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The Chartered Society for Worker Health Protection

OXFORD

# Workplace Exposure Measurements of Emission from Industrial 3D Printing

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### Abstract

Particle and gaseous contaminants from industrial scale additive manufacturing (AM) machines were studied in three different work environments. Workplaces utilized powder bed fusion, material extrusion, and binder jetting techniques with metal and polymer powders, polymer filaments, and gypsum powder, respectively. The AM processes were studied from operator's point of view to identify exposure events and possible safety risks. Total number of particle concentrations were measured in the range of 10 nm to 300 nm from operator's breathing zone using portable devices and in the range of 2.5 nm to 10 µm from close vicinity of the AM machines using stationary measurement devices. Gas-phase compounds were measured with photoionization, electrochemical sensors, and an active air sampling method which were eventually followed by laboratory analyses. The duration of the measurements varied from 3 to 5 days during which the manufacturing processes were practically continuous. We identified several work phases in which an operator can potentially be exposed by inhalation (pulmonary exposure) to airborne emissions. A skin exposure was also identified as a potential risk factor based on the observations made on work tasks related to the AM process. The results confirmed that nanosized particles were not measured from the workstation air thanks to the closed system and suitable risk control procedures. Still, handling of metal powders and AM materials that can act as skin irritants such as epoxy resins were found to pose a potential risk for workers. This emphasizes the importance of appropriate control measures for ventilation and material handling that should be addressed in AM operations and environment.

Keywords: additive manufacturing; gas-phase compounds; industrial printers; nanoparticles; occupational health

### What's Important About This Paper?

This study considered the user perspective to identify exposure events and possible safety risks from additive manufacturing (AM) machines. Specific work phases resulted in potential inhalation exposure to nanosized particles, and dermal exposures to metals and epoxy resins. Control measures for ventilation and materials handling should be addressed in AM operations and work environments.

# Introduction

Additive manufacturing (AM), more popularly known as 3D printing has been in industrial use since 1990s (Kruth, 1991; Wohlers, 2020). The term AM is used in industrial scale manufacturing and 3D printing is often used in case of affordable desktop printers (ISO/ASTM, 2021). AM is a group of technologies where 3D objects are built by adding layers on top of each other (Gibson *et al.*, 2010). AM is emerging as a general-purpose technology akin to computers and electric drives (Akmal *et* 

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*al.*, 2022). It is used in a plethora of applications from simple prototypes to end-use parts such as jet engine parts and dental devices (Yan and Gu, 1996; Akmal *et al.*, 2018, 2020; Kamal and Rizza, 2019; Wohlers, 2020; Salmi, 2021). With popularity of desktop 3D printing rising, there has been significant attention and publicity for this technology (Schelly *et al.*, 2015; Kukko *et al.*, 2020). Questions about occupational health issues have risen both with desktop 3D printers but as well as in industrial AM environments (Chan *et al.*, 2018; Roth *et al.*, 2019; Stefaniak *et al.*, 2021).

Today, there are several different AM techniques and materials available in the market. Here, we concentrated on three techniques commonly used in an industrial setting, namely powder bed fusion (PBF), material extrusion (MEX), and binder jetting (BJT). PBF uses a laser or an electron beam to fuse material together in a powder bed. A blade or roller will then bring a new layer of powder and a laser will fuse this layer. This is then repeated until the whole part is printed (ISO/ASTM, 2021). The materials used in this method are generally different polymers and metals (Wohlers, 2020). When metal powder parts are printed it takes place in a vacuum or inert atmosphere consisting of argon and nitrogen. MEX is commonly used in desktop 3D printing, but it is also utilized in industrial applications. In this method, thermoplastic material filament goes through a heated extrusion system, which moves to create geometries layer by layer (ISO/ASTM, 2021). This method typically uses plastic filaments such as acrylonitrile butadiene styrene (ABS) and polylactic acid (Bumgarner, 2013; Stephens et al., 2013). However, material options for desktop 3D printers have increased lately. The new materials include several plastic materials, polyether ether ketone PEEK, Nylon, soft rubber-like materials, composite materials, and biodegradable materials (Wohlers, 2020). In BJT, a roller or blade brings one layer of powder, into which binding agent is applied to the relevant area by inkjet head (ISO/ASTM, 2021). This is then repeated until the whole object is ready and can be cleaned up from the extra powder. The materials used with this method are gypsum powder, sand, and metals (Gibson et al., 2010). There is no need for separate support structures as the powder supports the part. This method often requires secondary processes such as debinding, sintering, and infiltration.

