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Potential exposure to airborne nanomaterials generated from 3-D printing processes

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Potential exposure to airborne nanomaterials generated from 3D printing processes

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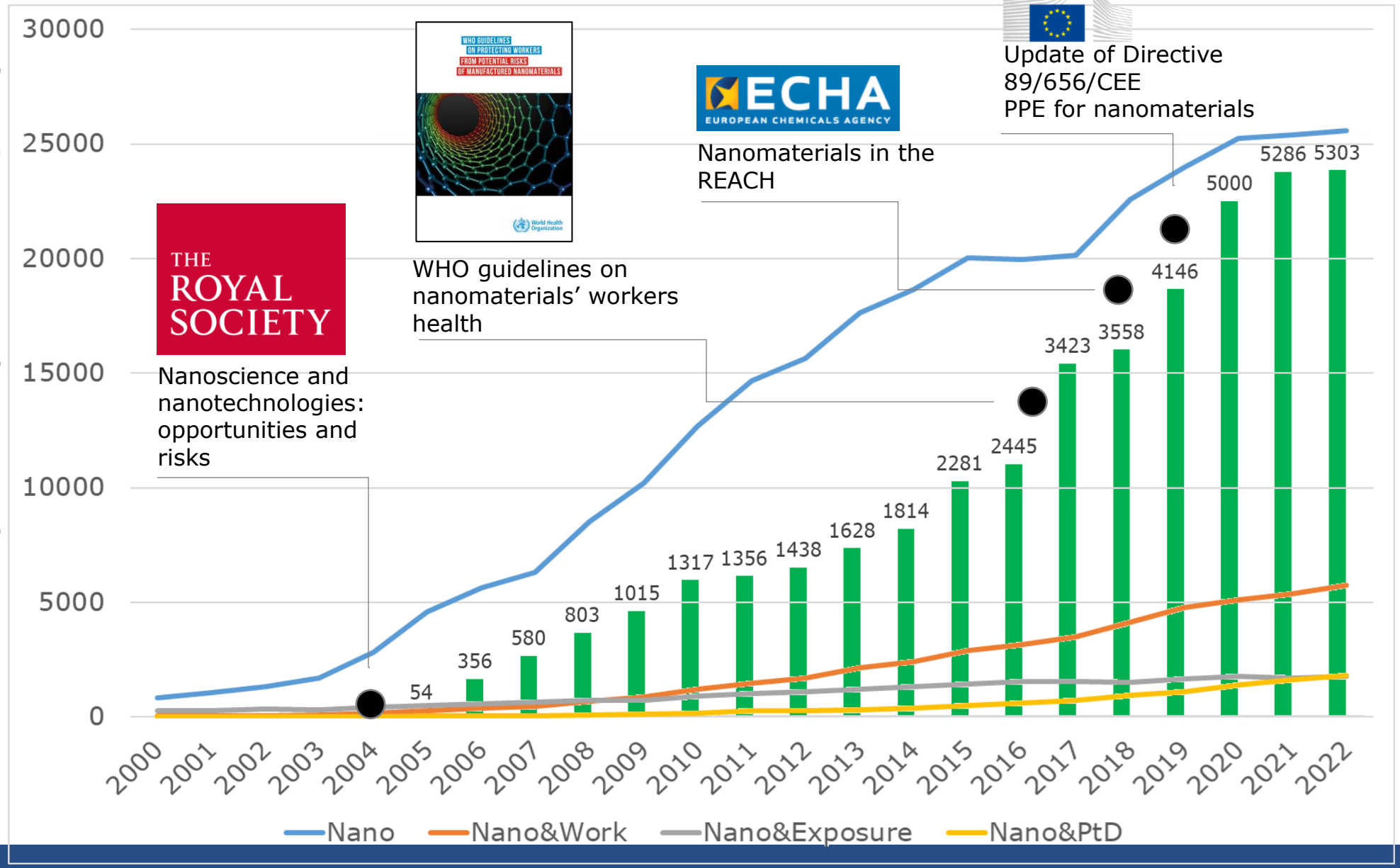
- Conclusions

20 years of responsible nanotechnology development

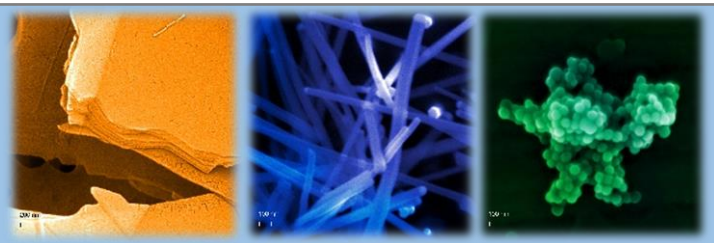


Exposure to NM in the workplace

- The emission of NMs in work processes can cause **potential risks** and adverse health effects for exposed workers
- **Nanoscale dimensions, shape factor, and unusual aerodynamic properties** are key parameters in assessing the risk of inhalation exposure to NMs
- **Few studies are currently available on workers' exposure assessment**, which take into consideration real working conditions, specific characteristics of the production sites and workers' biomonitoring
- Currently, **no specific occupational exposure limits (OELs)** for NMs are defined by law. The WHO in 2017 proposed a list of OELs for several NMs based on a systematic literature review
- Other studies propose **nano reference values** (NRV) that take into account not only mass but also particle number concentration (PNC) of NMs

It is necessary to implement **suitable and effective methodologies** to prevent workers exposure in production processes involving NMs

Nano and advanced materials as key enabling technologies



Nanomaterial (NM) is a natural, incidental or manufactured material consisting of solid particles, aggregates or agglomerates, where **50% or more** of these particles in the **number-based size distribution** have one or more external dimensions in the size range **1-100 nm**. [**EC, 2022**]

Advanced materials (AdMa) are rationally designed to have **new or enhanced properties**, and/or targeted or enhanced structural features, including materials from innovative manufacturing processes that enable the creation of targeted and improved structures [**OECD, 2022**]

The **key enabling technologies (KETs)** on which innovative applications will be based to improve citizens' lives and environmental impact, exploit the innovative properties of nanomaterials and new advanced materials.

