 (1.14)	43.37 (1.08)	40.92 (1.10)	-	-	-	-
	<100 nm/total	0.794	0.975	0.844	0.812	-	-	-	-
PLA2 ^{e)}	GM (GSD)	2,174 (1.20)	45,690 (2.50)	1,582 (1.55)	5,939 (1.24)	1,321 (1.15)	26,129 (2.34)	1,209 (1.50)	6,221 (1.22)
	range	374-3,497	2,469-474,000	1,283-21,711	1,431-11,138	1,079-2,035	1,601-199,900	820-15,071	3,467-20,156
	CMD (nm)	84.44 (1.15)	188.18 (1.26)	82.90 (1.11)	59.64 (1.16)	-	-	-	-
	<100 nm/total	0.543	0.119	0.553	0.708	-	-	-	-

^{a)} Geometric mean (geometric standard deviation): GM unit (particles/cm³)

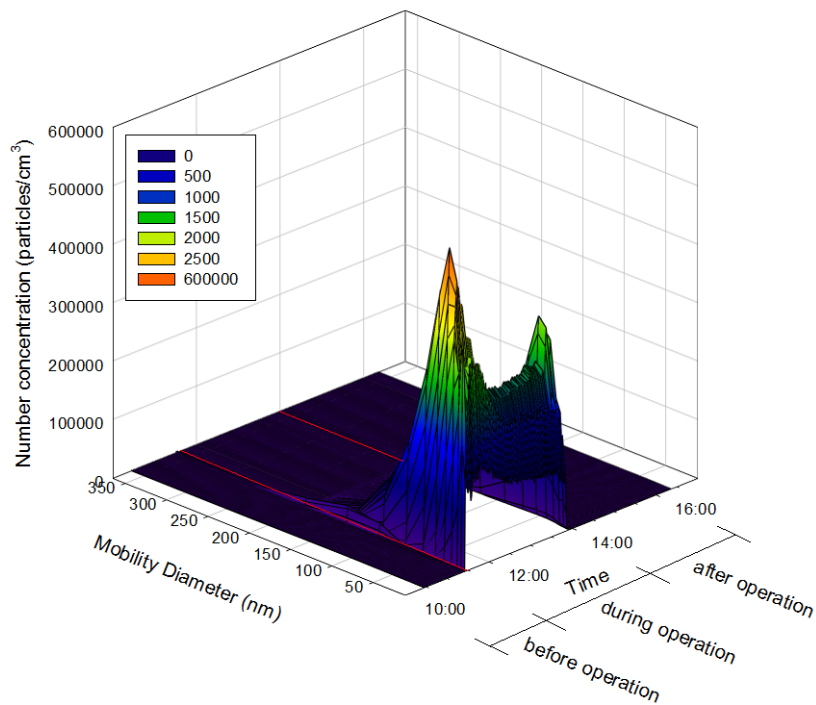
^{b)} Count median diameter, Geometric mean (geometric standard deviation)

^{c)} acrylonitrile-butadiene-styrene (ABS) (Cube, 3D systems, USA)

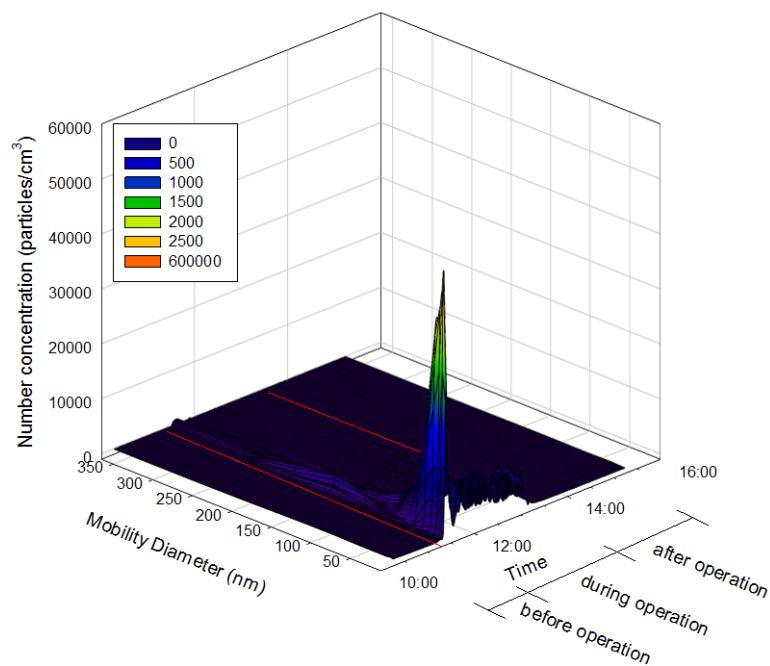
^{d)} polylactic acid (PLA1) (Cube, 3D systems, USA)

^{e)} polylactic acid (PLA2) (3DISON plus, Rokit, Korea)

