Occupational exposure to nanoparticles: monitoring and management in industrial settings

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Outline

- Nanoparticle emissions in industrial settings
- Experimental methods
- Case studies:
  - Production of cosmetics
  - Ceramic tile ablation
  - Ceramic tile sintering
  - Atmospheric plasma spraying
- Exposure management
- Conclusions

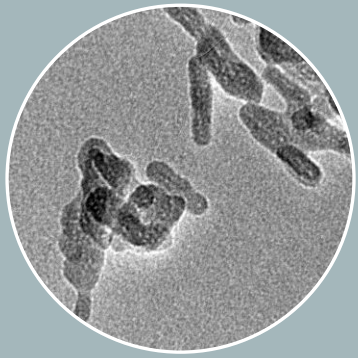
Framework

Safe production and Use of Nanomaterials in the Ceramic Industry

www.cerasafe.eu

NANOPARTICLE EMISSIONS IN INDUSTRIAL WORKPLACES

Nanoparticles in industrial settings



Manufactured (MNM)

Intentional, commercial purposes (2011/696/EU; 1-100nm, >50%)

Process-generated (PGNP)

Emitted during highly energetic (thermal or mechanic) processes

Background (BG)

Natural or anthropogenic origin

EXPERIMENTAL METHODS

Instrumentation

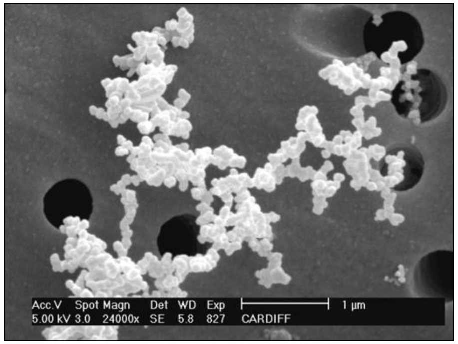
Particle counters
(particle number)

Part. counters & sizers
(size distribution)

Optical particle counters
(particle mass)

Cascade impactors
(fixed site and portable)

Handheld monitors
(particle number, Black Carbon)



Microscopy
(SEM, TEM, AFM)

Handheld
gas monitors

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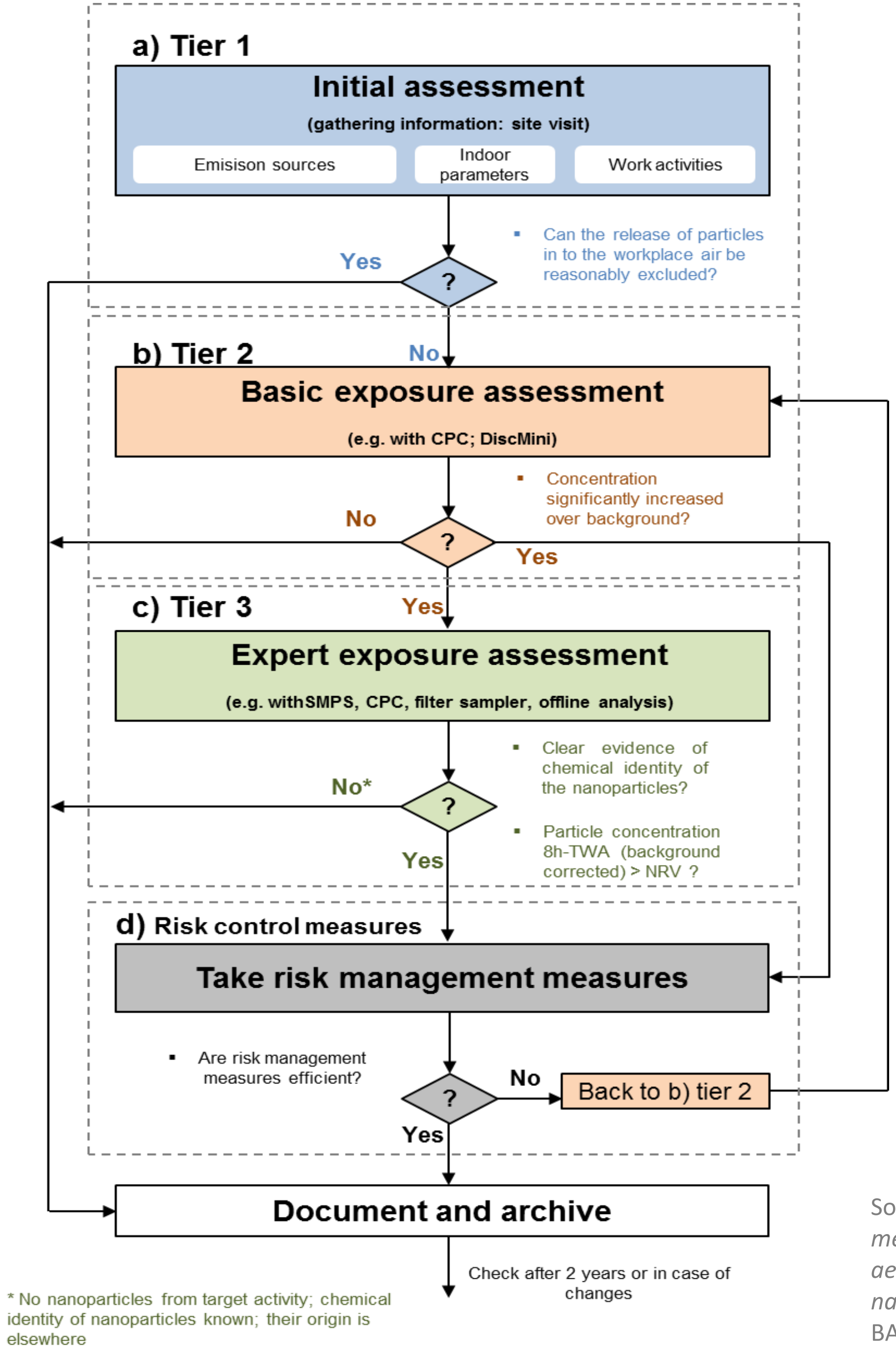
Measurement strategy



… for N and mass concentrations

Source: *Tiered approach to an exposure measurement and assessment of nanoscale aerosols released from engineered nanomaterials in workplace operations*, BAuA, BGRCI, IFA and VCI, Germany. 2011.

Measurement strategy

OUTDOOR

EMISSION AREA

DiscMini
(10 - 700 nm)

NanoScan SMPS
(10 to 420 nm)

TEM
samples

WORKER AREA

CPC TSI 3775
(4-1500 nm)

DiscMini
(10 - 700 nm)

Grimm 1.108
(300nm – 20 µm)

