

CONSIDERATIONS CONSIDERING THE EVOLUTION OF GAS EMISSION TYPE FORMALDEHIDE AND VOLATILE ORGANIC COMPOUNDS IN THE DLP PRINTING PROCESS WITH ECOLOGICAL RESIN

Mircea Dorin Vasilescu¹,

¹ Polytechnic University Timisoara, Mechanical Faculty, Department MMUT, Sq. P. Victoriei, no. 2, mircea.vasilescu@upt.ro

ABSTRACT: In this paper, the author proposes an exploratory study in which it is possible to observe the evolution of formaldehyde emission in a printing process in which mask stereolithography (MSLA) is used. To conduct the experiment, individual sensors and a device are used to determine the two types of gas emission. These allow us to observe the evolution of emission in several points considered in relation to the integrated 3D printing system. From the experimental tests performed at the level of the space in which the printing process is performed, the change in formaldehyde and volatile organic compound is smaller during the printing process. It can also be seen that it is important to control and reduce the level of formaldehyde and then to control that which is generated for the volatile organic compound.

KEYWORDS: 3D printing, MSLA/DLP printing, sensors, Arduino, resin,

1. INTRODUCTION

In this study, the author intends to determine if there is gas emission and the evolution of them in the 3D printing space using mask stereolithography (MSLA). The role of this paper is exploratory and, at the same time, with the obtained data, it is possible to take into consideration that the digital light processing (DLP) process can be present in the laboratory in work with the students.

It is important to note that the study of emissions generated by the process of 3D printing with plant basis resin is less studied in scientific articles [1,2]. Most of the studies are oriented toward the analysis of the emissions generated by printing processes based on the thermoplastic process or/and the laser beam for particles. In 3D printing processes with thermoplastic material, some authors determinate the existence of emission of gases and/or particles at a different level. Both types of emitted physical elements can produce various changes in the proper functioning of the human respiratory system [3,4]. The minimum value of the standard emission parameter for total volatile organic compounds (TVOC) is $0.4 * 10^{-6}$ grams / m³ [5].

Some elements used in the printing process can affect the environment in which the printer or worker is positioned. Some studies of PLA-type material emission are carried out with commercial devices [6-8], and others are studied for ABS [7]. Different materials were comparatively analysed in relation to emission in other papers [9,10].

2. MATERIALS AND METHODS

2.1 Materials and printer

In this study, an eco-friendly resin with ecological properties of ANYCUBIC type is used [11]. This type of resin is in accordance with the printer taken into consideration by the author of this study. For generating the part body, an ANYCUBIC PHOTON printer is used [12]. The body of the parts is of gear type. It has three distinct areas. In the lower part of the printed structure, there is a compact surface generated by five layers with an exposure time of 60 seconds. The second part is that of the supports that has a cylindrical form. The solidification time is in accordance with the type of resin and in this situation is 11 seconds per layer. The last part is the gear body, and this is the largest volume of printed material.

2.2 Sensor for measuring the TVOC and HCHO emission

For measuring air quality, a system with a device and various sensors is used. From the last chapter, it is possible to observe that one must use three important types of gas sensors. First, the gas sensor is the total volatile organic compound gases (TVOC). The second is that for formaldehyde (HCHO). To determine the level of emission of the same gas, it is possible to use a commercial apparatus. In this study, a device is used to measure HCHO and TVOC gas emission. The data obtained by optical visualisation from the measuring device are loaded into a spreadsheet. Data are put in the table at a time of one minute. The data obtained from the sensors are saved on an SD card and transferred to a spread sheet in EXCEL.

From the point of view of the individual sensor, the first author proposes using a MOX sensor siloxane resistance type SGP30 type [13] to determine VOC emissions [14]. The accurate measurement value of emission has 15% precision and a sampling rate of one-second value output range from 0 ppb to 60000 ppb for TVOC.