Literature related to occupational health issues of AM has concentrated on affordable desktop 3D printers, which usually use the MEX method (Stefaniak *et al.*, 2021). These studies have shown that the desktop 3D printers emit especially nanoparticles (particles with diameter below 100 nm) (Stephens *et al.*, 2013; Kim *et al.*, 2015; Azimi *et al.*, 2016; Yi *et al.*, 2016; Mendes *et al.*, 2017). Emissions of nanoparticles are shown to be strongly dependent on the printing material (Stephens et al., 2013; Steinle, 2016; Mendes et al., 2017; Poikkimäki et al., 2019) and also to some extent, on the color of the filament (Yi et al., 2016). It has also been shown that an increase of the nozzle temperature increases the emission of the nanoparticles (Deng et al., 2016; Mendes et al., 2017; Poikkimäki et al., 2019) as well as malfunctioning of the 3D printer. To this end, jammed filament in the heated extruder nozzle can increase emissions (Yi et al., 2016; Mendes et al., 2017). However, exposure to gaseous and particulate contaminants in other AM methods has gained less attention (Runström Eden et al., 2022; Stefaniak et al., 2021). Exposure to particles and volatile organic compounds (VOCs) has been studied during PBF and BJT (Afshar-Mohajer et al., 2015; Graff et al., 2016; Mellin et al., 2016; Ljunggren et al., 2019; Väisänen et al., 2019; Zisook et al., 2020; Runström Eden et al., 2022). These studies showed that there exists notable exposure to contaminants not only during the 3D printing but especially during pre- and post-processing phases.

Nanoparticles are suggested to cause adverse health effects such as pulmonary and cardiovascular diseases, cerebral toxicity, genotoxicity, and cancer (Savolainen et al., 2010), but not all the effects are yet known. Effects to the health depend on toxicology of the nanosized compound i.e. effected by different factors, e.g. size, surface chemistry, shape, protein absorption gradient, and surface smoothness or roughness (Sharifi et al., 2012). Thus, it is not appropriate to consider nanoparticles only as a homogeneous group, when assessing the risk to the worker. Measurements of urine metals indicated that AM operators had a higher body burden of the metals present in the metal powder than the office controls (Ljunggren et al., 2019). During the use of polymer-based AM some health effects such as asthma and allergic rhinitis have been reported (House et al., 2017; Chan et al., 2018). Now, there are healthbased occupational exposure limit values (OELVs) only for few types of nanoparticles (i.e. engineered nano-TiO<sub>2</sub>, carbon nanotube [CNT], and carbon nanofiber [CNF]) which sets a challenge for risk assessment. Therefore, some precautionary principle-based nano reference values (NRVs) have been given for engineered nanoparticles (SER, 2012).

Different AM methods cause different chemical emissions, depending on both the fusion method and the materials used (Roth *et al.*, 2019; Stefaniak *et al.*, 2021), which may be harmful. This raises the occupational hygiene question, are operators exposed to contaminants during the AM process and to what extent? To determine this, we measured particles and selected gaseous thermal decomposition contaminants from the workstation and nanoparticles from the operator's

breathing zone. Nanoparticles in this study refer to incidental and unintentionally generated nanoparticles. These should not be misinterpreted as engineered nanoparticles. We focused on three different industrial scale AM technologies: PBF, MEX, and BJT (ISO/ ASTM, 2021) in three different work environments.

## Methods

### Measurement sites

The study was conducted in three different workplaces (WPs) that utilized altogether four different industrial AM machines (Table 1). Particles and selected gaseous thermal decomposition contaminants were studied from the workstation and nanosized particles from the operator's breathing zone during process-related work tasks. In all WP, general ventilation was mechanical. During the measurements, AM processes were almost continuous and only short breaks occurred between manufacturing periods. There were no other particle emitting processes occurring in the AM rooms simultaneously.

### Instrumentation and measurement locations

The location of the measurement locations, the purpose of the measurement, the equipment used for the measurement, and the measured contaminants measured are presented in Table 2. Particles were measured with a water-based condensation particle counter (N-WCPC3788, TSI Inc.) and similarly, nanoparticle size distribution (5.5–350 nm) with a Scanning Mobility Particle Sizer (SMPS+C, series 5.400, Grimm Aerosols GmbH, Germany). Fine and coarse particles were measured with optical particle counters, size range 0.265–31 µm with DustMonitor 1.109 (Grimm Aerosol GmbH, Germany) and 0.3–10 µm