Advanced manufacturing
- Additive manufacturing
- Autonomous systems
- Sensor technology
- Industry 4.0
- Robotics

Advanced (nano)materials
- Biomaterials
- 3D printing and design
- Chemicals, polymers, metals, glass
- Rapid prototyping

Life-science technologies
- Neurotechnology
- Bioengineering
- AI in biology
- Bioelectronics
- Medical engineering

Micro/nano-electronics and photonics
- Integrated circuit design
- Quantum computing
- IoT sensors and tokens
- High-performance computing

Artificial intelligence
- Deep Learning
- Quantum AI
- Robotics
- Autonomous systems
- AI-as-a-service

Security & connectivity technologies
- Standards (5G, SigFox...)
- Network architectures
- Cryptography
- IoT networks & protocols
- Distributed ledgers

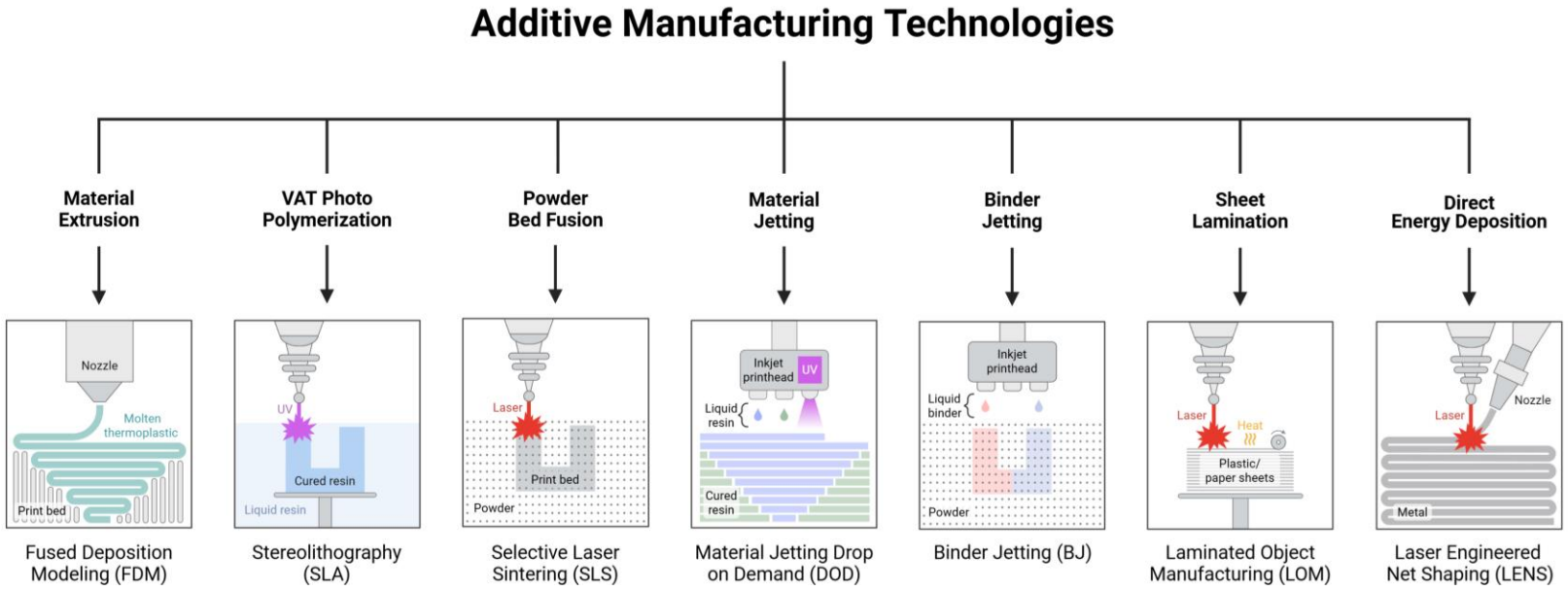
European Commission
Horizon Europe
2021-2027

Overview of 3-D printing technologies

ISO/ASTM 52900:2021
Additive manufacturing — General principles: Fundamentals and vocabulary

Additive Manufacturing
Process of joining materials to make parts from 3D model data, usually layer upon layer

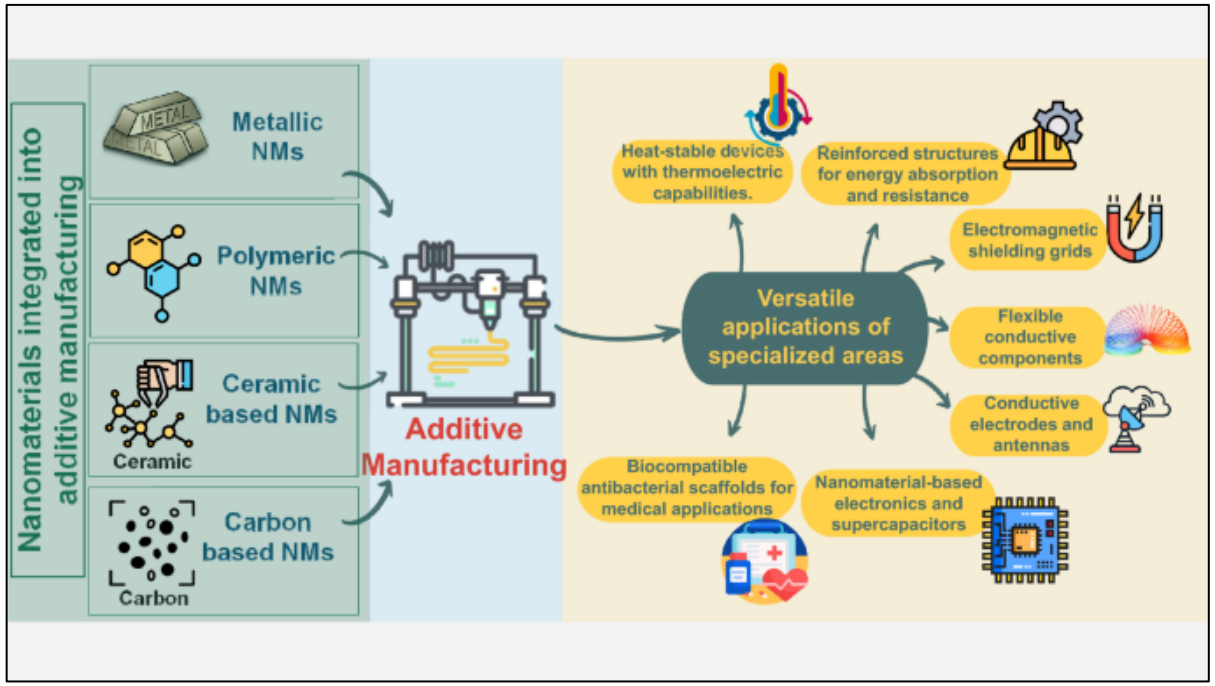
3D Printing
Fabrication of objects through the deposition of a material using a print head, nozzle or another printer technology (often used in a non-technical context synonymously with AM)



