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Article

Fused Filament Fabrication 3D Printing: Quantification of Exposure to Airborne Particles

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Abstract: Fused Filament Fabrication (FFF) has been established as a widely practiced Additive Manufacturing technique, using various thermoplastic filaments. Carbon fibre (CF) additives enhance mechanical properties of the materials. The main operational hazard of the FFF technique explored in the literature is the emission of Ultrafine Particles and Volatile Organic Compounds. Exposure data regarding novel materials and larger scale operations is, however, still lacking. In this work, a thorough exposure assessment measurement campaign is presented for a workplace applying FFF 3D printing in various setups (four different commercial devices, including a modified commercial printer) and applying various materials (polylactic acid, thermoplastic polyurethane, copolyamide, polyethylene terephthalate glycol) and CF-reinforced thermoplastics (thermoplastic polyurethane, polylactic acid, polyamide). Portable exposure assessment instruments are employed, based on an established methodology, to study the airborne particle exposure potential of each process setup. The results revealed a distinct exposure profile for each process, necessitating a different safety approach per setup. Crucially, high potential for exposure is detected in processes with two printers working simultaneously. An updated engineering control scheme is applied to control exposures for the modified commercial printer. The establishment of a flexible safety system is vital for workplaces that apply FFF 3D printing.

Keywords: 3D printing; exposure assessment; occupational safety; ultrafine particles

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1. Introduction

3D printing is applied widely for the manufacturing of complex structures using various materials, such as plastic, metal, and ceramics [1–4]. This revolutionary technique finds application in various sectors, including fabrication of biomedical devices [5], electronics and aerospace [2], while providing a rapid prototyping technique for composite materials [2]. Nowadays, research around 3D printing includes process optimisation for medical implants [6], biodegradable materials [7], 3D printing of fibre reinforced polymers [8], and recycled polymeric materials [9]. Especially for the case of polymer 3D printing, FFF is considered one of the most common techniques, where thermoplastic material is deposited layer-by-layer for the production of various polymeric components [10–12]. At the same time, process hazards are commonly disregarded from the process design. The 3D printing exposure assessment literature [10] has revealed that FFF activities can lead to exposure to ultrafine particles and volatile organic compounds.

Ultrafine particles are the airborne particles with a diameter less than 100 nm, produced from natural or human sources (incidental, e.g., vehicle exhaust) [13]. It has been demonstrated that due to high respiratory system penetration [14], nanoscale particles can cause a variety of adverse health effects [14]. UFPs can penetrate the cellular membrane and lead to the production of ROS. UFPs' induced cytotoxicity is originated by the developed oxidative stress, causing DNA damage, oxidation, and denaturation of proteins and enzymes and disruption of mitochondria leading to cell apoptosis, as well as greater adverse health effects such as inflammation, chronic respiratory illnesses, and cancer [15].

A key concern of FFF activities is the health effects and safety problems that they may induce, due to the emission of UFPs and VOCs. During FFF 3D printing, UFP are generated near the extrusion nozzle due to high concentrations of semi-volatile organic compounds (SVOCs) emitted from the heated filaments. Three proposed mechanisms contribute to particle formation following the evaporation of VOCs and SVOCs from the heated filaments: Nucleation of SVOCs (condensation into primary particles), particle growth due to condensation of VOCs, and particle agglomeration [16–18]. Health surveys examining FFF 3D printer emissions have been performed but are currently limited. Gumperlein et al. conducted a randomized, cross-over design study, where healthy human volunteers were exposed to ABS 3D printer emissions for 1 h [19]. No acute effects on inflammatory markers in nasal secretions or urine were found. However, a slight increase in exhaled nitric oxide was noted, which could be induced by eosinophilic inflammation from inhaled UFPs. Moreover, in a health survey, Chan et al. found that about 60% of participants using 3D printing in commercial prototyping businesses, educational institutions, and public libraries reported weekly respiratory symptoms [20]. The same study also determined that working more than 40 h per week was significantly associated with asthma or allergic rhinitis diagnosis. In addition, in a case report study, House et al. found that a self-employed businessman with a history of childhood asthma operated ten 3D printers with ABS filaments in a small work area and after 10 days working with ABS printing, he experienced chest tightness, shortness of breath, and coughing [21].

Furthermore, human exposure to VOCs due to FFF activities can be pervasive and has been a topic of concern due to the mutagenic, genotoxic, and carcinogenic potential of chemicals emitted by specific materials. Several VOCs are also considered potent central nervous system toxicants. They can be metabolized quickly and yield several toxic metabolites that can be excreted through the urinary system [22–24]. These studies indicate a strong correlation between 3D printing emissions and adverse health effects; however, they highlight that additional and extensive examinations are needed to further study the potential toxicological effects of the emitted UFPs and VOCs.

Seeing that a crucial exposure hazard of the FFF 3D printing processes is the emission of nanoscale particles, the establishment of safety approaches can be based on nanomaterial safety frameworks. An efficient nanosafety strategy can be formed based on the STOP principle as suggested by the OECD [25]. This methodology places substitution of materials with safer alternatives as top priority, diminishing inherent hazard to a great extent. Technical measures, such as process isolation and local ventilation, can be used to contain the hazard at the source, before coming into contact with employees. Organisation of the process can be adjusted based on a safety prospect (e.g., risk awareness, standard operation procedures). The last barrier of safety from ultrafine particle exposure is using personal protective equipment such as gloves, respirators, lab coats, and eye protection.

The main determinant factor for the emission potential is considered to be the nozzle temperature and typically emissions can be increased by multiple orders of magnitude when increasing the nozzle temperatures. Other secondary parameters are bed temperature and nozzle diameter, along with a variety of printing parameters [10]. Figure 1 presents the main emission hazards displayed in 3D printing processes. Several works in the latest years have studied these emissions with results varying widely based on material and process parameters [10,26]. In the 3D printing literature, various filament materials have been explored in terms of exposures that they can cause [26]. Examinations of the more specialized filament materials include filaments that incorporate nanomaterial additives such as CNTs [27] or metal additives [28]. CF-reinforced filaments have not been explored in the exposure assessment literature as of yet, albeit being a highly promising material alternative for applications requiring enhanced mechanical properties [8]. The present study examines occupational exposures to ultrafine particles within a 3D printing workplace. CF-reinforced filament materials are applied in most of the cases examined. In one of the setups examined in this work, the CF reinforcement is achieved through modification of a commercial 3D printer, which presents a unique exposure profile.

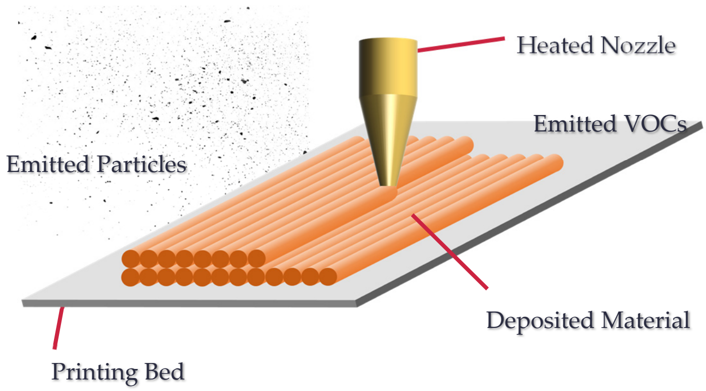

Figure 1. Airborne emissions in FFF 3D printing.

Crucially, the rapid development of the FFF technique, the variety of commercial printers and materials, as well as the diverse requirements of the print parts, have led to current FFF workplaces typically applying a multitude of devices and materials in different combinations. These are defined based on the final target properties of each printed part, and the number of parts required for each batch. It is an integral objective of this work to reveal that within such a workplace, each process setup entails a different profile of potential occupational exposure. As will be shown through the presentation of the different cases, understanding of the exposure potential of each process setup is vital, since it can lead to the optimization of the safety system on a case-by-case basis.

Additionally, since the focus of the study is strongly placed on studying the potential for occupational exposure of the employees involved in the 3D printing operations of the workplace under investigation, the data obtained from the instruments are examined and interpreted on the basis of comparison with reference values. As will be shown in the next sections (Section 2.4), these values have been derived from the nanotechnology field, similarly to relevant publications [29]. To account for the variability in emissions based on print process phases, the present study introduces an additional short term (15 min) exposure threshold, to more closely reveal exposure episodes of high priority.

Thus, within this study, a comprehensive exposure assessment measurement campaign in a workplace employing 3D printing processes is presented. Several novelty elements are introduced in this research. These are related to:

- The materials studied.
- The variety of process setups examined.
- The direct focal point in employee exposure, through the comparison with exposure thresholds.

2. Materials and Methods

Several methodologies have been suggested and implemented for nanoparticle exposure assessment. Two of the most widely applied are the OECD Harmonized Tiered framework [30] and the NIOSH NEAT technique [31]. These two techniques present many similarities, such as the use of count-based instrumentation and the use of real time measurements, as nanoparticle concentrations are expected to vary widely temporally and spatially.

Currently, there are two fully developed methodologies that can be applied for the assessment of the risks associated with FFF. Standard ANSI/CAN/UL 2904 [32] describes the suggested approach in order to determine the emission rates of hazardous substances for specific 3D printing configurations. OECD has developed a framework [30] for evaluating the exposure of employees to nano-objects, which, as expressed in the previous section, is highly compatible with the process. The studied workflow employs a multitude of different 3D printers, filaments, workspaces and printing parameters, thus evaluating the release rates for a few specific combinations would provide limited results. Therefore, our goal was to examine the levels of exposure for the operators of 3D printers as well as the specific phases of the processes that would entail higher risk. To that end, our methodology was based on the OECD framework [30] and on previous studies conducted in workplaces with one or more printers [33,34]. Exposure assessment experiments were designed to study exposure potential with one or two printers functioning simultaneously.

Before conducting the exposure measurements, an initial screening of the workrooms was performed and information regarding the work practices was collected. Based on that information and the aforementioned methodologies, a measurement campaign most suitable for the present setting, as defined by the information gathering session, was designed and subsequently implemented. The experiments were designed with consideration of these requirements as well as employee and workplace availability constraints.