For HCHO, it is possible to use a sensor dedicated to measuring these formaldehyde elements [15] made by SeeedStudio – Grove. A WSP2110 sensor is used to measure the emission [16] with an output range of 1 ppm to 50 ppm. The optimal mathematical regression equation (1) type power with a percentage R2 99.78% for HCHO.

$$\text{ppm} = 1.4857(R_s/R_0)^{-2.194} \quad (1)$$

Parallel to the last type of sensor, an MS1100 [17] was used to detect formaldehyde, toluene, benzene, and other VOC gases. It is important to note that this MS1100 sensor is placed at the same time in the printed space and another in the enclosure. The optimal mathematical regression equation is polynomial type (2) with a percentage value R2 of 98.63% for HCHO.

$$\text{ppm} = 7.4123(\text{Volt})^2 - 25.564(\text{Volt}) + 17.367 \quad (2)$$

3. RESULTS

3.1 Evolution of TVOC emission in the printing process

The SGP30 sensor allows us to determine the evolution of volatile organic compound gas emissions. In Figure 2a, we can see the evolution of emissions for the base area of the printed structure. A tendency to increase the level with the appearance of two zones can be observed, one of intermediate maximum and one of intermediate minimum. In the area of generating the supports Figure 2b, it can be seen the existence of two zones of maximum value with an approximately equal value and of two zones the last in the final part of the process of printing the supports with a value approximately equal to that in the initial phase.

The area of generation of the wheel body is as in the other cases of measuring this type of emission the most agitated with a trend line as can be seen in Figure 1, which is very slightly increasing.

The evolution of emissions determined using the proposed device could be observed in relation to the three zones considered in Figure 3a, for the lower part of the structure and, respectively, in its intermediate area in Figure 3b. In the first area, the existence of an evolution with a maximum point can be observed, and at the end of the analysed area, with a decrease in

emissions by one third of the value of the increase on the first analysed part. In the second zone, an oscillating evolution can be observed with two points of minimum and two of maximum located at approximately the same emission value. However, the trend is to increase the level of emissions.

In the printing part of the wheel, a scattering of the measured mean values with two points critical of half a maximum around half thickness of the wheel and of a minimum in the generation part of the hole in the cylindrical part of the wheel can be seen in Figure 5.

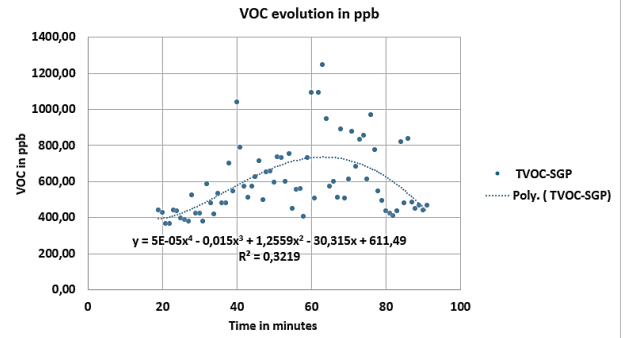


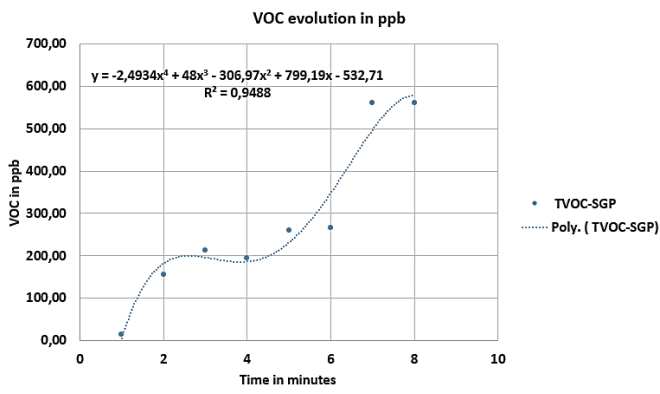
Figure 1. The evolution of TVOC emission is determined with the SGP30 sensor in the printing gear zone.

