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Health and safety in 3D printing

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Abstract

Fused deposition modelling, or 3D printing, is an additive manufacturing technique that is quickly gaining popularity because of its ability to produce usable parts with several geometries. It provides multiple advantages in everyday life. However, the emerging risks of using 3D printers at home is an issue that needs to be addressed. It is estimated that a person spends, on average, 80-90% of their time inside a building, up to 60% of that time is at home. Therefore it is essential to control the pollutants in the indoor environment. This paper evaluated the Volatile Organic Compounds (VOCs) and nanoparticle emissions during 3D printing with the most common Poly-Lactic Acid (PLA) and Acrylonitrile Butadiene Styrene (ABS) materials. Real-time aerosol monitors were used to characterise particulate emission, and laboratory analysis was used to check the VOCs levels. During printing, an increase of VOCs and nanoparticles was observed. This increase was more significant during printing with ABS filaments than during printing with PLA filaments. The nanoparticles size emitted for the ABS filament was smaller than the particles emitted for the PLA filament. A carcinogen substance like benzene was found during printing. The pollutants levels observed may cause health problems, and it is recommended that printing be avoided without engineering controls in place, e.g. a good ventilation and extraction system.

1. INTRODUCTION

3D printing initially is used to create prototypes and models, but nowadays is also used for the production of end-use products (Rett et al., 2021) thanks to its ability to create usable parts with several geometries. Fused Deposition Modelling (FDM) is an increasing component of additive manufacturing technology (Babagowda et al., 2018).

The 3D printers market is growing very fast. In 2018, 1.42 million units of 3D printers were sold, and this number is expected to reach 8.04 million units by 2027 (Grand View Research, 2019). Poly-Lactic Acid (PLA) and Acrylonitrile Butadiene Styrene (ABS) are the most widely used filament materials in 3D printers.

Nowadays, in many houses, schools and offices, 3D printers are used without concerns about health effects. 3D printers emit volatile organic compounds (VOCs) and ultrafine particles during the printing process (Wojtyła et al., 2017; Byrley et al., 2018). In most cases, it can take several hours or even days to print, with the likelihood of a person sitting nearby for several hours (Hall et al., 2019). In Europe, people may spend more than 20 hours per day indoors (Working group 13, 1997) and so it is very important to control the indoor air pollutants to avoid negative health impacts.

According to a study conducted in seventeen 3D printing firms, 59 per cent of employees have respiratory conditions, and workers who work 40 hours a week on printers are more likely to have respiratory-related diagnoses (asthma or allergic rhinitis) (Chan et al., 2018).

Particle Number Concentrations (PNCs) and Volatile Organic Compounds (VOCs) were monitored as part of a multimetric approach.

VOCs are gases that contain a variety of chemicals and are released from liquids or solids with a high vapour pressure at room temperature (US EPA, 2014b).

VOCs are easily volatilized at room temperature, they are classified in four groups:

(i) Very Volatile Organic Compounds (VVOCs) with T_b: < to 50–100 °C (e g. propane, butane, methyl chloride)

(ii) Volatile organic compounds (VOCs) with 50-100 °C < T_b < 240-260 °C (Formaldehyde, d-Limonene, toluene, acetone, ethanol (ethyl alcohol) 2-propanol (isopropyl alcohol), hexanal)

(iii) Semi-Volatile Organic Compounds (SVOCs) with 240-260 °C < T_b < 380-400 °C

(iv) Particulate Organic Matter (POM) with T_b > 380 °C (e.g. Pesticides (DDT, chlordane, plasticizers (phthalates), fire retardants (Polychlorinated Biphenyl (PCBs), Polybrominated Biphenyl (PBB) (US EPA, 2014a).

This study aims to identify contaminants emitted during 3D printing and make recommendations for healthy 3D printing practices.

2. MATERIALS AND METHODS

2.1 3D printer and filaments

The selected printer was a Creality Ender 3·D with the capacity to build 220x220x250 mm (Figure 1). There is a single extruder, one heated plate, and sidewalls on the printer, but no cover or extraction device.