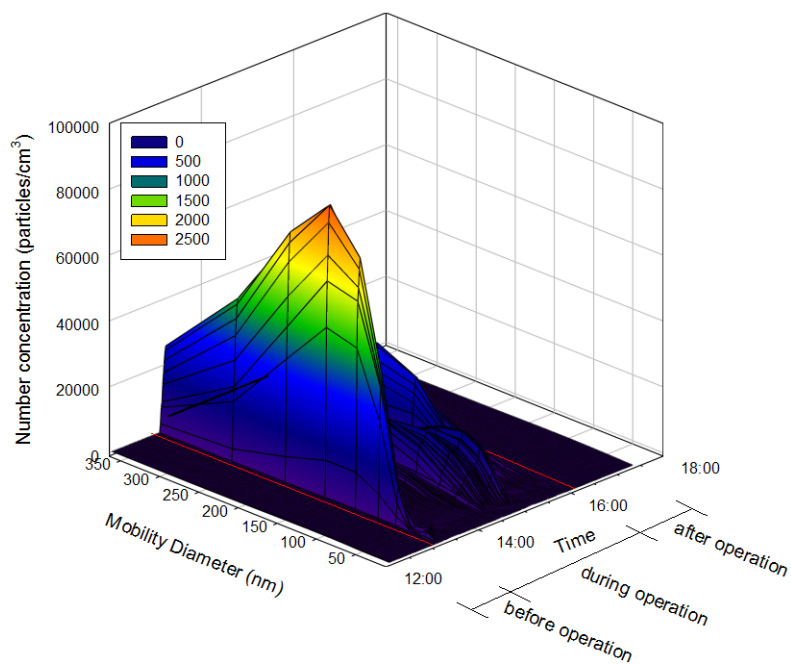
Figure 3 shows the SMPS output during sampling. In the figure, the red line indicates the duration of printer operation. During 3D printer operation, the number concentration rapidly increased for all cartridges. The use of the ABS cartridge produces the highest number concentration, whereas the PLA1 cartridge emitted the smallest particles size. Particles of less than 100 nm size were produced rapidly when the ABS and PLA1 cartridges were used, whereas the use of the PLA2 cartridge produces particles larger than 100 nm.



(a) ABS cartridge



(b) PLA1 cartridge

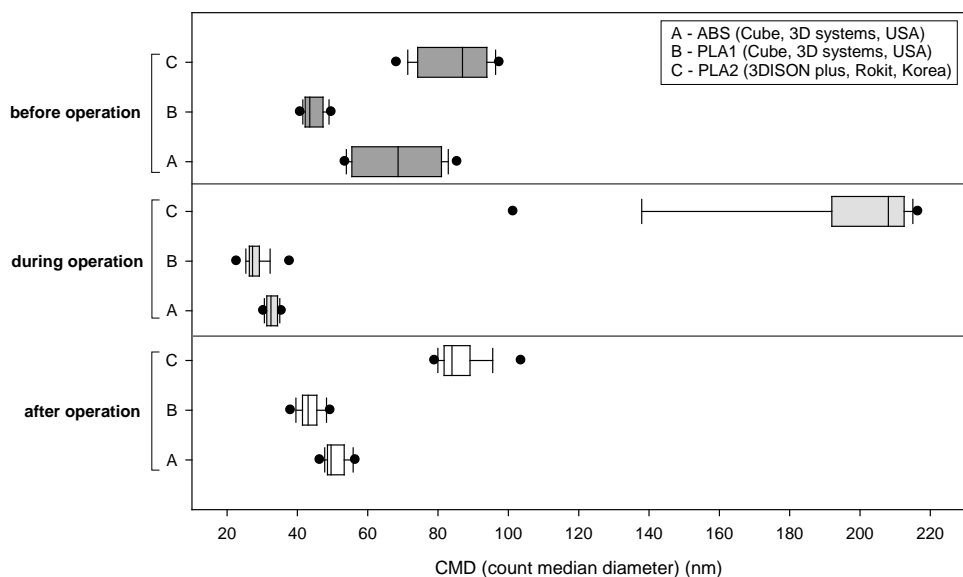


(c) PLA2 cartridge

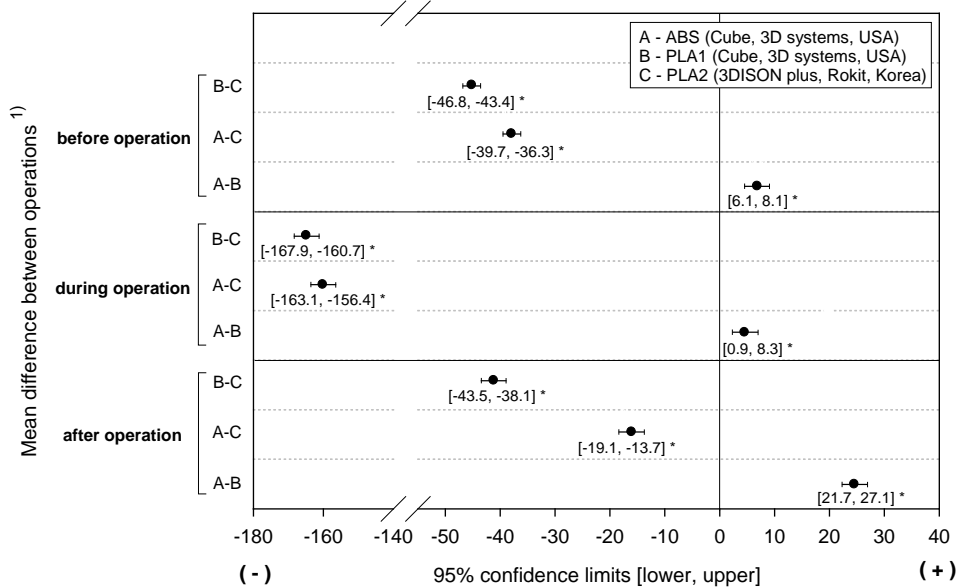
Figure 3. SMPS output for the various size categories before, during, and after 3D printer operation.

