Evaluation of an innovative filtration system for Particulate Matter (PM) and Volatile Organic Compounds (VOCs) emitted by Desktop 3D printers

R. Sarda Estève[(a)*], N. Roux[(b)], A. Franz[(b)], D. Baisnée[(a)] and F. Truong[(a)]

(a) Commissariat à l'Energie Atomique CEA/DRF/LSCE, 1 route de l'Orme, 91190, Saint Aubin, France
(b) Zimple, 17 rue Rodier, 75009 Paris, France, www.zimple3d.com

* Corresponding author. Tel: +33(0)169089747 ; fax:+33(0)169088546
E-mail address: sarda@lsce.ipsl.fr

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Preliminary results

The study presented here is under refinements to be submitted in Atmospheric Environment in 2017.

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ABSTRACT

An increasing interest in desktop 3D printers for prototyping, tooling or building commercial objects has been observed during the last past years. These printers are now commercially available, and they are intensively used in closed offices or rooms. Recently numerous studies have shown that commercially available desktop three-dimensional printers with single or multiple filaments are Particulate Matter (PM) and Volatile Organic Compounds (VOCs) big emitters. The particles emitted are often in the ultrafine mode below 2.5 µm (PM2.5) or ultrafine mode below 1 µm (PM1). The gases emitted have molecular masses up to 180 $g.mol^{-1}$. This complex mixture which is produced during the heating phase and the printing process is particularly toxic and is thermoplastic dependent. During the extrusion and the deposition process of Acrylonitrile Butadiene Styrene (ABS), the average particles concentration found for the 3D printer tested was 373 539 $nb\#.cm^{-3}$ and 78 part per billion (ppb) for the identified gases. The average aerodynamic particle size diameter (AD) has been found to be in the Ultrafine Particle range (HFP, <100 nm). To reduce the health impact and the indoor production of PM and VOCs of these printers, a compact and low-cost filtration device has been developed. This filter combines a total filter coupled with a charcoal membrane. The results obtained have shown that the device removes 99% of the ultrafine particles and more than 90% of the gases. This study suggests that a cleaning process must be implemented in each 3D printer to reduce the health impact of the end user.

1. INTRODUCTION

The appearance of printing devices which includes photocopiers, laser and inkjet printers started in the early 1960s. The introduction of the low-cost material in 1984 set off a revolution in the use of printers for professional and personal activities. Then the printing technologies have continued to evolve until the emergence of 3D printers around 2009 allowing the creation of physical objects [1].

The health impact resulting from the use of printers and photocopiers has been studied for some forty years [2]. Today, the known risks associated with the use of photocopiers and printers are due to Ozone (O3), Volatile Organic Compounds (VOCs) and particulate matter (PM) emissions [3] [4]. Photocopiers are now equipped with ozone filters, which reduces the risks [5]. Nowadays, the few studies on particles and gases emissions from 3D printers show that this type of devices also generates PM (<1 µm) containing an enormous amount of Ultrafine Particles (UFP<150 nm) and VOCs during the different printing processes. Both gases and particles that are emitted have toxic effects [6] [7] [8].

The majority of 3D printers use a manufacturing technique by deposition of molten polymer (MPD), also called fused filament fabrication (FFF): 3D models are printed by fusion of a polymer filament. The thermoplastics commonly used are Acrylonitrile Butadiene Styrene (ABS) or PolyLactic Acid (PLA) as feedstock. The emissions of gases and particles depend on the type of filament used, the heating temperature and the model of the printer. Both PLA and ABS are considered as active emitters [9]. To limit the health impact of using this type of printer in a closed environment, the Zimple Company has developed a universal device: Zimpure (Paris, France) that traps all particles and gases during the printing phases regardless of the type of printing and the brand of the 3D printer used. The emission rates of a 3D printer and the efficiency of Zimpure which can be implemented directly next to the heated nozzle have been investigated in this study.

2. METHODS

The Zimpure filter has been tested in February 2017 at the Commissariat à l'Energie Atomique, France. As shown in Figure 1, the 3D printer was placed into an aluminium enclosure of 0.243m3 (L75cm, l55cm, h59cm). The enclosure was perforated by three holes to run the tubing from the measuring instruments to the printer. The diameter of the holes was corresponding with the diameter of the tubes. In this way, data were collected directly and simultaneously inside the enclosure. The printer and Zimpure were plugged out of the enclosure, and the cable feed runs through another hole. The printer was preliminarily connected with an SD card containing the file of the 3D object. A cube of 32 cm^3 was printed in order to have the same flow during all the printing process. Before the experiment, the enclosure has been flushed with filtered air. Then, a constant air flow of 16L/min was provided to the chamber in order to simulate an aeration system. The print lasted two hours, with 5 minutes warm-up time. Lastly, the object printed weighted 22g, including the raft.