TEM
samples

Quantitative:
- Particle number
- Mass
- LDSA
- Mean diameter

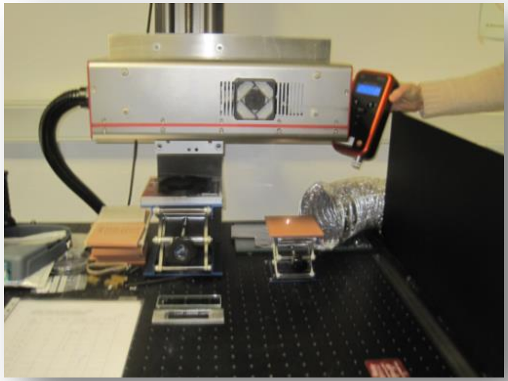
Range: 5 nm – 20 µm

Non-quantitative:
- Particle morphology
- Chemical composition
- Mineralogy

Measurement strategy

WORKER AREA

EMISSION AREA



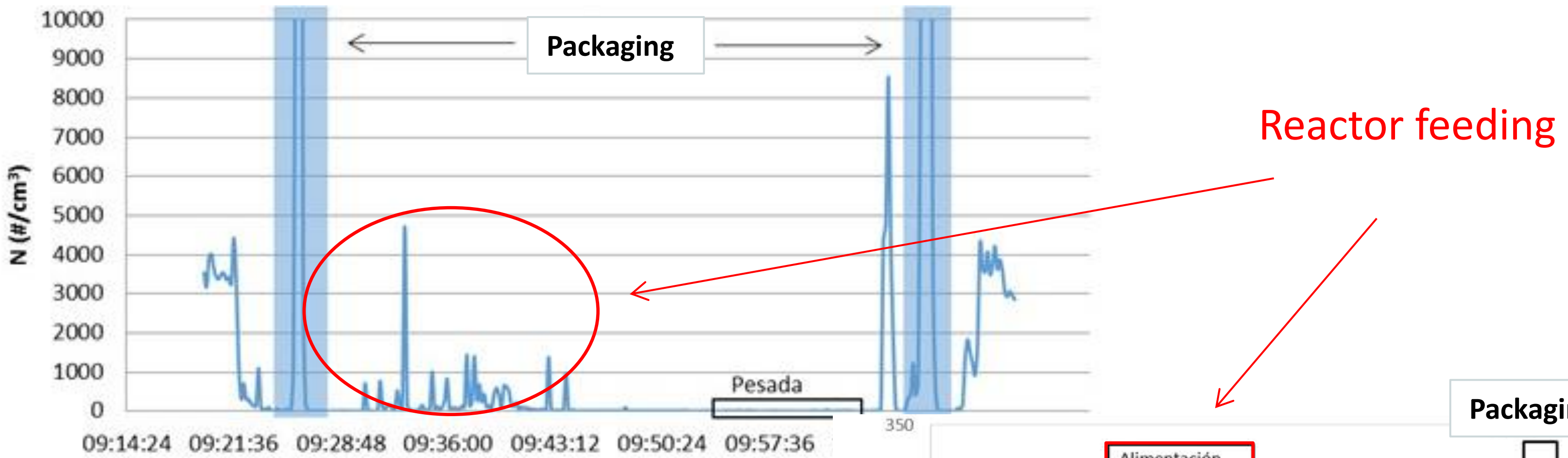
INDOOR BACKGROUND

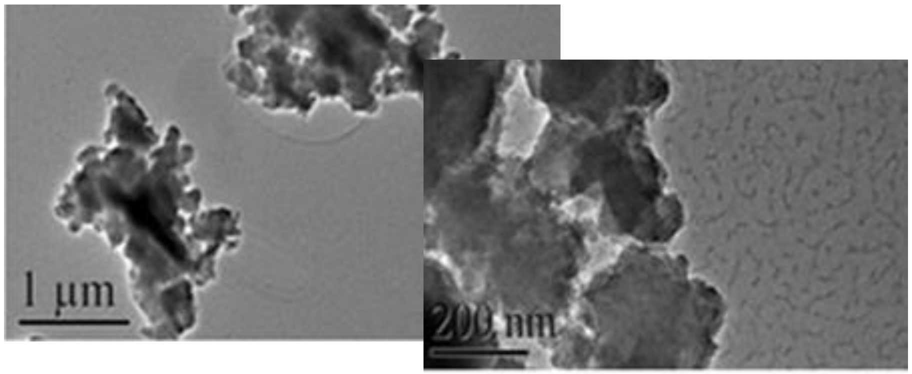
OUTDOOR BACKGROUND

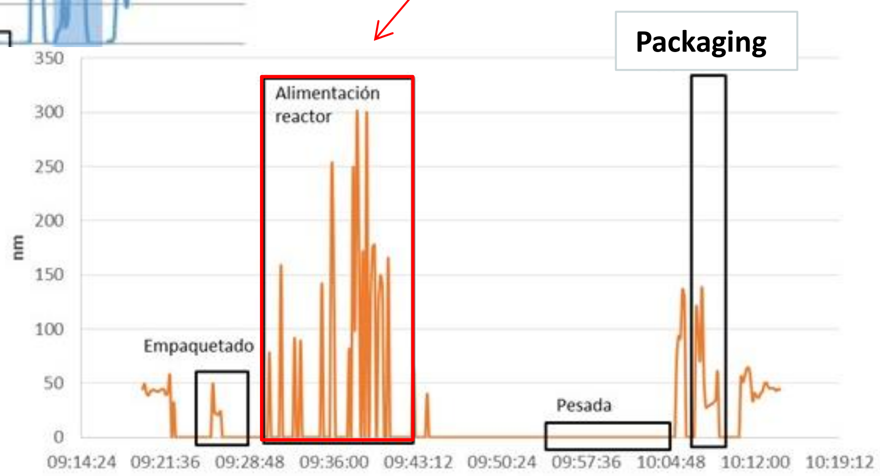
Case study:
Production of cosmetics

Reactor feeding: production of cosmetics

- Amorphous silica: 10-20 nm, powder
- $N_{10\text{-}700\ nm}$ increased up to 1000-4000/cm^3, mean diameter 60-300 nm
- Suggests release of aggregates





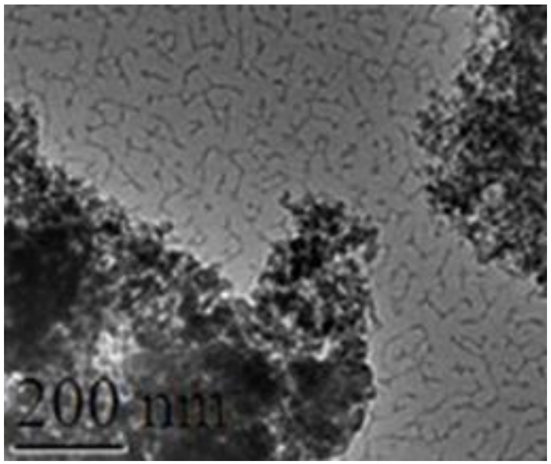


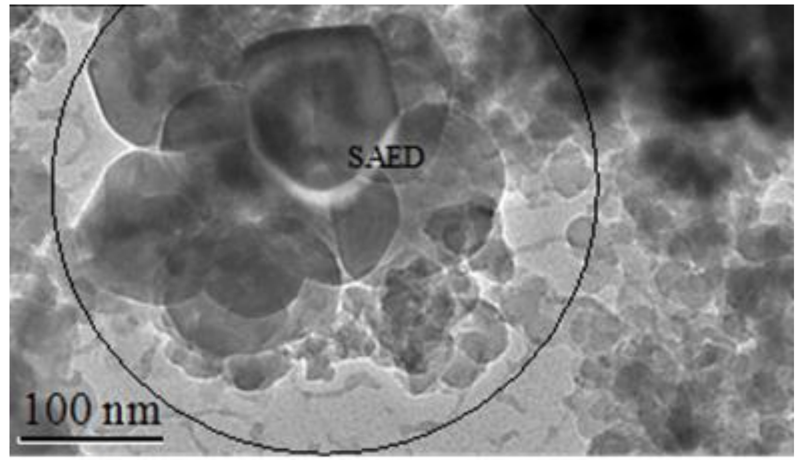
Low statistically significance due to concentrations close to DL

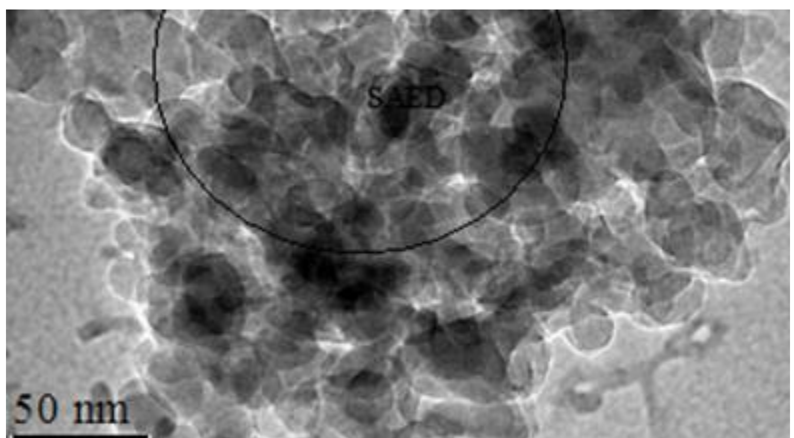
Toxicity of aggregates?

Fugitive emissions of MNMs

- Hydroxiapatite (10-20 nm; aqueous suspension)
- High presence of amorphous silica (nanometric), not used in this formula! Source unknown. Samples collected from the breathing zone

