House Keeping

1. Questions/Comments/Feedback - Let us know via the question area in your attendee control panel
2. Discussion - Microphones will be unmuted at the end of webinar
3. Be Patient - Allow others to finish speaking
4. Slides and recording will be sent to all attendees and available on website

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Event name : LIFE NanoMONITOR Webinar - 13 December 2018

NanoMONITOR is partly funded by the European Commission Life+ with grant agreement LIFE14 ENV/ES/000662

ENVIRONMENT
LIFE Programme

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Hands on Training on methodologies to Conduct Exposure Assessment Studies in Workplaces

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ITENE CEAM AEON yordas Group Formerly THE REACH CENTRE

LIFE NanoMonitor Webinar **13th December, 2018**

NanoMONITOR is partly funded by the European Commission Life+ with grant agreement LIFE14 ENV/ES/000662

ENVIRONMENT LIFE Programme

Outline

1. Sources of NM release
2. Methodology
3. NMs in urban environments
4. Conclusions

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ENVIRONMENT
LIFE Programme

1 Sources of NM release

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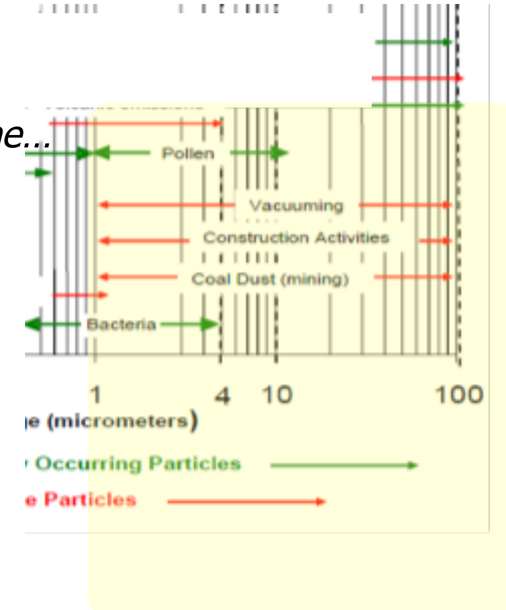
Sources of NM release

Different origins

Natural:

- *volcanic emissions, forest fires, marine…*



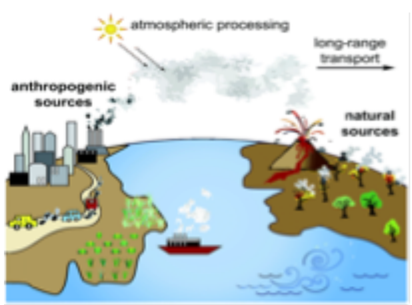
Anthropogenic

- Incidental:

  Traffic emissions, machinery, burning…

- Manufactured:

  Engineered Nanomaterials



Clean air at the Alps	< 1 000 part/cm^3
Clean air at the office	2 000 – 4 000 part/cm^3
Urban poutdoor air	10 000 – 20 000 part/cm^3
Contaminated outdoor air (smog)	> 50 000 part/cm^3
Cigarrete smoke	> 50 000 part/cm^3
Industrial Works (welding)	100 000 – 1 000 000 part/cm^3

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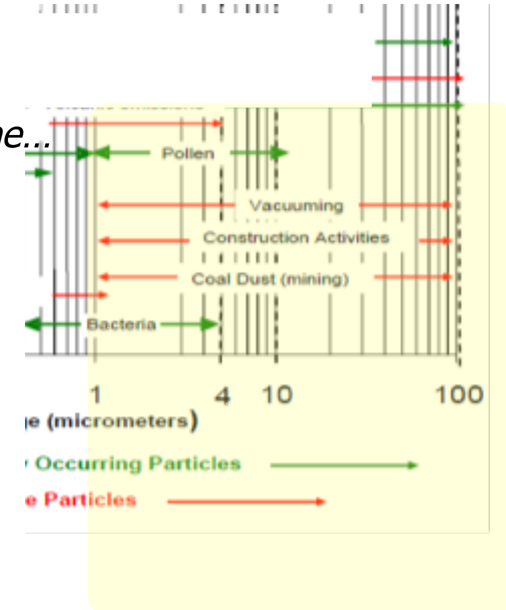

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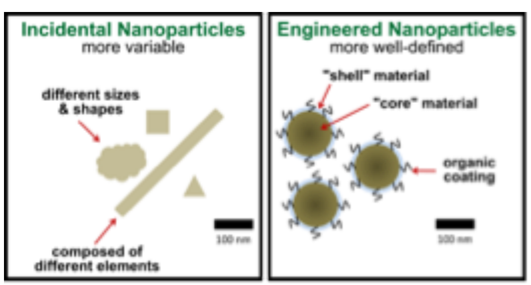

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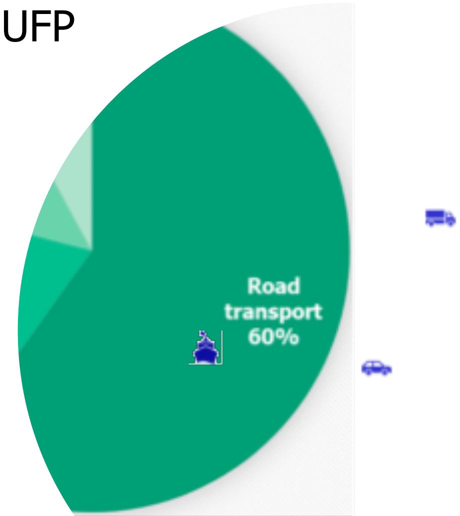
Sources of NM release

Emissions from vehicles & INMs

From the total particle number emissions, 84% lies within the UFP size range, and mainly is due to vehicle transport:

- Road transport >60%
  - semi-volatile engine emissions,
  - solid particle engine emissions,
  - brake wear and resuspension,
- Non-road transport ~19% (including ship traffic)
- Domestic combustion ~13%
- Other: Incinerators, smelters, power plants, and industries in urban areas



The large majority of commercially produced particles are highly polydispersed

↳

not expected NM appearance!