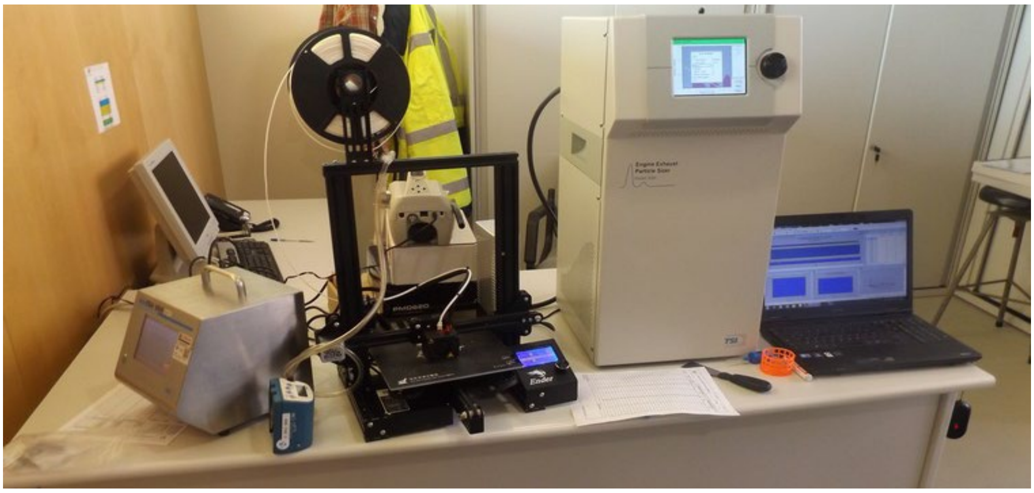


Figure 1. Ender 3D printer, printing

The 3D printer supports several filaments, but the study was only tested the two filaments most commonly used in the market, the thermoplastics ABS and PLA. PLA is typically made from renewable sources such as corn (low greenhouse gas emissions), is biodegradable, and inexpensive. ABS (acrylonitrile, 1,3-butadiene, and styrene) is a petrochemical filament. PLA is more rigid and stiffer than ABS, but hobbyists mostly use it due to its low heat resistance. ABS is a more robust plastic for prototyping because it is softer and less strong, but it is still tough and lighter.

The extruder is heated to a temperature where the filament begins to melt (190ºC for PLA and 230ºC for ABS), Extrusion-based printing relies on the extrusion of material in a layer-by-layer manner (Rett et al., 2021).

2.2 Sample design

A chamber was used in many studies and reports to collect particles and VOCs released during printing (Kwon et al., 2017; Byrley et al., 2018 ;Gu et al., 2019). The chamber may concentrate the pollutants. This study aimed to assess nanoparticles and VOCs emissions in a real-world setting for a non-professional consumer in a typical household.

A room with the dimensions of 9 x 2.5 x 5 meters was selected. This study was carried out measuring pollutants emitted during printing for ABS and PLA. The measurement equipment was located near the printer, around 10 cm (Figure 1).

2.3 Particulate measurements

PNCs were measured with a Condensation Particle Counter CPC 3007 (TSI Inc., Shoreview, MN), Particulate Matter respirable mass concentrations were measured with a Side Pak Personal Aerosol Monitor AM510 (TSI Inc., Shoreview, MN), and particle size distributions were measured with an Engine Exhaust Particle Sizer (EEPS 3090; TSI Inc., Shoreview, MN), Table 1.

Before the sampling phase began, the instruments were calibrated according to the manufacturer's instructions, and "zeroing" was done every day before sampling.

Table 1 Direct reading instruments used for monitoring the particulate fraction

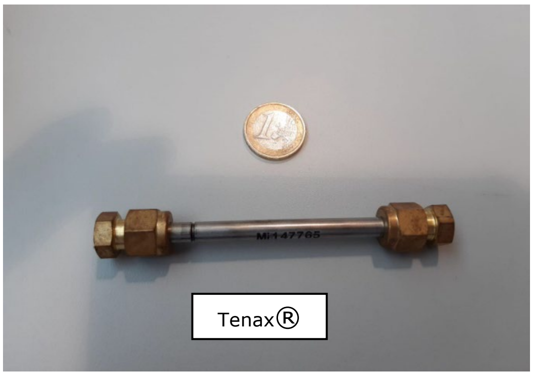
Instrument			Measured parameters	Particle size range
	Condensation particle counter (TSI Inc., Shoreview, MN) CPC -3007	Condensation nuclei counter	Particles number concentration	0.010 to 1 µm
	EEPS (TSI Inc., Shoreview, MN) Model 3090	Engine Exhaust Particle Sizer Spectrometer	Ultrafine particle size distribution (nanoparticles)	0.0056 to 0.56 µm
	Side Pak (TSI Inc., Shoreview, MN) Model Am510	Laser photometer	Particle mass concentration and size distribution	(PM_4) Respirable fraction

2.4 Volatile organic compounds (VOCs)

VOCs were sampled with a personal pump, a Tygon tubing air sampling and a Tenax® TA sorbent tube.

The pump selected was the Gil Air Plus; the pump is designed to provide a stable, controlled flow rate of approximately 20 to 5,100 cc/min. All the pumps used were annually maintained to avoid pulsations and fluctuations in the flow rate.

The sampler flow rate was checked and adjusted to (50 ml/min) before each sampling using a calibrated MesaLabs Bios DryCal Defender 530. It was also checked after the test was complete (Figure 2).