Emerging use of NMs and AdMa in 3-D printing processes

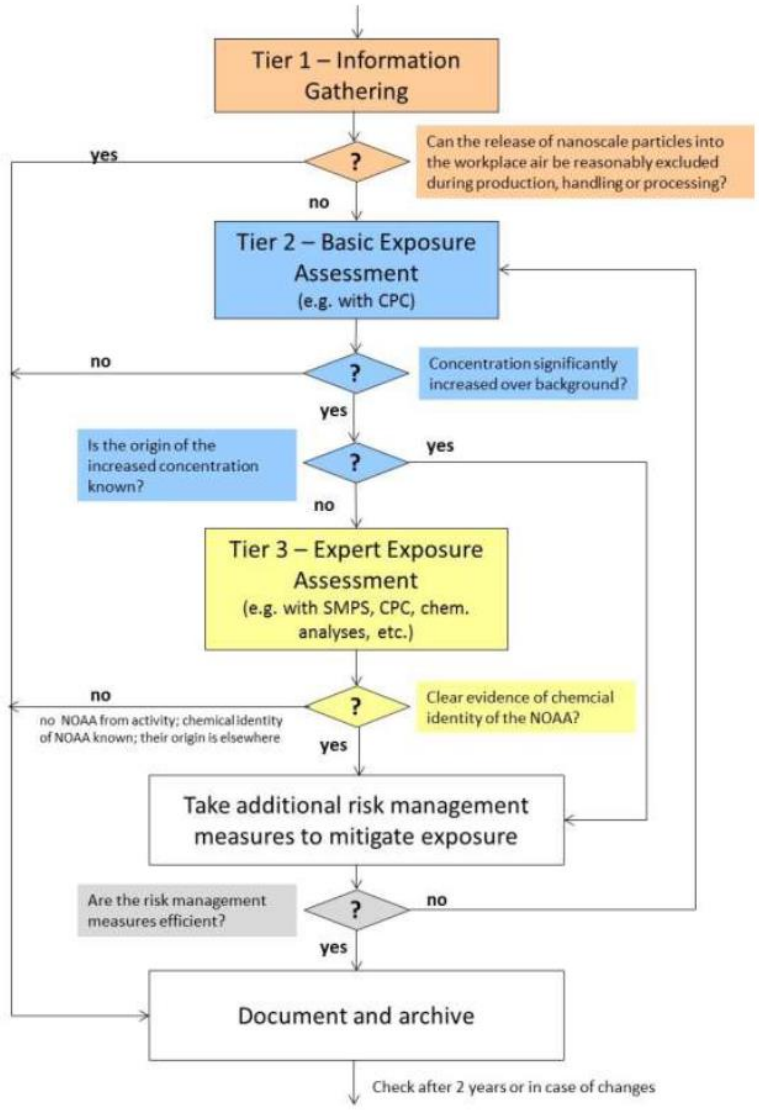
Key points of interest

- **Unique properties and applications**
- **Sources of airborne NM** in 3-D printing processes (e.g. material extrusion, powder bed fusion, pre/post-processing activities)
- **Other emissions of harmful substances** (e.g. VOC, SOA, gases, fumes)
- **Mechanisms of release** (e.g. thermal degradation, mechanical abrasion, volatilization)
- **Exposure pathways** (inhalation, dermal contact, ingestion)
- **Health risks of airborne NM** (i.e. respiratory issues, cellular toxicity, long-term exposure concerns)



Source: Rahman M. et al, Progress in Additive Manufacturing, 2024,9: 1197-24

Harmonized tiered methodological approach for workplace exposure to NM



- OECD-CEN harmonized tiered approach for NM exposure assessment
- Materials/processes information (focus on plastic materials for 3D printing processes)
- Glove box experimental laboratory tests on powders emissions of pristine materials
- On field exposure scenario measurements
- Off-line characterization on sampled materials
- Toxicological analysis (in collaboration with STAMI)

OECD ENV/JM/MONO(2015)19 Harmonized tiered approach to measure and assess the potential exposure to airborne emissions of engineered nano-objects and their agglomerates and aggregates at workplaces.

Source: OECD, 2015

European Committee for Standardization (CEN) EN 17058:2018 Workplace exposure - Assessment of exposure by inhalation of nano-objects and their aggregates and agglomerates.

Source: CEN, 2018

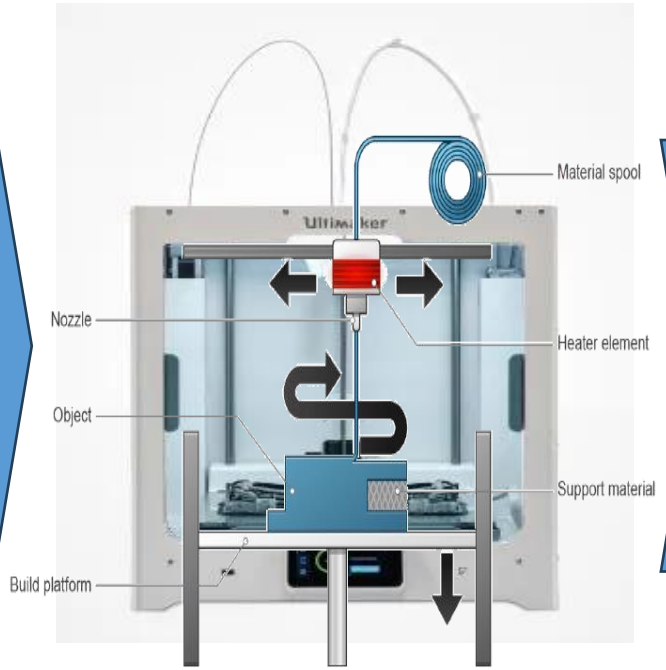
Case Study 1: Fused deposition modeling (FDM)