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Sources of NM release

ENMs presence in urban infrastructures

ENMs are widely used in the context of the outdoor urban environment:

- Textiles and fabrics (e.g. ropes, sails, tents, traps): flame retardancy,
- In Concrete: self-cleaning surfaces, photocatalytic pavements
- In Steel: anti-crack, smoother surfaces, temperature restriction
- In Wood: moisture adsorbents, prevent discoloration, water repellance
- In Glass: temperature control, block UV & glare
- In Paints and Coatings: scratch resistant, Hydrophobic surfaces
- In Monitoring: sensors (stress, strain, vibration, cracking, corrosión…)
- Fuel additives: to enhance fuel efficiency
- Autos: High-performance tires
- Road markings: Antireflection layers

Roof panels of St Pancras Station in London (10000 m^2, 18000 Glass panels) with TiO_2 ENM photocatalyst & Self-cleaning

conventional glass   self-cleaning glass

Church "Dives in Misericordia", Rome, made by using self-cleaning concrete

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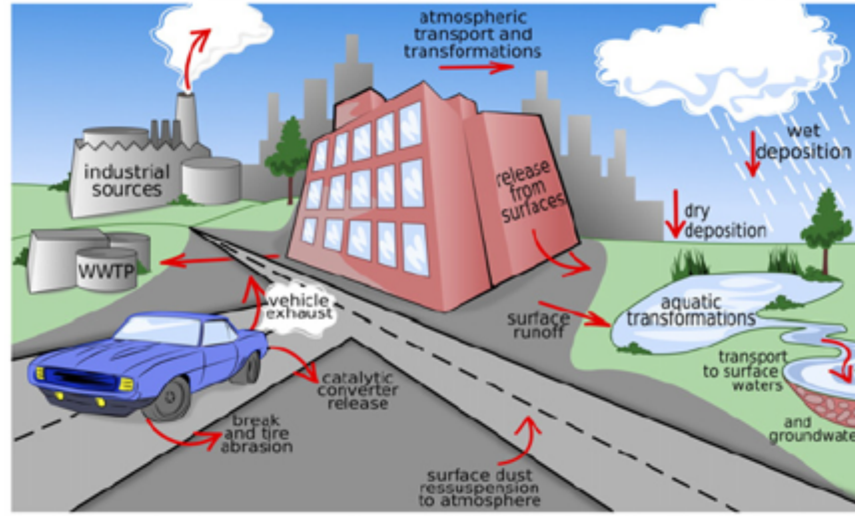
Sources of NM release

How they release in urban environment?

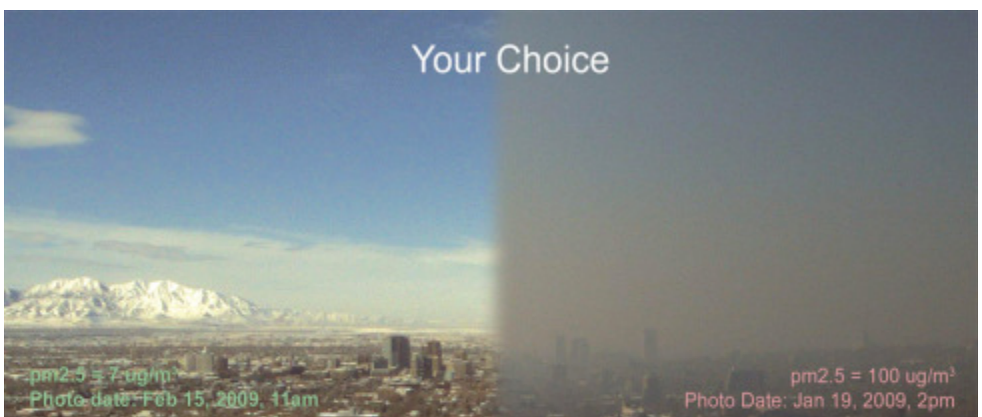
- Matrix formulation (type and concentration of binder and fillers) → a higher proportion of binder decreases release of ENMs.
- Weather conditions, triggering ENM erosion that can lead to air/water transport and deposition of these ENMs into/onto soil, surface water, and impervious surfaces.
- Loosely bound ENMs on the surface coatings by:
  - UV irradiation
  - mechanical damage
  - wash off



- Sources and pathways of outdoor urban nanomaterials in the environment -

Source: Baalousha et al, Sci.Tot. Env. 557–558 (2016) 740–753

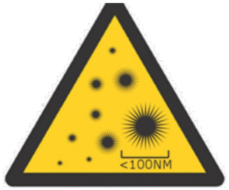
- Temperature, especially in hot geographical locations, may result in faster weathering (corrosion) of the paint, enhancing release of ENMs. **But no studies are found that record the impact of temperature.**
- City structure, densely packed high-rise buildings limit air exchange and hence, the dispersion of NMs, further elevating their concentrations.