2.1. Instrumentation

The conducted measurements evaluated the exposure to particles of sizes 10 nm to 25 µm (Figure S1) near an operator's breathing zone. Technically, the breathing zone corresponds to a hemisphere (generally accepted to be 30 cm in radius) extending in front of the human face, centred on the midpoint of a line joining the ears. The base of the hemisphere is a plane through this line, the top of the head and the larynx [35]. The location of the measurement points was defined in each case based on a potential location that an operator/employee could be working on, in this way representing a breathing zone location. Additionally, instrument positions were within 30–50 cm from the printers. The various measurement setups can be found in the Supplementary Information (Figures S2–S6).

Instruments providing number-based measurements were selected since primary emitted particles are usually of ultrafine or near ultrafine size [10,26]. Larger particles measured are considered the result of agglomeration [36]. Two instruments (*CPC 3007* and *Aerotrak 9306-V2*, *TSC Inc., Edina, MN, USA*) were used in order to observe particle count concentrations for multiple size channels. The *CPC* instrument displays particle concentration in a fixed range channel, for all particles measured, at 10 nm–1 µm. The *Aerotrak* instrument displays the capability to adjust the measurement size range channels. The channels were adjusted to display the sub-micron size range with detail, as follows:

1. Channel 1: 300–400 nm
2. Channel 2: 400–500 nm
3. Channel 3: 500–600 nm
4. Channel 4: 600 nm–1 µm
5. Channel 5: 1–2.5 µm
6. Channel 6: 2.5–25 µm

Particle size distribution was recorded using *NanoScan SMPS 3910 (TSC Inc., Edina, MN, USA)* in the range of 10–420 nm. It is noted that although portable equipment was used, a fixed-location measurement protocol was applied for each case, as done in other relative studies [29,33,34,37]. The measurement's objective was not to represent personal exposure through a worker's 8 h shift. Such kinds of exposure campaigns require a set of different instruments, that the operators may equip themselves with and monitor concentrations on their actual breathing zone. In this way, exposure while workers are moving or performing different tasks is defined [38].

Printing-related events such as filament loading, and print start were time-logged as to enable the assessment of a correlation between these events and hazardous emissions. Before the prints initiated, the background measurements took place. This means that the background concentrations were assessed through the "time variance" approach rather than the "spatial variance" approach (e.g., concentration in an adjacent room), as concentrations before the emission generating activity [30]. The background readings were taken for at least 30 min.

2.2. Description of Studied Cases

The presented cases are performed within a pilot line scale 3D printing workplace with focus on composite materials. Measurement campaigns are presented in an order of increasing complexity and novelty of evaluated activities. Printing using a carbon fibre reinforced filament is used as a starting point (Case 1) before moving to multiple printers (Case 2) and the resulting higher exposure load. Additionally, two methods for continuous fibre deposition are presented with varying levels of safety controls applied (Case 3, 4).

Basic information regarding the processes and the workrooms were collected as presented in Table 1. The summary of this information allows an easy identification of differences and similarities between cases. Information such as printing temperature and speed are included in Table 1; however, the goal of this work is to present the wide range of exposure levels during different activities of a 3D printing workplace and not to directly compare printing parameters.

Table 1. Information gathering as a pre-assessment in 3D printing processes exposure measurements.

		Case 1	Case 2	Case 3		Case 4	
				3a	3b	4a	4b
Process		FFF 3D printing	FFF 3D printing	Continuous Fibre Reinforcement (CFR)		Continuous Fibre Reinforcement (CFR)	
3D printer		*Raise3D Pro2 Plus-* enclosure cap removed	*Raise3D Pro2* *Raise3D Pro2 Plus*	*Markforged Industrial X7*		Modified *Prusa i3 MK3S*	
		Raise 3D Technologies Inc., Irvine, CA, USA.		*Markforged, Watertown, MA, USA*		*Prusa Research a.s., Prague, Czech Republic*	
Workroom Ventilation/Air Filtration		Negative pressure mechanical ventilation, air purifier with HEPA filter	Negative pressure mechanical ventilation, air purifier with HEPA filter	General ventilation through an open window	Air purifier with HEPA filter	No ventilation	Mechanical ventilation (10 ACH), local exhaust
Workroom	Volume	45 m^3	45 m^3	15 m^3		20 m^3	40 m^3
	Temperature	~30 °C	~30 °C	~20 °C		~20 °C	~20 °C
	Humidity	40%	40%	40%		40%	40%
Filaments Used (colour)		Non-commercial TPU with Carbon fibres 27.2% *w*/*w* (black)	*MasterFill PLA Pro* (natural) *PolyFlex™ TPU95* (orange) *PolyMide™ CoPA* (black) *Spectrum PETG* (yellow)	*Markforged 800cc Onyx FR* (black) + *Markforged Carbon Fiber*		*Easyprint PLA* (natural) + *Markforged Carbon Fiber*	
Process	Measurement Duration	Full or near full 8 h workday				≈2 h	
	Time Per Print	45 min	10–30 min	4–6 h		10–20 min	
	Object	Square mono-shell tower (1 × 1 × 5 cm)	Square mono-shell tower (1 × 1 × 2 cm)	Fan (radius ≈ 10 cm)		Rectangular (1 × 4 × 0.2 cm)	
	Nozzle Temperature	210–230 °C (increasing)	PLA-215 °C TPU-230 °C CoPA-250 °C PETG-250 °C	Onyx-275 °C CF-230 °C		200 °C	
	Bed Temperature	Not heated	Not heated	Not heated		50 °C	

Table 1. *Cont.*

	Case 1	Case 2	Case 3		Case 4	
			3a	3b	4a	4b
Operator Involvement	Filament loading-unloading Print starting Removal of failed prints, purged material Regular monitoring		Print Starting Remote monitoring		Filament loading-unloading Print starting Removal of failed prints, purged material Regular monitoring	
Incidental Emissions	Negligible transfer of particles from 3D printing at adjacent room	Negligible transfer of particles from 3D printing at adjacent room	No incidental emission expected		No incidental emission expected	
Enclosure Specifications	No enclosure	Built-in non-airtight enclosure with dedicated air fan equipped with HEPA filter	Built-in non-airtight enclosure without air filtration/removal.		No enclosure	

2.3. Experiment Setup

2.3.1. Case 1—TPU 27.2%CF

Case 1 consists of a printability test for a TPU filament produced within Horizon 2020 project Repair3D [39]. The novelty of this case lies in the reinforcement of the filament through the inclusion of 27.2% wt chopped carbon fibres. During printing, the enclosure was removed, due to material-specific ergonomic limitations.

2.3.2. Case 2—Multiple Printers

For Case 2, two printers were operated on the same room and four filament materials were used (MasterFill PLA Pro by 3DHUB Greece (Moschato, Greece), PolyFlex™ TPU95 and PolyMide™ CoPA by Polymaker B.V. (Utrecht, The Netherlands), Spectrum PETG by Spectrum Filaments (Pęcice Małe, Poland)). Each printer has a built-in non-airtight enclosure (enclosed plexiglass frame with visible openings) equipped with a HEPA filter. Such enclosures have been implemented by 3D printer manufacturing companies or are custom-made on an aim to reduce exposure potential [40], but also to facilitate higher quality prints, due to the stabilization of the temperature inside the printer. This reduces probability for the occurrence of defects such as warping, in specific materials. However, similarly with Case 1, the enclosure cap was removed during TPU printing. Moreover, enclosure caps were removed while filaments were either loaded or unloaded, while enclosure doors were briefly opened multiple times mainly near the print start.

2.3.3. Case 3—CF Co-Deposition (Semi-Industrial)

Two particle exposure measurements were conducted for Case 3 during the printing of test artifacts for characterization purposes. Prints were performed using the *Markforged Industrial X7* printer and fire-resistant PA filament. The process was mostly isolated with the operator only briefly entering the room a few times. For the first measurement (Case 3a), controls consist of the printer's built-in non-airtight enclosure and an open window. A dehumidifier equipped with a HEPA filter was employed for the second measurement (Case 3b) and was placed with the air inlet facing the printer.

2.3.4. Case 4—CF Co-Deposition (Custom)

The experimental equipment measured in Case 4 consisted of a commercially available FFF 3D printing system (*Prusa i3MK3*), equipped with a modified printhead (Figure S7) to incorporate continuous fibre coextrusion into its function. The toolhead included a custom designed liquefier with two entry orifices and a single extrusion point. A continuous fibre multifilament yarn is inserted along with thermoplastic 3D printing filament and both materials are mixed inside the heated liquefier forming a composite feedstock that is extruded from the nozzle. Regarding materials utilized during the experimentation, PLA filament by *Primacreator* (Malmö, Sweden) was combined with carbon fibre with thermoplastic PA-based sizing. In addition to the instruments used in previous cases, for Case 4 the scanning mobility particle sizer *NanoScan SMPS 3910* was also used, enabling the observation of particle size distribution throughout the process.

2.4. Point of Reference for Result Interpretation

The results that will be displayed in the following paragraphs are generated from experiments performed for exposure assessment. Therefore, they are representative of exposure levels of employees working in the same space. It is highlighted that this does not correspond to personal exposure (e.g., concentrations inhaled by the worker while performing various tasks within the 8 h shift) but the concentrations that a worker could be exposed to, provided that they remain in the workroom. In order to assess if these exposure levels are within hazardous ranges, comparison with occupational exposure limits is needed. It is important to note that since ultrafine particles are the main hazard of the 3D printing processes, the focus of the analysis will be placed on the ultrafine particle emissions (*CPC 3007* readout). Nevertheless, data for larger particle sizes will be displayed and discussed as well, particularly in the cases that significant fluctuations are present.