Fused Deposition Modeling (FDM)

Material extrusion technique that uses a continuous filament of thermoplastic material fed into a heated extruder (150-250°C) and deposited on a platform to fabricate a part layer by layer

Source materials

- polyamide PA12 (i.e. nylon)
- thermoplastic polymer (ABS)



Final printed products

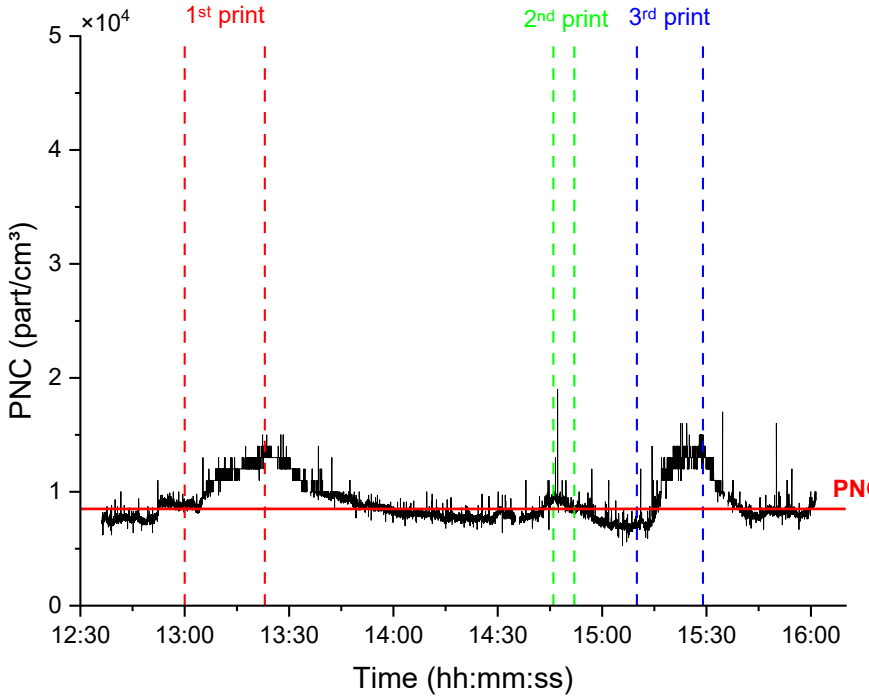
polimeric objects 5x5 cm size

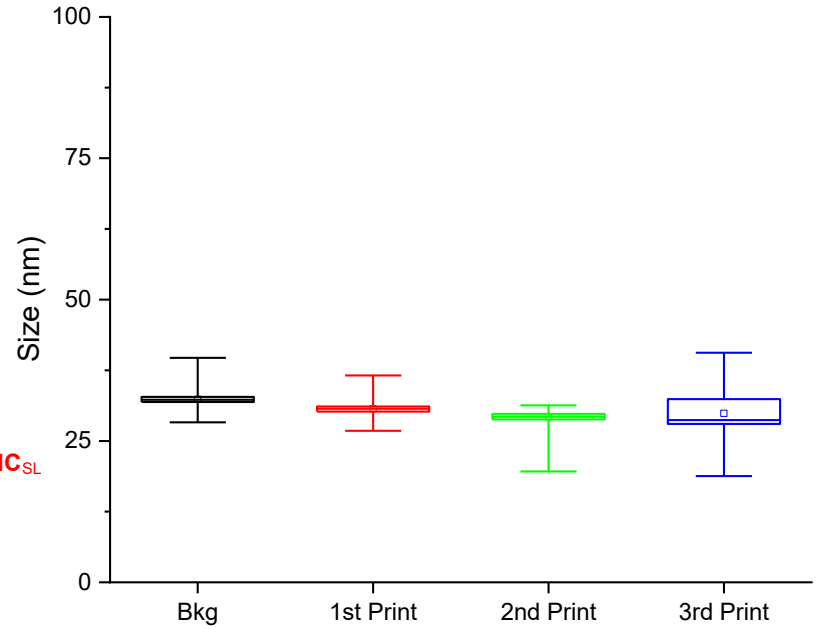
Exposure conditions

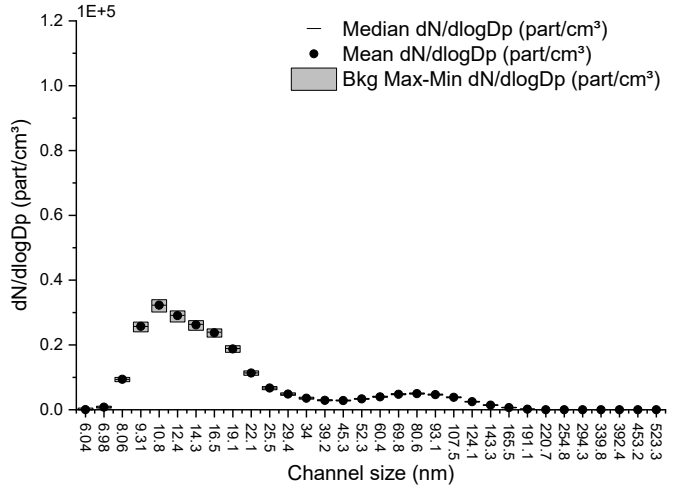
- Average process length: 17 min
- Open printing system
- Manual starting/monitoring/finishing process by the operator

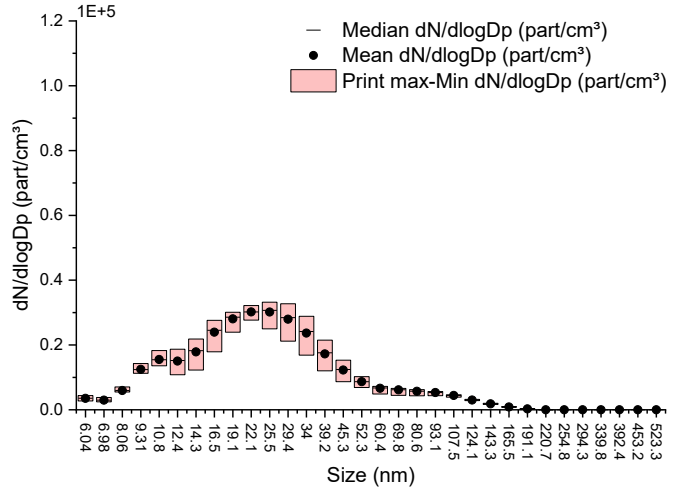
Case Study 1a: PA12 FDM 3D printing exposure scenario