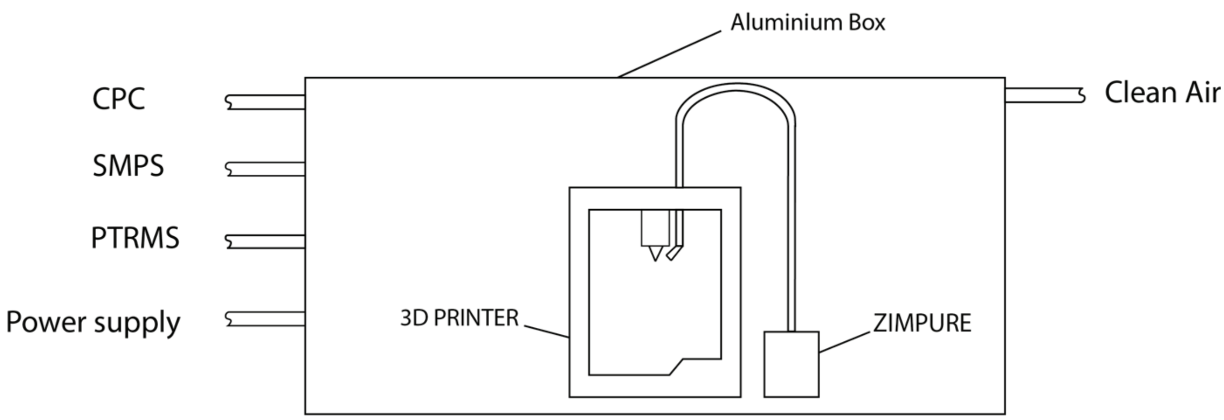

Figure 1. Design of the experiment

The aspiration rate has also been tested by measuring the emissions of the 3D printer while printing outside the aluminium enclosure, with the ultrafine particles counter and mass spectrometer placed above it.

2.1 INSTRUMENTATION DESCRIPTION

The experiment was performed on a Zortrax M200, using grey ABS filament [10]. The extruder temperature used while printing ABS was 230°C. The heated bed temperature was 110°C. To characterize the PM and the gas phase, a set of instruments has been used during all the experiments.

- **CPC 3022 (TSI)** [11], measuring UFPs from 7nm to 300nm. It was necessary in order to know precisely the emission rate of the particles released by the 3D printer. The CPC Counter was connected to a computer, and the data points collection period was 20 seconds.
- **FIDAS (PALAS)** [12], a real time dust monitor measuring particles from 250nm to 10µm. It enabled a vision of the emission of bigger particles than the one measured by the CPC.
- **U-SMPS 1050 X / 1100 X / 1200 X** [13] calibrated to measure particles from 4nm to 700nm. This instrument provides a precise distribution of the sizes of the particles released by the 3D printer.
- **PTRMS** [14] (Proton Transfer Mass Spectrometer) measuring Volatile Organic Compounds (Gases).

2.2 PARTICLES AND GASES MEASUREMENT

Measurement preparation

All these experiments were done in the aluminium enclosure, in order to have a closed system where ambient air and environment do not interfere with the measurement. Before each measurement, the aluminium enclosure was cleaned with filtered air to remove particles from the previous experience. Then, the printing process was launched, and the aluminium enclosure closed.

Particles measurement

Particle sizes were scanned using the SMPS and the real time dust monitor. The SMPS provided results for particles with a diameter between 3 and 700 nanometers. Bigger particles, from 250 nm to 10µm, were scanned as well, using the real time dust monitor. This experiment revealed that the particles released by the 3D printer are in the ultrafine mode, below 100nm diameter. In the light of this information, the next experiments were performed focused on the 3-150 nanometers range in order to be more accurate.

VOC measurement

With the mass spectrometer, every atomic mass was scanned in order to visualize the peaks of emissions. Two peaks were very much in evidence: the atomic mass 105 (protonated, which represents 104+1), and the atomic mass 107 (protonated too, 106+1). These peaks respectively correspond to Styrene and Ethylbenzene, known to be respectively carcinogenic and toxic [15] [16].

Aspiration measurement

As described above, all these experiments were conducted in a closed enclosure. Even if Zimpure is efficient in a closed chamber, it has been though for open printing configurations by aspirating the particles directly near the extruder nozzle, where they are released. That's why the aspiration rate was also tested by placing the CPC and the mass spectrometer probe directly above the printer. In this way, it was possible to test to what extent Zimpure aspirates the nanoparticles and gases released.