with OPS3330 (TSI Inc.). Selected gaseous contaminants that are carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), and concentration of VOCs were also measured. CO<sub>2</sub> concentration was measured with generic measurement indicator (MI70 with a probe GMP70, Vaisala, Finland) and similarly, CO with Dräger gas detector (X-am 5600 with Dräger Sensor® XXS CO, Dräger Safety, Germany). Photoionization detector (ppbRAE3000 PGM 7340, RAE Systems Inc.) with a UV-lamp (10.6 eV) was used to measure nonspecific total concentration changes of VOCs. VOCs were also sampled for laboratory analysis with the flow of 0.1 l min<sup>-1</sup> into Tenax TA Carbograph 5TD absorbent tubes in WP1 and WP3. Samples were analyzed with a gas chromatograph using a thermodesorption mass selective detector. Qualitative analysis of chemical compounds was determined using Wiley and NIST mass spectral libraries and pure reference substances.

Stationary measuring points were placed close to the AM machines at the height of approximately 1.5 m from the floor. No significant air flows were directed, nor any work activities occurred in close proximity to the stationary measuring points. The stationary measuring points represented the general concentrations in the AM process rooms. The distance to the nearest AM machine was less than 3 m. The particle concentration of incoming air was measured in front of the supply air terminal. The measurement point was considered to represent the background reference air originating from the outdoors through the filtration. Sampling lines were used only when absolutely necessary. The length of the sampling line was kept as short and straight as possible to avoid particle losses and was a maximum of 1.6 m for all measuring points. Conductive tubing lines were used. It was ensured that no bends formed in the sample line. The line losses of

Table 1. Measurement sites and AM	technologies in use at each site.
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Workplace	Area of AM room	AM machine	AM technique and fusion temperature	Materials
WP 1, university research laboratory, mechanical general ventilation	16 m × 8 m ×4 m	2 printers in use, enclosed, not venti- lated, several other printers in same room but they were not used during measurement times	BJT (zprinter 450) ~50 °C MEX (uPrint SEPlus) ~300 -310 °C	Gypsum powder and acrylonitrile- butadiene styrene (ABS)
WP 2, commercial company, mechanical general ventilation	11 m × 6 m × ~ 3 m	3 printers, enclosed, integrated ven- tilation, AM process takes place in a gas atmosphere	PBF (EOS M 290 DMLS printers) ~1700 °C	metals (titanium alloy)
WP 3, commercial company, mechanical general ventilation	6 m × 3 m × 3 m	2 printers, enclosed, integrated ven- tilation, a broken exhaust air pipe in the one AM-machine was found during measurements	PBF (EOSINT P380 and P350 printers) ~100 - 230 °C	plastic polymers PrimeCast® 101, PA2200 (polystyr- ene, polyamide)

Measuring point	Location	Purpose	Contaminant	Equipment
Back- ground	Measured at front of the sup- ply air terminal	The particle concentration of incoming air. Rep- resent the incoming air originating from the out- doors through the filtration	Particle number concentra- tion 5.5–350 nm	SMPS+C, series 5.400, Grimm Aero- sols GmbH, Germany
			Particle number concentra- tion 265 nm to 31 µm	DustMonitor 1.109, Grimm Aerosol GmbH, Germany
			CO <sub>2</sub>	MI70 with a probe GMP70, Vaisala, Finland
			VOC	MiniRAE 2000 PMG-7600 (10.6 eV), RAE Systems Inc.
Stationary	Close to the AM machine at the height of 1.5 m	Represent the general concentrations in the AM process room	Particle number concentra- tion 2.5 nm to 3 µm	N-WCPC 3788, TSI Inc.
			Particle number concentra- tion 300 nm to 10 µm	OPS3330, TSI Inc.
			CO <sub>2</sub>	MI70 with a probe GMP70, Vaisala, Finland
			СО	X-am 5600 with Sensor® XXS CO, Dräger Safety, Germany
			VOC	ppbRAE3000 (10.6 eV), RAE System Inc.
			VOC in WP1 and WP3	Tenax TA Carbograp 5TD with 0.1 l min <sup>-1</sup>
Worker breathing zone	Worker chest/ shoulder	Personal exposure	Particle number concentra- tion 10–300 nm, average par- ticle size, theoretical LDSA <sup>a</sup>	DiSCmini, Testo AG, Germany
			10 nm to 10 μm theoretical LDSA <sup>b</sup>	PartectorTEM, NANEOS, Switzerland

<sup>a</sup> Fierz *et al.* (2011).

<sup>b</sup> Fierz *et al.* (2014).

particles were not corrected. Further, blank zeros and inlet air flows were verified prior to the measurements for online particle measurement instruments.