3.2 Evolution of HCHO emission in the printing process

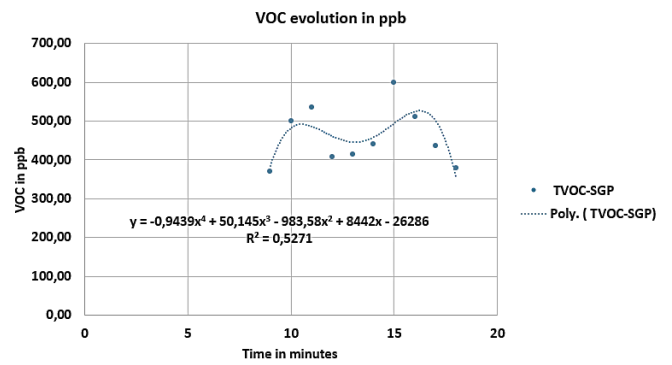
The first of the independent sensors used to determine these types of emissions was the MS1100 type located inside the closures. In Figure 4a, in the generated part of the bottom element, the tendency to emit these emissions decreases by a minimum point at the printing time of 2 minutes. In the sports printing area of Figure 4b, a slight increase in emissions can be observed in the second phase, followed by a decrease in them in the final part. One of the reasons for this variation in emissions may be contact with the solid part in the first interval.

In the area of printing the gear Figure 6, an oscillating evolution of emissions with areas of high values and with minimum values can be observed, respectively. If in the first zone between 50 and 60 minutes the variations can be attributed to the striated cylindrical output surface of the gear on the final part of printing, the decrease in the determined values can be put on the reduction of the printing surface.

The second of the independent sensors proposed to be used by the author for the de-termination of these types of gases emitted was the HCHO, which is located inside the enclosures. From Figure 8a, in the bottom generation part of the printed element, the tendency to emit such emissions increases by a minimum point at the printing time between 4 and 6 minutes.

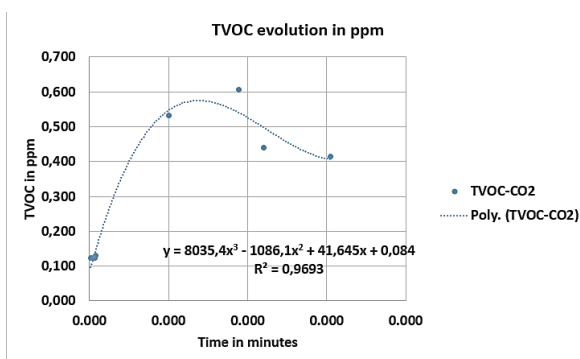


(a)

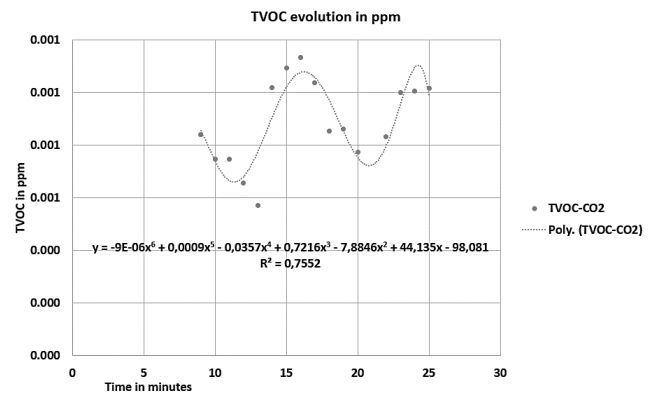


(b)

Figure 2. The evolution of TVOC emission determined with the SGP30 sensor (a) bottom; (b) supports.

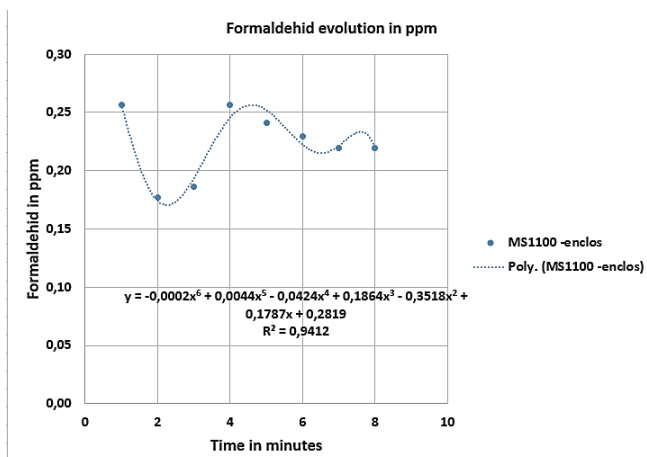


(a)