The data measured by the SMPS are presented as the GM (GSD) of the count median diameter (CMD) in Figure 4(a). For all cartridges, before and after operation, the particle size was less than 100 nm. During 3D printing, the CMD using the ABS was 33 (1.11) nm, while for the PLA1 and PLA2 cartridges it was 28 (1.14) nm and 188 (1.26) nm, respectively. 3D printing using ABS and PLA1 produces nano-particle emissions.

Figure 4(b) shows the result of an analysis of variance using a *post hoc* Tukey test to indicate significant differences between cartridges (ABS, PLA1, and PLA2). Depending on the printing operation, statistically significant differences were found in the CMD of particle between cartridges ($p < 0.05$). Before and after operation there was a similar trends, while Figure 4(b) shows that during operation particles produced using the PLA2 (indicates C) cartridge had the highest CMD, whereas particles produced using the PLA1 (indicates B) cartridge had the lowest CMD.



(a)



(b)

Figure 4. (a) The number concentrations according to the count median diameter (CMD) measured by the SMPS (median (line within box), upper quartile, and lower quartile (top and bottom part of the box, respectively), the maximum excluding outliers and the minimum excluding outliers (upper and lower bars on whiskers, respectively), and outliers (black circles)). (b) Mean difference in the count median diameter (CMD) between the cartridges (difference between means (black circles), and the 95% confidence outliers (upper and lower bars on whiskers)).

Figure 5 shows the number concentration measured by the CPC. As soon as 3D printer began, the total number concentration of particles increased rapidly and when using the ABS cartridge the concentration continued to increase up to the instrument detection limit (500,000 particles/cm³). The total number concentration of particles when using the PLA1 and PLA2 cartridges displayed a similar trend. After finish the 3D printer operation, the particle concentration decreased gradually.

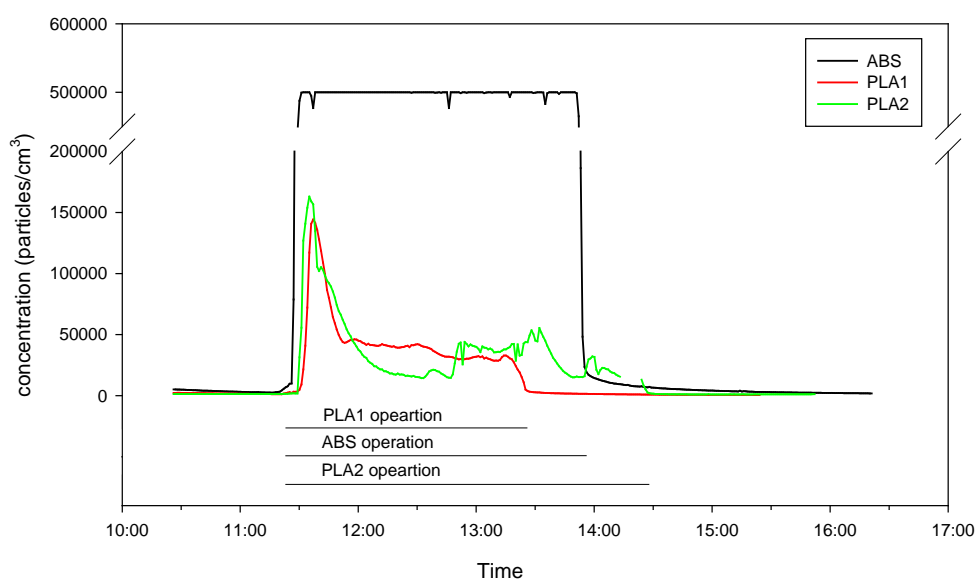


Figure 5. Real-time monitoring by CPC during 3D printing with the use of ABS, PLA1, and PLA2 cartridges (maximum CPC concentration is 500,000 particles/cm³).

3.1.2. Mass concentration of particle

Table 2 shows the measured mass concentrations of the particles emitted for each cartridge. During 3D printer operation, the GM (GSD) of the particles emitted for each cartridge was ABS; 63.74 (1.10) $\mu\text{g}/\text{m}^3$, PLA1; 31.89 (1.01) $\mu\text{g}/\text{m}^3$, and PLA2; 153.20 (1.69) $\mu\text{g}/\text{m}^3$. The mass concentration of particles using the PLA2 cartridge was the highest, and there were statistically significant differences between the levels before and during operation for all cartridges. Figure 6 shows a comparison of the mass concentration of particles emitted with each cartridge (ABS, PLA1, and PLA2). Statistics analysis of variance used a *post hoc* Tukey test to identify any significant differences between the cartridges. During printer operation, the mass concentration of particles during the use of the PLA2 cartridge was higher than for the other cartridges ($p < 0.05$). Before operation and after operation shows similar trend, while Figure 6 shows that during operation particles produced using the ABS (indicates A) cartridge had the highest mass concentration, whereas particles produced using the PLA2 (indicates C) had the lowest mass concentration.