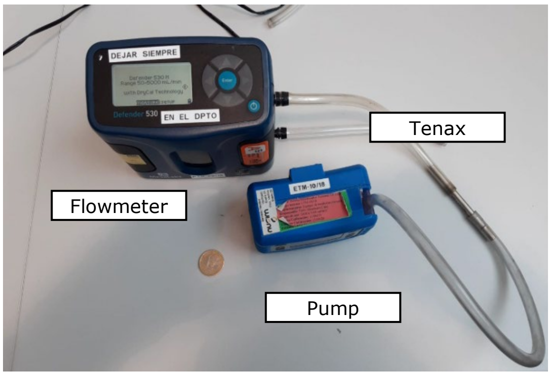


Figure 2. Tenax® TA sorbent tube (left) and pump calibration (right)

The sampling time selected was 100 minutes. Once sampling was completed, the Tenax® TA sorbent tube was refrigerated (temperature between 0 to 5ºC) and sent to the laboratory, located in the same building, for analysis. The laboratory analysed 49 different VOCs. (Table 2). The laboratory procedure for analysis was based on the UNE-EN 14662 "Ambient air quality. Standard method for measurement of benzene concentrations" and NIOSH Method 2549 "Volatile Organic Compounds screening". The limit of quantitation (LOQ) for VOCs is 0.1 ng. It was used the Gas Chromatograph (Agilent 5975C), thermal desorption (MARKES UNITY 2), an HP-INNOWax Column and ancillary elements were used.

Table 2. Nano reference values, based on the benchmark level (IFA)(Deutsche Gesetzliche Unfallversicherung, 2020)

Description	**Density**	**Benchmark level (8-h TWA)**
Biopersistent granular nanomaterial in the range 1-100 nm	>6,000 kg/m^3	20,000 particles/cm^3
Biopersistent granular nanomaterial in the range 1-100 nm	<6,000 kg/m^3	40,000 particles/cm^3
Non-bio-persistent nanomaterial in the range 1-100 nm		Applicable OEL.

2.5 Limits

With regard to nanoparticles levels, there are currently no air quality regulations relating to the control of exposure to airborne nanoparticles because the safe level of nanoparticle exposure is still contentious, and there are no universally accepted standard measurement techniques or instruments. Nevertheless, it's clear that the nanoparticle's surface plays an essential role in the toxic effects. The environment particle concentration numbers are a better metric for evaluating risks than the traditionally (and officially) used mass-based approach (van Broekhuizen et al., 2012), because nanoparticles have extensive surface area to volume ratios compared to the same material in bulk (Schmid & Stoeger, 2016; Instituto Nacional de Seguridad e Higiene en el Trabajo (INSHT), 2015).

There are multiple nanoparticles with different sizes distribution and heterogeneous composition; a benchmark concentration level was suggested by the German Institut für Arbeitsschutz (IFA). The 3D printer filaments (PLA & ABS) have a density of less than 6,000 kg/m^3, and the proposed reference level for nanoparticles is 40,000 particles/cm^3.

There are many VOCs, to simplify the indoor air quality reference levels; in some literature, the term Total Volatile Organic Compounds (TVOC) is used but it is not well defined in any of the relevant papers. The definition that is more accepted is the sum of all VOCs which elute between and including n-hexane and n-hexadecane on a non-polar capillary column.

The recommended value of TVOC for an indoor environment is 200 μg/m^3 (Working group 6, 1992; Working group 13, 1997; Mečiarová et al., 2017). Nevertheless, there are some VOCs with no recommended safe level for exposure, e.g. benzene, and others have individual exposure limits. This is also the reason for evaluating all the VOCs individually; Public Health England published a guide for indoor VOCs benchmark levels, Table 3. Related to dust, the time-weighted average (TWA) for respirable dust is 3 mg/m^3 (LEP 2019, 2019). It is a mass-based approach with similar legislation in most countries.

Table 3. Indoor air quality guidelines for selected VOCs (Public Health England, 2019)

VOCs	Limit Values in μg/m³		Source
	Short Term	Long term	
Acetaldehyde (75-07-0)	1420 (1h)	280 (1day)	Health Canada (2018)
α-Pinene (80-56-8)	45000 (30 min)	4500 (1day)	EPHECT (Trantallidi et al., 2015)
Benzene (71-43-2)	No recommended level exposure		World Health Organisation (2010)
D-Limonene (5989-27-5)	90000 (30 min)	9000 (1 day)	EPHECT (Trantallidi et al., 2015)
Formaldehyde (50-00-0)	100 (30 min)	10 (1year)	World Health Organisation (2010)
Naphthalene (91-20-3)	-	3 (1 year)	Agency for Toxic Substances & Disease Registry (2005), USA
Styrene (100-42-5)	-	850 (1 year)	Health Canada (2018)
Tetrachloroethylene (127-18-4)	-	40 (1 day)	Health Canada (2018)
Toluene (108-88-3)	15000 (8h)	2300 (1 day average)	Health Canada (2018)
Trichloroethylene (71-01-06)	No recommended level exposure		World Health Organisation (2010)
Xylenes-mixture (1330-20-7)	-	100 (1 year)	Health Canada (2018)

3. RESULTS AND DISCUSSION

Table 4 shows the concentration particle number measured with the CPC and the EEPS. An increase of nanoparticles levels was observed during printing for the different tests; this increase was more acute with ABS filament printing at 230ºC.