Measuring time varied from 3 to 5 days and was divided between working and non-working hours. An 8-h time-weighted particle concentration was calculated from stationary measuring point to determine particle concentration inside AM room during daytime. All AM-related work phases that required an operator presence were performed on working hours. Similarly, a 16-h time-weighted average particle concentration was calculated outside working hours to indicate concentration levels inside AM room in a circumstance different from daytime. Outside working hours (non-working hours), the AM process continued automatically without operator supervision.

European standard EN689 recommends personal sampling for exposure measurements (European Committee for Standardization, 2018). Therefore, to obtain the operators' personal exposure during different AM-related work tasks, particle number and lung deposited surface area (LDSA) concentrations were measured from operator's breathing zone with portable diffusion size classifiers, i.e. DiSCmini (Testo AG, Germany) with measurement range 10-300 nm and PartectorTEM (NANEOS, Switzerland) with measurement range 10 nm to 10 µm. The portable instruments were placed on the operator's belt or a backpack and the sample inlets were mounted on the operator's chest (i.e. breathing zone) with Tygon<sup>®</sup> sampling line. The process required the presence of the operator only during working hours, thus all operator's personal exposure measurements were conducted during working hours. The duration of the operator's work tasks varied between 2 and 158 min. This was considered for assessing the exposure. An institutional ethics review was conducted for the study.

#### Description of AM-related work tasks

The AM process included several work phases. Here, the AM process was divided to different work phases illustrated in Fig. 1. Service and repair were not needed during the measurement periods.



Figure 1. Work phases including tasks relating to AM process from operator's exposure point of view.

Work phases started from the preparation, which included inspecting the AM machine, adding or changing used material and especially for MEX, waiting for the printer nozzle/printing chamber to warm up. With PBF and BJT techniques, preparation phase included also preparing the powder bed, which was depended on the AM technique used. With BJT the powder adding was not necessary, but with PBF the bulk material was added into cassettes by scooping or vacuuming from closed vessels. Preparation phase required the presence of operator. The AM phase itself was automatic and required only couple of checks from operator since the process operated without problems.

The post-processing phase was the most laborious part of the AM process for producing end-use parts. In case of the MEX post-processing, the AM object was manually removed from the build platform. The support structures were removed mechanically with a chisel and then washed in a washer. The build support structure broke into several pieces during removal, but no visible dust formed. In the post-processing of BJT, the AM object was also removed manually from the printer. Unfused gypsum powder was vacuumed and the surface treatment was applied manually with chemicals such as epoxy resins and cleaning solution for to harden and brighten the BJT-fabricated object. In metal PBF, the manufactured object was fused to the build platform and wire cutting (electrical discharge machining) was used to remove the object from the build platform and to remove support structures. The wire cutting was not included in this study. With plastic PBF, the loose powder supported the object and no external supports were needed for heat sink that are required for metal PBF. The extra powder was removed with suction, a brush or compressed air blow. The manufactured object was finished with sandpaper in front of a localized exhaust ventilation system.

Maintenance for all three techniques included cleaning of the machine. Cleaning contained vacuuming inside the AM machine, wiping with alcohol, and visual nozzle inspection. Vacuuming was used especially in PBF. For PBF and BJT, re-use and recycling of the material were normal maintenance tasks which also occurred in this study.

The workers at all sites were wearing working clothes. The use of protective gloves varied between work tasks. The gloves were mainly used during the handling of post-processing chemicals. When metal powder was handled in WP2, protective clothing (Tyvek coverall) and a respirator with hood and particle filters were used.

## Results

### Particle concentrations in the AM workspace

During the measurements, AM processes were almost continuous. Only short breaks occurred between manufacturing periods. The exact particle concentrations in the AM rooms of WP2 and WP3 are presented in Supplementary Table S1 (available at *Annals of Work Exposures and Health* online) for further information. The data from WP1 were only partially usable and not shown in the table.

In WP1, a university research laboratory using both MEX and BJT, the nanoparticle data from stationary measurement point placed in the AM process room was not valid due to instrument malfunction. In this case, only background concentration was measured. The average background concentration of nanoparticles was  $2.2 \times 10^3$  cm<sup>-3</sup> during working hours and  $9.1 \times 10^3$ cm<sup>-3</sup> during non-working hours on 3 days measurement period. During the working hours, the background concentration was very low indicating good filtration of the incoming air. The higher particle concentrations during non-working hours were most likely due to the mixing of room air at the measuring point, as the ventilation rate was decreased after working hours. The same phenomenon was also observed with fine particles. The background concentration of fine particles increased as well from 24.2 to 51.5 cm<sup>-3</sup> after working hours on 3 days measurement period.