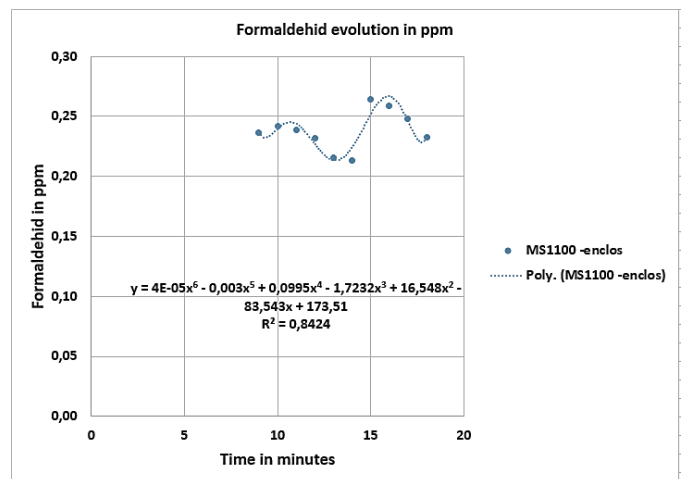


(b)

Figure 3. The evolution of TVOC emission is determined with the bottom sensor of the device sensor (a) bottom; (b) supports.



(a)



(b)

Figure 4. The evolution of HCHO emission is determined with MS1100 (a) bottom; (b) supports.

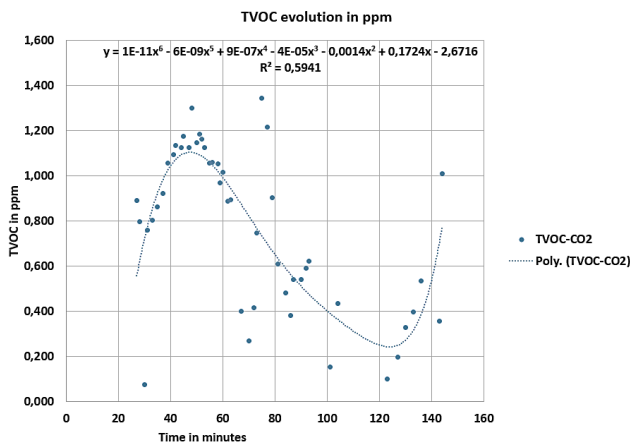


Figure 5. The evolution of TVOC emission is determined with the device sensor in the printing gear zone.

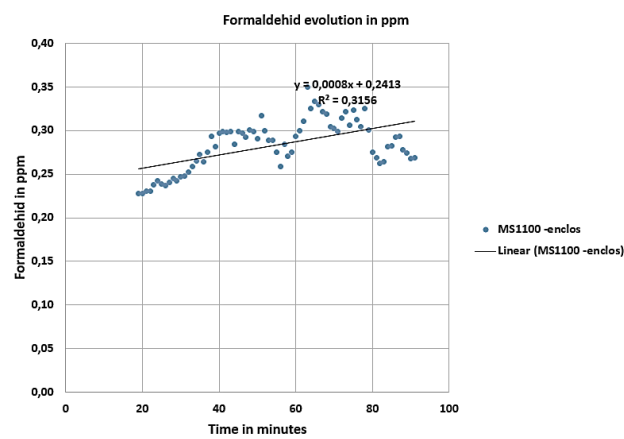


Figure 6. The evolution of HCHO emission is determined with MS1100 in the printing gear zone.

In the sports printing area, Figure 8b, it is possible to observe the existence of a decrease zone in the first zone of the printing process to a minimum value of 15 minutes, respectively, with a linear evolution of emission in the final part of their printing.

In the last part of the printing that generates the gear Figure 7, it is possible to see a very high scattering of the emission values with an interval between a minimum of almost 50 ppb and a maximum of about 90 ppb. The tendency to emit such emissions is slightly ascending.