On the 7th of February, while printing ABS filament, an average concentration of 6,276 particles/cm^3 was observed, with the concentration rising from 3,684 particles/cm^3 to 8,000 particles/cm^3 in 1.5 hours (Figure 3A and Figure 3B).

Table 4. Nanoparticles emitted during 3D printing

Material	Date	Printing Temperature	CPC (part/cm³)	EEPS (part/cm³)
PLA	20/02/2019	190ºC	3,780	3,000
PLA	24/07/2019	190ºC	3,531	3,450
ABS-PLA	11/02/2019	190ºC	20,000 to 3,400	14,000
ABS	07/02/2019	230ºC	6,276	6,400
ABS	21/02/2019	230ºC	15,521	14,000
ABS	08/02/2019	230ºC	40,239	72.791
ABS	25/07/2019	230ºC	8,723	10,000

Typical submicron particle size distributions are shown in Figure 3C, with the majority of the particles emitted during printing being less than 100 nanometers with a number peak of about 15 nm.

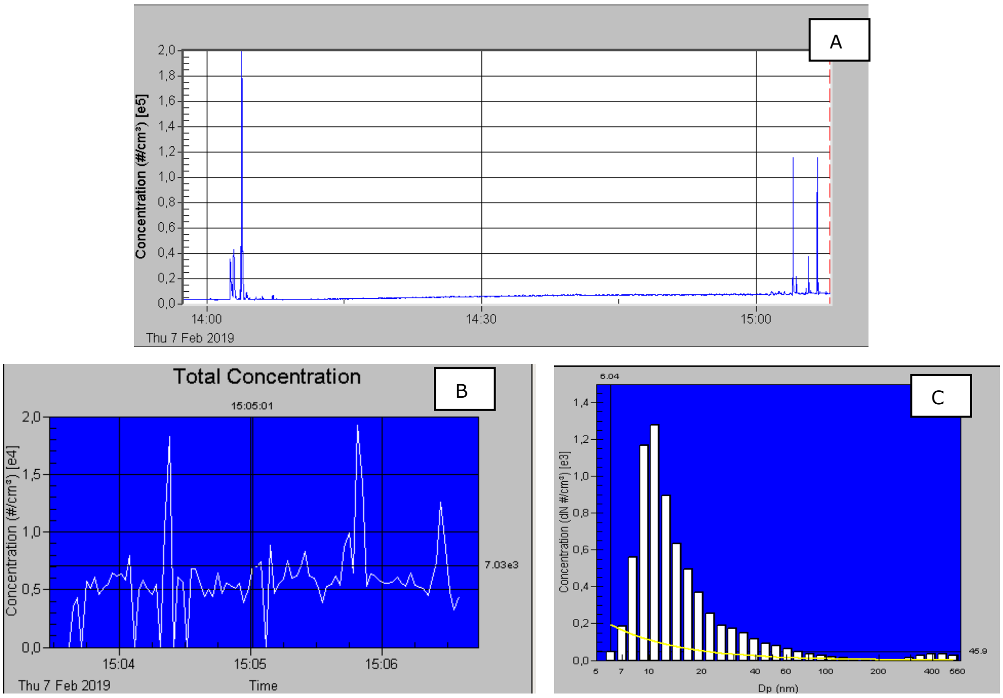


Figure 3. Nanoparticles during ABS printing. A (CPC concentration), B (EEPS concentration), C (EEPS size distribution)

On the 20th of February, during printing PLA filament, an average concentration of 3.780 particles/cm^3 was observed, Figure 4A and Figure 4B. The concentration remained steady during printing. Typical submicron particle size distributions are shown in Figure 4C. Most of the particles emitted during printing were less than 200 nanometers with a number peak around 80 nm.