In a commercial company WP2, where metal objects were manufactured with PBF, the higher nanoparticle concentration was measured during working hours than after a workday. The average nanoparticle concentration varied from  $6.2 \times 10^3$  to  $15.8 \times 10^3$  cm<sup>-3</sup> during working hours and from  $3.4 \times 10^3$  to  $13.1 \times 10^3$ cm<sup>-3</sup> during non-working hours in the AM room. The corresponding background nanoparticle concentration varied from  $7.3 \times 10^3$  to  $18.8 \times 10^3$  cm<sup>-3</sup> and from  $4.9 \times 10^3$  to  $9.2 \times 10^3$  cm<sup>-3</sup>, respectively. Nanoparticle concentration measured from the AM room followed nicely the concentration measured from the background (Fig. 2a) in WP2. The AM room concentrations were relatively low and close to the background concentrations indicating that there were no strong indoor sources for particles. In this study, the highest average fine particle concentration was measured in WP2, where concentration during working hours varied from 20 to 50 cm<sup>-3</sup> and from 20 to 120 cm<sup>-3</sup> during non-working hours in the AM room. At the same time, the background concentration decreased comparatively from 10 to 40 cm<sup>-3</sup> during working hours and from 10 to 30 cm<sup>-3</sup> during non-working hours. There was an increase in the fine particle concentration in WP2 during third measurement day which was due to the maintenance work phase performed inside the AM room (Fig. 2b).

In a commercial company WP3, where PBF technique was used to print plastic objects, the highest nanoparticle concentration was measured in AM process room after one workday. The average nanoparticle concentration measured were from



**Figure 2.** Nanoparticle (a) and fine particle (b) concentrations in WP2 measured from the AM room (black line) and from the background (gray line). Water-based condensation particle counter N-WCPC3788 measures particles in the size range from 2.5 nm to 3 µm. Scanning Mobility Particle Sizer SMPS+C measures particles from 5.5 to 350 nm. Optical particle counters OPS3330 measures particles from 300 nm to 10 µm and DustMonitor 1.109 from 265 nm to 31 µm.

 $9.5 \times 10^3$  to  $30.0 \times 10^3$  cm<sup>-3</sup> during working hours and from  $6.8 \times 10^3$  to  $84.9 \times 10^3$  cm<sup>-3</sup> during non-working hours in the AM room. At the same time, the average background particle concentration varied from  $2.8 \times 10^3$  to  $11.6 \times 10^3$  cm<sup>-3</sup> during working hours and from  $2.3 \times 10^3$  to  $3.9 \times 10^3$  cm<sup>-3</sup> during non-working hours. In this case, the measurement results from the AM room showed strong concentration peaks which cannot be explained by the changes in the background concentration (Fig. 3a). Nanoparticle concentration over  $100 \times 10^3$  cm<sup>-3</sup> was measured when both AM machines printed polystyrene and polyamide simultaneously. The concentrations of fine particles during AM of plastics were relatively low and did not show strong fluctuation during the measurement periods in WP3 (Fig. 3b). The concentration measured from the AM room followed the concentration measured from the background, thus the operation of the AM machine did not have an influence on the fine particle concentration here. The average fine particle concentration varied from 10 to 20 cm<sup>-3</sup> during working hours and almost the same (20 cm<sup>-3</sup>) during non-working hours in the AM room. The background concentration of fine particles decreased slightly from



**Figure 3.** Nanoparticle (a) and fine particle (b) concentrations in WP3 measured from the AM room (black line) and from the background (gray line). Both AM machines printed simultaneously on the second measurement day after 2 a.m. Water-based condensation particle counter N-WCPC3788 measures particles in the size range from 2.5 nm to 3 µm. Scanning Mobility Particle Sizer SMPS+C measures particles from 5.5 to 350 nm. Optical particle counters OPS3330 measures particles from 300 nm to 10 µm and DustMonitor 1.109 from 265 nm to 31 µm.

working hour concentration of 10–60 to 20–40 cm<sup>-3</sup> after working hours.

# Particle concentrations in AM-related work tasks

The AM process included several work phases. Here, the AM process was divided to different work phases illustrated in Fig. 1. Service and repair were not needed during the measurement periods. In general, work tasks that took place in the AM process room followed the concentrations measured from the stationary measurement point. Elevated nanoparticle concentrations were measured during post-processing tasks performed outside the printing room at WP2 and WP3. In WP1, all the tasks were performed inside the AM process room. The average nanoparticle concentration on operator's breathing zone varied from  $0.6 \times 10^3$  to  $17.4 \times 10^3$  cm<sup>-3</sup> during tasks outside the AM room (Supplementary Table S2, available at *Annals of Work Exposures and Health* online).