3. RESULTS

3.1 UFP CONCENTRATION EMISSIONS

Particles released size

The number of particles function of their sizes can be seen in Figure 2. Data were acquired by the SMPS. The repartition is a Gaussian curve centered on 17nm: This is the particles size the most released (6000p/cm^3). The particles released are sized between 6nm and 100nm. They are ultrafine particles, also called nanoparticles. The thermoplastic fusion does not release particles bigger than 100nm. After turning on Zimpure (Figure 3) almost no particles remain:

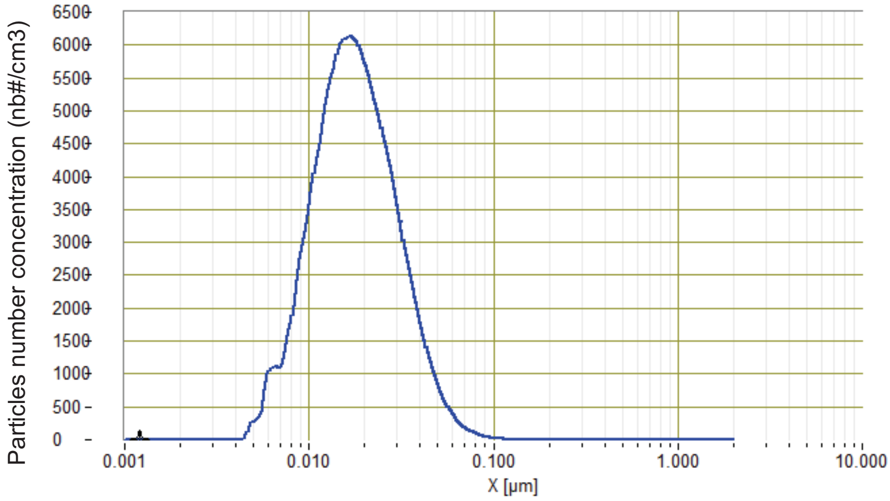

Figure 2. Particles size distribution without Zimpure

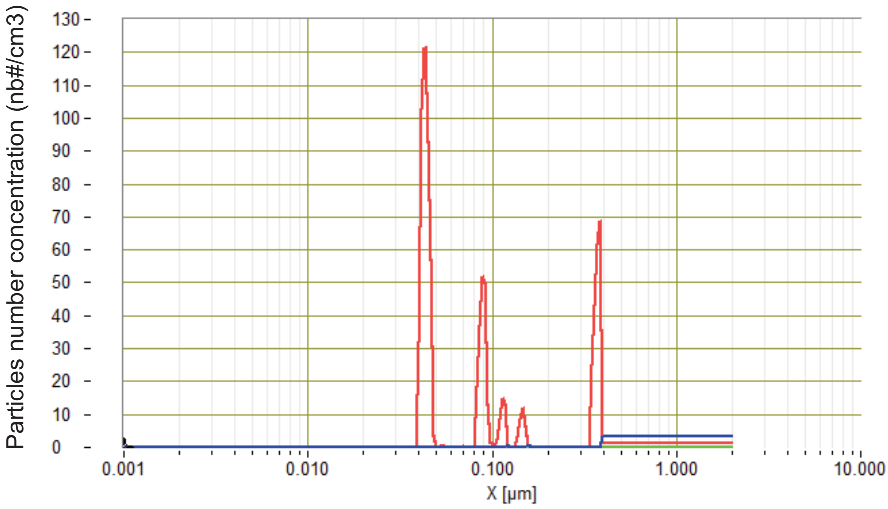

Figure 3. Particles size distribution with Zimpure

Ultrafine particles concentration emissions

In Figure 4, acquired by the CPC counter, the particles concentration during a print in the closed enclosure is observed. The print was launched at 13:43, when the air contained in the aluminium enclosure was Clean Air Blank (1). The printer started to warm up, so it released a few particles. The first peak corresponds with the printing of the raft (2). This peak is due to the high plastic flow used during this process. Then, during the printing phase, the concentration stabilized around 373 539 particles/cm^3. (3)

Zimpure was turned on at 14:54. As shown in Figure 4, the concentration drastically decreased from this point to reach around 170 p/cm3 (4).