Table 2. The mass concentration before, during, and after 3D printer operation

cartridge		concentration (unit: $\mu\text{g}/\text{m}^3$)	
		GM (GSD) ^{a)}	range
ABS	before operation	58.34 (1.06)	54.23-67.88
	during operation	63.74 (1.10)	58.02-91.40
	after operation	51.93 (1.06)	49.61-64.51
PLA1	before operation	32.32 (1.01)	31.90-34.19
	during operation	31.89 (1.01)	31.61-33.36
	after operation	32.10 (1.03)	31.64-38.57
PLA2	before operation	11.19 (1.01)	11.12-11.60
	during operation	153.20 (1.69)	11.43-387.43
	after operation	11.33 (1.20)	10.43-47.34

^{a)} Geometric mean (geometric standard deviation)

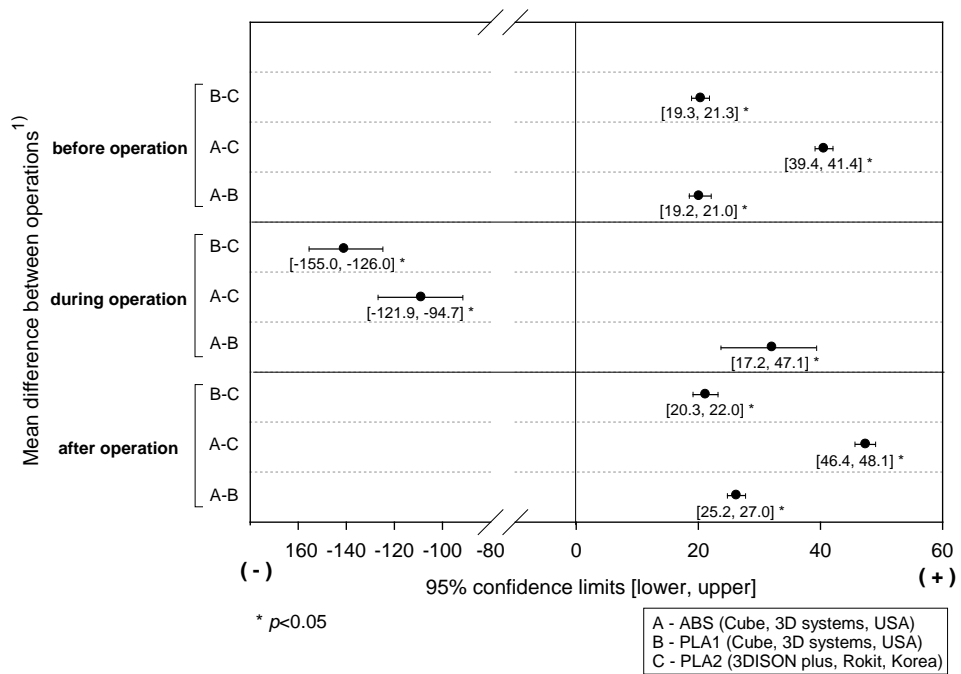


Figure 6. Mean difference in the mass concentration of particles between the cartridges (difference between means (black circles), and the 95% confidence outliers (upper and lower bars on whiskers)).

The data measured by the PC filter are presents in Figure 7. The mass concentrations measured during the use of the ABS and PLA2 cartridges increased during printer operation, while for PLA1 the concentrations were similar to those before operation. During operation, the mass concentrations were about 1.9 times and 2.1 times higher than before operation when the ABS and PLA2 cartridges were used, respectively. During 3D printer operation, the mass concentration of particles measured when the PLA2 cartridge was used was higher than for the other cartridges. After operation, the mass concentration decreased compared to the levels before and during operation for all three cartridges.

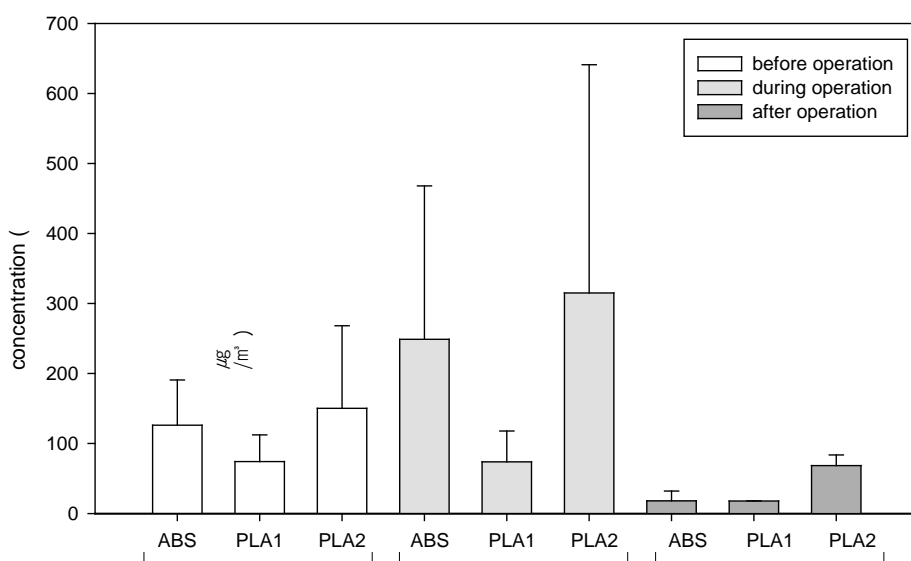


Figure 7. Particle mass concentration measured using a PC filter (error bars indicate the standard deviation of the mean (n=3)).