A significant barrier to performing this assessment thoroughly is the absence of health-based occupational exposure limits for ultrafine particles emitted from FFF 3D printing activities. Crucially, even if a general, all-encompassing exposure limit existed, it would be quite questionable to regard all material emissions of the same hazard levels, given the wide diversity of materials used for FFF 3D printing. These barriers can be attributed to the newness of the field and the limited risk awareness. In similar studies, only one exposure threshold has been proposed at 40,000 ultrafine particles/cm^3 [29]. This is not a 3D printing-dedicated exposure limit, but a derived threshold based on limits proposed for bio-persistent nanoparticles of a density lower than 6000 kg/m^3 [41]. This means that this is not a health based or regulatory binding limit. While, as already expressed, the threshold is not representative of the hazard of the materials emitted, it can be a useful benchmark for assessing levels of risk.

Most importantly, it should be noted that these values correspond to mean workplace concentrations on an 8 h time-weighted average. Short spikes in concentration, corresponding to high emission events could be deficiently represented in an averaging of the concentrations. However, they are crucial in interpreting exposure assessment data and should not be neglected. A rule of thumb of retaining a 15 min exposure threshold of 2 × OEL has been supported from nanomaterial safety experts [42]. Therefore, for the following measurements and assessments, these two reference values will be used:

40,000 #/cm^3 of ultrafine particles as an 8 h TWA–occupational exposure threshold;
80,000 #/cm^3 of ultrafine particles as a 15 min threshold.

An additional note is that even if exposure thresholds are not exceeded, safety science has established that measures ought to be considered in case of high upsurges in emissions. In this case, decision making through the ALARP (As Low As Reasonably Practicable) principle is paramount. The ALARP principle states that measures taken to reduce the residual risk shall be applied as far as this is reasonably practicable [43]. Based on this concept, since adverse health effects as a result of exposure to UFPs cannot be excluded, measures can be taken to prevent or reduce the magnitude of the emissions to the extent that it is reasonably practical, meaning that no excessive costs are required, or the process is not hindered in any significantly disruptive manner through the additional control systems.

For all measurement cycles described in the Results section, the Concentration/Time plots for all instruments applied will be presented. The 15 min mean of the concentrations will also be displayed, to assess exceedance of the short-term threshold. A table of summarized information for the most crucial events will be presented. The highlight findings of each measurement will be discussed. It is noted that the background concentrations were not subtracted from the process concentrations, following the result presentation scheme applied in relative works of the literature that have evaluated UFP concentration in 3D printing workspaces [34,37]. This scheme is also applied in other nanosafety-focused exposure measurement studies [44] and studies investigating the emissions of ultrafine particles as a potential Indoor Air Quality pollutant [45]. Consistently to the presentation scheme utilized in these works, a linear scale is used for the presentation of concentration data, as opposed to selecting a logarithmic scale, which is more compatible to the presentation of emission rates [46].

To mitigate measurement errors, all instruments were calibrated according to the manufacturer's guidelines on the predefined dates. Moreover, a 15 min moving average of the measured concentrations and the time series data was used to smooth out short-term fluctuations and highlight longer-term trends.

3. Results

3.1. Case 1—TPU 27.2%CF

Figure 2 presents particle concentrations during printability tests of TPU filament with 27.2% wt CF addition. *Aerotrak* reading remained close to background. Real-time *CPC* readings and the 15 min moving average of the concentrations are compared to the recommended 15 min STEL of 80,000 #/cm^3. It is observed that this value is exceeded for about 20 min. Two prevalent peak concentration events are observed, during the removal of the previously employed filament (150,000 #/cm^3), and the filament loading of the CF reinforced TPU (230,000 #/cm^3). This process presents increased potential for exposure risk in the short term, due to the enclosure cap being removed and the particles escaping to the workroom. This is an issue that is generated by a simple space management problem, since the built-in enclosure of the printer cannot accommodate the spool holder and the TPU filament being placed above the nozzle. In order to address this, we recommended and implemented a simple enclosure extension using four plexiglass sheets through a stable structure (Figure 2). This simple process utility can be placed on the printer when the cap is removed, to extend the enclosure and contain emitted particles, while preserving enough space for the TPU filament and spool holder to be located within. Table 2 presents a comparison of observed concentrations with reference thresholds.

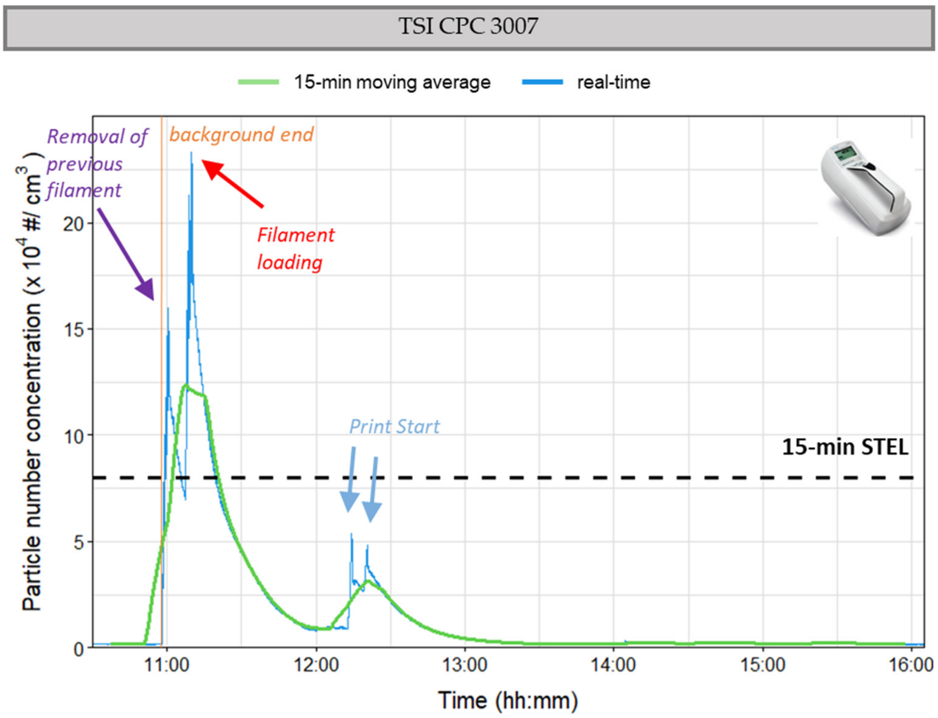

Figure 2. *Cont.*

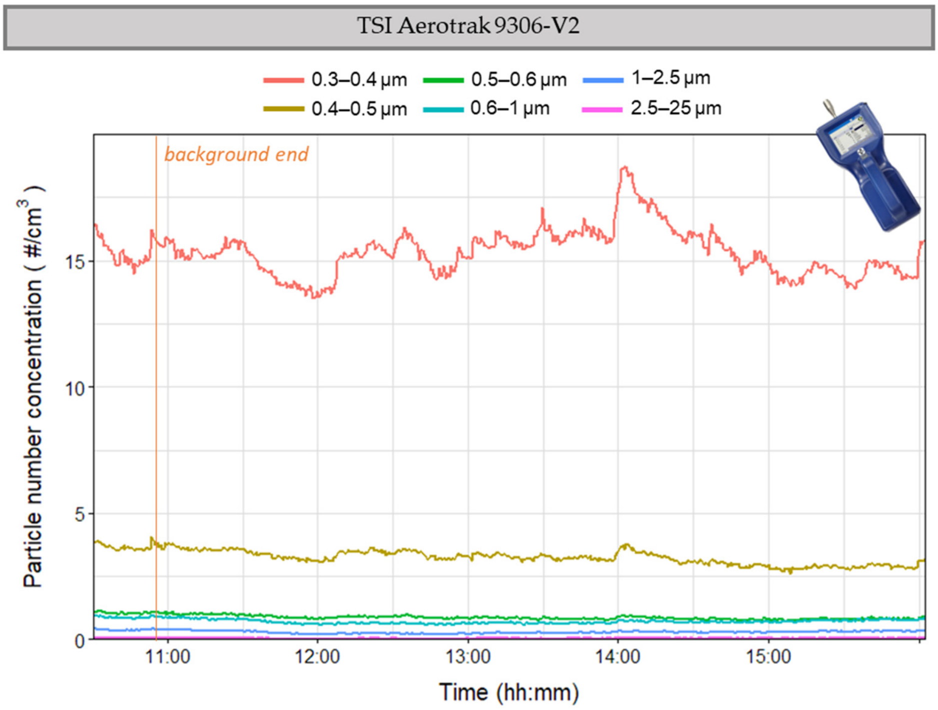

Figure 2. Particle Concentrations for Case 1.

Table 2. Measurement Overview for Case 1—Comparison with exposure thresholds.

Concentration Peaks (#/cm³)	**Max. Peak (#/cm³)**	**Peak Time (hh:mm)**	**Max. 15 min Mean (#/cm³)**	**Corresponding Emission Events**	**15 min Threshold Exceeded (80,000 #/cm³)**
	233,000	**11:09**	**123,700**	**Filament Load**	**Yes**
Background Mean (#/cm³)	6400				
Full Workday Concentration Mean (#/cm³)	12,500				
Eight hour threshold exceeded (40,000 #/cm³)	No				

3.2. Case 2—Multiple Printers

For the first cycle, measurement started with loading of PLA and PETG filaments, which led to the first peak in the concentration of ultrafine particles. It is apparent from the measurement data analysis that the printing processes generate peak concentrations significantly higher than the background (Figure 3). Filaments were unloaded and loaded multiple times and a number of print starts were attempted creating corresponding peaks for UFPs and a few peaks for larger particles. PETG was replaced by CoPA, which was used for a print shortly after being loaded and PLA was replaced by TPU, which was loaded twice and then used for a 40 min continuous print. At this time, there was an increase in concentration for particles of sizes over 300 nm. For these last three events a respective peak was detected by *CPC 3007* while the other instruments observed a slow increase during the second half of the 40 min print but only in the size range of 300 nm to 400 nm (Figure 3).