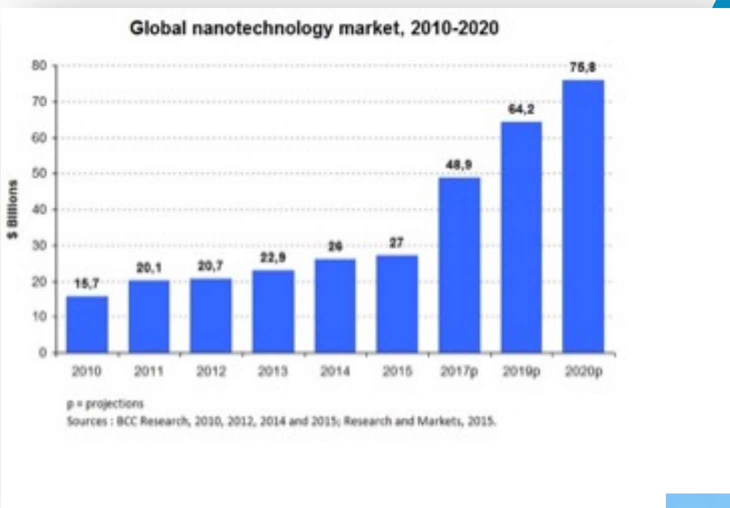
Mexico city *(source: https://fieldguidetonature.wordpress.com/)*

Sources of NM release

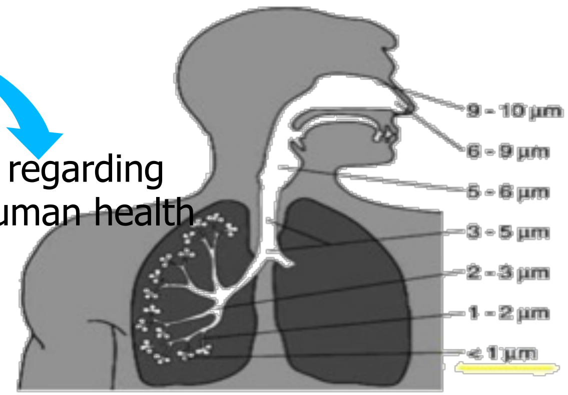
Why nanomaterials? Why now?



Understanding new particle formation in occupational /urban environments is important to estimate particle number concentrates and related human exposure



Uncertainties regarding exposure / human health



Increasing market/applications

Graffiti protesting the establishment of nanotechnology laboratories on the Bastille fortress in Grenoble, France

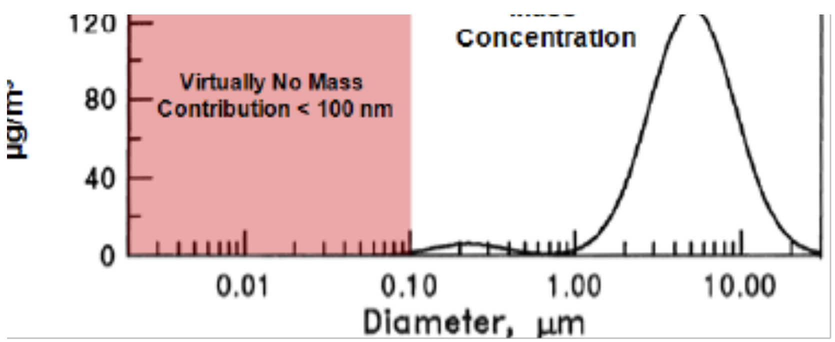
Low market penetration / Consumer confidence

Sources of NM release

Why nanomaterials? Why now?

Although NMs contribute a negligible portion of the total mass of particulate matter, they are the dominant fraction in terms of particle number, reaching orders of magnitude higher than larger particles, thus a major proportion of emissions **remains unregulated through ambient air quality standards**.

Limits?
Metrics?



Occupational
Exposure
Limits

Sources of NM release

Factors determining the exposure

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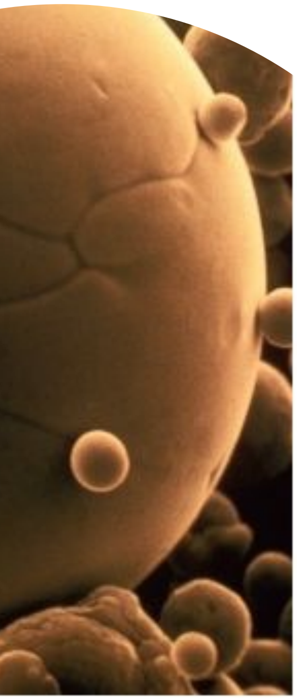