Real Time measurements









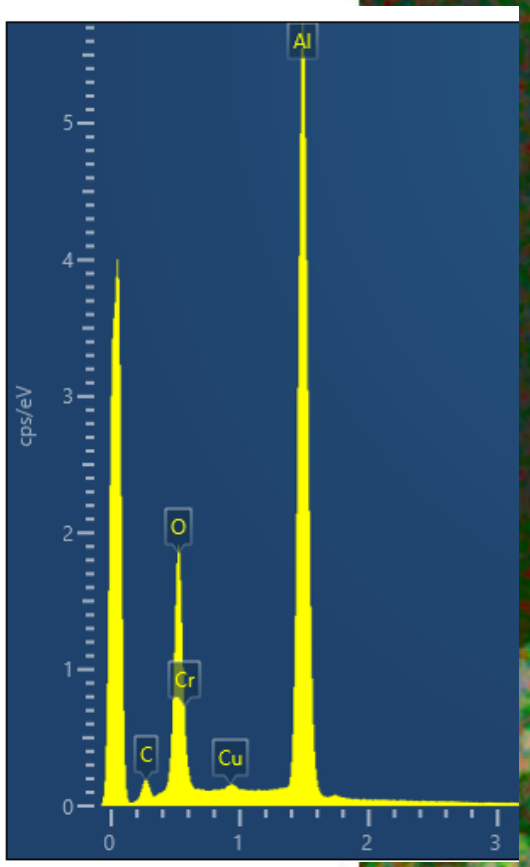
$$PNC_{SL} = Avg_{bkg} + 3\sigma_{bkg} = 8500\ part/cm^3$$

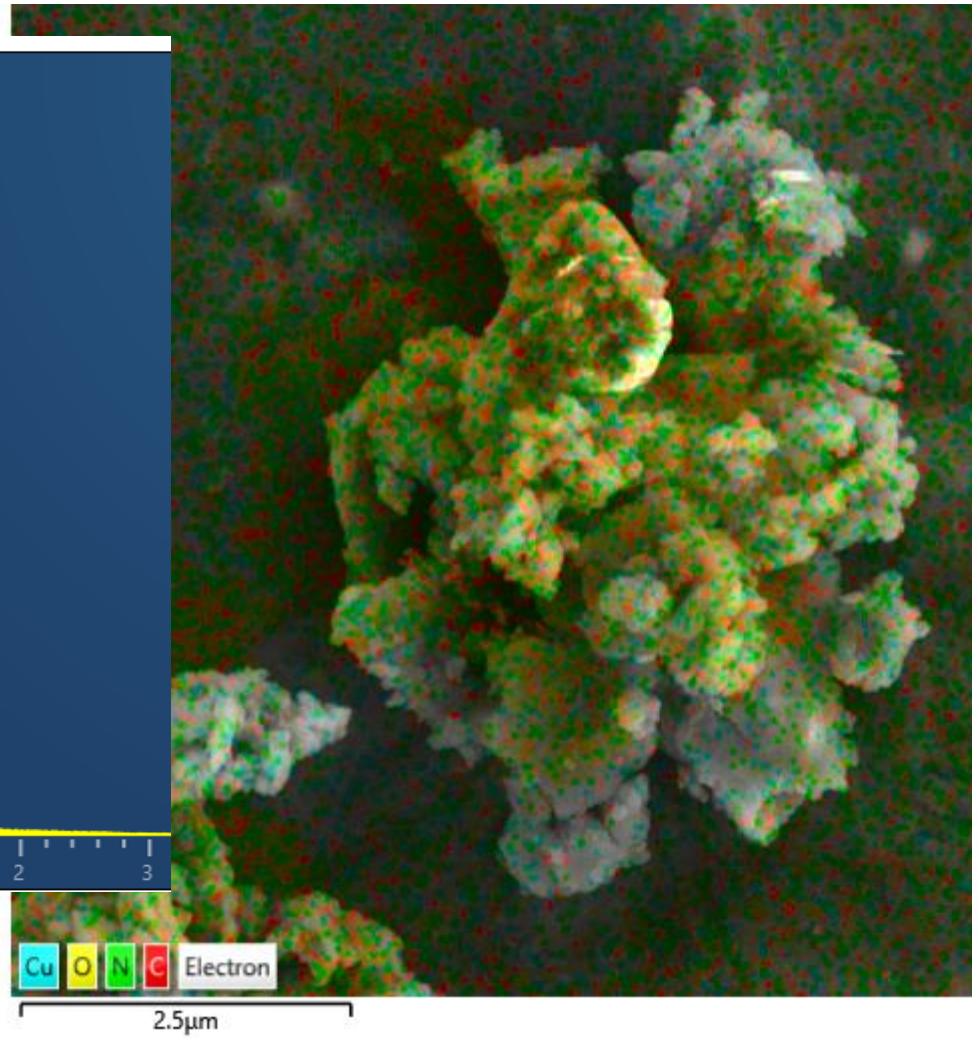
Toxicological study on PA12 (in collaboration with STAMI)

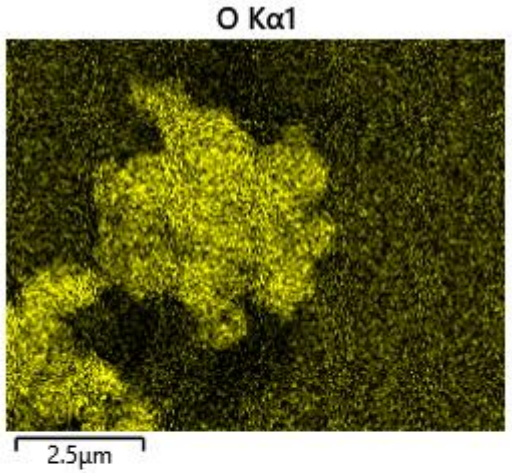
No significant reduction in cell metabolic activity was observed in any of the exposed groups compared to the control, as determined by the AlamarBlue assay. Consistently, the LDH release assay did not show any increase in membrane damage