3.2. Gaseous material

Table 3 shows the TVOC concentrations during sampling. When the PLA1 and PLA2 cartridges were used, TVOCs were not detected. When the ABS cartridge was used, during 3D printing the average the GM (GSD) and maximum TVOC concentrations were 154.9 (3.4) ppb and 453.3 ppb, respectively. The TVOC concentration rapidly decreased after 3D printer operation, but some TVOCs were still detected 15 min after printing finished (Figure 8).

Table 3. TVOC concentrations before, during, and after 3D printer operation

cartridge		concentration (unit: ppb)	
		GM (GSD) ^{a)}	range
ABS	before operation	N.D ^{b)}	N.D
	during operation	154.9 (3.4)	0 – 453.3
	after operation	57.9 (5.1)	0 – 449.7
PLA1	before operation	N.D	N.D
	during operation	N.D	N.D
	after operation	N.D	N.D
PLA2	before operation	N.D	N.D
	during operation	N.D	N.D
	after operation	N.D	N.D

^{a)} Geometric mean (geometric standard deviation)

^{b)} Not detected

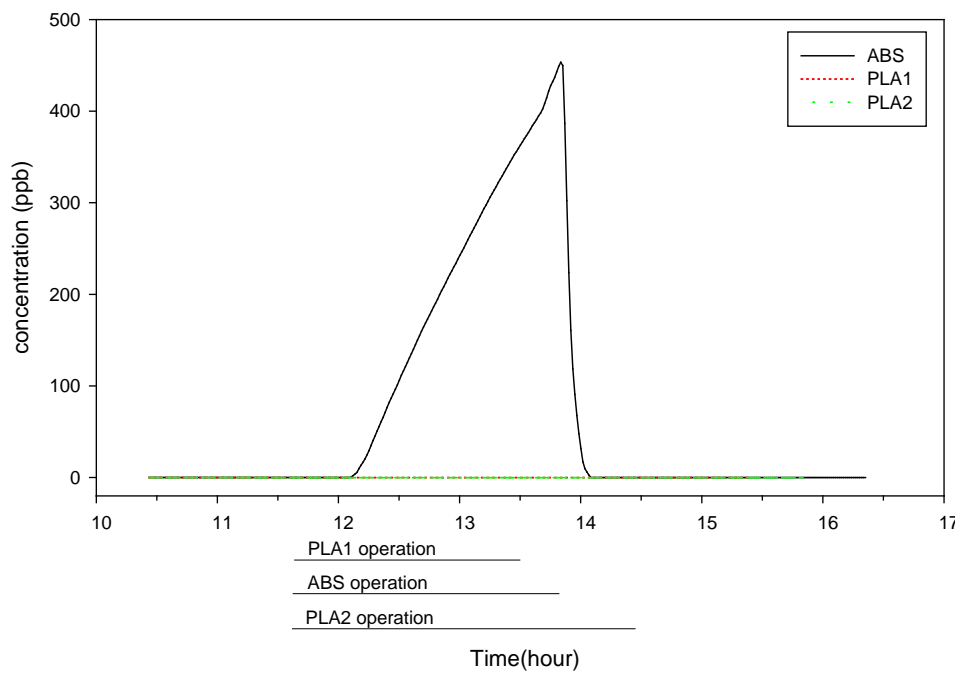


Figure 8. Real-time monitoring of TVOC concentrations during sampling.

Table 4 shows the concentration of aldehydes and the indoor/outdoor (I/O) ratio. During emission sampling, formaldehyde, acetaldehyde, and isovalderaldehyde were detected. The concentration of these aldehydes increased during 3D printer operation. Formaldehyde was the most abundant aldehyde when the PLA2 cartridge was used, whereas acetaldehyde and isovalderaldehyde were detected when ABS was used.

During operation, the indoor concentration of aldehydes was higher than that outdoor, except for isovalderaldehyde when the PLA1 cartridge was used. When the ABS cartridge was used, Isovalderaldehyde and acetaldehyde concentrations were 11.9 times, and 3.2 times, respectively, higher than the outdoor concentration. When the PLA2 cartridge was used, formaldehyde concentrations were 5.2 times higher than the outdoor concentration. The LOD of the aldehyde compounds is presented in Appendix 1.