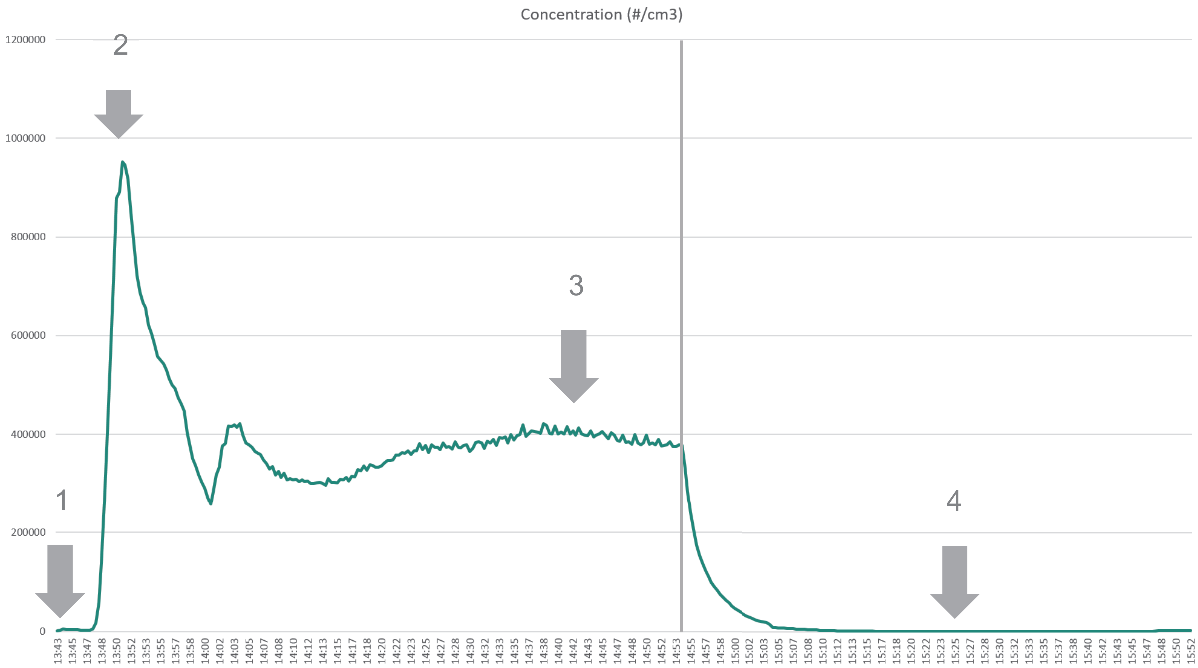

Figure 4. UFP concentration (nb#/cm3) in the aluminium enclosure acquired by the CPC

- Average UFP Concentration while printing without Zimpure: 373 539 (#/cm^3) *(Period: 13:43 to 14:54).*
- Average UFP Concentration while printing with Zimpure after stabilization 170 (#/cm^3) *(Period: 15:16 to 15:47).* Efficiency: 99.9%

3.2 VOCs EMISSIONS

To characterize the emission of the VOCs emitted during the printing phase, a Compact PTRMS (C22, Ionicon Analytik Innsbruck, Austria) has been used. The PTRMS has been calibrated with a Restek 110 (Hydrocarbons Mixture, Restek, France). A full scan from m/z 21 to m/z 250 experiments shows that two protonated compounds (M/z+1) were explicitly emitted: m/z 105 (styrene) m/z 107 (Ethylbenzene). Figure 5 shows the fine variability in ppb of m/z 59 (Acetone) and m/z 101 (Hexanone), two ketones often used as solvent in the industrial chemistry, and of m/z 105 (Styrene) and m/z 107 (Ethylbenzene), the two major toxic and even carcinogenic compounds found during the full scan procedure. The concentration of these compounds was monitored continuously during the cleaning and warming up phases with free

VOCs (1 and 1’), the printing process (2) and the filtration procedure (3). A continuous flow of clean air of 16 liters per minute (LPM) was introduced to the enclosure to ensure a correct ventilation. The mean concentration of Acetone and Hexanone in the air laboratory were respectively 50 ppb and 10 ppb. The calculated residence time in the enclosure was 16 minutes, and no external contamination has been observed regarding the levels of the two ketones during the experiment. The mean concentration during phases (1 and 1’) was below 10 ppb for all the species. During the extrusion process, an increase of m/z 105 and 107 up to 78 ppb and 45 ppb respectively was observed (2). During the phase (3) the concentration of m/z 105 and m/z 107 returned to very low concentration in 45 minutes.