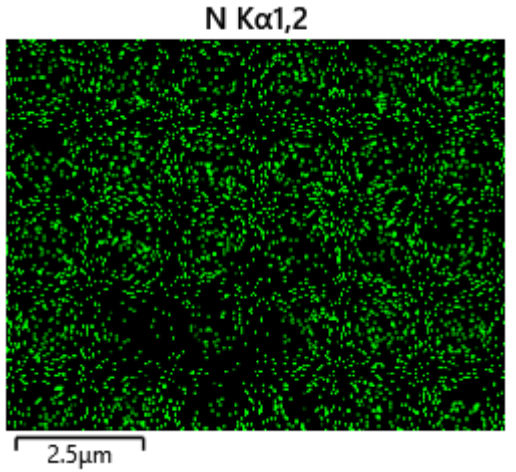
Case Study 1a: PA12 FDM 3D printing exposure scenario

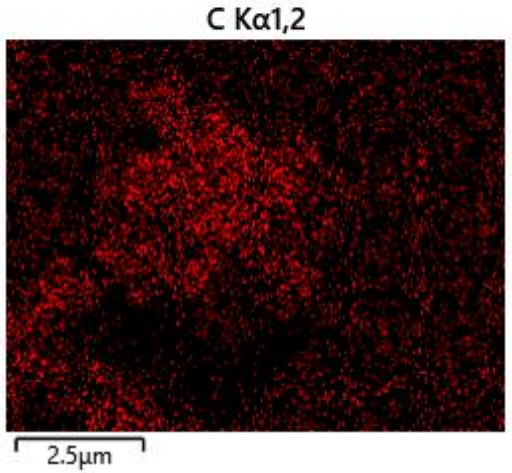
Off-line SEM-EDS analysis on sampled airborne materials