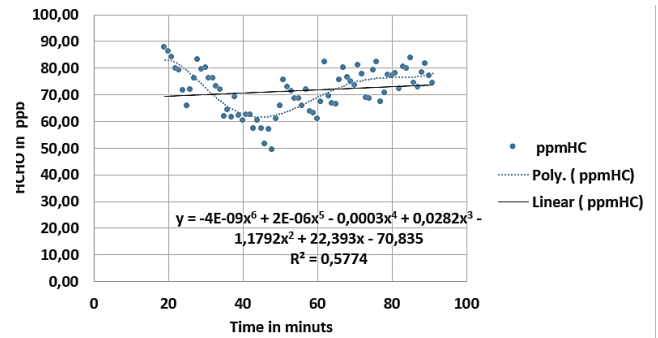
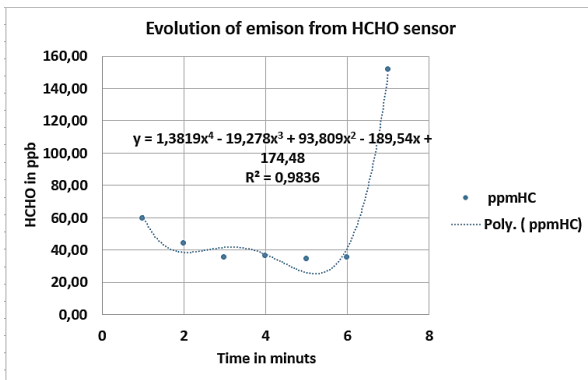
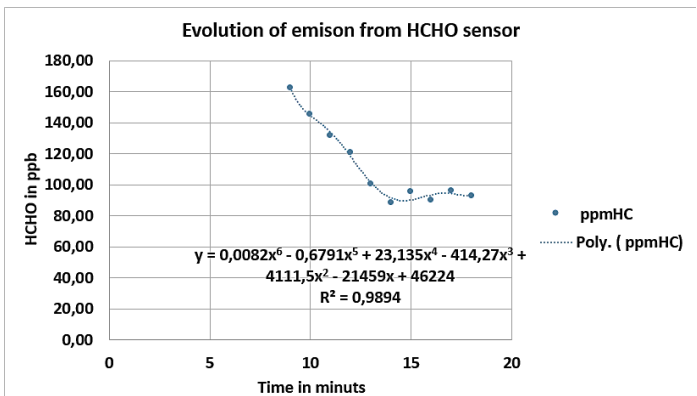


Figure 7. The evolution of HCHO emission is determined with the HCHO sensor in the printing zone gear zone.



(a)



(b)

Figure 8. The evolution of HCHO emission determined with the HCHO sensor (a) bottom; (b) supports

4. DISCUSSIONS AND CONCLUSIONS

The HCHO data determinate with the MS1100, the HCHO sensors and the device have different minimum and maximum values.

From the point of view of the comparative analysis of the determinate emission of HCHO gases in the enclosure with the MS1100 sensor, the maximum percentage is in the gear zone of the printed structure. Minimum values are in the support zone Figure 9.

Zone	MS1100			
	Min	Max	Δ TVOC	%
Bottom	0,18	0,26	0,08	31,58%
Support	0,21	0,26	0,05	20,07%
Gear	0,23	0,35	0,12	48,36%
Total			0,25	

Figure 9. Evolution of HCHO gas emission with MS1100.

From the point of view of the comparative analysis of HCHO gas emission determinate in the enclosure with the device, the maximum percentage is in the

bottom zone of the printed structure. The minimum values are in the gear zone, Figure 10.

Zone	HCHO			
	Min	Max	ΔHCHO	%
Bottom	0,03	0,15	0,12	51,09%
Suport	0,09	0,16	0,07	32,25%
Gear	0,05	0,09	0,04	16,66%
Total			0,23	

Figure 10. Evolution of HCHO gas emission with HCHO.

From the point of view of the comparative analysis of HCHO gas emission determinate in the enclosure with the device, the maximum percentage is in the gear zone of the printed structure. The minimum values are in the bottom zone Figure 11.

Zone	Device			
	Min	Max	ΔHCHO	%
Bottom	0,017	0,087	0,07	23,26%
Suport	0,078	0,154	0,08	25,25%
Gear	0,037	0,192	0,16	51,50%
Total			0,30	

Figure 11. Evolution of HCHO gas emission with a device.

From [18] a good value for HCHO is presented in Figure 16 according to the table data Figure 14. From the comparative analysis of the emissions for the sensors considered to achieve the determination of the emission level, all three sensors warn of a medium-level polluted area in the support area and less polluted in the other two.