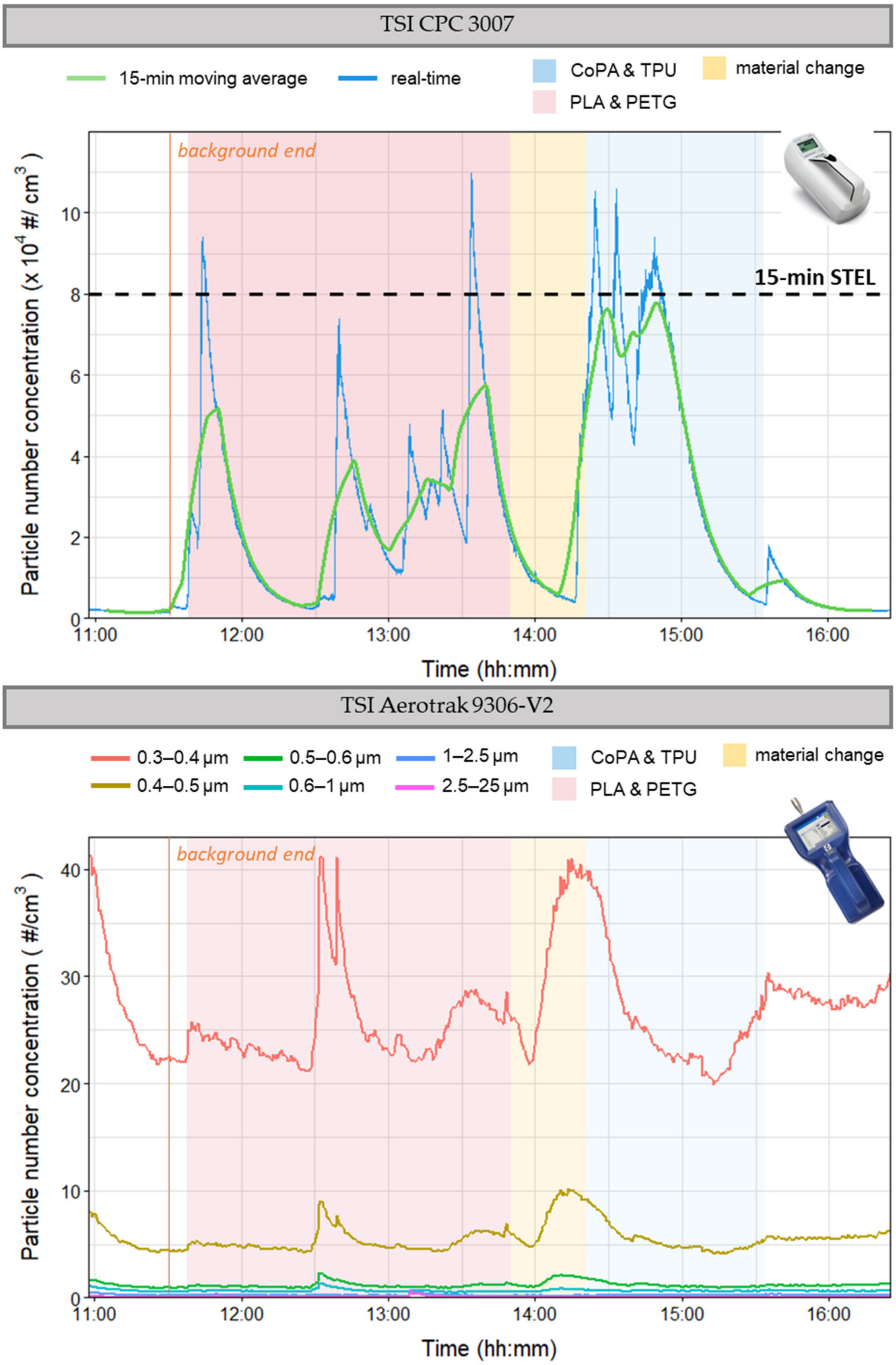

Figure 3. Particle concentrations for Case 2.

Table 3 presents the crucial data concerning ultrafine particle concentrations. The loading process phases and print start procedures lead to the high concentration peaks. It can be an uncomplicated control measure to ensure that operators are not present within the vicinity of the printer during these stages.

Table 3. Measurement Overview for Case 2—Comparison with exposure thresholds.

	Max. Peak (#/cm^3)	Peak Time (hh:mm)	Max. 15 min Mean (#/cm^3)	Corresponding Emission Events	15 min Threshold Exceeded (80,000 #/cm^3)
Concentration Peaks (#/cm^3)	**110,000**	**13:34**	**77,800**	**Filament Loading/Unloading (PLA to TPU) Print Start (CoPA)**	**No**
Background Mean (#/cm^3)			1700		
Full Workday Concentration Mean (#/cm^3)			16,900		
Eight hour threshold exceeded (40,000 #/cm^3)			No		

It can be calculated that for none of the maximum concentration peak cases is the 80,000 #/cm^3 15 min threshold surpassed. However, it can be observed that several of the high-emitting activity events lead to concentrations that approach this value. Specifically, the last emission event leads to a 77,800 #/cm^3 15 min mean concentration, coming in succession of two events in which the 15 min mean concentration reached values as high as 50,000 #/cm^3. Caution is recommended in terms of safety since direct exposure to all these emission events could constitute hazardous levels of exposure. Interestingly, the full workday concentration mean (16,900 #/cm^3) does not exceed the 40,000 #/cm^3 value, revealing that not exceeding the threshold should by no means be a conclusion to the exposure assessment investigation. An important detail is that for calculations of the 8 h concentration means, the remaining hours of the typically 5 to 7 h print processes were considered to display the 8 h workday's mean background concentration. For the 15 min moving average each value was calculated for 15 min time period centred around the respective time point (450 s before and 450 s after).

3.3. Case 3—CF Co-Deposition (Semi-Industrial)

For Case 3, measurements were performed during print sessions for artifacts manufactured for characterization purposes. Here, the measurements were divided in two sessions, in which the main difference between the processes was the application of a HEPA-filter equipped air purifier in Case 3b, as an exposure control mechanism. Case 3a is a printing process without the application of any controls.

3.3.1. Case 3a

After activating *Markforged Industrial X7* following idle periods, a purging process has to be performed to remove filament material exposed to air humidity. Purging lasts for a few minutes and is the main source of particle emissions as seen in the first case of measurements, reaching values as high as 60,000 #/cm^3. Secondary emission events are observed during the printing and at every print start, although of much lower magnitude than the purging process (approx. 20,000 #/cm^3) (Figure 4).

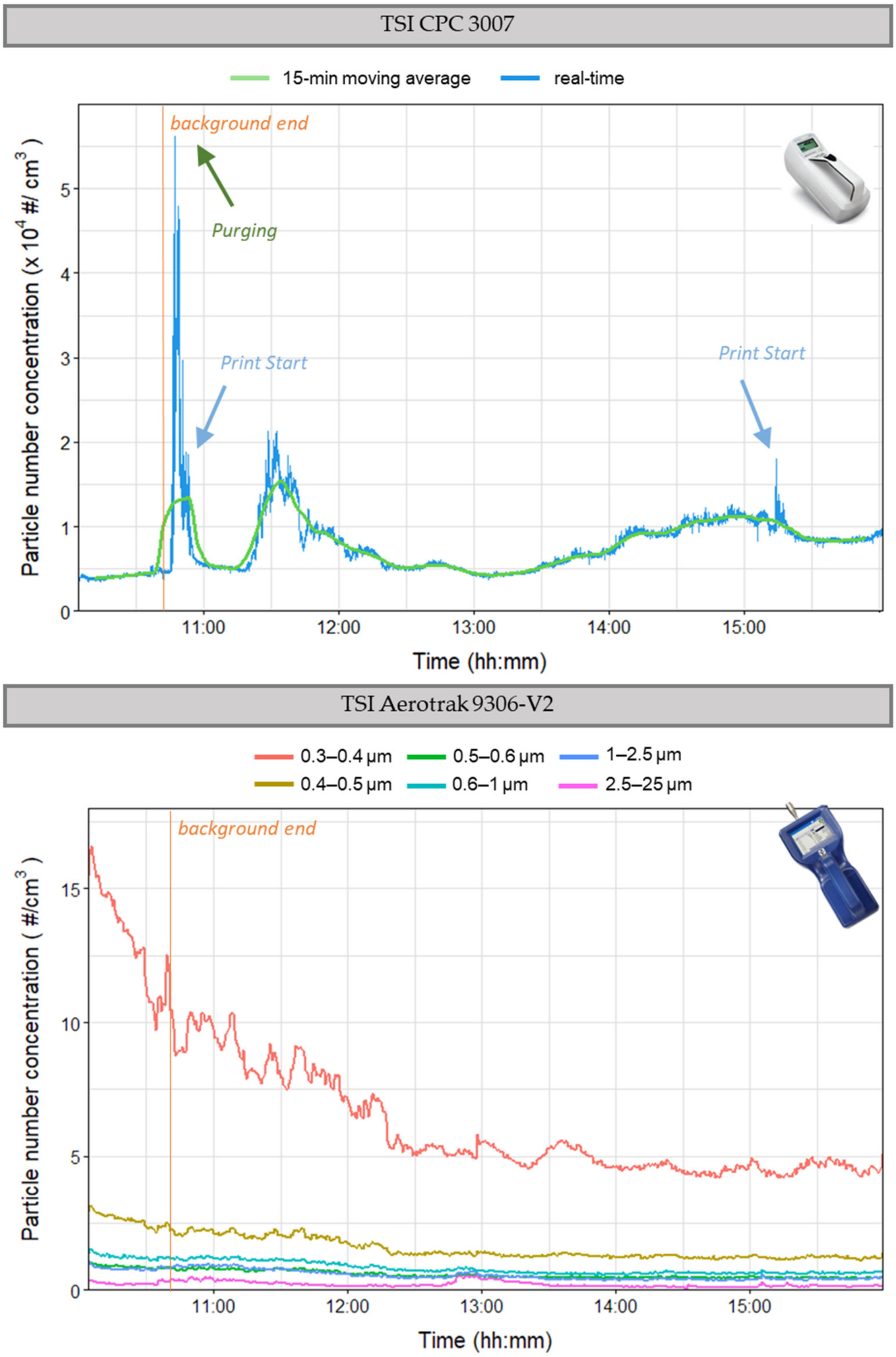

Figure 4. Particle concentrations for Case 3a.