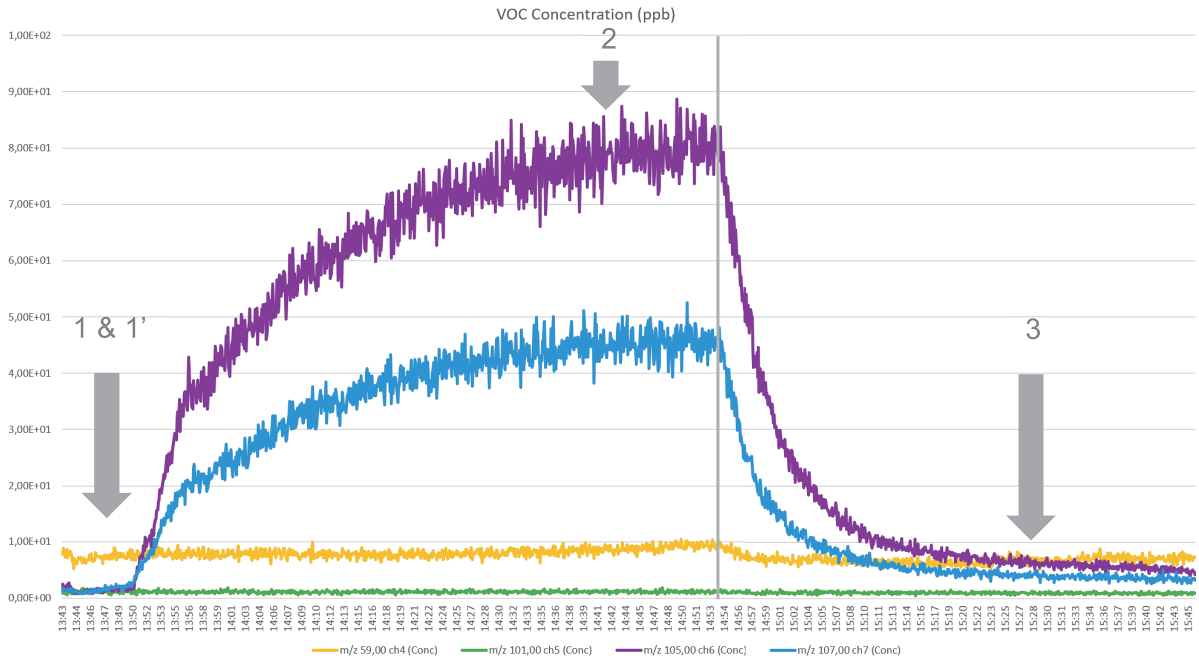

Figure 5. VOC concentration in the aluminium enclosure acquired by the mass spectrometer

- Average VOC Concentration while printing without Zimpure: *(Period: 14:30 to 14:54)*
  - Styrene: 78 (ppb)
  - Ethylbenzene: 45 (ppb)
- Average VOC Concentration while printing with Zimpure after stabilization *(Period: 15:50 to 15:52)*
  - Styrene: 1.38 (ppb) Efficiency: 98.2%
  - Ethylbenzene 0,79 (ppb) Efficiency: 98.2%

3.3 ASPIRATION RATE

UFP Aspiration rate

To know if the aspiration technique was efficient, the CPC and PTRMS probe were placed directly above the printer, while the 3D printer was printing. The experiment started in ambient air (1). After the printing of the raft (2), the measurement ran for 30 minutes without Zimpure (3). Then Zimpure was turned on and the measurement ran for another 30 minutes (4). We observed that Zimpure aspirates more than 99% of the nanoparticles released by the 3D printer.

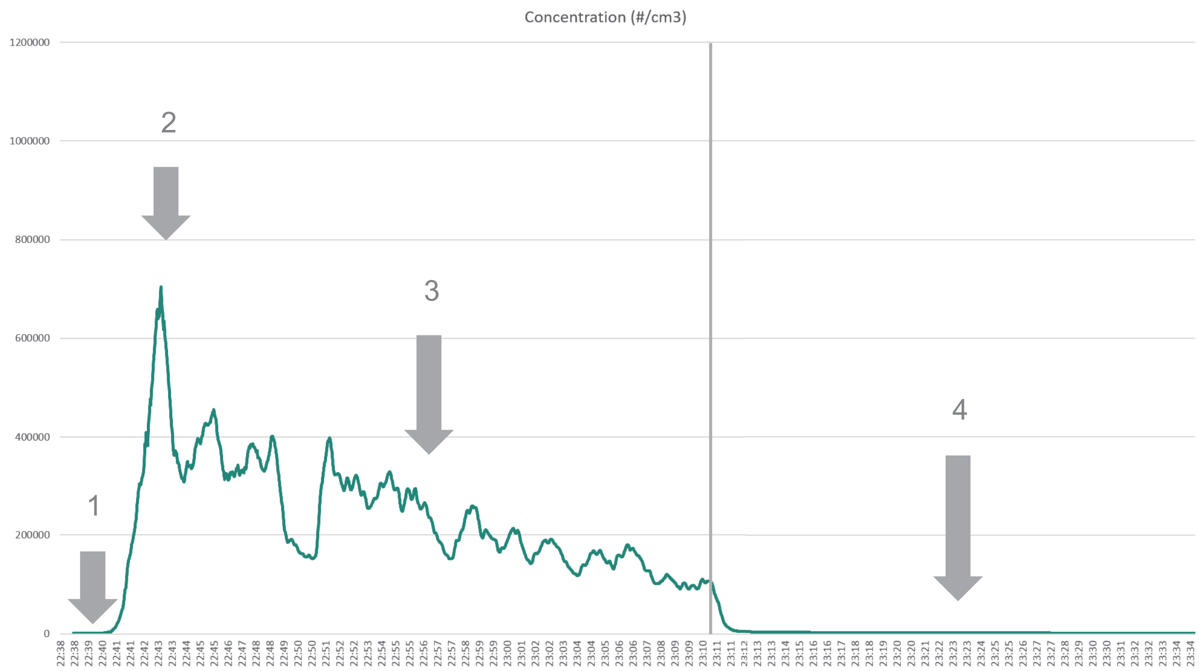

Figure 6. UFP Concentration measured directly above the printer outside the aluminium enclosure