Table 4. Aldehyde concentrations during use of the 3D printer cartridges

cartridge	substance	concentration (ppb) ^{a)}				I/O ratio ^{b)}		
		before operation	during operation	after operation	outdoor	before operation	during operation	after operation
ABS	formaldehyde	39.3 (6.6)	68.0 (12.7)	43.8 (21.2)	21.3 (10.7)	1.8	3.2	2.1
	acetaldehyde	<LOD ^{c)}	31.9 (6.2)	11.6 (1.7)	<LOD	<LOD	3.2	1.2
	isovalderaldehyde	<LOD	90.8 (22.5)	37.6 (17.2)	<LOD	<LOD	11.9	4.9
PLA1	formaldehyde	26.4 (16.4)	54.0 (23.3)	40.4 (6.0)	23.9 (13.0)	1.1	2.3	1.7
	acetaldehyde	11.2 (2.1)	30.4 (5.0)	10.8 (1.5)	10.9 (1.7)	1.0	2.8	1.0
	isovalderaldehyde	<LOD	<LOD	14.6 (12.0)	<LOD	<LOD	<LOD	1.9
PLA2	formaldehyde	111.0 (59.1)	155.9 (24.3)	114.7 (41.7)	30.2 (5.7)	3.7	5.2	3.8
	acetaldehyde	<LOD	18.4 (14.7)	<LOD	<LOD	<LOD	1.9	<LOD
	isovalderaldehyde	<LOD	27.2 (33.9)	<LOD	<LOD	<LOD	3.6	<LOD

^{a)} Arithmetic mean (standard deviation)

^{b)} Indoor/outdoor (I/O) ratio

^{c)} Limits of detection

Table 5 shows the benzene, toluene, ethyl benzene, and m, p-xylene concentrations. Benzene concentrations were at the LOD for all cartridges. The toluene, ethyl benzene, and m, p-xylene concentrations increased during printing. When the ABS and PLA2 cartridges were used. When the PLA1 cartridge was used the concentration during printer operation was lower than that before operation, but higher than the outdoor concentration, and toluene concentrations were higher than when the other cartridges were used. During printing, the highest ethyl benzene concentration (16.4 times higher than the outdoor concentration) was recorded when the ABS cartridge was used. When the PLA2 cartridge was used, m, p-xylene was detected at higher concentrations (2.9 times higher than those outdoors) than when the other cartridges were used.

Table 5. BTEX concentrations during use of the 3D printer cartridges

cartridge	substance	concentration (ppb) ^{a)}			
		before operation	during operation	after operation	outdoor
ABS	benzene	<LOD ^{b)}	<LOD	<LOD	<LOD
	toluene	<LOD	3.7 (5.5)	2.5 (3.5)	<LOD
	ethyl benzene	<LOD	11.5 (7.0)	2.0 (1.2)	0.7 (0.6)
	m, p-xylene	<LOD	<LOD	0.6 (0.2)	<LOD
PLA1	benzene	<LOD	<LOD	<LOD	<LOD
	toluene	29.5 (28.2)	16.2 (15.3)	20.5 (25.0)	4.9 (7.6)
	ethyl benzene	1.5 (1.0)	0.8 (0.5)	1.0 (0.5)	0.6 (0.2)
	m, p-xylene	1.5 (1.0)	0.8 (0.4)	0.9 (0.4)	0.5 (0.1)
PLA2	benzene	<LOD	<LOD	<LOD	<LOD
	toluene	1.5 (1.6)	2.7 (3.9)	10.6 (9.3)	1.3 (1.0)
	ethyl benzene	<LOD	1.2 (0.7)	1.6 (1.0)	<LOD
	m, p-xylene	<LOD	1.3 (0.8)	1.8 (1.1)	<LOD

^{a)} Arithmetic mean (standard deviation)

^{b)} Limits of detection (ppb): 21.29 (benzene), 0.52 (toluene), 0.45 (ethyl benzene), 0.45 (m, p-xylene)

Table 6 shows the phthalate concentrations when each cartridge was used. The phthalate concentrations were almost at the LOD and all outdoor samples were below the LOD. All DnOP and DMP samples were below the limit of detection (LOD) for all cartridges, and the DEP and DEPH were also below the LOD when the PLA2 cartridge was used. This result shows that the concentration of the phthalates that were present at levels above the LOD increased during printing. When the PLA1 cartridge was used, the concentration of DEP and DBP after printing was slightly higher than that during operation.

Table 6. Phthalate concentrations during use of the 3D printer cartridges

cartridge	substance	concentration (ppb) ^{a)}		
		before operation	during operation	after operation
ABS	DMP	<LOD ^{b)}	<LOD	<LOD
	DEP	<LOD	2.2 (0.8)	1.0 (0.6)
	DBP	<LOD	0.7 (0.2)	<LOD
	DEPH	<LOD	1.4 (0.3)	<LOD
	DnOP	<LOD	<LOD	<LOD
PLA1	DMP	<LOD	<LOD	<LOD
	DEP	<LOD	0.9 (0.4)	1.0 (0.4)
	DBP	<LOD	<LOD	1.5 (1.2)
	DEPH	<LOD	1.4 (0.2)	<LOD
	DnOP	<LOD	<LOD	<LOD
PLA2	DMP	<LOD	<LOD	<LOD
	DEP	<LOD	<LOD	<LOD
	DBP	<LOD	2.7 (3.2)	<LOD
	DEPH	<LOD	<LOD	<LOD
	DnOP	<LOD	<LOD	<LOD

^{a)} Arithmetic mean (standard deviation)

^{b)} Limits of detection (ppb): 0.40 (DMP), 0.67 (DEP), 0.81 (DBP), 1.25 (DEPH), 0.75 (DnOP)

4. Discussions

In this study, the particulate and gaseous emissions from a 3D printer process were determined. In addition, the impact of use of various 3D printer cartridges on emissions was investigated.