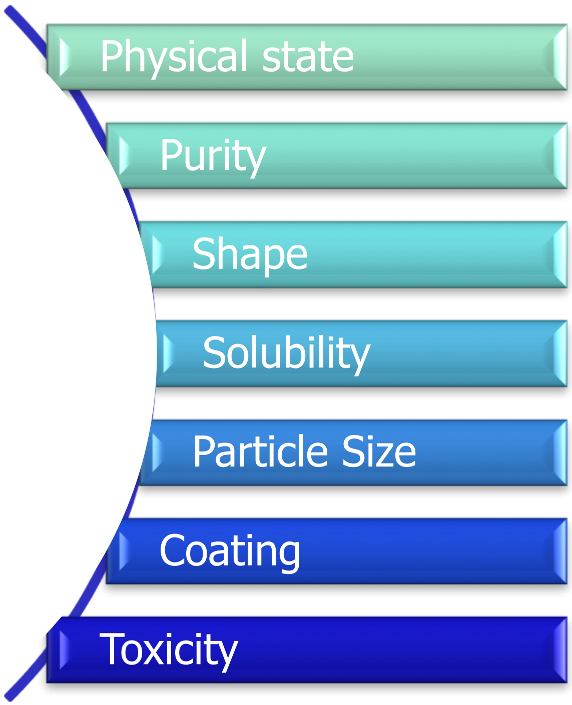

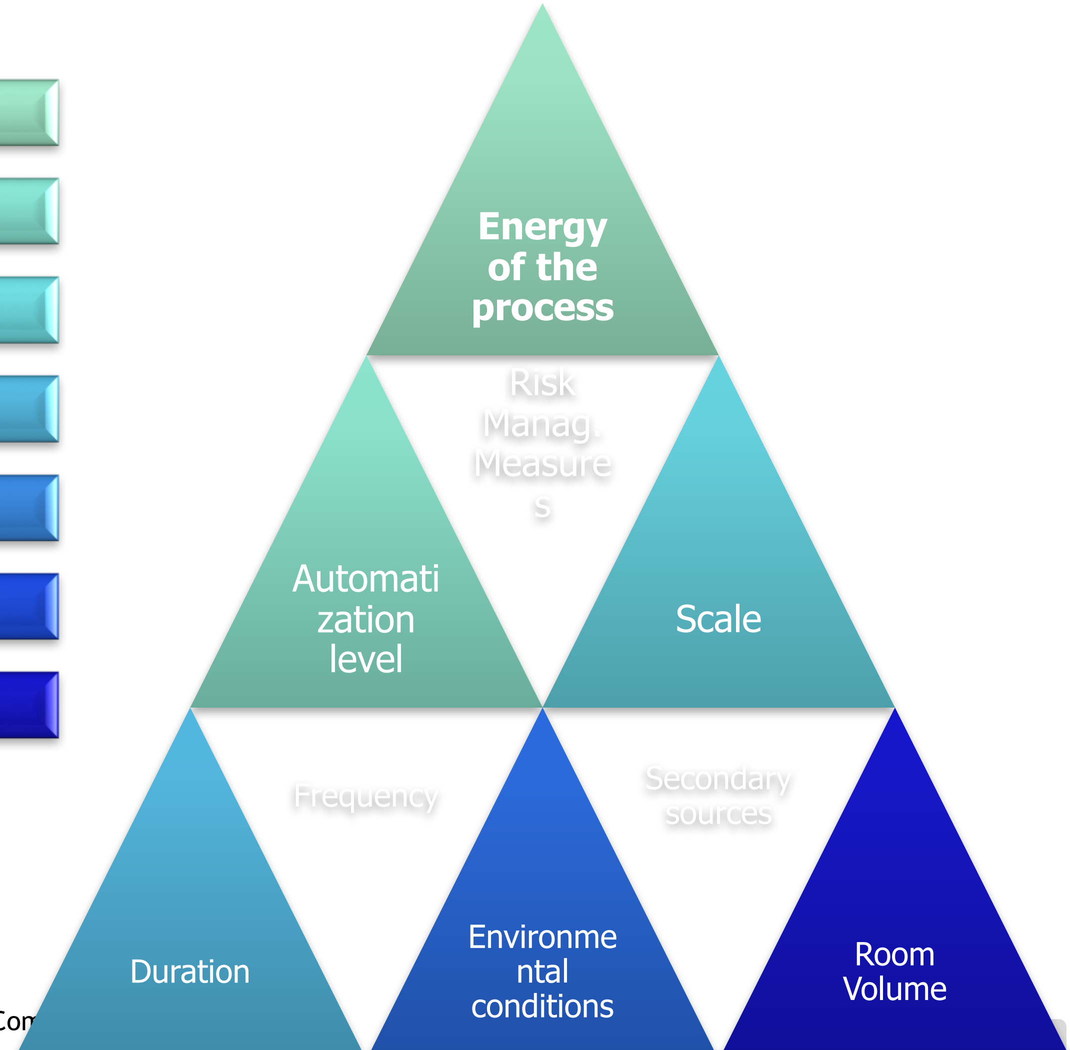

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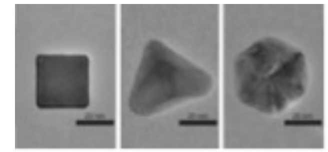
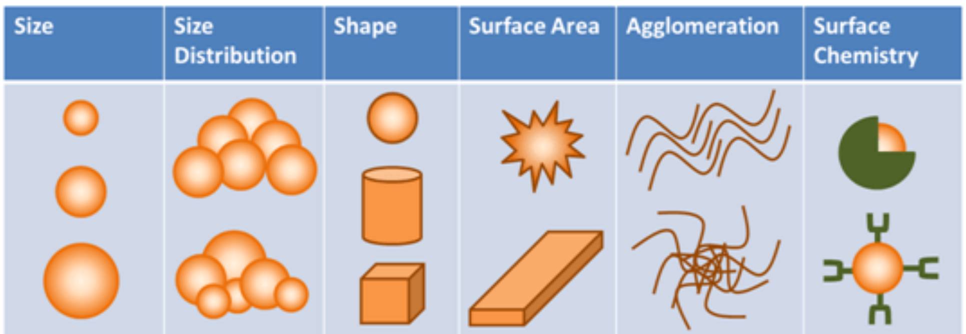
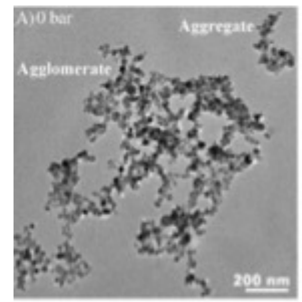
Sources of NM release

Challenges from the measuring element

- NMs can be manufactured with various shapes, coatings, and surface functionalities.