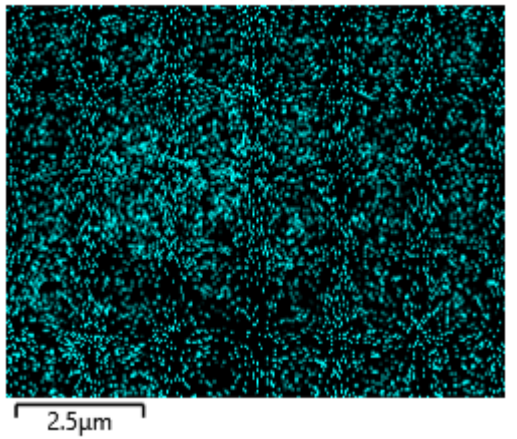






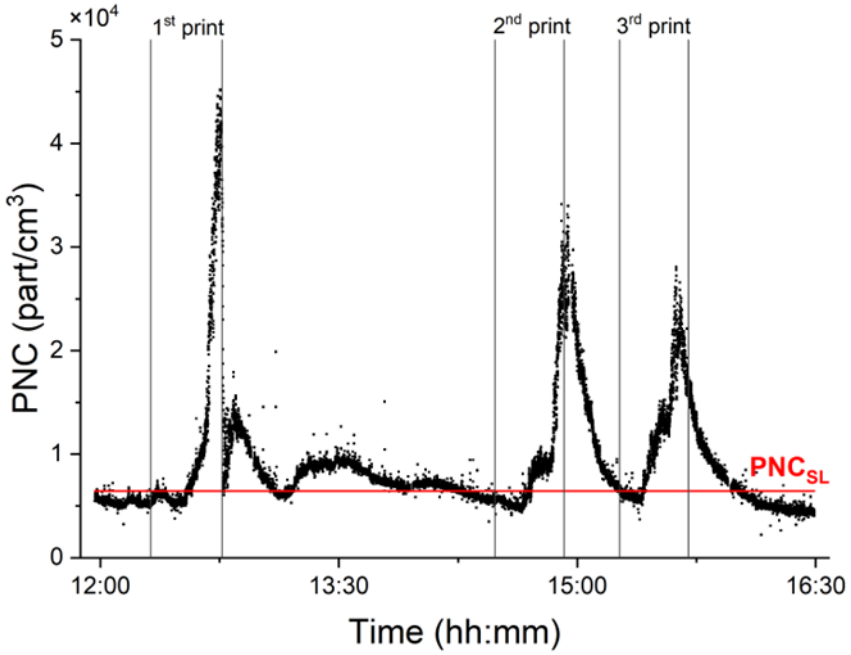


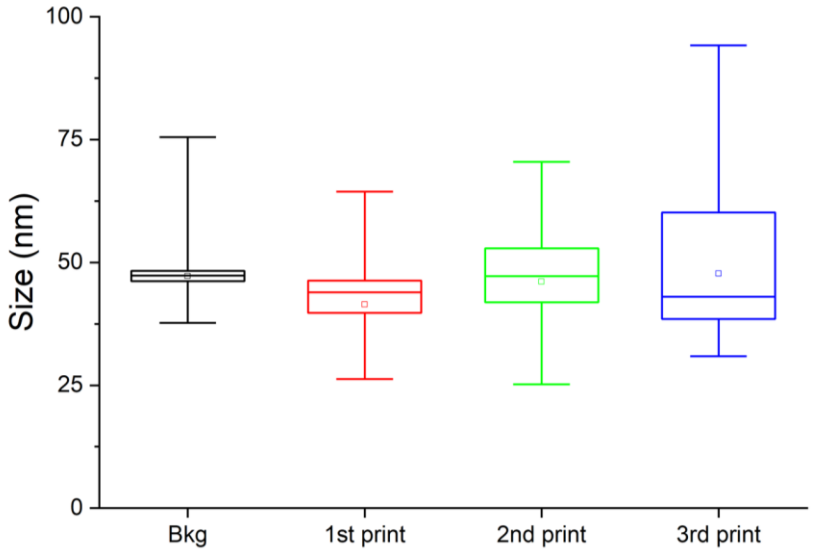


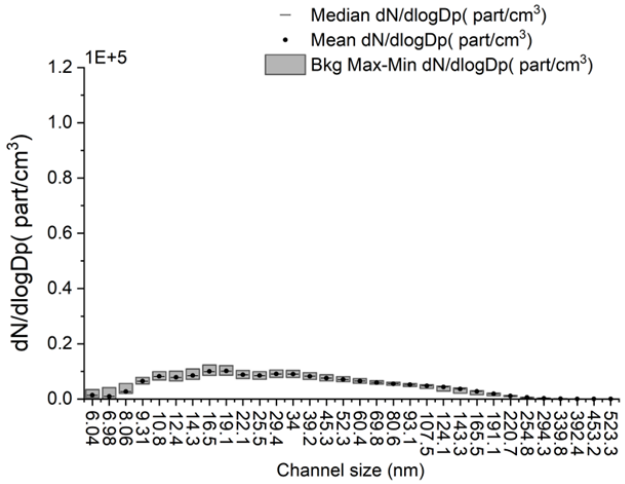


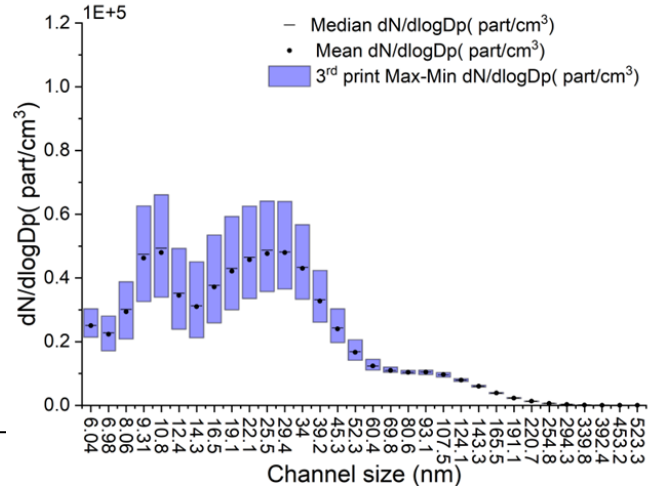
Case Study 1b: FDM ABS 3D printing exposure scenario

Real Time measurements









$$PNC_{SL} = Avg_{bkg} + 3\sigma_{bkg} = 6400\ part/cm^3$$

Literature evidence on ABS toxicity

Exposure to Acrylonitrile Butadiene Styrene (ABS) can cause health effects, primarily due to the fumes and particles released during processes like 3D printing. Inhalation of ABS fumes and particles can lead to respiratory issues such as headaches, nausea, eye and throat irritation, and potentially even damage to lung cells. Occupational exposure to the chemical acrylonitrile has been linked to central nervous system effects and blood changes, and it is also classified as a human carcinogen (IARC, Group 1).

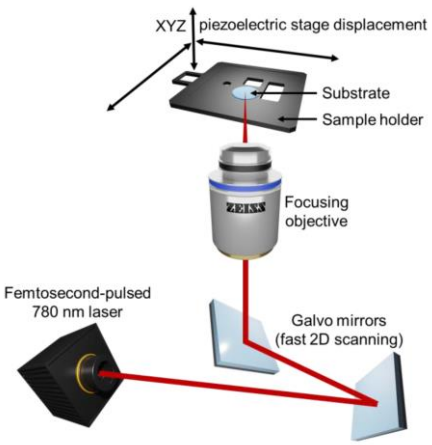
Case Study 2: Two-photon polymerization

Two-photon polymerization (2PP)

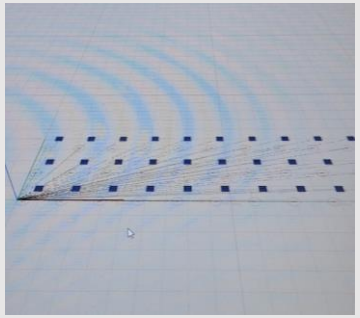
Falls into the group of stereolithography (SLA)-based additive manufacturing technologies, specifically a high-resolution variant known as two-photon lithography (2PL) or direct laser writing. It is a form of vat photopolymerization that uses a pulsed laser to create sub-micron features with high precision in photosensitive resins.

Source material

- UV-curable photoresins (PR)