3.3.2. Case 3b

UFP concentrations are much higher during the second case of measurements (Figure 5) and a significant increase of the number of larger particles is recorded unlike Case 3a (Figure 4). During the purging event, the UFP concentrations reached a peak of approximately 110,000 #/cm^3, while larger particles, in the size bins of 300–400 nm and 400–500 nm reached values of approximately 60 #/cm^3 and 20 #/cm^3, respectively, which were the largest recorded values for any of the processes tested. This can be possibly related to the chopped CF additives leading to larger particles release comparing to the conventional FFF cases where agglomeration of UFPs is considered the main mechanism for the production of particles >0.1 µm. The disparity during purging indicates a higher number of particles escaping the enclosure. This outcome is probably the effect of the improperly placed air purifying device pulling particles from the enclosure (Figure 6).

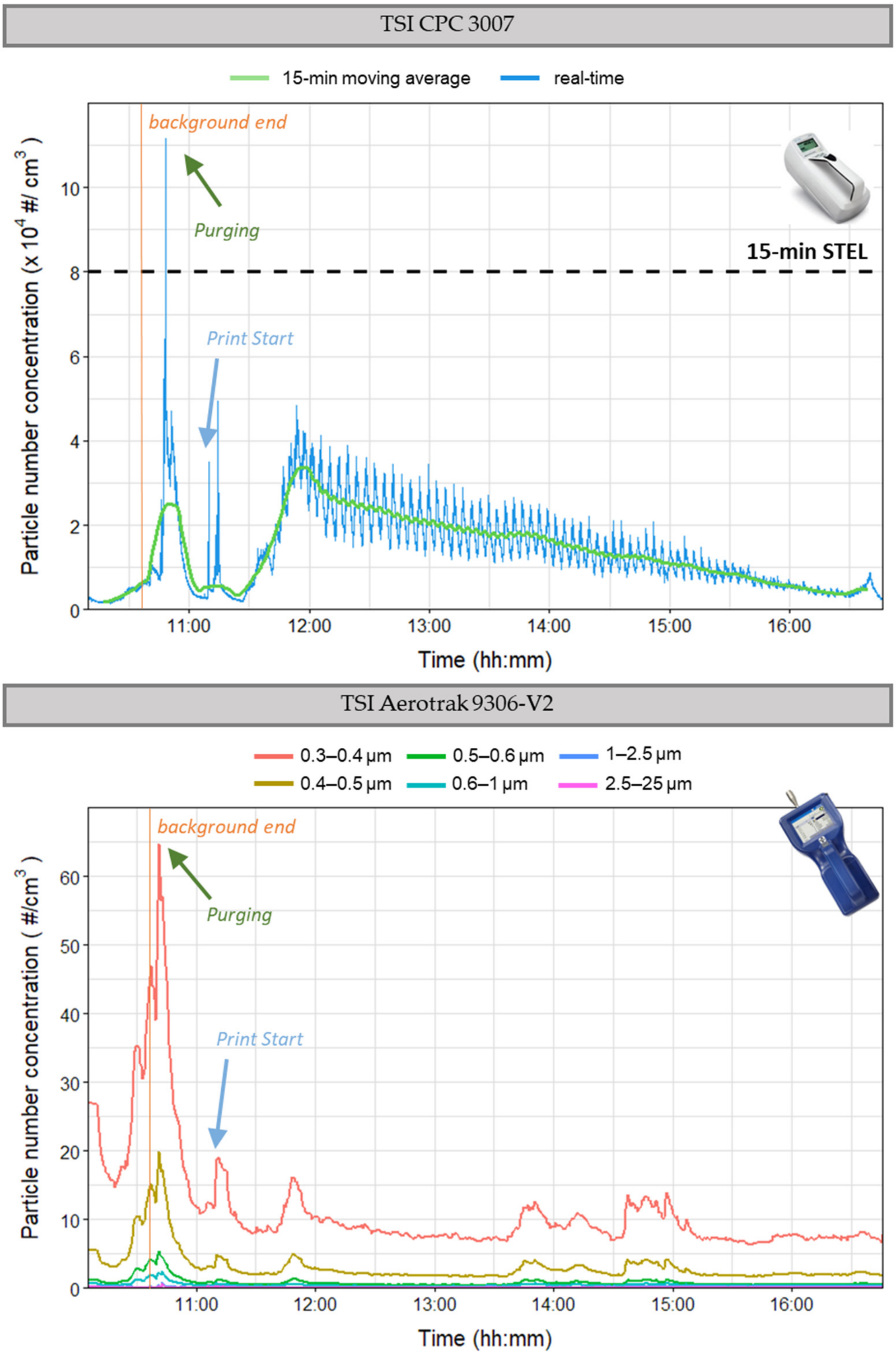

Figure 5. Particle concentrations for Case 3b.

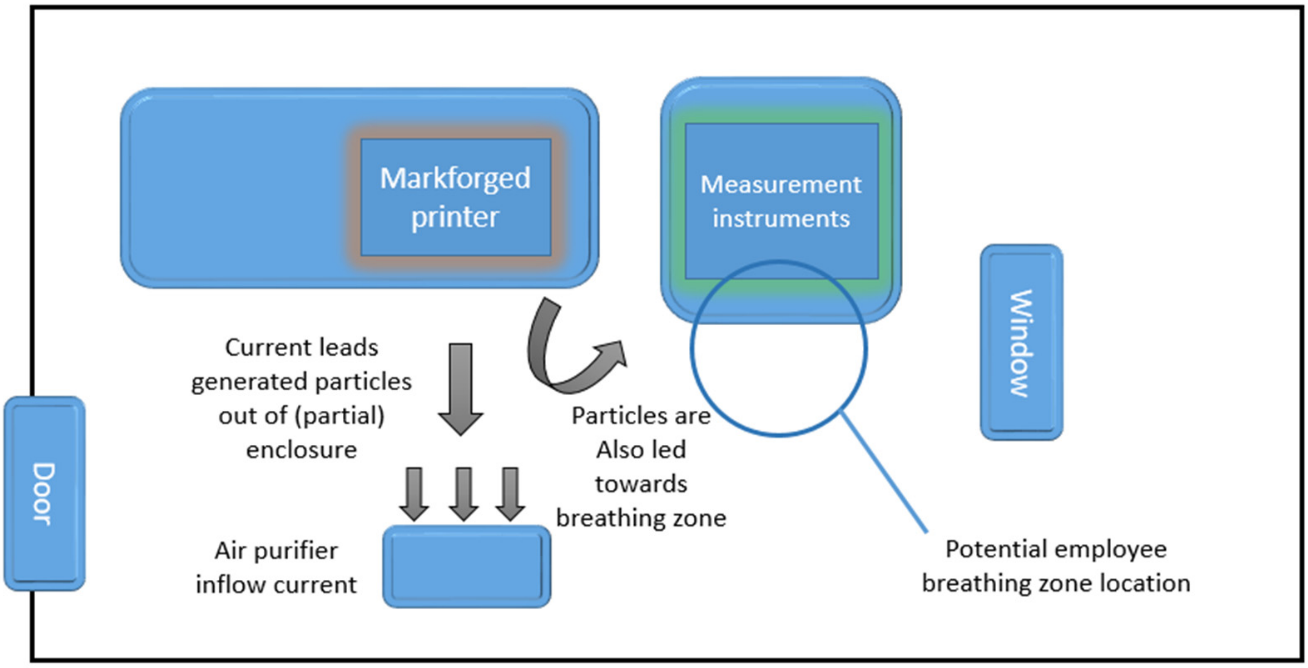

Figure 6. Potential interpretation of increased concentrations after control use in Case 2.

The repeating peaks recorded during the second measurement are considered the result of the printed artifact's design since the distance between two consecutive peaks coincides with the printing time of each layer, as calculated by the printer's dedicated slicer software. The object being printed was a fan (radius ~10 cm), and the unique emission pattern may have been caused by the different emission profiles of the centre of the fan and the blades. This may be an indication that the deposition pattern is an additional determinant mechanism of the rate of generation of the particles. As described in Table 4, in none of the cases were the 8 h or 15 min thresholds exceeded.

Table 4. Measurement Overview for Case 3—Comparison with exposure thresholds.

Case	Case 3a No Controls	Case 3b Air Purifier Active
Background Mean (#/cm^3)	4100	3400
Max. 15 min mean (#/cm^3)	15,400	33,800
Corresponding emission events	Printing	Printing
15 min threshold exceeded (80,000 #/cm^3)	No	No
Full Workday Concentration Mean (#/cm^3)	6800	11,800
Eight hour threshold exceeded (40,000 #/cm^3)	No	No

3.4. Case 4—CF Co-Deposition (Custom)

For Case 4, measurements of airborne particle emissions were performed during a modified continuous CFRP 3D printing process. In this measurement campaign, measurements were divided in two sessions. The difference between the processes was the lack of application of Engineering Controls (e.g., general ventilation, local ventilation) in Case 4a, as an exposure control mechanism for emissions removal. In Case 4b, CFRP printing processes were performed with the application of Engineering Controls. Overall, the main objectives of this campaign were the comparison of effectiveness of Engineering Controls in exposure mitigation and the evaluation of operators' exposure risk to the emissions.

3.4.1. Case 4a

Modifications have been made on a *Prusa* 3D printer, in order to be able to print and co-deposit polymer and CF simultaneously. Materials used in printing were PLA and CFs coated with Nylon (polyamide) for sizing purposes, providing in this way better adhesion with the polymer material.