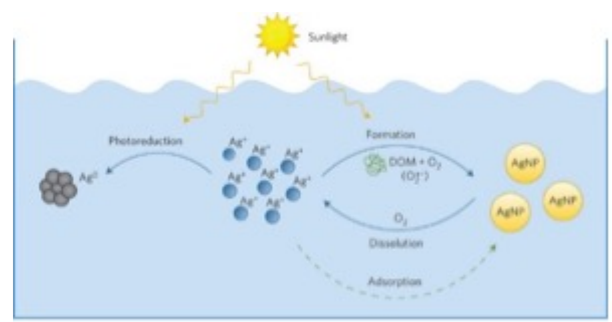




De Volder, Univ. Cambridge, NanoManufacturing

- NMs can exist as single or aggregated particles.

- NMs can undergo a number of potential transformations that depend on both the properties of the ENM and the local environment.



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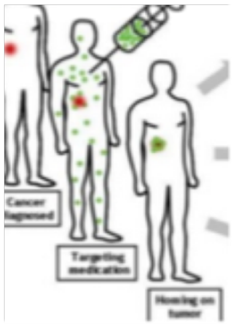
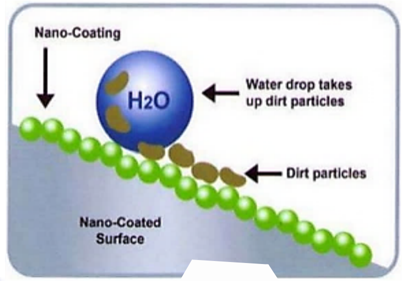
Sources of NM release

Challenges from the measuring process





EMISSION SOURCE	RELEASE POTENTIAL	SPECIFICATIONS
1. Point source or fugitive emissions		
Liquid-phase reaction	Likely	Single particles
Flame spraying	Likely	Single particles
CVD	Not Excluded	Single particles
Top-down (milling)	Not excluded	Single particles
2. Handling and transfer of bulk manufactured nanomaterial powders with relatively low energy		
Weighing of powders	Likely	Single particles and aggregates < 1000nm
Harvesting	Likely	
Manual packaging (Bagging)	Likely	
Bag emptying of powders	Likely	Single particles and aggregates < 1000nm Large aggregates 1 to 20µm
Melt Blending	Likely	Embedded particles. Limited release of fully dissociated NPs
3. Dispersion of either (liquid) intermediates containing highly concentrated (> 25%) nanoparticles or application of (relatively low concentrated < 5%) ready-to-use products		
Spraying of liquid	Very Likely	Single aggregates as well as large agglomerates
Spraying (gas)	Very Likely	
Injection Moulding	Very Likely	Single particles and aggregates < 1000nm
Brushing and rolling	Very Likely	Embedded particles Limited release of fully dissociated NPs
Sonication of nanodispersions	Very Likely	Single particles and aggregates < 1000nm
4. Activities resulting in fracturing and abrasion of manufactured nanoparticles-enabled end-products		
Abrasion of nanoproducts	Not excluded	Embedded particles. Limited release of fully dissociated NPs

Source: LIFE **NanoMONITOR “Guidance on the sampling methods and analytical techniques for the measurement and monitoring of engineered nanomaterials in the environment”**

Sources of NM release

Limit Values for NMs

NIOSH - National Institute for Occupational Safety and Health (EEUU)

Recommended Exposure Limit (REL)		
Tipo de nanomaterial	***Recommended Exposure Limit* (REL)**	**Efecto considerado**
TiO_2 ultrafino (<100 nm)	0,3 mg/m^3	Tumores en los pulmones
Nanotubos de carbono y nanofibras	0,001 mg/m^3	Inflamación pulmonar y fibrosis

IFA - Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (Alemania)

Recommended Benchmark Levels (RBL)	
Tipo de nanomaterial	***Recommended Benchmark Level* (RBL)**
Metales, óxidos metálicos y otros nanomateriales granulares biopersistentes de densidad > 6 000 kg/m^3	20 000 partículas/cm^3 (entre 1 nm y 100 nm)
Nanomateriales granulares biopersistentes de densidad < 6 000 kg/m^3	40 000 partículas/cm^3 (entre 1 nm y 100 nm)
Nanotubos de carbono	0,01 fibras/cm^3
Partículas líquidas ultrafinas	MAK[a] o AGW[b]

BSI - British Standard Institution (UK)

Benchmark Exposure Levels (BEL)	
Tipo de nanomaterial	***Benchmark Exposure Level* (BEL)**
Insoluble	0,066 x WEL[a] 20 000 partículas/cm^3
Soluble	0,5 x WEL
CMAR[b]	0,1 x WEL
Fibroso[c]	0,01 fibras/cm^3

SER - Social and Economic Council of the Netherlands (Holanda)

Nano Reference Values (NRVs)		
Tipo de nanomaterial	***Nano Reference Value* (NRV)**	**Ejemplos**
Nanomateriales granulares biopersistentes de densidad > 6 000 kg/m^3	20 000 partículas/cm^3 (entre 1 nm y 100 nm)	Ag, Au, CeO_2, CoO, Fe_xO_y, La, Pb, Sb_2O_5, SnO_2
Nanomateriales granulares y fibrosos biopersistentes de densidad < 6 000 kg/m^3	40 000 partículas/cm^3 (entre 1 nm y 100 nm)	Al_2O_3, SiO_2, TiN, TiO_2, ZnO, negro de humo, nanoarcilla, C_{60}, dendrímeros, poliestireno, nanofibras para las cuales se han descartado efectos similares a los del amianto
Nanofibras rígidas y biopersistentes para las cuales no se descartan efectos similares a los del amianto	0,01 fibras/cm^3	SWCNT, MWCNT, fibras de óxidos metálicos para las cuales no se descartan efectos similares al amianto
Nanomateriales granulares no biopersistentes	Límite de exposición profesional en escala no nanométrica	Lípidos, NaCl

Safe levels of NM exposure are still ambiguous!