The highest number concentration  $17.4 \times 10^3$  cm<sup>-3</sup> was measured from the operator's breathing zone during post-processing, when PBF printed plastic object was finished manually by sanding with a sandpaper in front of the ventilated grinding table in WP3 (Fig. 4a). At the time, the background concentration was relatively stable (Fig. 4a, gray line) while the breathing zone concentration showed strong fluctuation and concentration peaks that differed from the base line. This clearly shows that the measured nanoparticles originated from the work process. During the sanding, LDSA varied from 8 to  $13 \mu m^{-2} cm^{-3}$  and the average particle size was at nano-range (<100 nm).

On AM process-related tasks carried out inside the AM room, the average nanoparticle concentration on operator's breathing zone varied from  $0.9 \times 10^3$  to  $4.8 \times 10^3$  cm<sup>-3</sup>. The highest average nanoparticle concentration  $4.8 \times 10^3$  cm<sup>-3</sup> as well as the highest LDSA concentration 20 µm<sup>-2</sup> cm<sup>-3</sup> in worker's breathing zone was measured during maintenance of the AM machine in WP2. As illustrated in Fig. 4b, there was a slight increase on nanoparticle number concentration on worker's breathing zone soon after the maintenance phase started and AM machine was cleaned. The concentration of background particles decreased at the time, but the average particle size measured was over nano-range (>100 nm) on worker's breathing zone. Relating to maintenance works, recycling also stood out from the results. Maintenance of the AM machine was mostly conducted inside the AM room, but recycling of the process materials was done outside (Supplementary Table S2, available at Annals of Work Exposures and Health online). The average nanoparticle concentration was  $9.3 \times 10^3$  cm<sup>-3</sup> during recycling of metal powders and average size was 40 nm

in WP2. The plastics used by the AM machine were also recycled in WP3. Handling of these recycled powders was performed under suction in both WPs.

#### Gas-phase compounds

The selected possible thermal decomposition products of used materials were measured. The average  $CO_2$ concentration varied between 419 and 484 ppm inside the AM rooms in all WPs. A slight variation at the same concentration levels were also seen on background concentrations as well. Measurable amount of CO was detected in only one WP, in WP2. The average CO concentration was 14 ppm at the AM room for 5 h over one night. There was an increase in nanoparticle concentration as the increased CO concentration was measured, but the origin of this concentration peak could not be identified. A process failure was ruled out while the surface of the printed metal object was faultless.

Total VOC concentrations varied between 40 and 230 µg m<sup>-3</sup> in laboratory samples measured in WP1 and WP3. The highest concentrations were measured in WP3. Alcohol compounds such as butanol and propanol, as well as traces of styrene and benzaldehyde in WP3, was detected in laboratory analysis (data not shown here). The butanol was probably originated from the particle measurement devices.

Concentration changes of VOCs were measured by photoionization detector (PID). Occasionally chemical solvents relating to AM process were handled and it affected the VOC results causing concentration peaks. The approximate average VOC concentration varied from 1 to 4 ppm near the AM machine as the background variation was from 1 to 2 ppm in WP1 and WP2. Unfortunately, the VOC data from WP3 were not reliable due to the instrument malfunction. The highest VOC-concentration peaks up to 14 ppm were measured after the surface treatment with cleaning solution and epoxy resins containing chemicals (Supplementary Fig. S1, available at Annals of Work Exposures and Health online) in WP1. AM processed metal objects are not typically treated with chemicals which explains smaller VOC concentrations in WP2.

### Discussion

The highest average nanoparticle concentration,  $40.4 \times 10^3 \cdot \text{cm}^{-3}$ , among studied AM rooms, was measured with plastics objects made by the PBF process in WP3. According to literature, almost similar number concentration of nanoparticles has been reported by MEX, BJT, and PBF techniques or even higher as printed without cover (Stefaniak *et al.*, 2021). Similar levels of nanoparticles have been also reported in office and public environments as well as in industrial



**Figure 4.** Nanoparticle concentration on operators' breathing zone. The plastic object was sanded outside the AM room (a), but the maintenance phase of a PBF printer performed inside (b). DiscMini measures particles in the size range from 10 to 300 nm. N-WCPC3788 measures particles in the size range from 2.5 nm to 3 μm. SMPS+C measures particles from 5.5 to 350 nm.