Measurements of airborne particle emissions during the modified continuous CFRP 3D printing process with no engineering controls can be seen below. Emission of significant concentrations of UFPs was confirmed from *CPC* results (Figure 7), being also higher compared to conventional 3D printing processes measured in previous cases. No significant emissions for microparticles were detected (Figure 7). As it can be seen from Figure 7, emissions during CF and PLA printing are higher, (peaks at 450,000 #/cm^3) compared to instances where only PLA is used (peaks at around 250,000–300,000 #/cm^3). Moreover, size distribution analysis results from *SMPS* (Figure S9) indicate that there is a significant difference in particle size distribution before printing and during the print activity. As it can be seen from Figure 8, comparing particles size distribution during printing with that of the background, it can be confirmed that UFPs of very small sizes are emitted during printing (approximately 10–15 nm in diameter). Moreover, the concentration of the emitted particles is very high (around 200,000–250,000 #/cm^3). Subsequently, modified continuous CFRP 3D printing processes display high UFPs emissions, presenting a significant occupational exposure hazard, related to the prototype status of the equipment, while only early stage of optimization has been implemented in the presently used device.

3.4.2. Case 4b

Given these very high emission values, the experiment was repeated after applying a set of engineering controls (general ventilation–10 ACH, or local ventilation–arm hood combined with general ventilation) for the purposes of emission removal and exposure mitigation.

Through using this setup, significant mitigation of exposure was achieved, concentrations during CF and PLA printing are significantly lower (peaks around 100,000 #/cm^3 with general ventilation & 80,000 #/cm^3 with general ventilation and arm hood in presence) compared to previous printing emissions with no engineering controls present (peaks at 450,000 #/cm^3). The workroom's general ventilation was approximately 10 ACH. This high amount of air changes may affect the emissions' removal capability of the arm hood, and, thus, the difference in emission removal is only minor when introducing the arm hood. Quite importantly, this level of controls leads to reduction of the 15 min UFP concentration, below the 80,000 #/cm^3 threshold. Thus, overall process safety is greatly benefited. On the other hand, emission peaks are still observed (Figure 9), therefore, the use of PPE is vital in this process setup as well. Moreover, size distribution analysis results from *SMPS* (Figure S10) indicate that there is a significant difference in particle size distribution before printing and during the print activity. The size distribution of the emitted particles (Figure 10) remained close to what was seen in the first experiment (Figure 8), showing that there is no size dependence in particle removal potential with or without the presence of engineering controls (local and general ventilation).

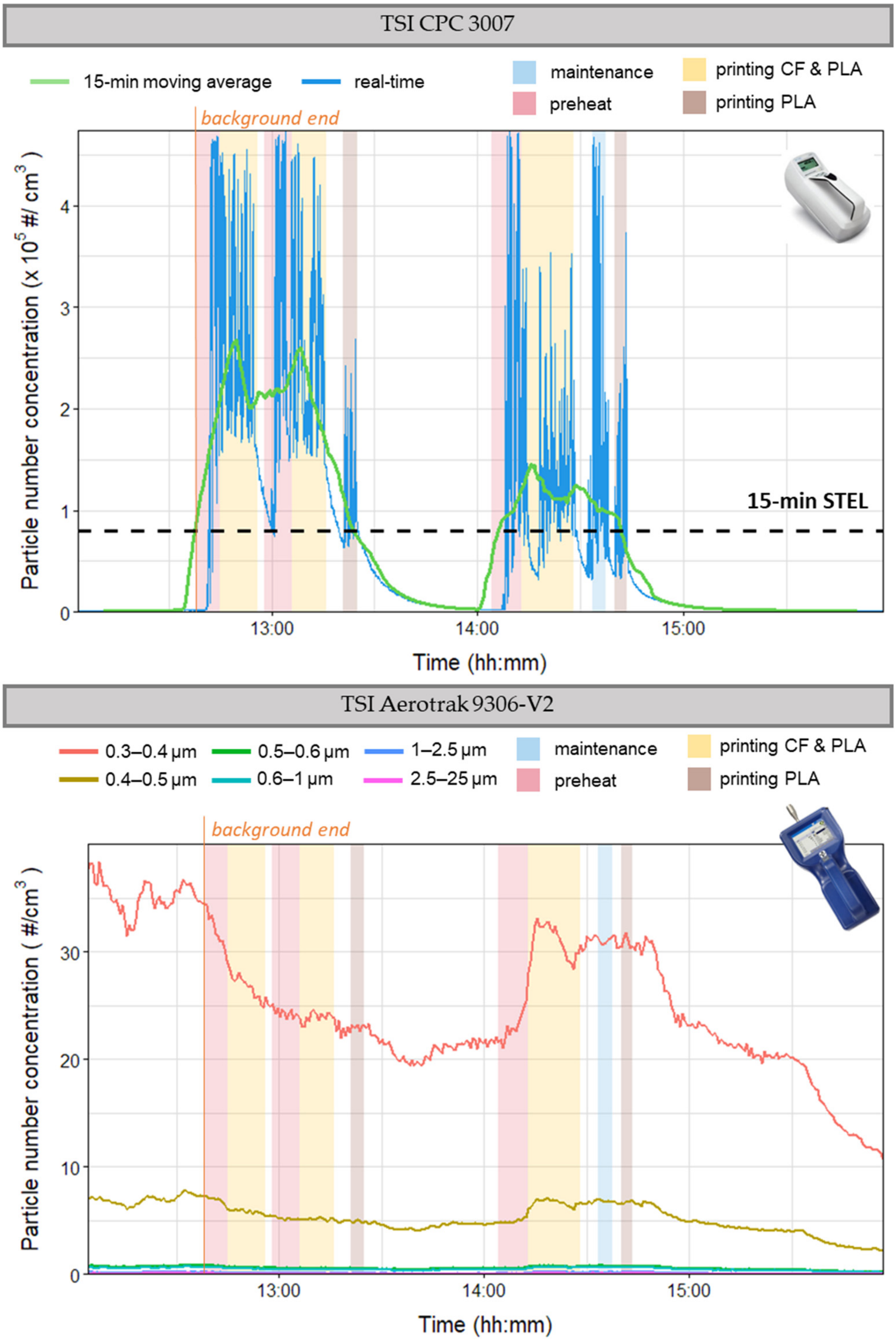

Figure 7. Particle concentrations for Case 4a.

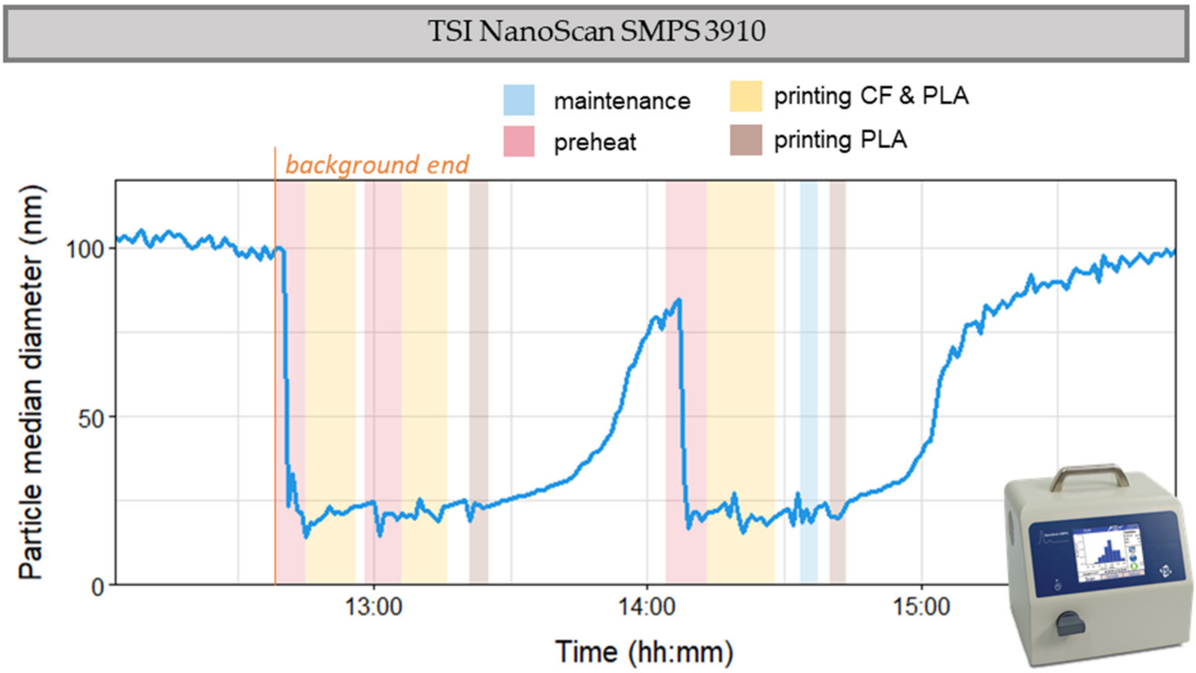

Figure 8. Median particle diameter for Case 4a.