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2 Exposure to NMs in workplaces

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Methodology

Nanosafety

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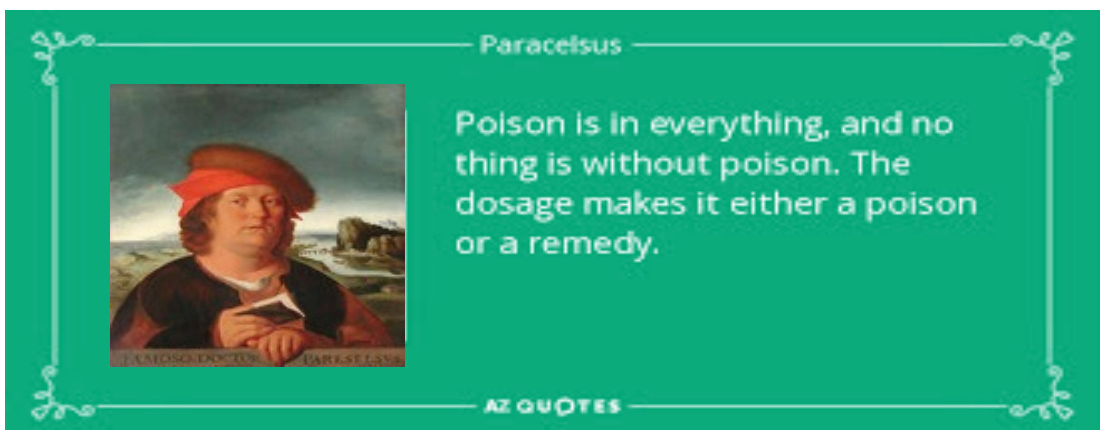
Risk = Hazard x Exposure

severity — probability

High Hazard	Low Hazard (?)
Low Exposure	High Exposure

Credits: Neil Hunt (Yordas Group)



Let's dosage!

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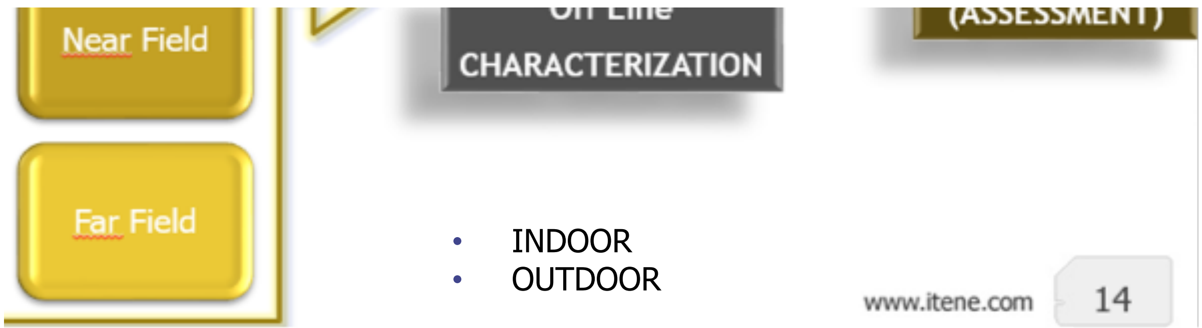
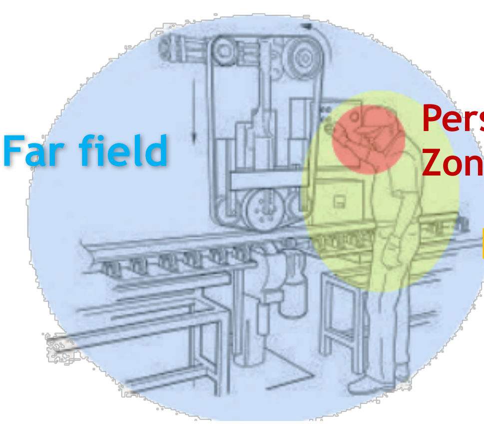
NEAT: Nanoparticle Exposure Assessment Technique



- INDOOR
- OUTDOOR

- With NMs
- Without NMs



Methner et al, J Occup Environ Hyg. (2010) Mar;7(3):163-76

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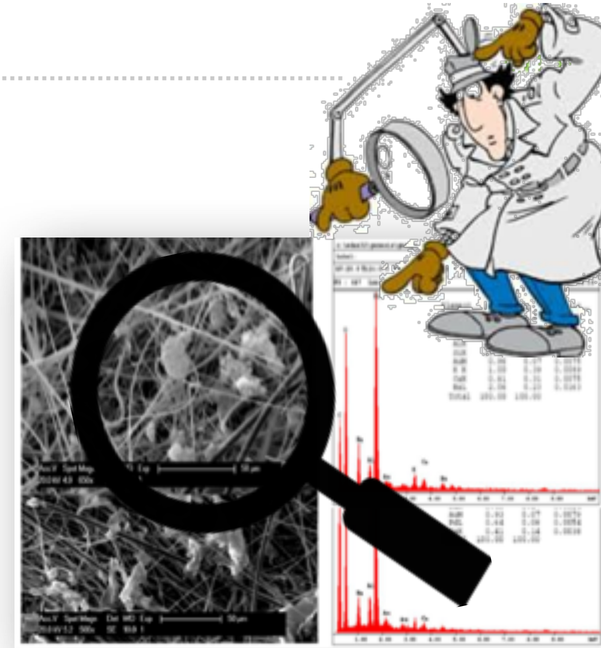
Methodology