WPs and processes, such as e.g. copy centers, restaurants, specific asphalt, and metal works (Viitanen et al., 2017). The measured concentration rose to upper level of an 8-h NRV value. NRVs for bio-persistent granular nanomaterials in the size range 1-100 nm particles with density smaller than 6000 kg m<sup>-3</sup> is  $40 \times 10^3$  and  $20 \times 10^3$  cm<sup>-3</sup> for higher density (SER, 2012), respectively. NRVs are given for engineered nanoparticles, but in this case these are used to interpret airborne nanoparticles generated at the WP. These values are intended to be a warning level and when exceeded, exposure control measures should be taken. In this sense, the NRVs may be adapted to the process-related nanoparticles as well. Since the AM process was automated, continuous operator-required work phases inside the AM room lasted up to about 2 h. Thus, the operator was not in fact exposed to this nanoparticle level. In addition, NRV could have been exceeded, if the operator had worked in the room all the time (8 h).

Both AM machines (EOSINT P380 and P350) present in the process room in WP3 were operated as closed systems and were ventilated. However, the exhaust pipe of one of the machines was not tightly attached enabling emissions from heated plastics into the AM room. According to recently published studies, a high-flow spot ventilation system and sealed enclosure with gas and particle filtration reduced the ultrafine particle and VOCs emissions from 3D desktop printers efficiently (Azimi *et al.*, 2017). Yi *et al.* (2016) and Viitanen *et al.* (2021) also reported less emitted particles when 3D printer was operated with enclosure than without. This highlights the importance of regular maintenance and systematic verification of correct operation of control measures that are essential for minimizing the emissions to the workspace and for protecting operator's health and wellbeing.

In this study, AM process related to work phases such as preparation, AM process itself, post-processing, and maintenance were recognized. The highest nanoparticle concentrations related to work tasks were conducted outside the AM room. All measured nanoparticle concentration during AM-related work phases were below the NRVs. However, it was not possible to measure all post-processing phases performed with the particle equipment used from workers' breathing zone inside the AM room in WP2, due to the reactive nature of the titanium alloy.

Reference time of NRV  $(40 \times 10^3 \text{ cm}^{-3})$  differs from the duration that the work phases had, and by noting the time correction and 8-h duration of the workday, the actual exposure would have been even lower. Although it is notable, that sanding was continuous for few operators for almost the whole workday. The highest average concentration peaks up to  $17.4 \times 10^{3} \cdot \text{cm}^{-3}$  on workers' breathing zone were measured during postprocessing phase, when the surface on the manufactured plastic object was finished by sanding outside the AM room. Earlier studies (Göhler et al., 2010; Gomez et al., 2014) have also reported nanoparticle releases during surface treatments, i.e. sanding with engineered nanoparticles coatings containing materials and with conventional materials. This study showed that the nanoparticles are released also from the conventional AM materials without the nanoparticle coatings. In this study, sanding was made in front of a suction outside the AM process room, which may have also affected the spreading of released particles.

Maintenance was found to be one of the most exposing work phases in this study. Handling of metal powders released particles and some of the bulk materials utilized in AM process were heavy metal powders. The operator sieved these powders before re-use. Caution should be taken, and the spreading of metal dust must be prevented because of the adverse health effects that they may cause (Jaishankar et al., 2014). Graff et al. (2016) also emphasized safety importance while handling metal powders in their study concerning AM. In case of maintenance tasks, the handling of powder materials was mostly done outside the AM process room, e.g. recycling of metal or plastic powders. In this case, the smallest nanoparticle number concentration of  $0.6 \times 10^3 \cdot \text{cm}^{-3}$  was measured outside the AM room during the post-processing of the manufactured object in a fume cupboard, which prevented spreading of dust. This as well as broken exhaust pipe (discussed earlier) emphasizes the importance of effective use of good risk management measures on preventing exposure. Inside the AM process room, powders were handled when the AM process was prepared or manufactured object was removed from the AM machine. Handling of powders may spread dust into surroundings, but by taking into account calm and steady working methods as well as technical measures, e.g. vacuuming excess dust, it can be prevented (WHO, 1999). To prevent potential exposure, appropriate control measures, e.g. efficient ventilation, covered AM machine, fume cupboards, suction, and suitable chemical protection gloves and clothing are needed.