- Average UFP Concentration while printing without Zimpure: 246 639 (#/cm3) *(Period 22:41 to 23:10)*
- Average UFP Concentration while printing with Zimpure after stabilization: 2 289 (#/cm3) *(Period 23:12 to 23:34)* Efficiency: 99,07%

VOC Aspiration rate

The Volatile Organic Compounds (VOC) concentration, acquired by the mass spectrometer, can be seen in Figure 7. The experiment started in ambient air (1). No VOCs were released during the warming up process (1'). The measurement ran for 30 minutes without Zimpure (2). Then Zimpure was turned on and the measurement ran for another 30 minutes (3). We observed that Zimpure aspirates more than 90% of the VOC released by the 3D printer.

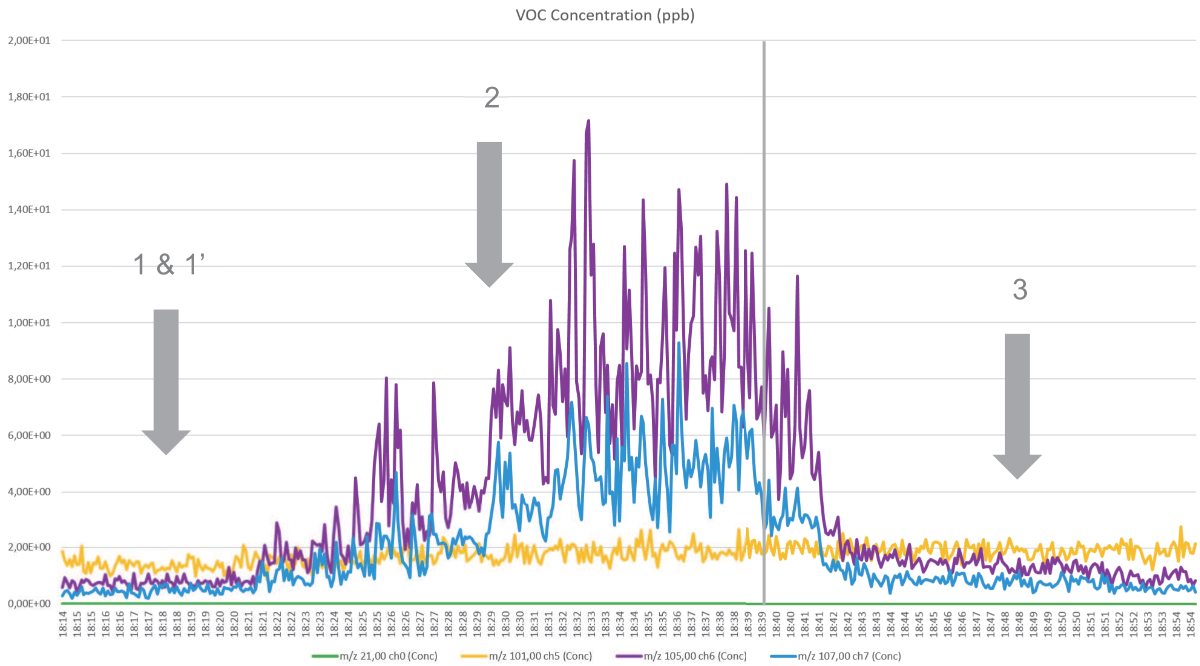

Figure 7. VOC Concentration measured directly above the printer outside the aluminium enclosure

- Average VOC Concentration while printing without Zimpure *(Period: 18:32 to 18:39)*
  - Styrene: 9.51 (ppb)
  - Ethylbenzene: 7.97 (ppb)

- Average VOC Concentration while printing with Zimpure after stabilization *(Period: 18:45 to 18:54)*
  - Styrene: 0.936 (ppb) <u>Efficiency: 90.15%</u>
  - Ethylbenzene: 0.402 (ppb) <u>Efficiency: 94.96%</u>

3.4 LIFETIME OF THE FILTER

Ultrafine particles concentration emissions (after 500h)

We repeated all these experiments with a filter which has been used for 500h. The results show that the filter is still filtering 99.7% of the particles and around 98% of the gases after this lifetime. In Figure 8, acquired by the CPC counter, the particles concentration during a print in the closed enclosure is observed. The print was launched at 15:56, when the air contained inside the enclosure was turned into Clean Air Blank (1). After the printing of the raft (2), the normal printing process started and the concentration stabilized around 65 696 particles/cm^3 (3)

Zimpure was turned on at 16:45. As shown in Figure 8, the concentration drastically decreased from this point to reach around 167 p/cm3 (4).