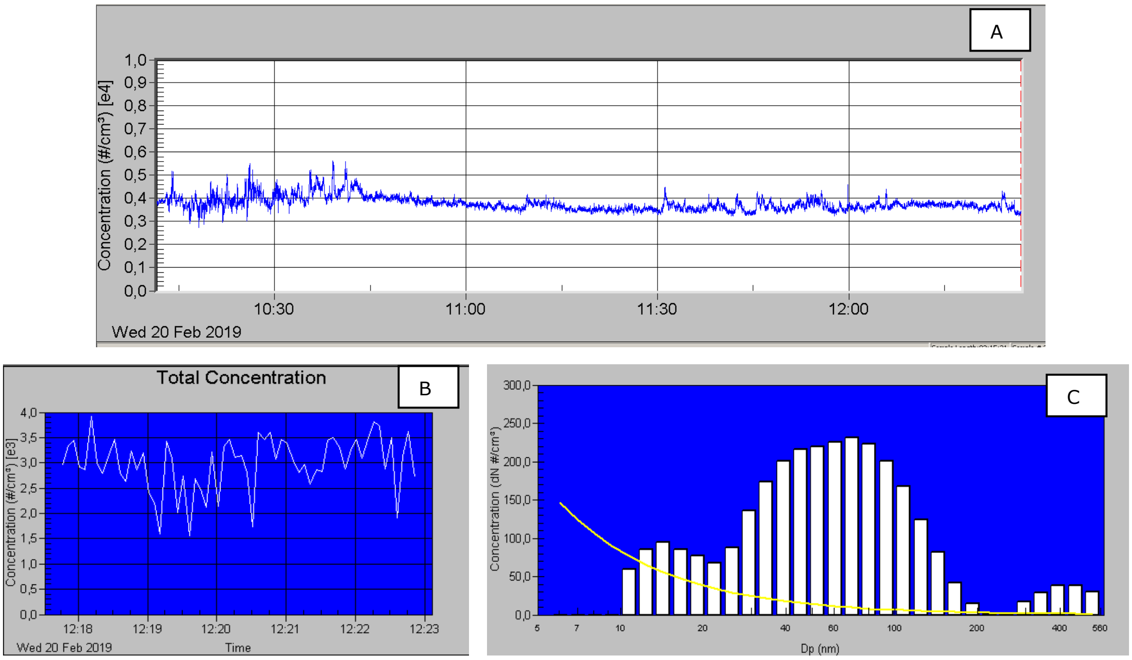


Figure 4. Nanoparticles during PLA printing. A (CPC concentration), B (EEPS concentration), C (EEPS size distribution)

On the 8th of February, during printing ABS filament, an average concentration of 40,239 particles/cm^3 was observed with the CPC (the average in the last hour was 50.276 nanoparticles/cm^3), Figure 5A, and 72,791 with the EEPS, Figure 5B, typical submicron particle size distributions are shown in Figure 5C. Most of the particles emitted during printing were less than 60 nanometers with a number peak around 15 nm. The high concentration of nanoparticles less than 10 nanometers can explain the difference between CPC and EEPS readings.

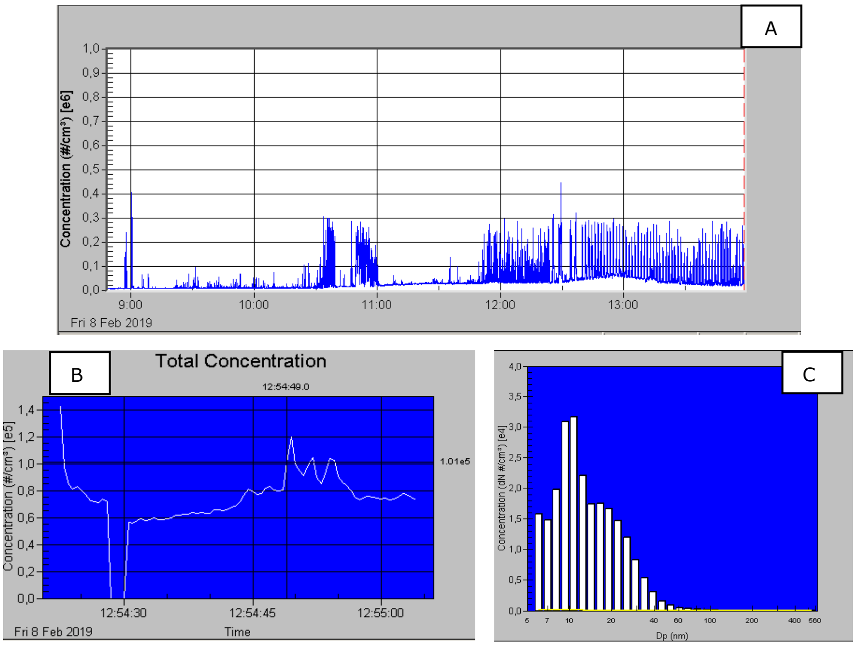


Figure 5. Nanoparticles during ABS printing. A (CPC concentration), B (EEPS concentration), C (EEPS size distribution)

On the 11th of February, when printing PLA filament, the concentration fell from 20,000 to 3,400 particles/cm^3 (Figure 6), indicating that the extruder had been contaminated with ABS filament from previous printing.

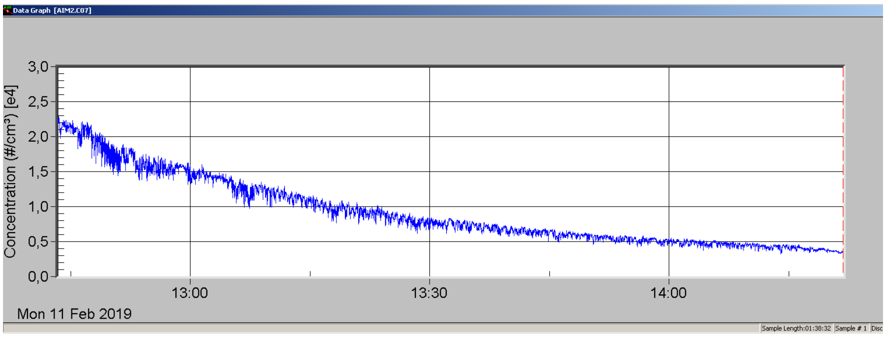


Figure 6. Nanoparticles during PLA printing (Contaminated with ABS). A (CPC concentration), B (EEPS concentration), C (EEPS size distribution

On the 21st of February, during printing ABS filament, an average concentration of 15,521 particles/cm^3 was observed with the CPC (Figure 7A), and 7,250 particles/cm^3 with the EEPS (Figure 7B) typical submicron particle size distributions are shown in Figure 7C. Most of the particles emitted during printing were less than 200 nanometers with a number peak around 15 nm.