The highest process temperature in AM machines was studied to be about 1700°C that was used with metals in WP2. Nanoparticles releases of up to  $10 \times 10^{6} \cdot \text{cm}^{-3}$ have been measured from industrial work processes related with high temperature, such as welding or smelting (Elinh and Berg, 2009; Gomes et al., 2012; Järvelä et al., 2016; Viitanen et al., 2017). Even with 3D desktop printers using different plastics that require different process temperatures, nanoparticle emissions in some cases have reached  $10 \times 10^{6} \cdot \text{cm}^{-3}$  (Mendes et al., 2017; Stabile et al., 2017). In this study, no significant nanoparticle emissions were observed in WP2. The average nanoparticle concentration measured was at the most  $8.7 \times 10^3 \cdot \text{cm}^{-3}$  in stationary measuring point in the AM room (Supplementary Table S1, available at Annals of Work Exposures and Health online). However, the nanoparticle formation during the AM process is likely to occur, but the closed printing system with tight cover efficiently prevented the emissions to the room in WP2. The AM machine EOS M 290 printers' enclosure sustained gas atmosphere and prevented nanoparticle release outside the printer effectively. This is supported by a higher background concentration of nanoparticles which was measured when the printing process was ongoing inside the AM room after workday.

Related to AM of metals, an event of relatively high concentration of CO was measured, but the source of the emission was not identified. CO is classified as a toxic substance if inhaled (ECHA, 2019). The concentration was 70% of the Finnish 8-h OELV 20 ppm set for the CO (HTP Values, 2020). Healthbased, non-binding indicative IOELV in EU is the same as Finnish national value. There was also an increase on nanoparticle concentration at the same time. However, the AM machine was tightly enclosed sustaining the inert atmosphere metal AM process needs. The process failure was ruled out because it would most likely have been seen on the manufactured object. This could potentially have been caused by the emissions released by a coffee roasting factory which was situated in the same building. CO emissions can be traced from coffee roasting (McCarrick

VOC concentration measured with PID was low although distinguishable from the background. Handling of chemical solvents mainly affected the VOC results causing occasionally quite high concentration peaks. Laboratory analysis revealed some amounts of propanol, butanol, and traces of styrene and bentzaldehyde. Possible sources for propanol and butanol were chemical solvents used in surface treatments or particle measurement devices. Mendes et al. (2017) also found butanol emissions originating from condensation particle counters that could have occurred in this case as well. In addition, styrene and benzaldehyde are listed as degradation products of ABS in literature review reported by Rutkowski and Levin (1986). With regard to chemicals used in AM process, some of them were recognized as skin irritants e.g. some epoxy resins, according to material safety data sheet. To this end, skin exposure should be avoided.

## Conclusions

In this study, the focus was on airborne particulate and gaseous emission related to three different industrial scale AM technologies: PBF, MEX, and BJT. For all technologies, adding material layer by layer was common, but the fusion methods vary greatly depending on the technique, affecting also ways in which workers may be exposed. In this study, the whole industrial scale AM process was studied in three different work environments.

Several AM-related work phases were identified, where operator can be exposed to particulate emissions and chemicals. Post-processing of the manufactured object by sanding increased nanoparticle concentration on operators' breathing zone. Further, nanoparticle concentration increased even up to upper level of NRVs inside the AM room, when the AM machine was not tightly enclosed, and the ventilation was reduced after workday. Overall, the results identified that all measured nanoparticle concentrations during AM-related work phases were below the NRVs, considering the contextual circumstances used in this study.

AM process and related work tasks contained handling of chemicals. In the PBF technique, the bulk material was powder, while MEX used more consistent plastic filament. In BJT, liquid post-processing chemicals were used more often. Chemical characteristics of the printing material should always be taken into account when planning the AM operations. For example, caution should be taken, in particular, the spreading of metal dust should be prevented when

handling metal powders with different reactivity for potential adverse health effects. In addition, some liquid chemicals were recognized as skin irritants. To this end, direct contact to skin should be avoided. To prevent potential exposure, appropriate control measures, e.g. efficient ventilation, AM machine with enclosure, fume cupboards, suction, and suitable chemical resistant gloves and clothing are necessary. Further, regular maintenance and systematic verification of the correct operation of control measures are essential. Considering that not all the different phases are performed inside the AM room, safety measures such as good ventilation are important throughout the AM process chain at the working site. It is important to conduct a comprehensive risk assessment that considers all chemicals involved in every phases of the AM process.

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# **Conflict of interest**

The authors declare no conflicts of interest.

## **Data availability**

The data underlying this article will be shared on reasonable request to the corresponding author.

# Supplementary data

Supplementary data are available at *Annals of Work Exposures and Health* online.

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