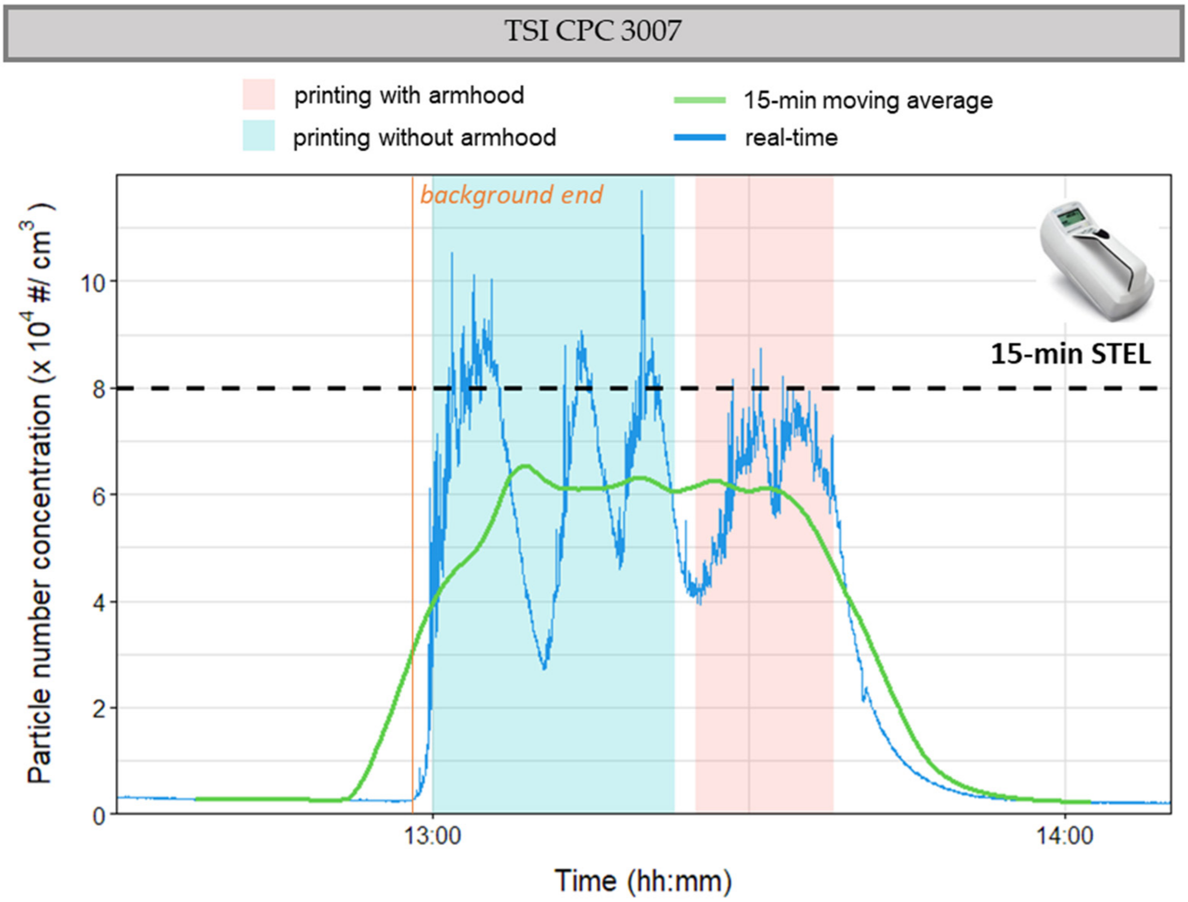

Figure 9. Particle concentrations for Case 4b.

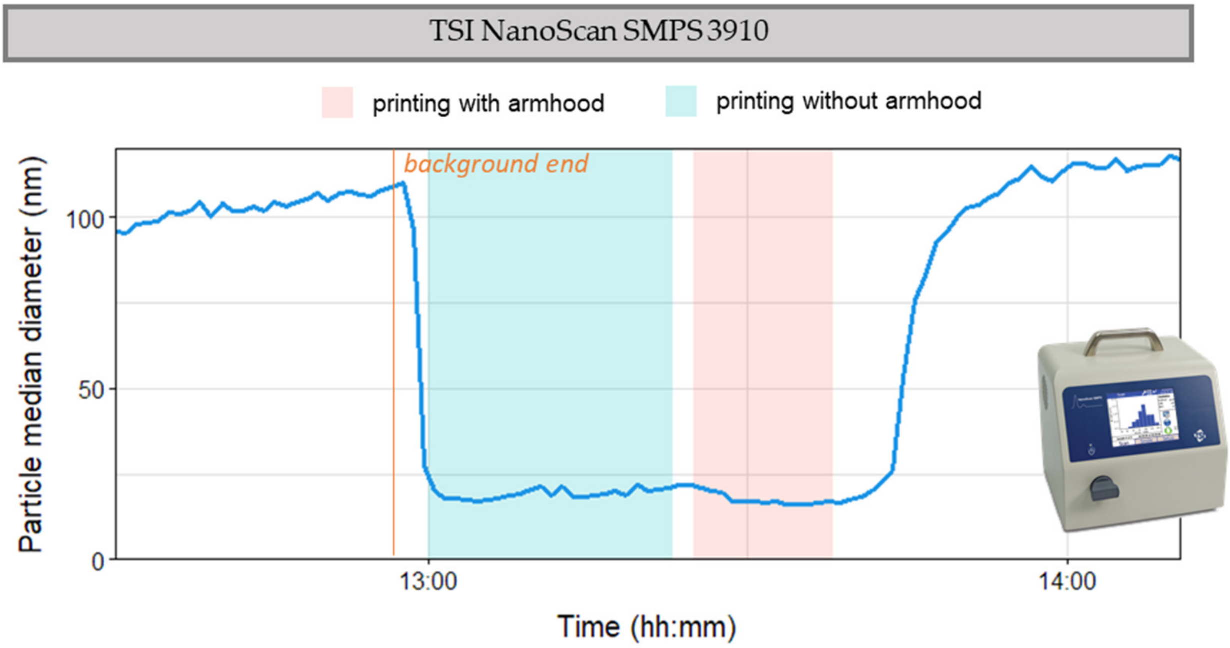

Figure 10. Particle size distribution for Case 4b.

4. Discussion

4.1. UFP Emissions

Analysis and interpretation of the findings, in cross-evaluation with process requirements as described by the process operators, led to several practical conclusions on the emission profile of the processes, as well as safety recommendations. Three-dimensional printing has been researched for UFP emissions during the various process phases and the use of enclosure and well-ventilated areas has been recommended as control measure [34]. Based on our study, filament loading and print start were the main causes of increased particle concentrations (Figures 2–5, 7 and 9) comprising of various particle sizes (Figures S9 and S10). It should be noted that for both of these events, the enclosure is open and an operator has to be present. While loading and unloading a filament, operators remove the enclosure cap in order to get access to the extruder. When a new print starts, a small amount of filament is purged, and the operator opens the enclosure door to remove it. Hence, the operator is potentially exposed to emitted particles at the initialisation phase of the 3D printing process.

As outlined by Zhang et al., the emitted particles are formed from the condensation of the volatile compounds during heating of the polymeric filament (nucleation) and subsequent particle growth and/or agglomeration reaching larger sizes [16]. Several studies report the emission of particulate matter for a variety of common filaments, such as ABS, PLA, Nylon, etc., showcasing that the emission profiles are dependent on the filament material due to the emission of different volatile compounds, as well as the process steps and the process conditions [17,37,47]. Stephen et al. pioneered the work on UFP emission measurements during 3D printing of ABS and PLA at different configurations exploring the effect of filament material and number of printers in UFP emission levels [37]. Similarly, Azimi et al. studied the UFPs and VOCs emissions from nine different filaments (including plastic materials and brick) using commercial 3D printers, showing that emissions are correlated to the printing material and the printing conditions, recommending relevant control measurements to mitigate exposure [46]. Due to the enhanced properties of the CFRPs, researchers have investigated the printability of different fibre-reinforced polymers [48,49]; however, the relevant occupational exposure studies are still lacking. Correlating the UFP emission with the process steps, the highest levels are generally observed near the start of printing processes, which is consistent with our findings. Concentrations gradually drop off as clearance rates (deposition, removal or agglomeration) surpass emissions [37].

For Case 3, purging was the main emission event, leading to concentrations of 110,000 #/cm^3, which were over twice as high as those for other instances within the same measurement cycles (Figure 5). Proper ventilation in the occupied spaces can be estimated based on the air changes per hour according to the Industrial Ventilation Standard for proper control of the occupational risk [50]. While for all measurements, the average concentration of UFP remained under the recommended 8 h TWA threshold of 40,000 #/cm^3 (Section 2.4), the 15 min threshold of 80,000 #/cm^3 is exceeded in Case 1 (Figure 2) and 4a (Figure 7), often for prolonged periods of time, close to 1 h; therefore, these peaks cannot be considered short time events. Therefore, proper control actions should be considered and implemented in the unvented and unfiltered indoor environments to mitigate the risks from the operation of 3D printers. This was successfully showcased in Case 4 (Figures 7 and 9), where the increase of the general ventilation to 10 ACH led to the reduction of the emission peaks from 450,000 #/cm^3 to ~100,000 #/cm^3. An additional minor exposure mitigation effect was achieved through the addition of a local exhaust unit (Figure S6).

With regard to the emission of particles in the sub-micron size, this has been demonstrated in the literature, although not as commonly as UFP emissions. Zhu et al. have reported the emission of significant concentrations of particles in the 0.25 µm to 0.28 µm size range, from ABS filaments. The authors recorded concentrations of airborne particles within the 0.25–32 µm sizes, showing that emissions for particles of sizes larger than 0.375 µm were very low. It is interesting to note that the study results showed increased concentrations further away from the printer, and the authors attributed this to a possible mechanism of primary ultrafine particle emission growth and coagulation [51]. Agglomeration of primary ultrafine particles initially emitted from the printing process to form larger particles has also been demonstrated by Youn et al. [36], while Yi et al. have argued that UFPs emitted by materials such as ABS display an increased tendency for agglomeration [52]. In another study, Seeger et al. have demonstrated that specific filament types, including ABS, can indeed produce emissions of particles in the 0.3–0.6 µm size range, although the emission rates were quite considerably lower (less than 1 per mil fraction) when compared to the ultrafine particle emission rates [53]. In the measurements of the present study, a definitive and conclusive trend on the sub-micron particle concentrations is not observed. In Cases 1 (Figure 2) and 3a (Figure 4), no concentration upsurges connected to the process steps are detected for sub-micron particles. In Case 3b (Figure 5), a similar pattern of concentration increase is observed for particles of 0.3–0.4 µm size, and to a lesser extent for sizes 0.4–1 µm, when compared to the timing of the ultrafine particle concentration upsurge. The purging and print start events could be the source of emissions for such larger particles, or the primary UFPs may rapidly agglomerate to form sub-micron particles. In Cases 2 (Figure 3) and 4a (Figure 7), concentration fluctuations for sub-micron particles are observed; however, they are not directly connected to any specific process step.