NEAT Technique… in practice



SEM/EDX		RATIO C_{ACT}/C_{BG} > CV	PROBABILITY OF EXPOSURE
NM BG	NM ACTIVITY		
✗	✓	✓	Highly Probable
✓	✓	✓	Possible
✗	✓	✗	Not Excluding
✓	✓	✗	
✗	✗	✗	Low Probability / Negligible
✗	✗	✓	

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Methodology

Risk assessment of exposure to NMs

STEPS:

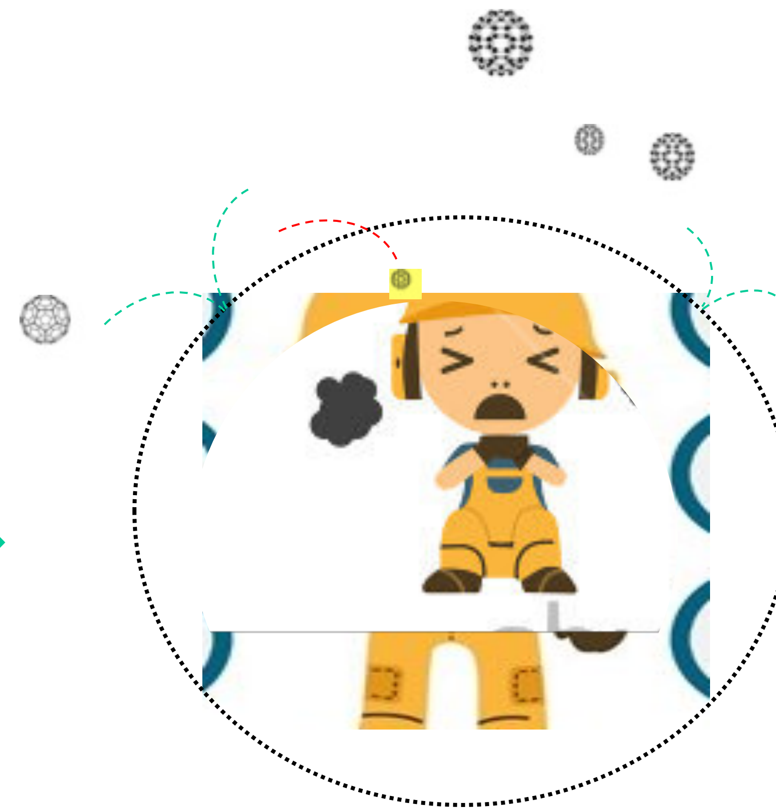
1 – Locate the risk

2 – Assess the risk (*Dose*)

3 – Application of the hierarchy of controls

4 - Reevaluate

Does it work for NMs?



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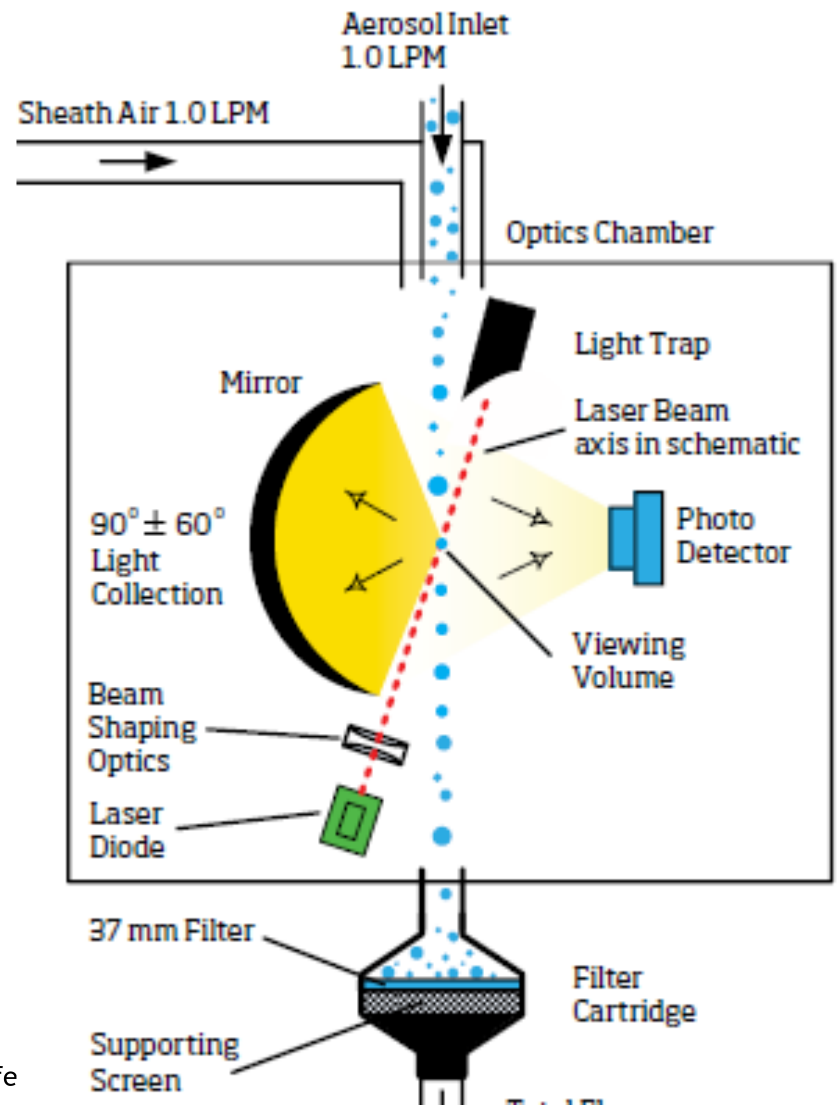
Methodology