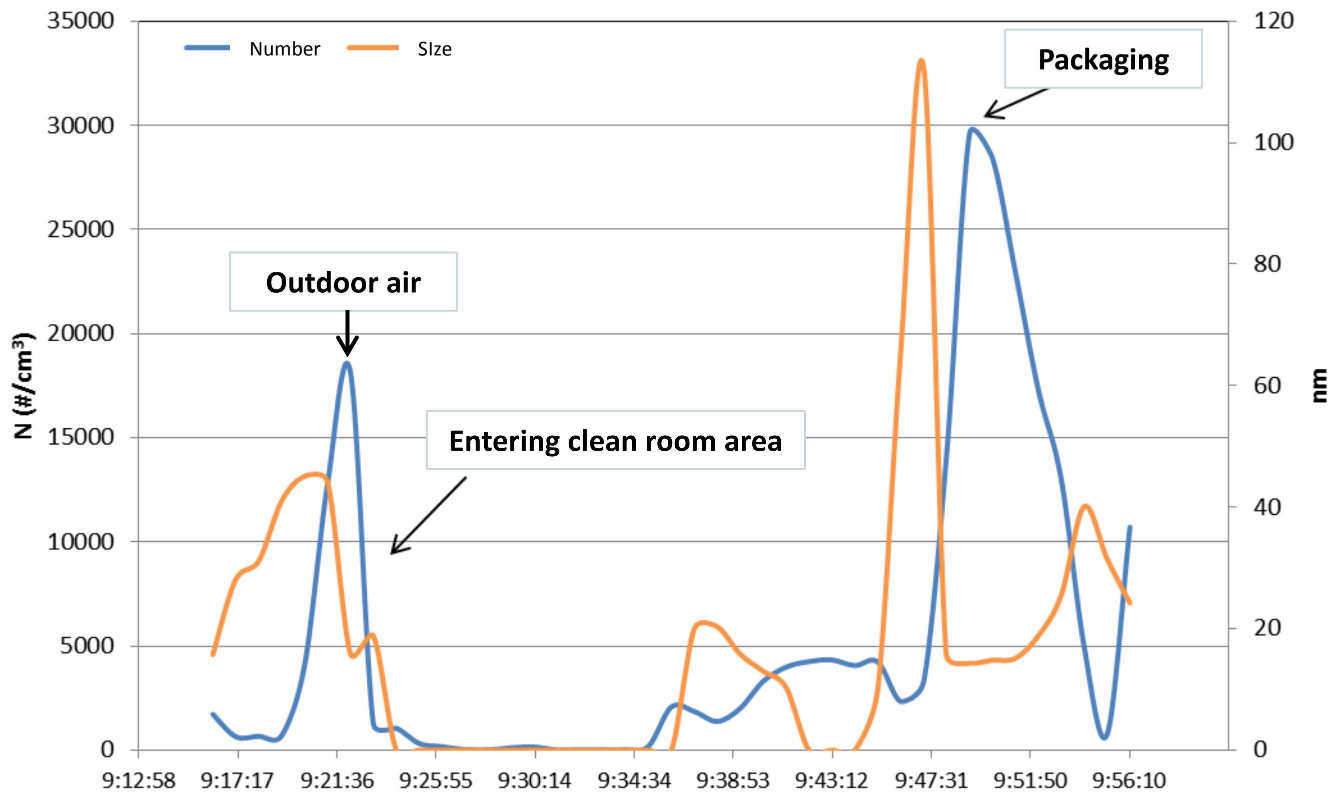






Process-generated NP emissions

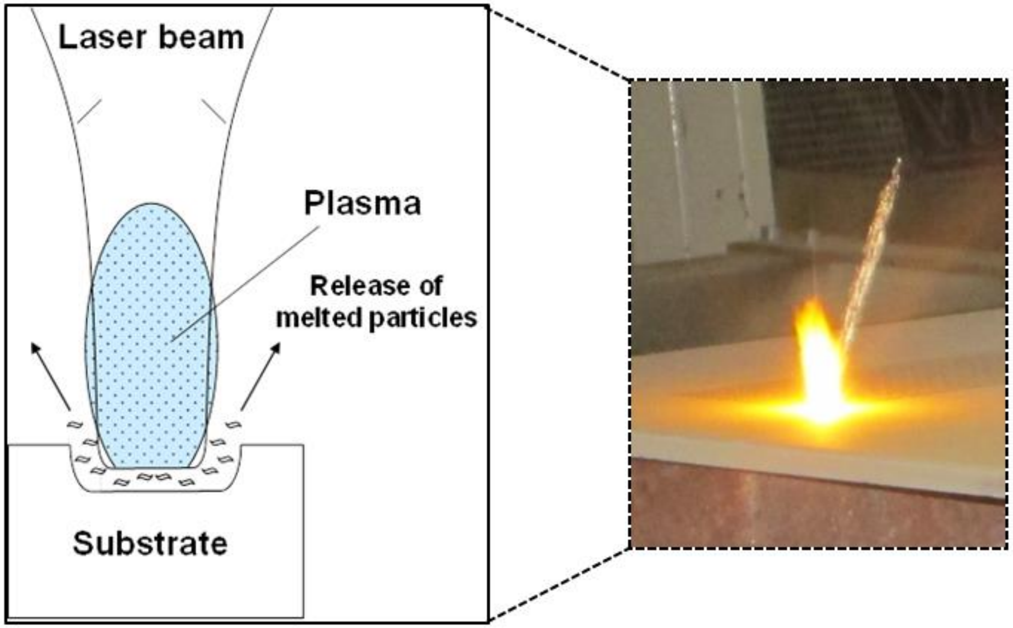
- Packaging of final product
- $N_{10\text{-}700\ nm}$ increased up to 30.000/cm³ (15 nm), statistically significant
- Source: new particle formation from organic vapours produced during thermal sealing of the tubes
- Mitigation strategies suggested (local exhaust)



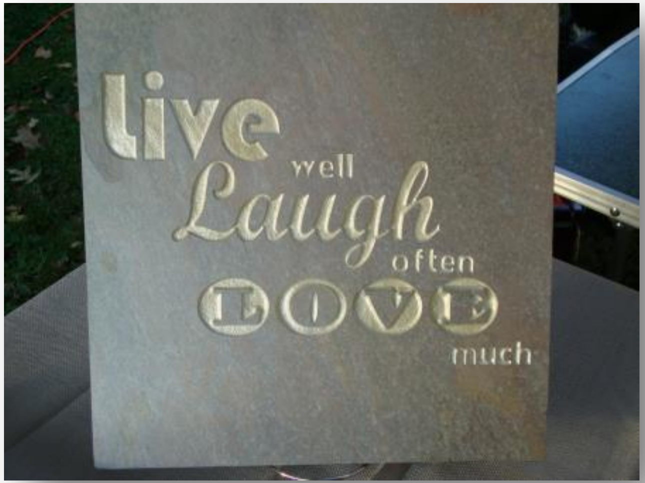
Case study:

Ceramic tile ablation

Laser-based tile ablation



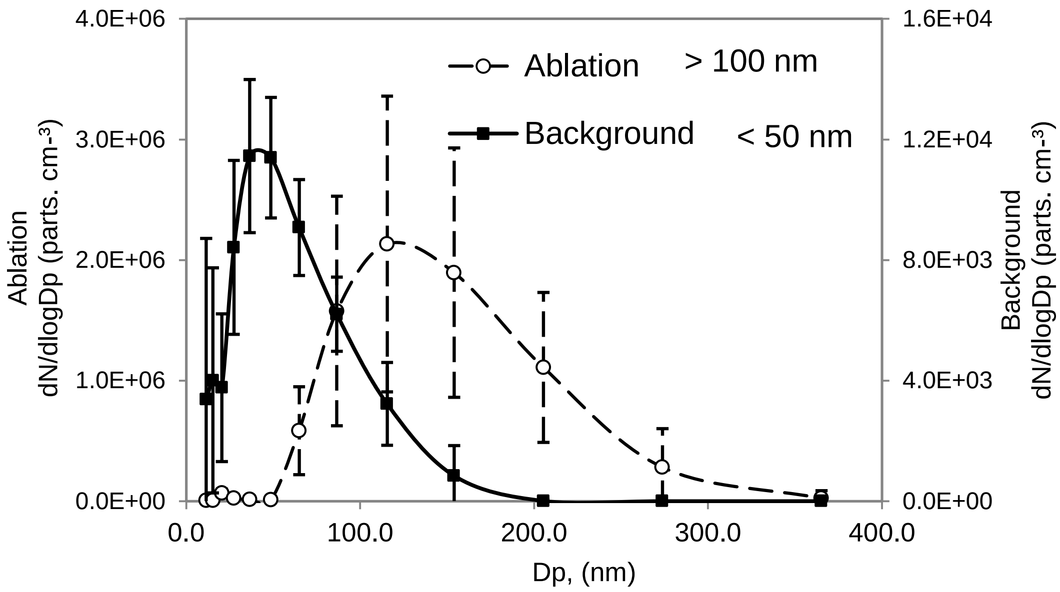
Modified from de la Fuente (2013)



Engravings by expelling material from a solid surface (raw porcelain) through irradiation with a pulsed laser beam. Mechanical process generating micro- and nano-scaled particle emissions.

Laser-based tile ablation

Coarse(r) particle emissions due to breakdown of the original material



Worker area concentratios

	$N_{mean} \pm \sigma$ (cm^{-3})	$PM_{2.5} \pm \sigma$ ($\mu g\ m^{-3}$)
Ablation	$3.8 \pm 1.9 \times 10^5$	650 ± 391
Bckg.	$1.3 \pm 0.9 \times 10^4$	5.9 ± 0.2