In the test chamber, ultrafine particle concentrations were higher than the outdoor concentration, with a typical particle size below 100 nm; i.e., nanoparticles (Ramachandran et al., 2011). Various characteristics of nanoparticles, including the size and morphology, are known to influence their toxicity, with small particles being more toxic than large particles (Peter et al., 1997). Nanoparticle can penetrate to the alveolus upon inhalation. Nanoparticles have a large surface area and can transfer toxic agents to blood vessels and tissue cells, leading to potential health hazards (Yoon, 2011).

During 3D printer operation, 500,000 particles/cm³ were measured by the CPC when the ABS cartridge was used. The CPC concentration range was 0 particles/cm³ to 500,000 particles/cm³. The results acquired from the CPC might be underestimated compared to the actual concentration. The CPC was used to measure the particle number concentration with a range of 20 nm to 1,000 nm, while the SMPS detectable size range was 10 nm to 420 nm, but the particle number concentration recorded by the SMPS was higher than that recorded by the CPC. This might be because of the maximum concentration range. The SMPS maximum concentration was 1,000,000 particles/cm³, while that for the CPC was 500,000 particles/cm³. The CPC also periodically inserts isopropyl alcohol (IPA) to

cause microscopic particles to grow into larger droplets that are easier to detect and count, which could lead to an underestimation of the particle concentration.

Despite the sampling process being conducted in a test chamber, the outdoor conditions and concentrations of the target materials had an impact on the test results, despite use of a charcoal and HEPA filter to filter the air entering the chamber. Prior to sampling, the background particle concentration was detected by the real-time instruments. Therefore, measurements of the 3D printer emissions only began when the particle number concentration in the chamber, as measured by the real-time instruments, was between 4,000 particles/cm³ and 6,000 particles/cm³.

To determine the mass concentration of particulate matter, a DustTrak and PC filter were used. On-line and off-line results displayed the same trend, but off-line sampling used a PC filter, whereas DustTrak calibration used a PVC filter. To facilitate more accurate evaluation of the particulate mass concentration, a PVC filter in off-line sampling should be used.

A ppbRAE monitor was used to calculate TVOCs, and at the same time the SMPS and CPC were used to calculate the number concentration of particulate matter. The use of IPA in the CPC could have affected the ppbRAE monitor when measuring the TVOC concentration.

The XAD-2 used for phthalate analysis might have a loss of sampler during desorption process. DEPH and DBP are also commonly used laboratory tools during sampling and analytical work (Park et al., 2010). Therefore, the phthalate concentration could have been underestimated.

The solution (CS₂) used to desorb BTEX included benzene. Determining the exact benzene concentration was problematic, and its LOD was higher than those of the other compounds.

Outdoor sampling was performed near the ventilation opening of a laboratory building. Therefore, the concentrations of VOCs, phthalates, and aldehydes were expected to be higher than the actual outdoor concentration, and the outdoor concentration was influenced by fine dust in the air. For outdoor sampling, a sealed location or performance of a measurement prior to sampling might improve the accuracy of measurements.

The emissions from the use of the ABS and PLA1 cartridges were measured in the 1 m³ chamber and acrylic box, inside the laboratory. The chamber and acrylic box were ventilated after sampling. The laboratory conditions might have resulted in a flow into the chamber due to natural ventilation, which could have affected the concentration of gaseous materials.

There was little difference between the components of each cartridges and the cartridge nozzle temperature setting conditions. The same product was produced during each experiment, but the printing time differed depending on the cartridge and company. The condition of most of the emissions differed due to the use of different cartridge. The use of the ABS cartridge resulted in the highest number concentration of particles, whereas when the PLA1 cartridge was used the lowest particle size and a low number concentration were recorded. The use of the PLA1 and PLA2 cartridges produced a similar number concentration, but with the PLA2 cartridge the particle size was larger.

This study had several limitations that should be addressed in future research. First, only two types of 3D printer (both FDM method) and two cartridge types (ABS and PLA) were experienced. More information could be obtained from a wider range of 3D printers and cartridges. Second, sampling was conducted in a chamber, and no exposure monitoring was undertaken. Furthermore, if the identification of all of the compounds within the cartridge were possible, it would improve the quality of data regarding 3D printer emissions for different printing methods and types of cartridge. In addition, further studies are needed to determine exposure factors together with an analysis of a diverse range of cartridge.

The users of 3D printer do not indicate the resulting concentrations of particulate matter and gaseous materials. According to the precautionary principle, effective management is necessary because the hazards associated with use of 3D printers are unknown. To prevent indoor air pollution from particle emissions during 3D printing, the installation of ventilation and use of personal protective equipment (PPE) is required.