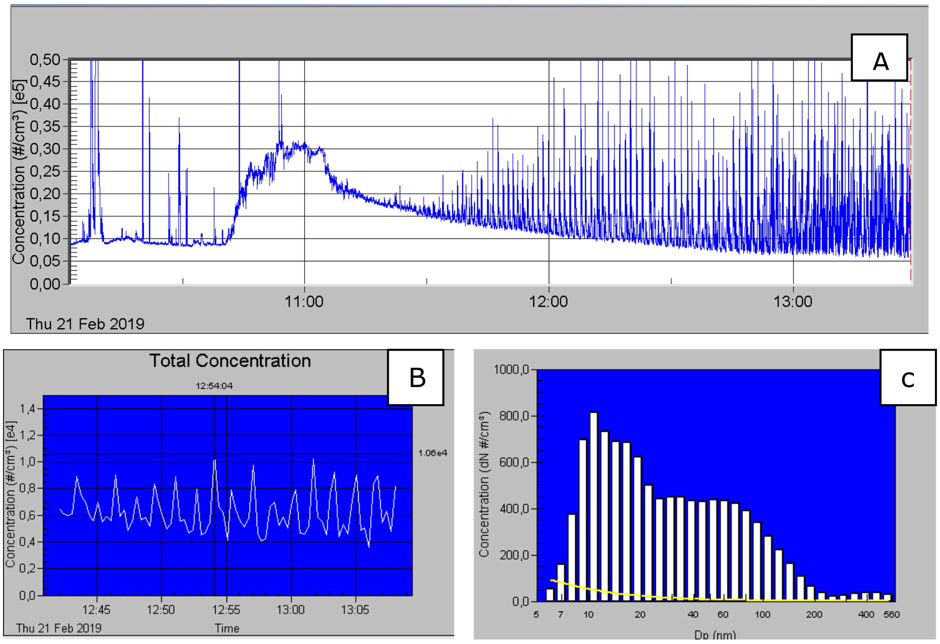


Figure 7. Nanoparticles during ABS printing (CPC concentration)

On the 24th of July during printing PLA filament, an average concentration of 3,531 particles/cm^3 was observed, the concentration remained steady during printing (Figure 8A and Figure 8B). Typical submicron particle size distributions are shown in Figure 8C. Most of the particles emitted during printing were less than 200 nanometers with a number peak around 80 nm.

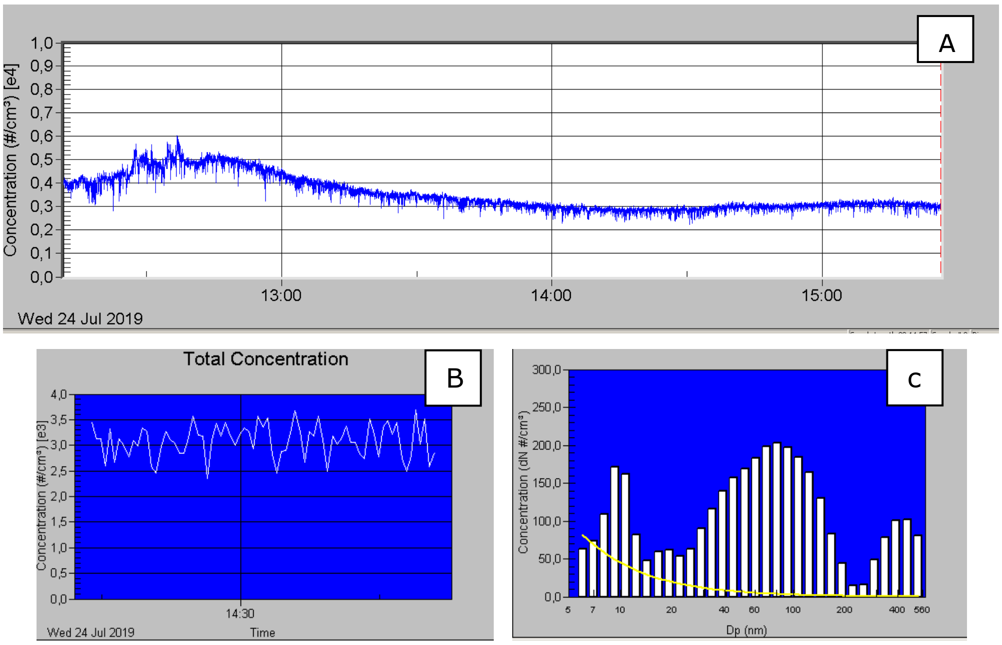


Figure 8. Nanoparticles during PLA printing. A (CPC concentration), B (EEPS concentration), C (EEPS size distribution)

On the 25th of July, during printing ABS filament, an average concentration of 8,723 particles/cm^3 was observed with the CPC (Figure 9A), and 10,000 with the EEPS (Figure 9B). Typical submicron particle size distributions are shown in Figure 9C. Most of the particles emitted during printing were less than 200 nanometers, with a peak around 15 nm. The high concentration of nanoparticles less than 15 nanometers can explain the difference between CPC and EEPS readings.