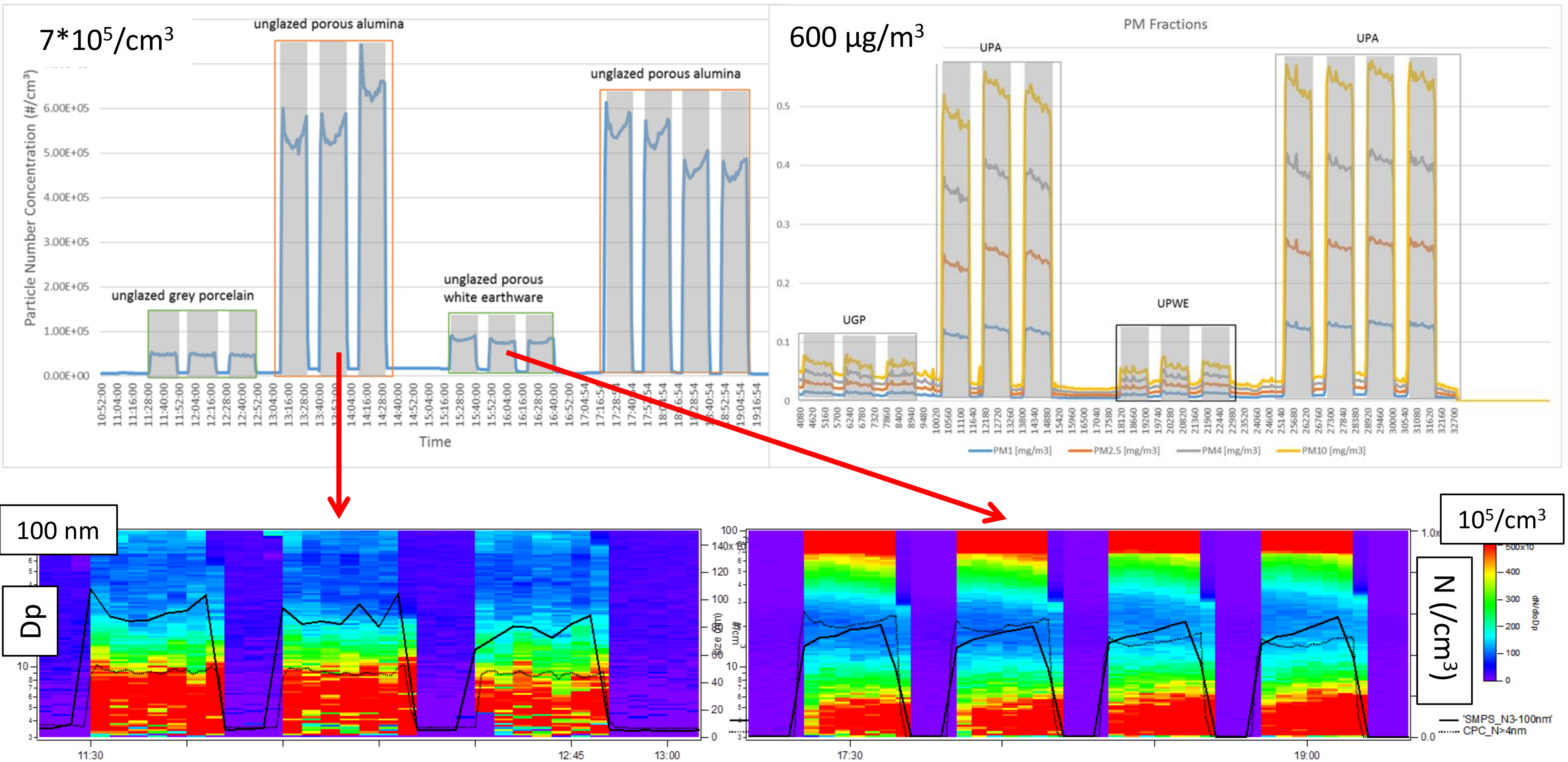
Particle mass concentration:

Statistically significant ($3*\sigma_{bg}$)

More effective metric because of coarse diameter of the particles

Fonseca et al. (2015) J. Aerosol Sci.

Laser-based tile ablation



Unglazed grey porcelain

Unglazed porous alumina

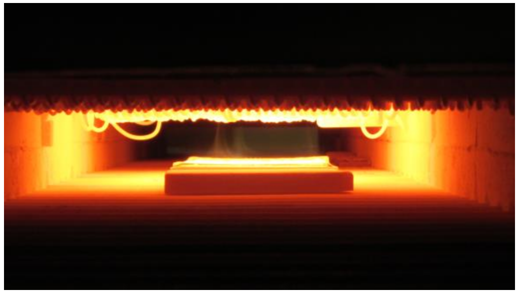
Very repetitive emission pattern, dependent on tile composition

Primary *vs*. Secondary emissions: soon to be tested with HTDMA

Case study:

Ceramic tile sintering

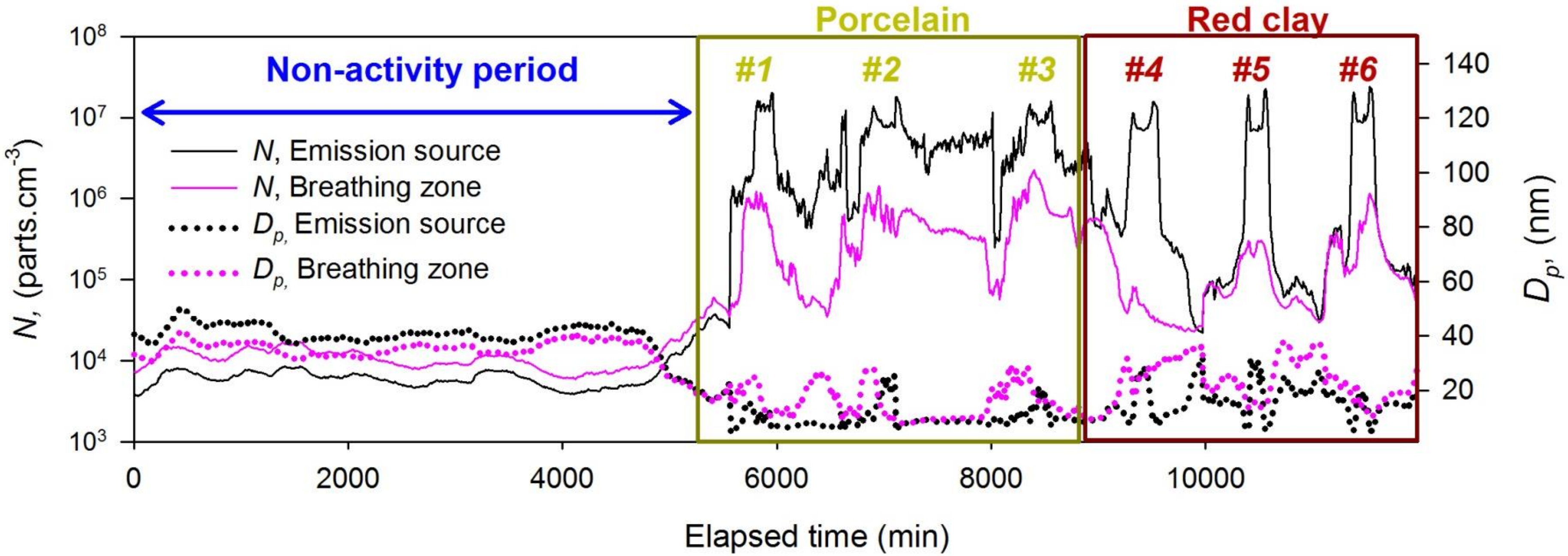
Laser-based tile sintering



Enhanced surface properties:

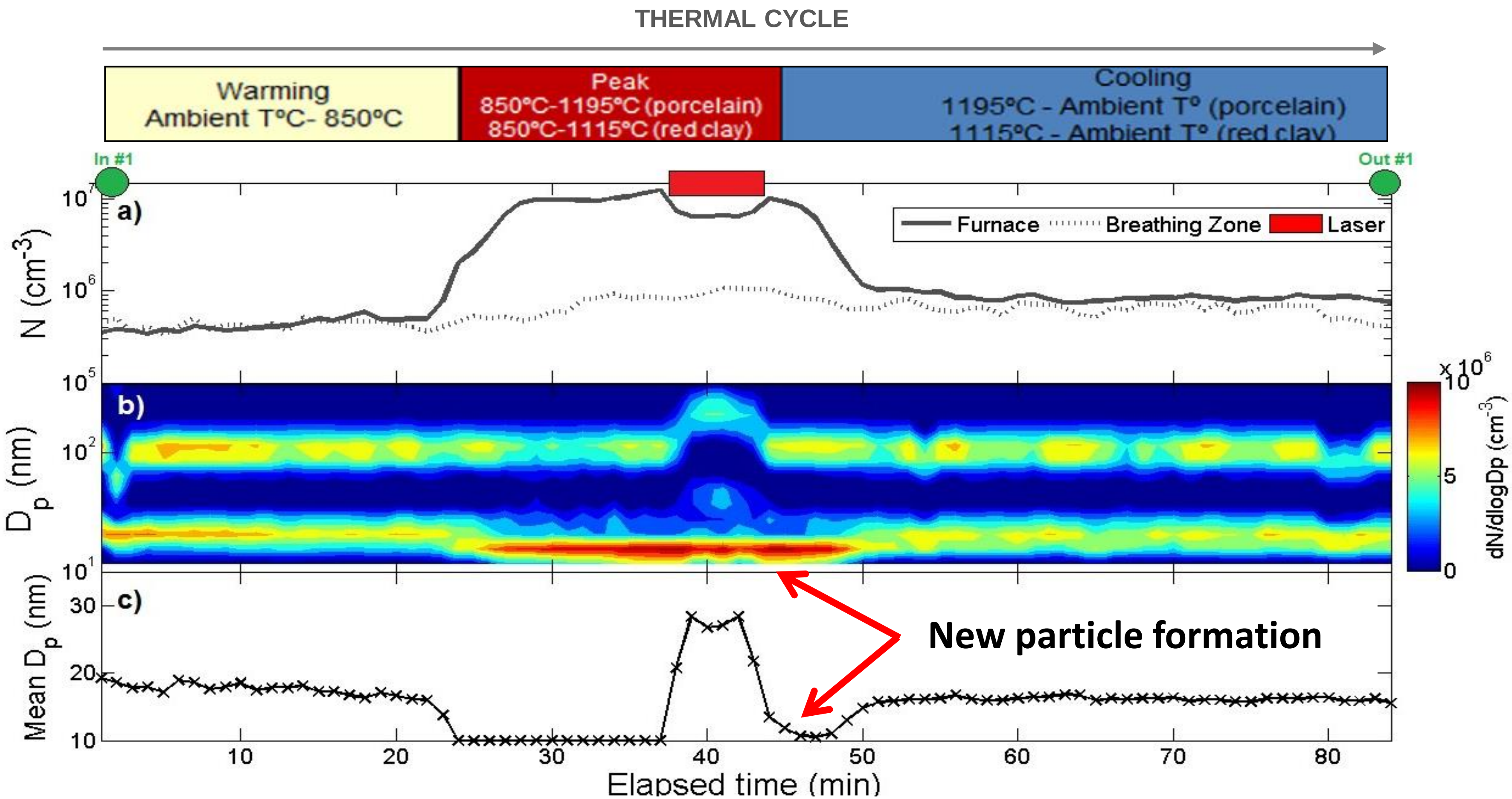
durability, new colours, pigmentation

of glass surfaces, etc.



	Source	Worker area
N	$>10^7/cm^3$	$>10^5/cm^3$
Dp	8-18 nm	13-27 nm

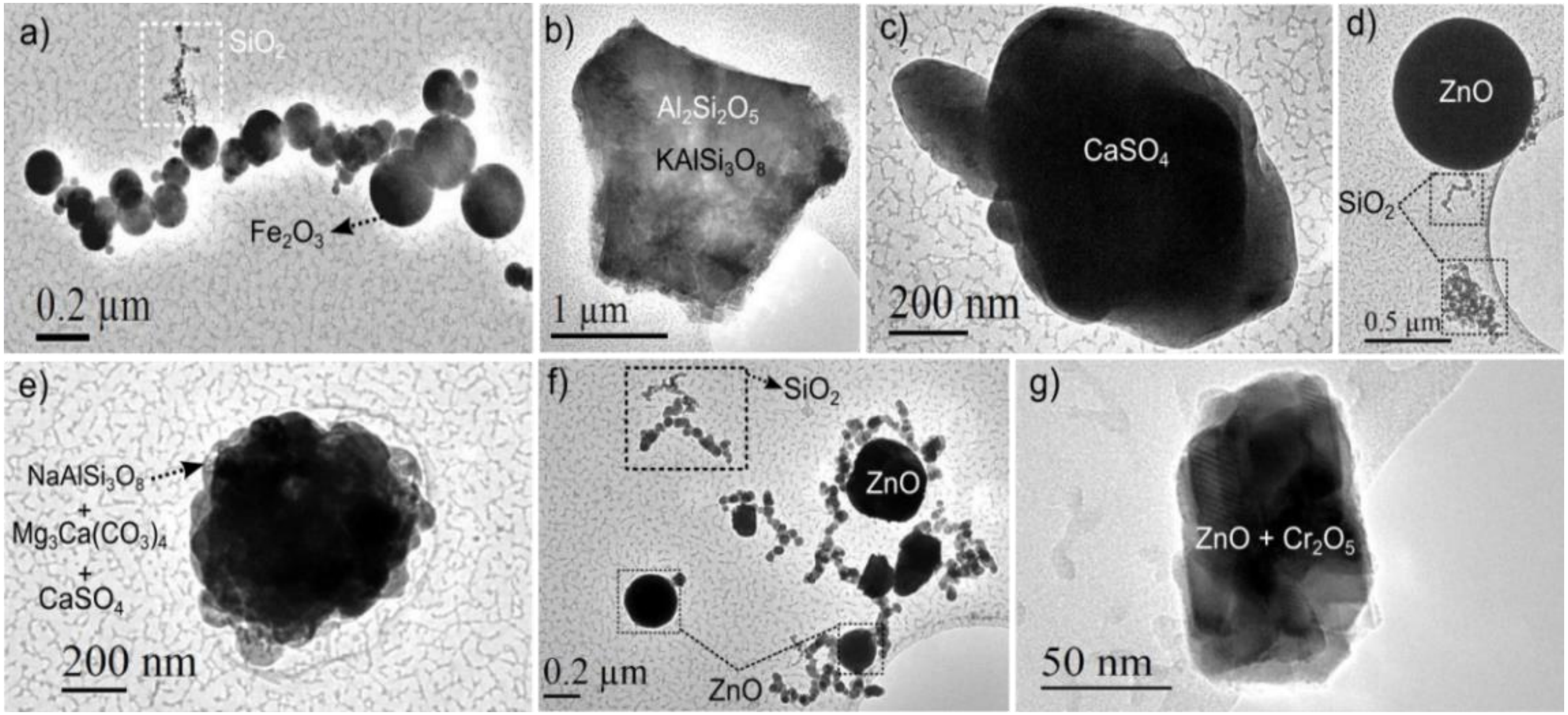
Laser-based tile sintering



NP emissions independent of the laser treatment: issue for ceramic sector in general. The laser seems to (partly) inhibit new particle formation

Fonseca et al. (2015) J. Aerosol Sci.; Fonseca et al. (2016) Sci. Total Environ.

Laser-based tile sintering



Spherical particles (10 nm – 1 µm) from melting of ceramic materials
Particle condensation and/or agglomeration

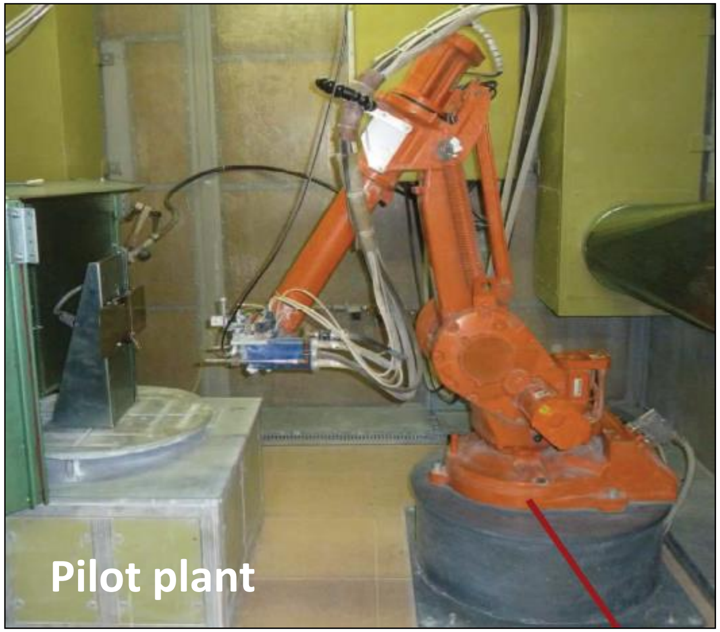
Fonseca et al. (2015) J. Aerosol Sci.; Fonseca et al. (2016) Sci. Total Environ.

Case study:

Atmospheric plasma spraying

Atmospheric plasma spraying

Highly energetic process to obtain high-performance coatings (e.g., thermal barriers)