Zone	MS1100	HCHO	Device	MS1100	HCHO	Device
Bottom	0,18 to 0,26	0,03 to 0,15	0,017 to 0,087	Moderate Pollution	Slight Pollution	Good
Suport	0,21 to 0,26	0,09 to 0,16	0,078 to 0,154	Moderate Pollution	Slight Pollution	Slight Pollution
Gear	0,23 to 0,35	0,05 to 0,09	0,037 to 0,192	Moderate Pollution	Good	Slight Pollution

Figure 14. AQI for HCHO gas emission.

From [18] a good value for TVOC is presented in Figure 16 according to the table data Figure 15. A perfect air quality concordance can be observed for the first printed areas and a difference between the values in the last two zones. In view of the data obtained, it can be said that from the point of view of TVOC emissions there are small problems with air quality in the printing space in the printing process.

Zone	SGP30	Device	SGP30	Device
Bottom	0,01 to 0,56	0,123 to 0,607	Good	Good
Suport	0,37 to 0,60	0,571 to 1,133	Slight Pollution	Slight Pollution
Gear	0,36 to 1,25	0,074 to 1,342	Slight Pollution	Slight Pollution

Figure 15. AQI for TVOC gas emission.

The VOC data determinate with the WSP2110 sensor and commercial apparatus have different minimum and maximum values.

From the point of view of the comparative analysis of TVOC gas emission determinate in the enclosure with the device, the maximum percentage is in the gear zone of the printed structure. The minimum values are in the supports zone Figure 12.

Zone	SGP30			
	Min	Max	ΔTVOC	%
Bottom	0,01	0,56	0,55	32,98%
Suport	0,37	0,60	0,23	13,79%
Gear	0,36	1,25	0,88	53,23%
Total			1,66	

Figure 12. Evolution of TVOC gas emission with SGP30

From the point of view of the comparative analysis of TVOC gas emission determinate in the enclosure with the device, the maximum percentage is in the gear zone of the printed structure. The minimum values are in the bottom zone, Figure 13.

Zone	Device			
	Min	Max	ΔTVOC	%
Bottom	0,123	0,607	0,48	20,91%
Suport	0,571	1,133	0,56	24,28%
Gear	0,074	1,342	1,27	54,81%
Total			2,31	

Figure 13. Evolution of TVOC gas emission with device

Air Quality Pollution Level Reference Table						
HCHO	0-0.08	0.081-0.1	0.101-0.2	0.201-0.5	0.501-1.0	1.001-1.999
	Excellent	Good	Slight Pollution	Moderate Pollution	Heavy Pollution	Serious Pollution
TVOC	0-0.5	0.501-0.6	0.601-1.5	1.501-3	3.001-6	6.001-12
	Excellent	Good	Slight Pollution	Moderate Pollution	Heavy Pollution	Serious Pollution
CO2	0-450	451-1000	1001-1500	1501-2000	2001-3000	3001-5000
	Excellent	Good	Slight Pollution	Moderate Pollution	Heavy Pollution	Serious Pollution
AQI	1	2	3	4	5	6
	Excellent	Good	Slight Pollution	Moderate Pollution	Heavy Pollution	Serious Pollution
ENVIRONMENT	1 GOOD	2 GOOD	3 POIUTE	4 POIUTE	5 POIUTE	6 POIUTE
	Excellent	Good	Slight Pollution	Moderate Pollution	Heavy Pollution	Serious Pollution

Figure 16. AQI for gas emission [18].

In this study, it was aimed to demonstrate that it is possible to extend the measured emission elements in the printing processes with ecological black resin. With this system, it is possible to determine the influence of emission on the MSLA or SLA printing process with resin and to make a comparison between these two printing processes.

An important aspect emerges, which is that of controlling emissions, which presents problems such as those of emissions such as HCHO and TVOC for printing with black ecological resin.