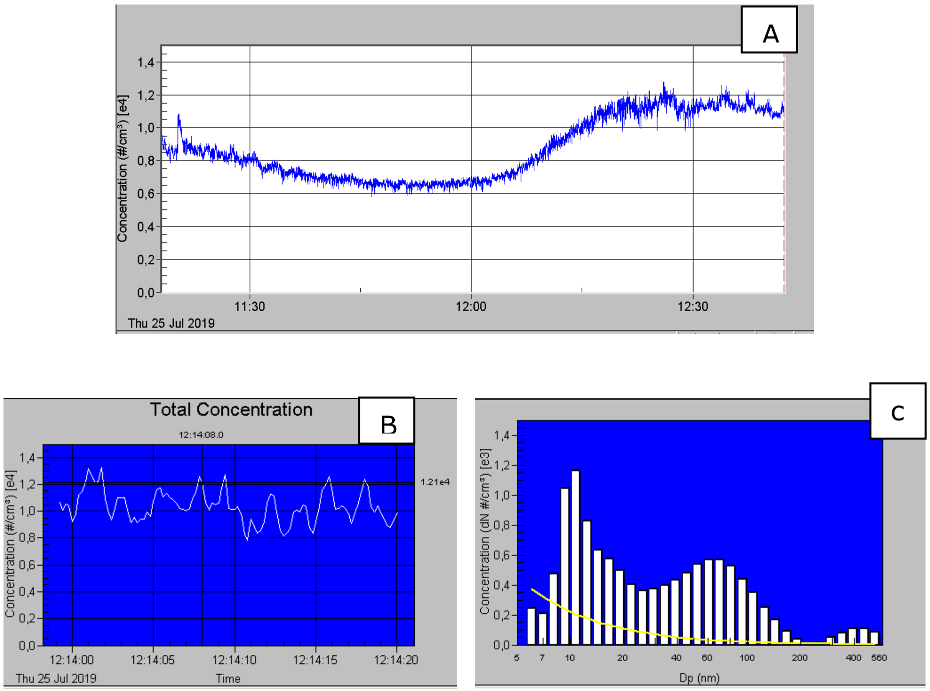


Figure 9. Nanoparticles during ABS printing. A (CPC concentration), B (EEPS concentration), C (EEPS size distribution)

The mass concentration levels measured with the side-pak AM510 were all less than 0.2 mg/m^3 (the threshold limit value (TLV) for respirable dust is 3 mg/m^3); there are no Health & Safety concerns in 3D printing if only this parameter is considered.

Table 5 shows the VOCs concentrations for PLA and ABS during printing.

Considering the Total Volatile Organic Compounds (TVOC), all the measurements were under the 200 µg/m^3 TVOC recommendations for indoor air quality.

Nevertheless, all the printing tests were carried out during shorts periods (2 to 5 hours) and a 3D machine in an actual situation can be printing for days. If the VOCs are analysed individually, an increase in those levels is observed in ABS printing. The benzene levels (with no safe levels for exposure) were an average of 0.8 µg/m^3 for PLA filament and 1.53 µg/m^3 for ABS.

An increase of other VOCs was observed: d-limonene, styrene, toluene, tetrachloroethylene, n-Hexadecane and naphthalene among others.

Regarding the nanoparticles levels during 3D printing, dangerous levels were observed when printing ABS filament at 230ºC. In some cases more than 40,000 nanoparticles/cm^3, in only a few hours, when a printing process can take several days.

It is highly recommended that engineering controls be undertaken (extraction system, good ventilation) before printing. The nanoparticles levels during PLA filament printing at 190ºC were lower than ABS, but it is also recommended that engineering controls be undertaken because the printing process can take several days, and the pollutants may concentrate during printing.

While analysing the typical submicron particle size distributions from PLA (Figure 4C, Figure 8C) and ABS (Figure 3C, Figure 5C, Figure 7C, Figure 9C), it was observed that ABS filaments at 230ºC emitted more and smaller particles than PLA at 190ºC.

The ABS particle size distribution has peaks around 15 nanometers and the ABS filament at around 80 nanometers.