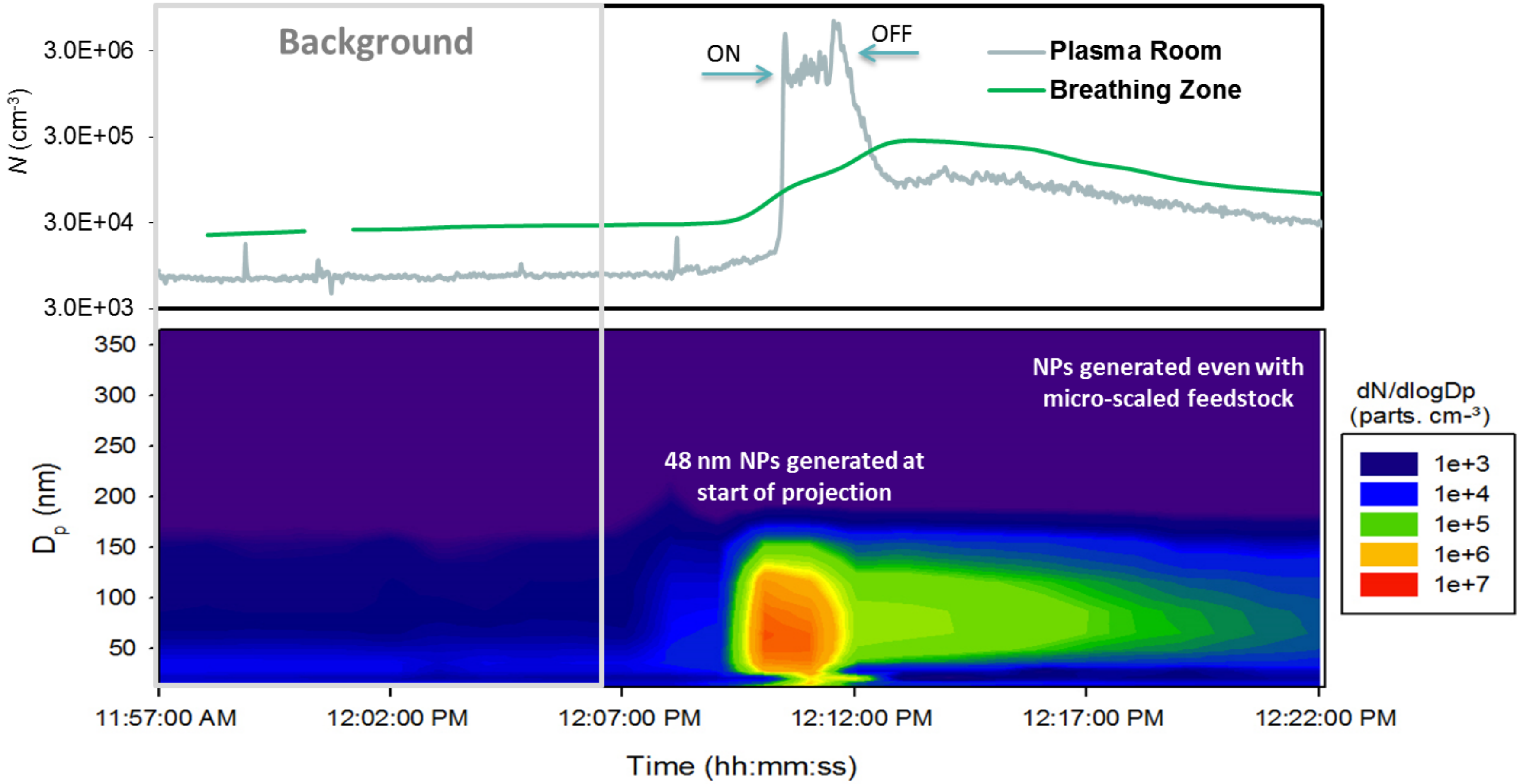


- Different types: atmospheric plasma, HVOF, arc discharge
- Spraying of ceramics or metals (powder or wire)
- High potential for NP emissions

Atmospheric plasma spraying

Pilot plant scale: micro-suspension

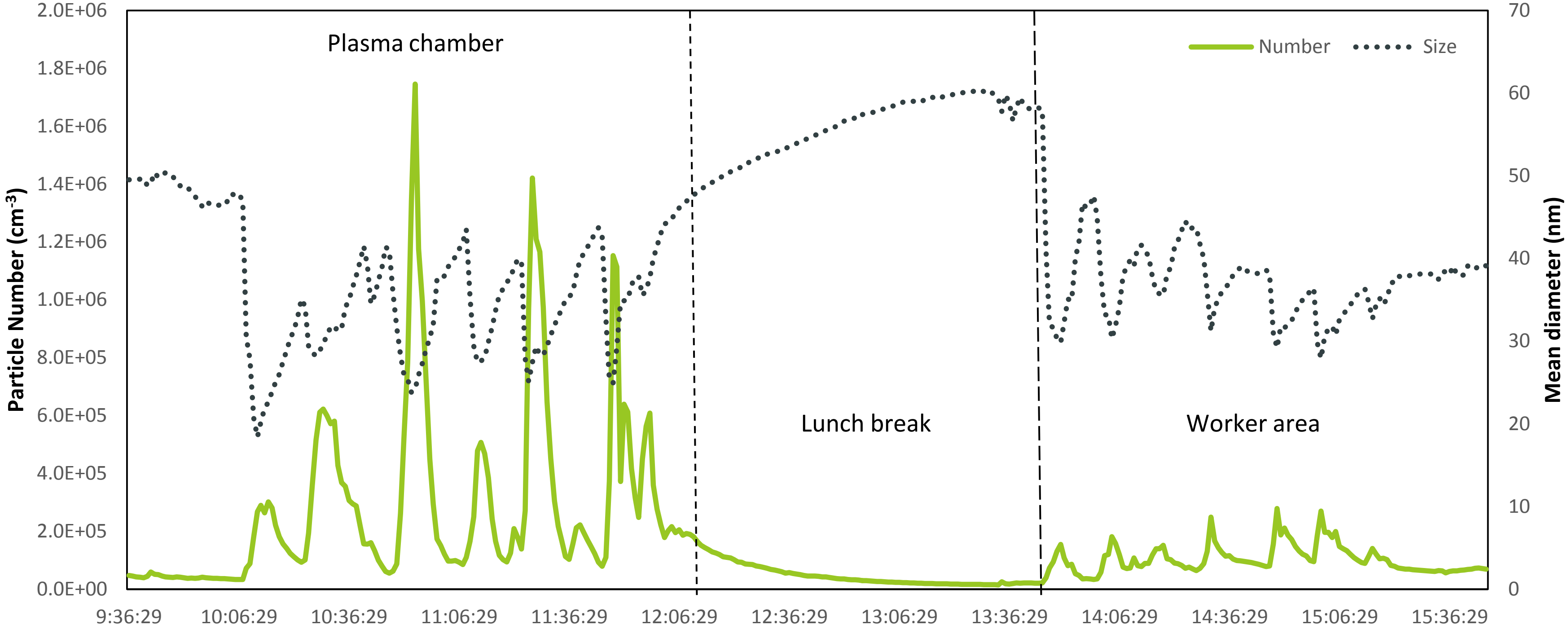
(ceramic glass powder <63 µm + 1% of fluidised nano 7 nm)

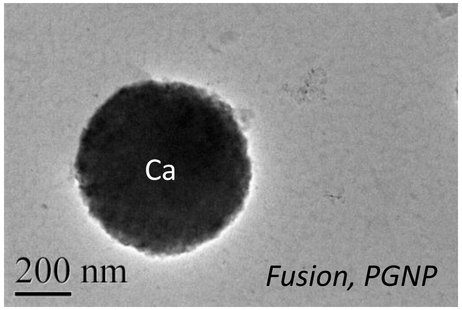


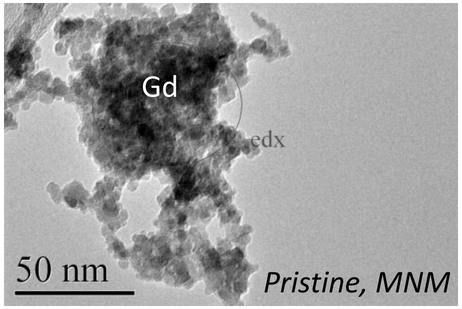
Viana et al. (2017), Sci. Total Environ.

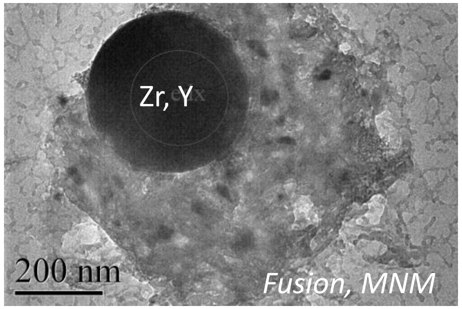
Atmospheric plasma spraying

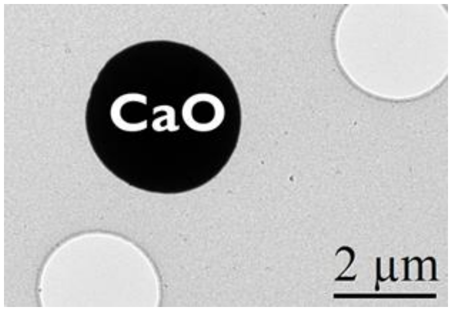
Industrial scale: metal coating WOKA 7205 (Nickel Chromium powder)