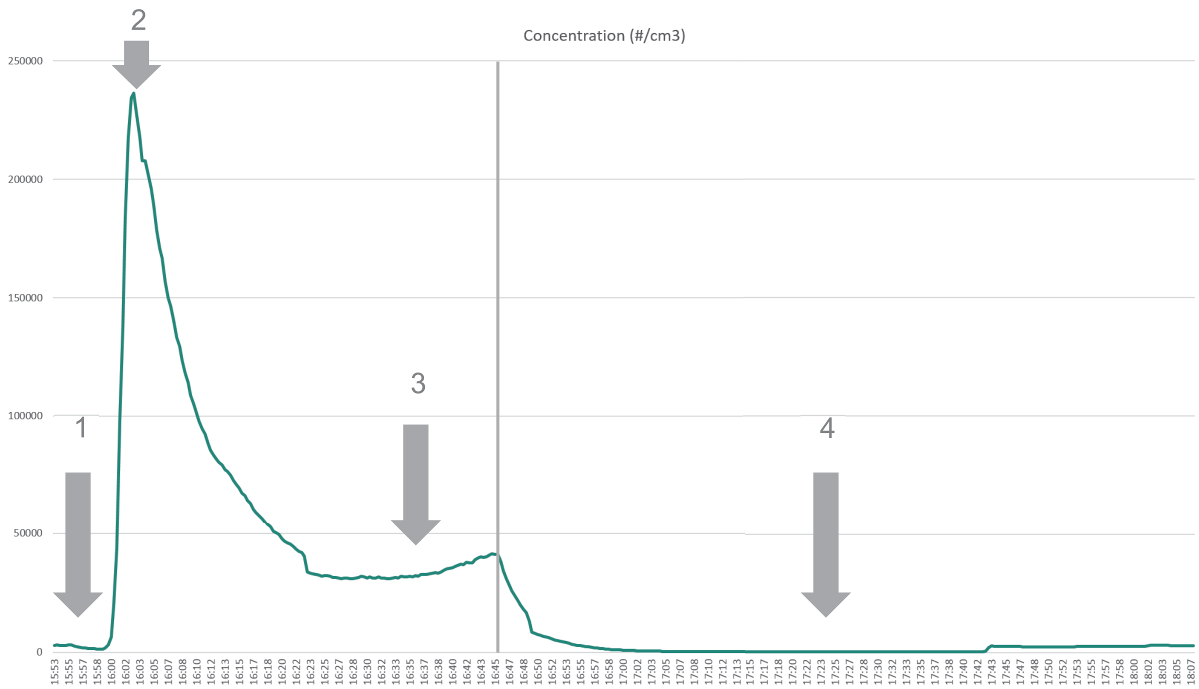

Figure 8. UFP concentration in the aluminium enclosure acquired by the CPC

- Average UFP Concentration while printing without Zimpure (500h): 65 696 (#/cm3) *(Period: 16:00 to 16:49).*
- Average UFP Concentration while printing with Zimpure (500h) after stabilization 167 (#/cm3) *(Period*: *17:14 to 17:42).* Efficiency: 99.7%

VOC concentration emissions (after 500h)

The Volatile Organic Compounds (VOC) concentration during a print in the closed enclosure, acquired by the mass spectrometer, can be seen in Figure 9. The print was launched at 15:56. After the cleaning and warming up phases (1 and 1'), an increase of m/z 105 and 107 up to 82 ppb and 47 ppb respectively is observed (2).

Zimpure was turned on at 16:45. As you can see on the curve, the concentration drastically decreased from this point to return almost to the concentration observed before the printing process (3).