Table 5. VOCs emission rates (μg/m^3) during 3D printing with different filaments

	Substance/material	PLA	PLA	PLA	PLA	ABS	ABS	ABS*
1	Hexane	< 0.49	< 0.53	< 0.42	< 0.44	1.25	0.59	< 0.50
2	2.4-Dimethylpentane	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
3	Isooctane	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
4	n-Heptane	0.58	0.57	< 0.42	< 0.44	0.61	< 0.47	< 0.50
5	n-Octane	< 0.49	< 0.53	< 0.42	< 0.44	0.67	< 0.47	< 0.50
6	Carbon tetrachloride	0.84	1.01	0.69	0.92	0.97	0.95	0.86
7	1.1.1-Trichloroethane	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
8	n-Nonane	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
9	Ethyl acetate	< 0.49	< 0.53	< 0.42	< 0.44	0.81	< 0.47	< 0.50
10	2-Butanone	0.92	< 0.53	< 0.42	< 0.44	0.75	< 0.47	< 0.50
11	Benzene	0.82	0.85	0.68	0.85	1.78	1.28	1.18
12	n-Dean	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
13	Trichlorethylene	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
14	4-methyl-2-pentanone	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	0.54	< 0.50
15	α-Pinene	0.78	0.76	0.7	0.6	< 0.52	0.69	0.68
16	Tetracloroethylene	0.85	0.87	0.82	0.81	0.81	0.69	0.75
17	Cloroform	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
18	Toluene	2.02	2.12	2.28	2.24	5.24	3.98	4.08
19	1.2-dicloropropane	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
20	1.2-Dicloroethane	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
21	N-butyl acetate	1.01	1.04	0.93	0.95	1.19	1.06	1.13
22	n-Undecano	0.88	0.94	0.77	0.81	0.86	0.92	0.95
23	b-Pinene	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
24	Ethylbenzene	1.13	1.08	1.37	1.31	1.66	1.47	1.42
25	p-Xilene	1.11	1.13	1.32	1.29	1.58	1.43	1.4
26	m-Xilene	3.15	3.06	3.78	3.84	4.35	3.93	3.71
27	n-Butanol	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
28	Bromodichloromethane	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
29	n-Dodecane	1.19	1.28	1.08	1.09	1.2	1.22	1.29
30	o-Xilene	1.58	1.57	1.8	1.78	2.13	1.92	1.85
31	d-Limonene	1.08	1.05	1.07	0.95	1.03	1.24	1.13
32	Propilbenzene	0.83	0.89	0.75	0.76	0.94	0.82	0.87
33	2-Ethiltoluene	0.66	0.7	0.63	0.63	0.79	0.68	0.73
34	3-Ethiltolueno	0.85	0.8	0.93	0.91	1.14	1	0.99
35	1.3.5-Trimethylbenzene	0.76	0.8	0.71	0.7	0.88	0.8	0.82
36	Styrene	0.87	0.83	0.79	0.69	1.23	1.21	1.19
37	4-Ethyltoluene	0.64	0.68	0.59	0.6	0.74	0.66	0.68
38	n-Tridecane	1.41	1.56	1.25	1.28	1.5	1.39	1.49
39	1.2.4-Trimethylbenzene	1.06	1.05	1.09	1.07	1.34	1.23	1.23
40	Dibromochloromethane	< 0.49	< 0.53	< 0.42	< 0.44	0.65	< 0.47	< 0.50
41	1.2.3-Trimetilbenceno	0.57	0.59	0.51	0.52	0.66	0.57	0.6
42	n-Tetradecane	1.61	1.71	1.4	1.42	1.62	1.53	1.67
43	Nonanal	2.12	1.66	< 0.42	1.41	1.58	2.04	2.16
44	1.2.4.5-Tetramethylbenzene	0.68	0.72	0.57	0.59	0.7	0.63	0.67
45	1.4-Dichlorobenzene	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
46	n-Pentadecane	1.75	1.87	1.51	1.53	1.8	1.66	1.8
47	Decanal	< 0.49	< 0.53	< 0.42	< 0.44	< 0.52	< 0.47	< 0.50
48	n-Hexadecane	2	2.1	1.74	1.7	1.97	1.84	2.1
49	Naphthalene	0.83	0.85	0.73	0.72	0.8	0.84	0.89

*5 meters away from the 3D printer

4. CONCLUSIONS

3D printing has become more and more common in people's daily lives. Many affordable models for home use can produce high-quality work. However, it is important to remember the contaminants released during printing and the potential health effects.

During the 3D printer operation, high particles levels were emitted; most of these emissions are lower than the respirable fraction (PM_4) and potentially could reach the lungs.

- Nanoparticle emission rates were higher for ABS at 230ºC than PLA at 190ºC. During the test, recommend exposure levels were exceeded after only a few hours of printing when printing can take days of work.
- The nanoparticle sizes emitted for the ABS filament at 230ºC were smaller than the particles emitted for the PLA filament at 190ºC.

- Hazardous chemicals such as d-limonene, styrene, toluene, tetrachloroethylene, n-hexadecane and naphthalene were released during printing. It is unclear if these chemicals are potent enough to cause harm when inhaled.
- Benzene levels were found during printing; as with any carcinogen substance, it is recommended to reduce the exposure limit to the minimum possible; it is highly recommended that engineering controls are taken during 3D printing.
- When possible, it is recommended that materials are printed at the minimum temperature possible, and engineering controls are used for reducing the pollutants' exposition.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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