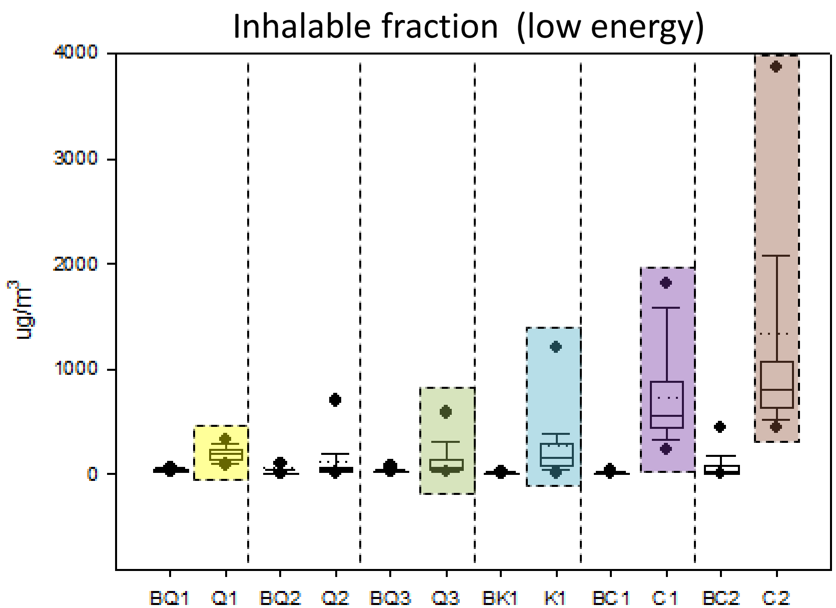


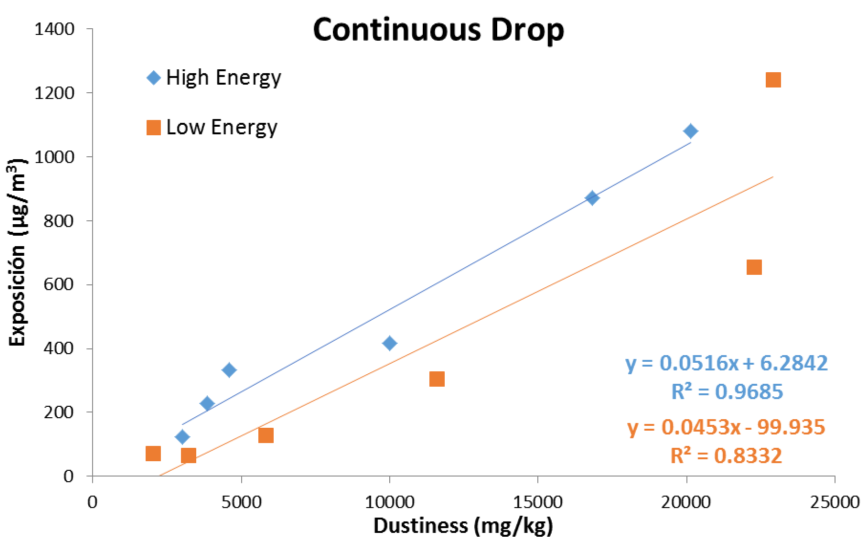


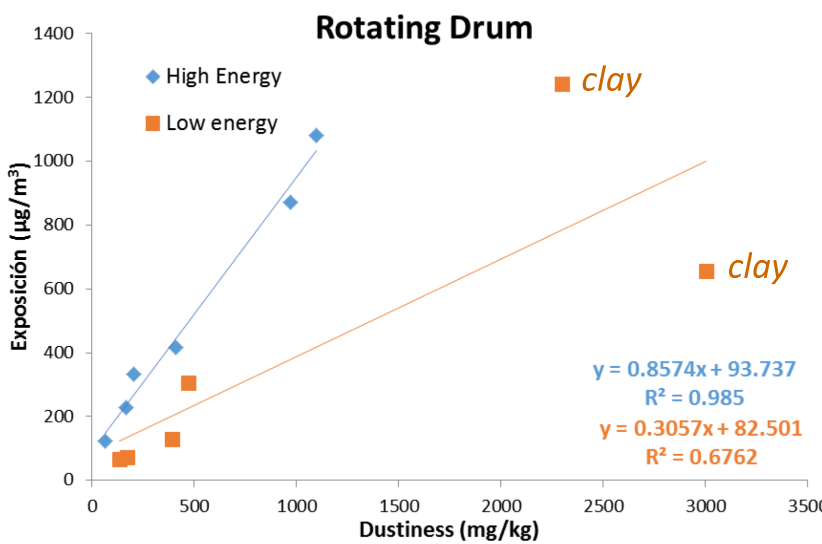
EXPOSURE MANAGEMENT

Case study: **Handling of raw materials**

Materials	d50 (µm)
Silica sand	120
Quartz 1	14
Quartz 2	3.8
Quartz 3	2.7
Kaolin	5.8







Case study: **Plasma spraying**

Leak identification

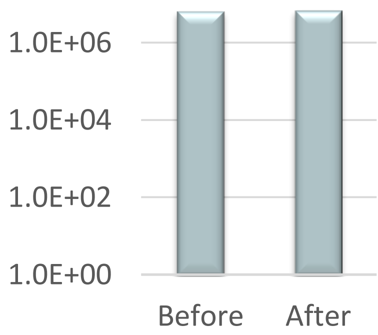
Sealing

New measurements

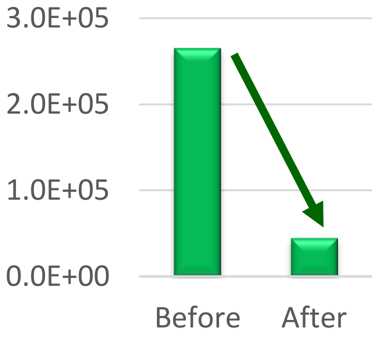
	INITIAL SITUATION	FINAL SITUATION
Breathin g zone	Ventilation by natural convection (ACH < 2)	Forced ventilation (~14 ACH) A precise protocol for opening and closing the plasma room
Plasma Room	Air entrance in the plasma room by a single point from the breathing zone	Air entrance in the plasma room from outside Improved air entrance distribution using a multipoint system surrounding the plasma plume Enhanced sealing of the extraction system

ACH: Air changes per hour (h^{-1})

Plasma chamber



Worker area



Reduction = 80-95% in terms of N in the worker area

However, N still > 50.000/cm^3

CONCLUSIONS

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Conclusions

- Different scenarios with potential for **occupational exposure** to NPs were assessed
- **Real-world operating conditions**, at pilot plant and industrial scales
- At times, **fine line between emission and worker area**
- **High NP concentrations** measured: >10^5/cm^3, up to 10^7/cm^3…
- … but also below DL: difficult to extract significant conclusions
- High exposure concentrations measured with but also in absence of MNMs
- Results highight the **relevance of process-generated NPs**
- Dedicated and properly implemented **mitigation strategies can reduce exposure by up to 80-95%**
- Major **knowledge gap**: toxicological characterisation of process-generated NPs. Also, aggregates *vs*. single particles?
- Need to assess **further scenarios under real-world operating conditions**
- **However, not possible to assess ALL scenarios: need for modelling**

Thank you for your attention!

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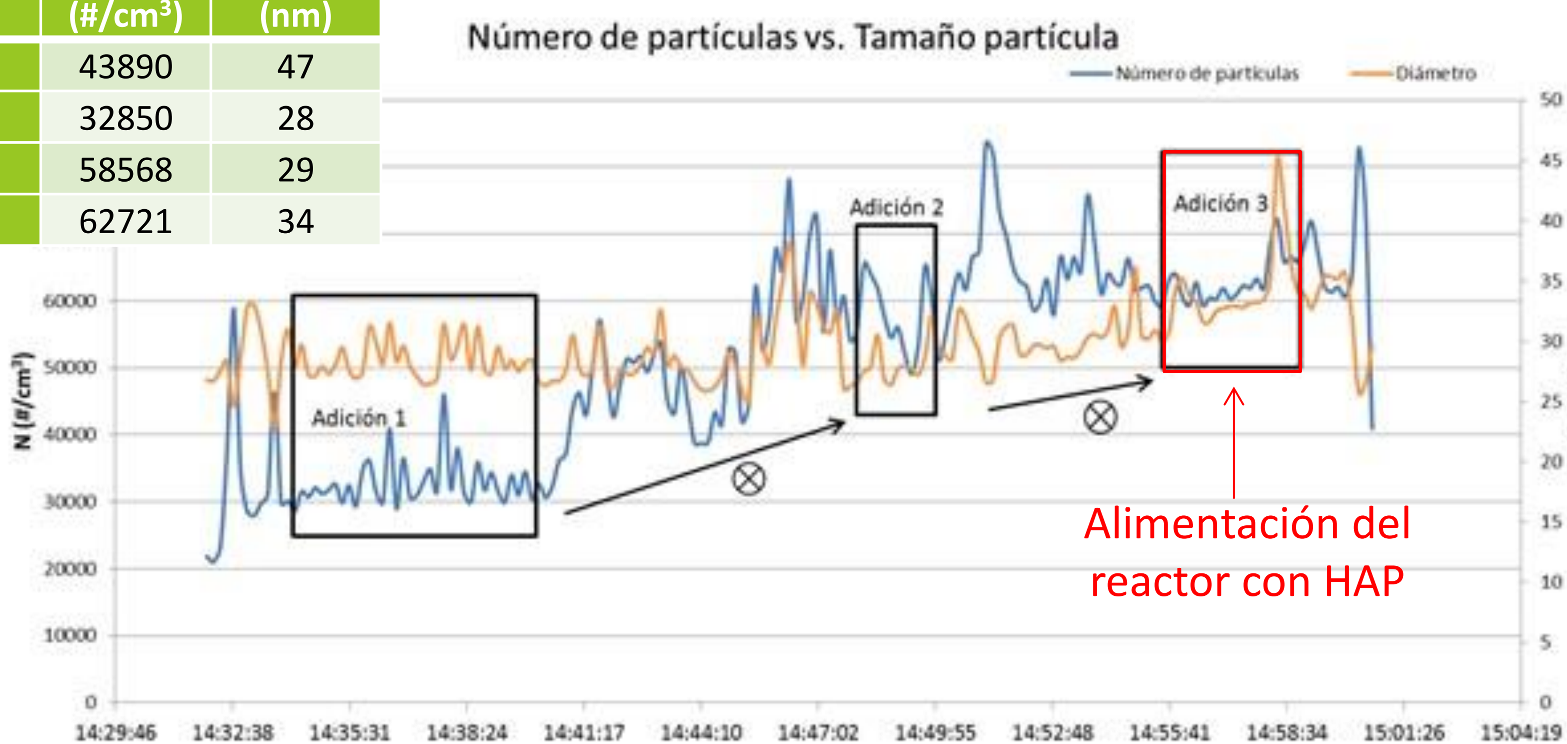
Escenarios de alimentación de reactores