5. REFERENCES

1. Vasilescu, M.D. Influence of technological parameters on the emission on DLP 3D printing process. *Rev.Chim.*, (Bucharest), 70, no. 12, 4387-4392, (2019).
2. Vasilescu, M.D. Study the influence of colour resin on the emission for DLP 3D printing process. *Nonconventional Technologies Review / Revista de Tehnologii Neconventionale*. Jun2020, Vol. 24 Issue 2, p60-63. 4p.
3. 7 In 1 Air Quality Formaldehyde Detector Monitor PM2.5/PM10/HCHO/CO2/VOC. Available online: <https://www.ebay.com/itm/7-In-1-Air-Quality-Formaldehyde-Detector-Monitor-Testing-PM2-5-PM10-HCHO-CO2-VOC/283812162455?hash=item421485eb97:g:JZwAAOSwNKleak6>, (2021).
4. Lifsetb, R. - 3D Printing and Industrial Ecology, *Journal of Industrial Ecology* 2017, Volume 21, Number S1, S6-S8.
5. 2.2 RESET™ Air Standard for Commercial Interiors. Available online: https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwi05Iic_NHtAhXIIIsKHfloDmgQFjAAegQIB-BAC&url=https%3A%2F%2Freset.build%2Fdownload%2FRESET_Standard_v2_2_2_Standard%2520for%2520CI%2520180131.pdf&usg=AOvVaw1-6oYyux1xbECnhT5zLnhG, (2021).
6. Mendes, L.; Kangas, A.; Kukko, K.; Mølgaard, B.; Säämänen, A.; Kanerva, T.; Ituarte, I.F.; Huhtiniemi, M.; Stockmann-Juvala, H.; Partanen, J.; Hämeri, K.; Eleftheriadis, K.; Anna-Kaisa Viitanen, A.K. - Characterisation of Emissions from a Desktop 3D Printer, *Journal of Industrial Ecology, Special Issue: Environmental Dimensions of Additive Manufacturing and 3D Printing*, 20 March 2017, S94-S106.
7. How Toxic Are ABS & PLA Fumes? 3Dsafety.org Examines VOCs. Available online: <https://3dprintingindustry.com/news/toxic-abs-pla-fumes-3dsafety-org-inquires-vocs-60796/>, (2021).
8. Denga, Y., Caob, S.J., Chenc, A., Guod, Y., - The impact of manufacturing parameters on submicron particle emissions from a desktop 3D printer in the perspective of emission reduction, *Building and Environment*, Volume 104, 1 August 2016, 311-319.
9. Steinle, P., - Characterisation of emissions from a desktop 3D printer and indoor air measurements in office settings, *Journal of Occupational and Environmental Hygiene*, Volume 13, 2016, 2, 121-132.
10. 3D Printing and Air Quality Risks!. Available online: <http://diy3dtech.com/3d-printing-and-air-quality-risks/>, (2021).
11. {Get 3 for the price of 2} Anycubic Plant-based UV Resin 0.5KG. Available online: <https://www.anycubic.com/collections/uv-resin/products/anycubic-plant-based-uv-resin?variant=40701789307042>, (2021).
12. ANYCUBIC 3D Printing Photon. Available online: <https://www.anycubic.com/collections/anycubic-photon-3d-printers/products/anycubic-photon-3d-printer>, (2021).
13. Adafruit SGP30 TVOC/eCO2 Gas Sensor. Available online: <https://learn.adafruit.com/adafruit-sgp30-gas-tvoc-eco2-mox-sensor>, (2021).
14. Davis, A.Y.; Zhang, Q.; Wong, J.P.S.; Weber, R.J.; Black, M.S. Characterization of volatile organic compound emissions from consumer level material extrusion 3D printers, *Building and Environment*, 2019, Volume 160, 106209, ISSN 0360-1323, <https://doi.org/10.1016/j.buildenv.2019.106209>.
15. Grove - HCHO Sensor. Available online: https://wiki.seeedstudio.com/Grove-HCHO_Sensor/, (2021).
16. WSP2110 VOC Gas Sensor. Available online: <https://www.winsen-sensor.com/sensors/voc-sensor/wsp2110.html>, (2021).
17. KS0451 Keyestudio MS1100 Formaldehyde Benzene VOC Gas Sensor. Available online: https://wiki.keyestudio.com/KS0451_Keyestudio_MS1100_Formaldehyde_Benzene_VOC_Gas_Sensor, (2021).
18. Air quality index. Available online: https://en.wikipedia.org/wiki/Air_quality_index, (2021).