5. Conclusions

This study confirmed the concentration of particulate and gaseous materials during 3D printing. We found that the concentration of particulate matter and gaseous materials differed depending on the cartridge type and manufacturer. The use of the ABS cartridge resulted in a higher particle concentration than the use of the PLA1 and PLA2 cartridges. The CMD and mass concentration of particles produced using the PLA2 cartridge was greater than for the other cartridges. The concentrations of aldehydes, BTEX, and phthalates, did not exceed threshold limits. The concentrations of particulate matter and gaseous materials increased during 3D printing.

The results can be used as a reference for evaluating 3D printer emissions and also provide basic data for further studies of the management of 3D printer exposure. This emission assessment also provides useful information regarding particulate matter and gaseous material emissions during 3D printer operation.

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Appendix

Appendix 1. Target aldehyde compounds from the standard solution and limit of detection (LOD)

No.	compound	LOD (ppb)
1	acetaldehyde	1.94
2	acetone	1.82
3	acrolein	1.84
4	benzaldehyde	0.42
5	butyraldehyde	0.96
6	crotonaldehyde	2.12
7	formaldehyde	1.26
8	gexaldehyde	2.06
9	isovaleraldehyde	2.44
10	m-Tolualdehyde	0.32
11	p-Toualdehyde	0.32
12	o-Tolualdehyde	0.32
13	propionaldehyde	1.92
14	valeraldehyde	0.45
15	2,5-dimethylbenzaldehyde	0.15

국문초록

3D printer 에서 발생하는 입자상물질과 가스상물질의 발생특성평가

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지도교수 윤 충 식

연구목적 3D (Three-dimensional) 프린터 사업은 교육용 자재와 전자부품, 등 활용영역이 확장되고 있고 최근에는 3D 프린터가 대중들에게 빠르게 보급되고 있으며 3D 프린터가 가동 되면서 발생하는 유해인자에 노출될 수 있다. 본 연구는 3D 프린터를 이용하여 제품을 제작하는 동안 입자상물질과 가스상물질의 공기 중 발생정도를 파악하고 카트리지에 따라 농도를 파악하고자 한다.

연구방법 입자상물질과 가스상물질의 측정은 FDM 방식의 3D 프린터를 챔버 안에서 가동 전, 중, 후로 나누어서 샘플링을 하였다. PLA (PLA1)

카트리지와 ABS 카트리지를 사용하였고, 다른 브랜드의 3D 프린터로 PLA (PLA2)에 대해 3 번 샘플링 하였다. 실시간측정법과 비실시간측정법을 동시에 샘플링하였다. 입자상물질의 측정은 실시간측정법으로 scanning mobility particle sizer (SMPS), condensation particle counter (CPC)를 사용하였으며, 입자의 중량농도 분석을 위해 DustTrak 을 사용하였고, 비실시간측정법으로 polycarbonate (PC) 필터를 open-faced 로 하여 채취하였다. 가스상물질의 측정은 ppbRAE 를 사용하였고, 비실시간측정법으로 프탈레이트류와 VOCs 를 XAD-2 와 charcoal 를 사용하여 저유량펌프로 채취하였으며, 알데하이드류는 2,4-dinitrophenylhydrazine (2,4-DNPH)로 채취하였다. 또한 실외공기를 대조군으로 선정해 함께 샘플링 하였다.

연구결과 (1) 입자상물질의 수농도: 3D 프린터를 가동하는 동안 입자의 수농도가 급격히 증가하였고, 입자크기 분포를 확인해보면 ABS 와 PLA1 에서 샘플링 시간 동안 100 nm 이하의 입자가 많이 발생함을 볼 수 있다. 또한 CPC 의 경우 ABS 를 사용하였을 때 프린터가 작동하는 전 시간 동안 500,000 particles/cm³ 의 노출 수준을 보였다. PLA2 카트리지는 프린터 가동하는 동안에는 100 nm 보다 큰 입자를 나타내었다.

(2) 입자상물질의 중량농도: DustTrak 으로 측정한 결과 프린터가 가동하는 동안 PLA2 에서 가장 높게 나타났고 PC 필터 중량분석결과도 동일하게 나타났다. (3) 가스상물질의 농도: 프탈레이트, 알데하이드,

VOCs 분석결과 프린터가동하는 동안 높아지는 경향을 나타내었고, 모든 물질에서 노출기준을 초과하지 않았다.

결론 본 연구를 통해 프린터를 가동하는 동안 나노입자와 VOCs, 알데하이드류, 프탈레이트류가 배출되었으며 사용하는 카트리지에 따라 농도가 다르게 나타났다. PLA 카트리지를 사용할 때 보다 ABS 카트리지를 사용할 때 입자상물질이 가장 많이 배출되었으며, 알데하이드류와 VOCs 가 ABS 와 PLA 카트리지를 사용할 때 배출되었다. FDM 방식의 3D 프린터를 가동할 때 발생 가능한 유해인자에 대한 연구가 부족하므로 사전주의원칙을 적용하여 노출관리를 해야 한다.

Keywords: FDM 3D 프린터, ABS, PLA, 나노입자, 알데하이드류

Student Number: 2013-21819