- Hidroxiapatita HAP (nanométrica, suspensión acuosa viscosa)
- Campaña#4: $N_{10\text{-}700\ nm}$ incrementa de 58000 a 62000/cm^3, con diámetros medios 29-34 nm (>diámetro original, 10-20nm). **Tendencia a incrementar con la adición de materiales micrométricos, no solamente con NPs. Especialmente durante los periodos de mezcla (reactor cerrado)**

Proceso	Número (#/cm^3)	Diámetro (nm)
Sala reactores	43890	47
Adición 1	32850	28
Adición 2	58568	29
Adición 3	62721	34



Ausencia de significación estadística debido a la escasa representatividad temporal

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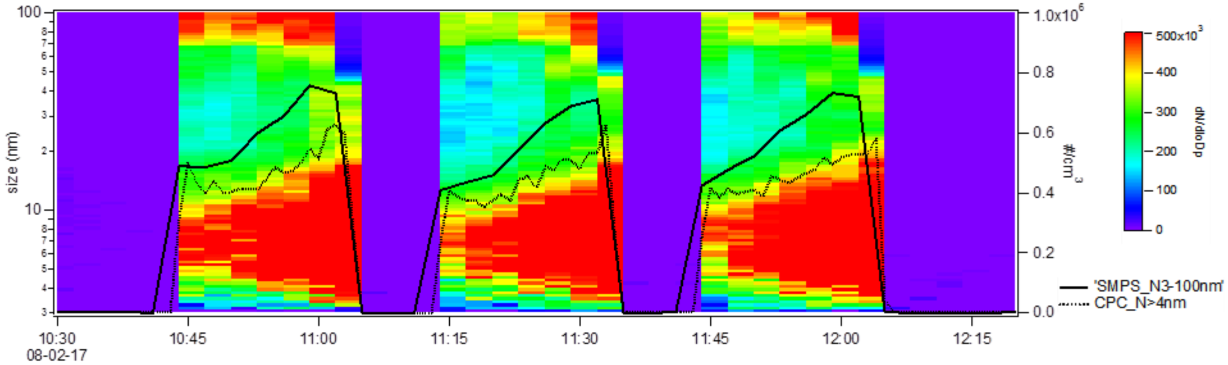
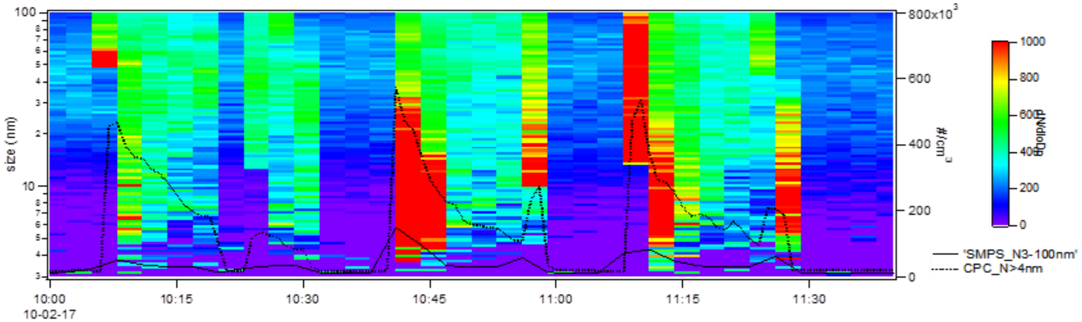
Laser-based tile sintering

- Innovative process to obtain enhanced surface properties (durability, new colours, pigmentation of glass surfaces, etc.)
- High potential for implementation at global scale

UGP, near-IR laser, high energy settings? Mistake in Word file?



UGP, mid-IR laser,



Looking to understand these emission patterns by looking into:

- Tile porosity
- Roughness
- Chemical composition
- Mineralogical composition
- Other variables?

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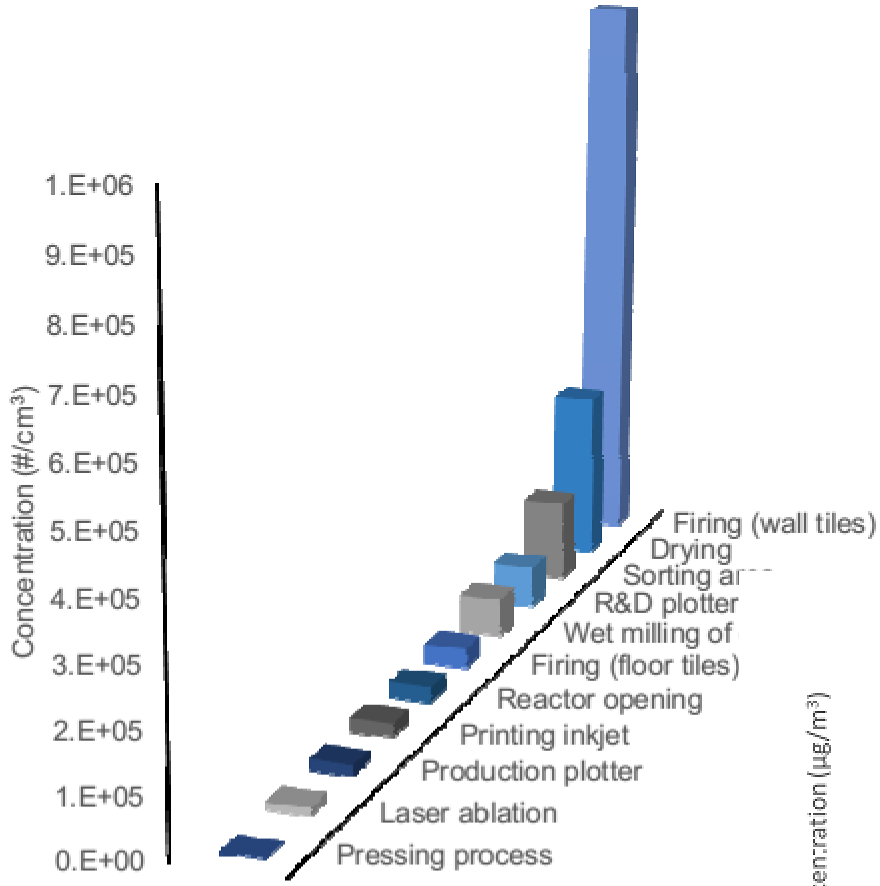

Figure 30. Mean particle number concentration in the selected s

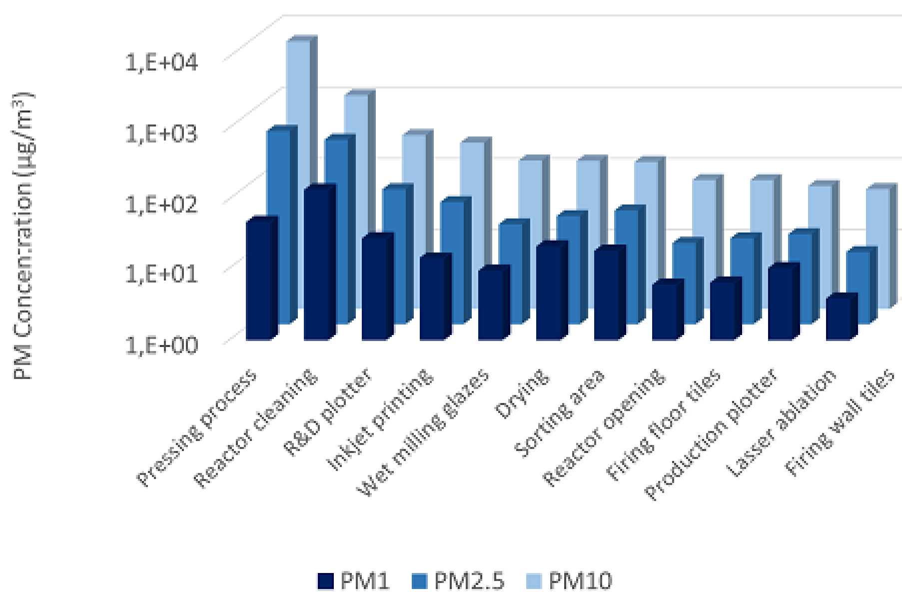

Figure 31. Mean values of PM_{10}, $PM_{2.5}$ and PM_1 emission of each sampling point