In terms of materials, it has been shown in this work that CF-reinforced filaments present the potential for causing significant exposures to UFP. Distinctive elements of the specific device, such as the purging phase of the *Markforged* can be a decisive factor for the exposure potential. On the other hand, employing more than one printer simultaneously within the same workroom is a definite indicator of higher exposure risk [37]. While printer enclosures are an important exposure mitigation factor, it is shown that specific materials, such as the TPU and CF-reinforced TPU studied in this work, may need to be printed without a full enclosure in place, negating any exposure protection effects. The modification of commercial 3D printer devices, which may be applied to introduce new functionalities, may lead to unpredictable changes in the exposure potential. A set of case-specific exposure assessment measurements is highly assistive in determining the exposure potential of the conventional and modified print processes. As seen in this work, the measurements can also confirm the exposure mitigation potential of any updated control schemes applied to reduce the exposure. All these cases consist of typical process setups that may be applied within a modern polymer 3D printing workplace, which manufactures parts for a variety of purposes. A flexible and modular strategy to address these exposures is recommended.

4.2. Hierarchy of Controls to Mitigate UFP Occupational Exposure

UFP concentration may vary temporary and spatially due to the emission source characteristics and the air exchange rates in the room [54]. In order to minimize exposure, it is preferable that operators monitor the process remotely and only enter the room when necessary. If an operator has to remain in the printer room for more than a few minutes, when performing such high-output processes with two printers operating, the use of a high efficiency respirator is recommended, as well as an air purifier for the removal of the UFPs [55]. Additional caution is suggested when the enclosure must remain open for the entire printing process and in synchronized filament load/print starts in multiple printers in the same workplace. Following the Hierarchy of Controls scheme (described in ISO 45001:2018 [56]), the action steps should be considered in order to minimise the exposure to UFP, such as proper ventilation system and use of sealed enclosure, installation of air cleaner in the operating room with the 3D printer. These engineering controls should be applied as priority controls. When further exposure mitigation is required, use of proper personal protective equipment, as well as periodic health examinations [57,58] is recommended, after engineering control options have been exhausted. A detailed Safe-by-Design scheme for FFF, based on the Hierarchy of Controls, has been presented in our earlier work [10]. The limitations introduced by exposure controls need to be evaluated as to prevent any conflict between the process and its safe execution. Furthermore, the impact of ventilations systems in the general airflow of the room should be examined in order to minimize the dispersion of emitted hazardous substances in the workroom. Park et al. evaluated the location of the installed ventilation system on the exposure to UFP during FFF printing, showing that ventilation studies should be performed on case-by-case basis [59]. Improper implementation of controls may lead to increased exposure and create a misleading perception of safety as showcased in Case 3b (Figure 6). The incorrect use of air purifiers or general dilution ventilation schemes may lead to increases in the exposure. For installations of such systems, expert consultation should be sought. Alternatively, the basic set of rules for general dilution ventilation should be followed at a minimum. These include [60]:

- Positioning exhausts or air purification devices as close to emission sources as possible
- Setting up ventilation configuration to position employees upwind of the dilution zone
- Using auxiliary fans to circulate air evenly across the room
- Adding make-up air (fresh, uncontaminated tempered air from outside the workspace) to replace existing air that cannot be recirculated in places where it will be most effective

Collectively evaluating the results of the various cases of this work, it can be observed that the different print processes display quite important variation in the ultrafine particle exposure potential. A thorough comprehension of this variability is crucial for a 3D printing workplace since the safety system applied can be adapted to account for these details. Following the Hierarchy of Controls and previous literature studies, relevant recommendations can be included to mitigate the exposure risks in a case-by-case basis in our study. Quite importantly, as shown from the Case 3a study, the purging process does not produce an output that ought to be monitored in terms of quality, as opposed to initial prints and pre-print purging. Therefore, this is a process sub-phase in which exposure can be avoided relatively uncomplicatedly. It is recommended that the process is remotely monitored to the extent that this is reasonably practicable. If the initial purging phase needs to be manually monitored, we recommend high efficiency respiratory protection (FFP3) since engineering controls are inapplicable in this stage. Furthermore, in case of constant operator presence, engineering controls and use of PPE is critical. Considering Case 4, operating the process through the setup described in this work necessitates the use of engineering controls (design and optimisation of general ventilation and local ventilation), as well as the use of an enclosure, which can lead to significant exposure mitigation [61].

4.3. Research Barriers and Potential for Further Work

As described earlier in this study, the aim was to present a set of case studies corresponding to a workflow that is representative of a typical work schedule for a 3D printing workplace performing prints of multiple material types and parts. The scope of the study entails a set of intrinsic limitations.

An important characteristic of this study is that no examination of the effects of nozzle temperature modifications or other types of print parameter (e.g., speed, layer height) changes took place in terms of the impact on the exposures, as commonly investigated in the 3D printing emission literature [62,63]. This was due to the fact that the investigation was centred on the workplace and its diverse set of 3D print devices and processes rather than focusing on a specific material and discussing its emission potential. The concept of assessing emission potential of material alternatives, as well as the impact of print parameters on the emissions, and the integration of the various tests in a methodology has been applied and discussed in our previous research work [64].

Similarly, another limitation was that repeatability of experiments was not examined. However, this has not yet been explored extensively in the literature, with studies typically presenting one instance of exposure measurements per case [29,33,34,37]. In some cases, there are multiple events occurring that may influence emissions during the measurement cycles, such as opening the print chamber door [65]. It is impractical to perform these tasks in the same order and time in additional experiments. In some studies, print errors/malfunctions occur, which are not reproducible, but crucial to be documented in terms of the impact they cause on emissions [29,33]. This repeatability hindrance is reflected in other areas of nanosafety, where there are difficulties to be encountered in reproducing the exact conditions in multiple experiments, especially in exposure campaigns of more complex processes that may include several process steps [66]. Additionally, with respect to the present study, it should be considered that the aim was to characterize the set of different processes taking place in the workplace as part of their production goals.

An additional limitation factor is that the examination concluded in Tier 2 of the protocol. This means that Tier 3 measurements, which would include collection of workplace air samples and characterisation of the particles retained (e.g., SEM) was not performed. This would be highly significant in this particular study, given that the previously unexplored CF-reinforced materials were studied. The Tier 3 examination would define whether CF fragments or particles containing CF fragments are emitted. It could also reveal whether any potential alteration in emitted particle morphology occurs (e.g., emission of higher aspect ratio particles, agglomerates, etc.).

Furthermore, as seen through Cases 3 and 4, application of controls to mitigate exposure to the emitted particles does not always show the results or the effectiveness that may be expected. This consists of a limitation in presenting a full exposure control strategy within the scope of this work. Future research work can focus on evaluating and comparing the efficiency of these different control strategies (e.g., arm hoods, dilution ventilation of various types, different air purifiers). This would facilitate understanding and adopting of these safety strategies from the part of the industry.

Quite importantly, the basis on which the exposure risk is being evaluated in this work is a nanotechnology-derived exposure threshold because no UFP exposure limits are applicable as of yet. Although this is the only relevant basis upon which to structure an exposure assessment, it is reasonable to argue that exposure limits should certainly take into consideration the type of material being printed, as well as the additive particle/agent. A fixed exposure threshold for UFP seems misrepresentative, given the extensive variety of thermoplastic materials being used for FFF 3D printing. This could be an area in which the emission/exposure research could make progress in the coming years, presenting high value and practicality for the 3D printing industry.

5. Conclusions

FFF 3D printing is a common manufacturing technique in the contemporary workplace. It, however, entails UFP exposure hazards, the quantification of which requires specific expertise and instrumentation. In this work, different FFF 3D printing process setups were examined, and their exposure profile was analysed and discussed, showcasing the exposure to particulate matter below 300 nm up to 4.5×10^5 #/cm^3. It is shown how a targeted response is required for each case in terms of safety. At the same time, the correct application of engineering controls was confirmed to result in exposure mitigation even for high-emitting processes, while inappropriate application of controls can lead to a misguided perception of process safety. Additional experiments in a control environment would provide vital insight on the UFP release mechanisms for the appropriate FFF process design and the required control systems. Exposure measurement campaigns similar to the present study can be the fundamental building block towards developing effective safety infrastructure within 3D printing workspaces, and, thus, ensuring the safe application of this highly promising technology.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/jcs6050119/s1, Figure S1: Detectable size ranges per instrument; Figure S2: Illustration of the Instrument configuration for Case 1; Figure S3: Illustration of the Instrument configuration for Case 2; Figure S4: Instrument setup for Case 3; Figure S5: Measurement setup for Case 4a; Figure S6: Measurement setup for Case 4b; Figure S7: 3D printer modified toolhead; Figure S8: Plexiglass Enclosure extension; Figure S9: Particle size distribution for Case 4a; Figure S10: Particle size distribution for Case 4b.

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Abbreviations

ACH	Air Changes per Hour
ALARP	As Low As Reasonably Practicable
ANSI	American National Standards Institute
CF	Carbon Fibre
CFRP	Carbon-Fibre-Reinforced Polymers
CNT	Carbon Nano-Tube
CoPA	Copolyamide
CPC	Condensation Particle Counter
DNA	Deoxyribonucleic Acid
FFF	Fused Filament Fabrication
FFP	Filtered Facepiece Respirator
HEPA	High Efficiency Particulate Air Filter
ISO	International Organization for Standardization
NEAT	Nanoparticle Emission Assessment Technique

NIOSH	National Institute for Occupational Safety and Health
OECD	Organisation for Economic Co-operation and Development
OEL	Occupational Exposure Limit
PA	Polyamide
PETG	Polyethylene Terephthalate Glycol
PLA	Polylactic Acid
PPE	Personal Protective Equipment
ROS	Reactive Oxygen Species
SMPS	Scanning Mobility Particle Sizer
STEL	Short-Term Exposure Limit
STOP	Substitution, Technical, Organisational, Personal protective equipment
TPU	Thermoplastic polyurethane
TWA	Time-weighted Average
UFP	Ultrafine Particles
UL	Underwriters Laboratories
VOCs	Volatile Organic Compounds

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