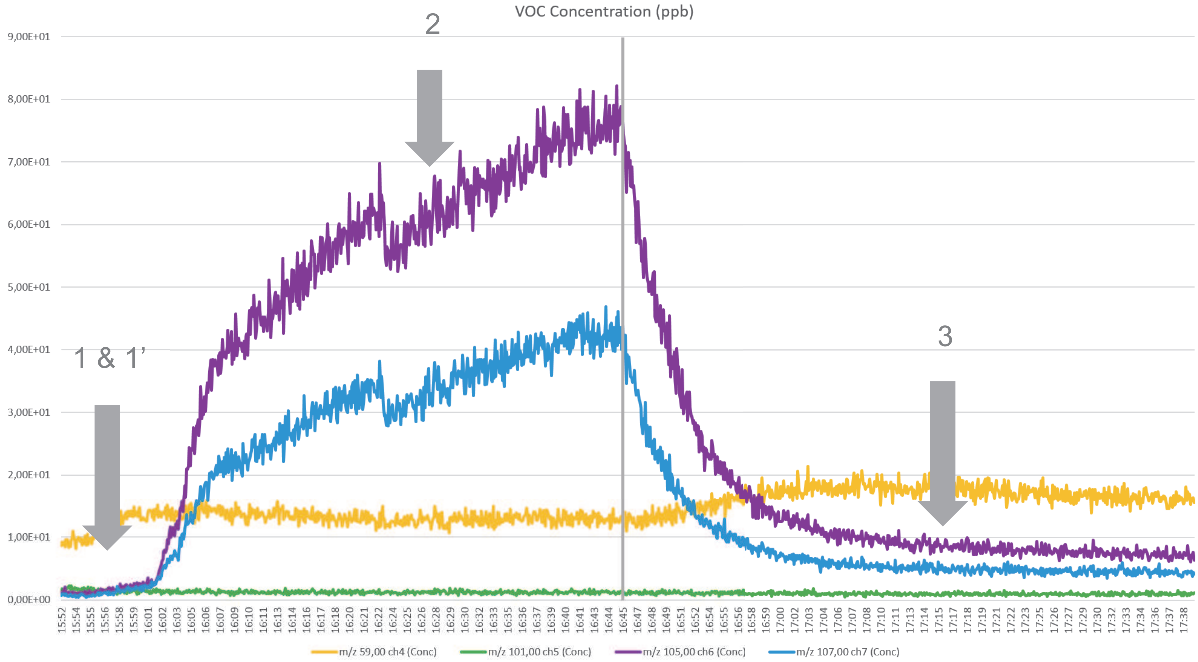

Figure 9. VOC concentration in the aluminium enclosure acquired by the mass spectrometer

- Average VOC Concentration while printing without Zimpure *(Period: 14:30 to 14:54)*
  - Styrene: 40 ppb.
  - Ethylbenzene: 21 ppb.
- Average UFP Concentration while printing with Zimpure (500h) after stabilization *(Period: 15:50 to 15:52)*
  - Styrene: 0.9 ppb. Efficiency: 97,8%
  - Ethylbenzene: 0.4 ppb. Efficiency: 98%

4. DISCUSSION

The particles and gases released by 3D printers have already been examined by researchers, and the results are unambiguous [7] [8] [9]. Because of their very small size (<0.1 microns), they do enter not only your bronchial tube or your lungs but also contaminate your blood. In this way, they potentially endanger all your organs. Styrene is “Reasonably anticipated to be a Human Carcinogen” [15]. It affects particularly liver, nervous system and vision. Ethylbenzene, one of the VOC highlighted in the results of this study, has an impact on the nervous system and is also harmful during periods when organs are developing [16]. Two complete studies about these chemical compounds produced by the Agency for Toxic Substances & Disease Registry are available [17] [18].

Contrary to what is usually thought, PLA is also a significant emitter. Actually, plastic filaments are never pure ABS or pure PLA. It's different from those used in plastic injection manufacturing for example. Many others toxic compounds can be found from one filament to another. Filaments are made up of a complex mixture of different polymers, in order to provide the best printing quality, layer adhesion, warping resistance, flexibility, and many other parameters. Like most plastics, PLA has the potential to be toxic if inhaled or absorbed into the skin or eyes as a vapor or liquid (i.e. during manufacturing processes).

Furthermore, there is a parallel with the beginning of the development of photocopiers or inkjet printers: manufacturers did not integrate filtering solution in their products. They were more focused on improving the technology or selling products than on consumers’ health. It had taken years before standards were created and respected. That is probably what is going to happen with 3D printing nowadays. In a few years filtering systems will be directly included in every 3D printer, but in the meantime, solutions have to be used. That’s what Zimpure proposes.

5. CONCLUSION

Considering this study and the numerous other studies published these last five years concerning FFF 3D printers and particles emissions, there are enough scientific contents to be aware of this issue. In the industry, standards and solutions are available for every process of material fusion, included thermoplastic fusion. That’s why it is possible to transpose it to personal 3D printers which are manufacturing boxes in the office, at home and even at school. Solutions exist, as you can see regarding the results of this study: Zimpure is a filtering system that can be implemented in each 3D printer, and its efficiency is now proved.

To conclude, 3D printing is a technology which is going to have more and more impact on our society. It has a positive contribution towards medical breakthrough and to the whole industry concerning tooling, prototyping and production. It is also an educative instrument. More and more schools decide to acquire 3D printers in order to develop innovative and stimulating projects with students. This issue has to be considered and treated seriously in order not to slow such a revolution. Zimpure is the first 3D printing filtering solution officially certified to solve this issue, and that could be compatible with all the 3D Printers.

6. ACKNOWLEDGMENTS

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