Final printed product

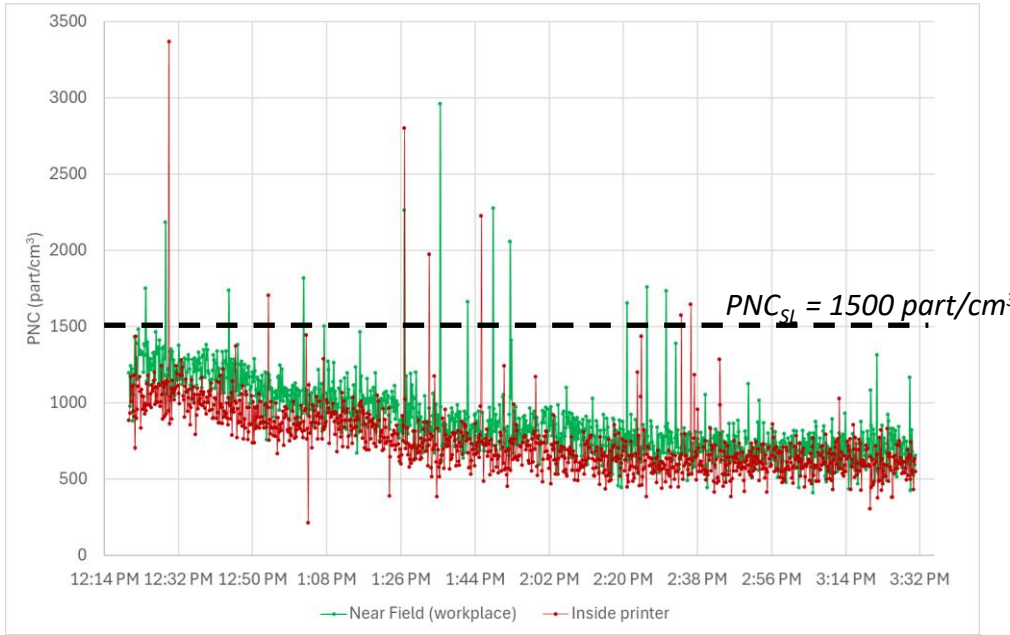


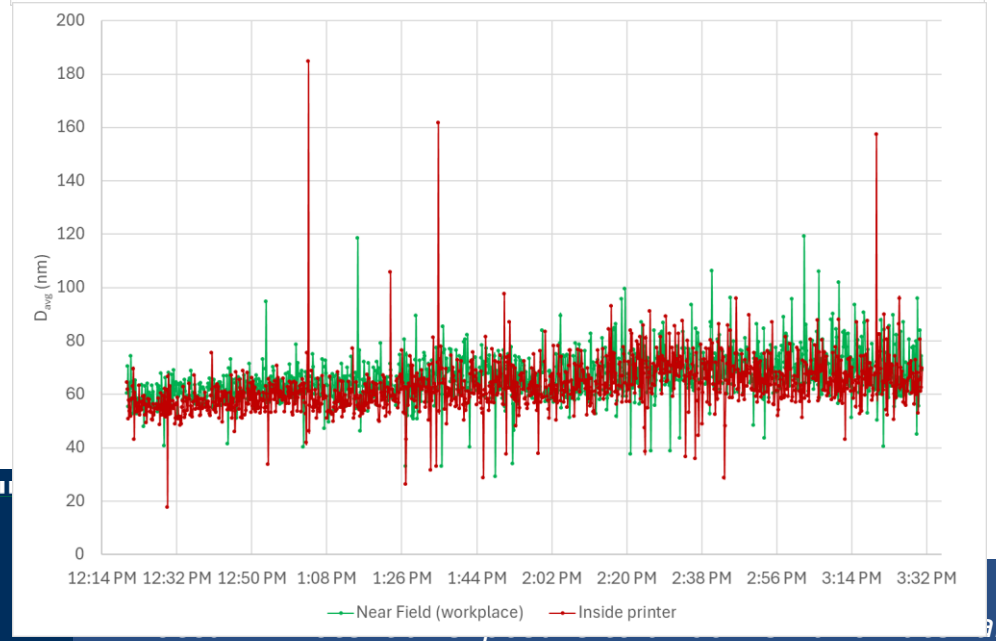
nanoresins array few nanometers size

Exposure conditions

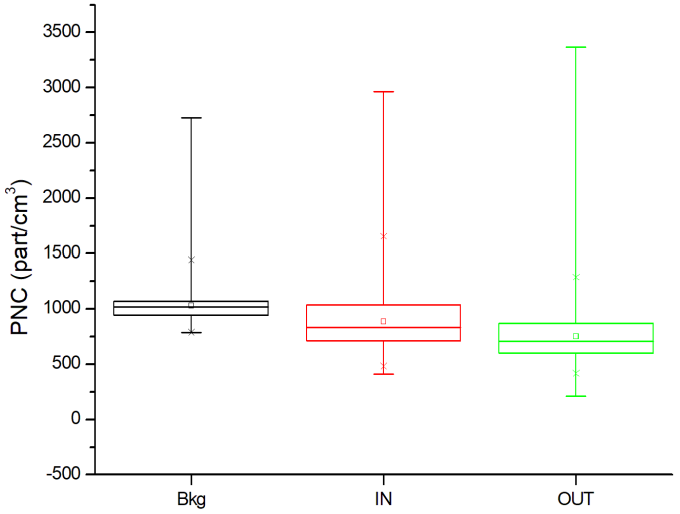
- Average process length: 3–24 hours
- Closed printing system with local exhaust ventilation
- Starting/finishing process from remote

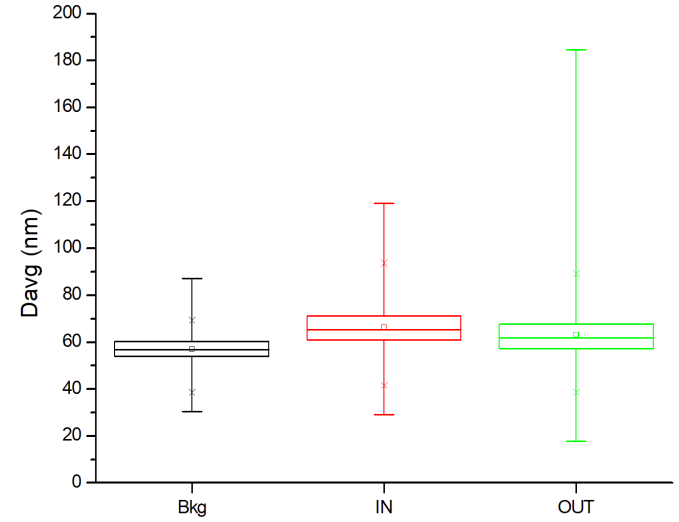
Case Study 2: 2PP PR 3-D printing exposure scenario

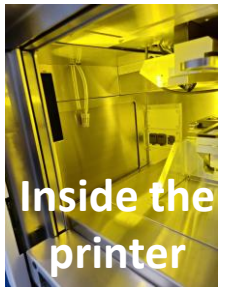




Real Time measurements







PR health effects

Skin contact with the PR can cause allergic dermatitis, while inhaling the fumes can cause respiratory irritation and an increased risk of occupational asthma. Eye contact and accidental ingestion can also cause irritation and damage to the eyes and digestive tract, respectively. The resin emits harmful VOCs, which can cause respiratory problems if inhaled in large quantities.

Conclusions

1. The **harmonized OECD-CEN tiered approach for NMs** has been successfully applied to characterize metrics relevant for inhalation of airborne particles in different occupational exposure scenarios for 3D printing processes.
2. The preliminary results indicate that:

   1. Airborne dust emissions from **PA12 are distributed primarily in the micrometer size range**. The FDM 3D printing process using PA12 filament also produces submicrometric particle emissions which cannot be strictly attributed to PA12 by SEM-EDS analysis. Preliminary in vitro toxicology studies have revealed **no significant health effects**.

   2. **ABS is recognized as a hazardous material** due to its potential carcinogenicity to humans. **Significant NMs emissions** occurred during the FDM printing process **3-4 times higher than background** in the near field of the workstation (average size range 9-80 nm).

   3. Although **PR is classified as toxic by inhalation**, **no significant emissions have been observed** when used in the 2PP lithography process, thanks in part to the effectiveness of the ventilation system adopted in the workplace.

3. Exposure mitigation recommendations depend on the type of process and may include **general containment measures** for 3D printers with **local exhaust ventilation.**
4. **Next steps of the study** will include a comprehensive analysis of relevant exposure metrics and case study comparisons, including **quantitative information**. **Toxicological studies on airborne materials** sampled in the workplace during the 3D printing process will also be explored.

Thank you for your attention!

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