Instrumentation

Based on aerosols technology

Different physical principles:

- Optical
- Eléctrical
- Gravimetric



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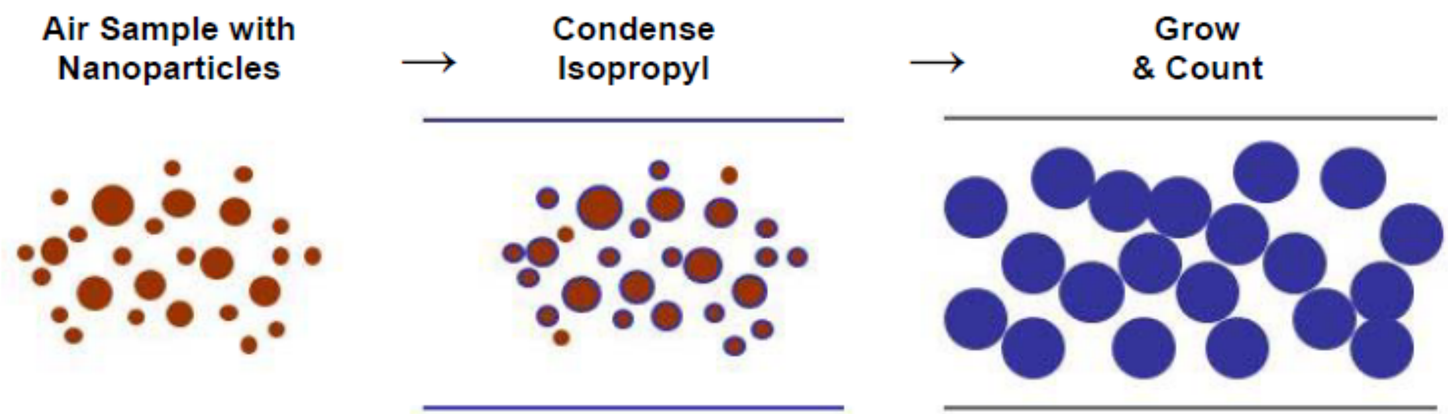

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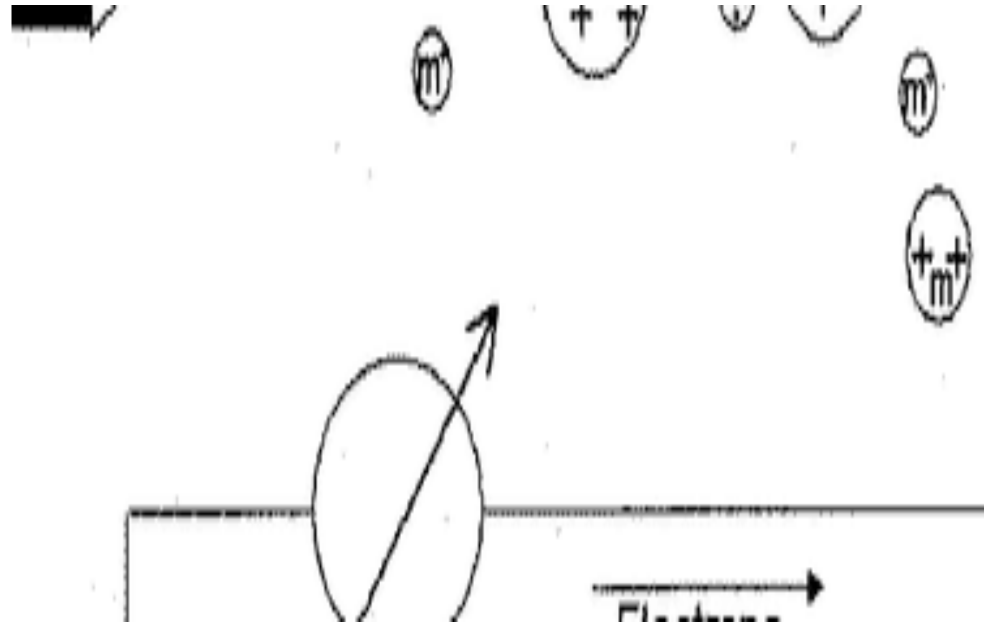

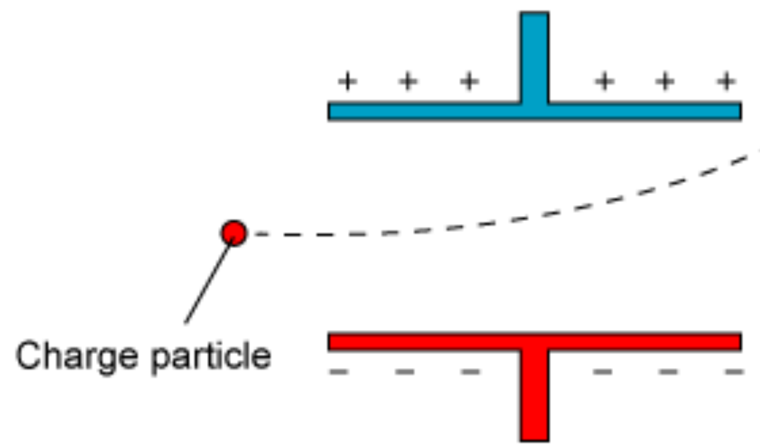

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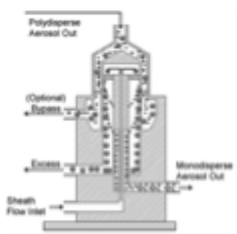

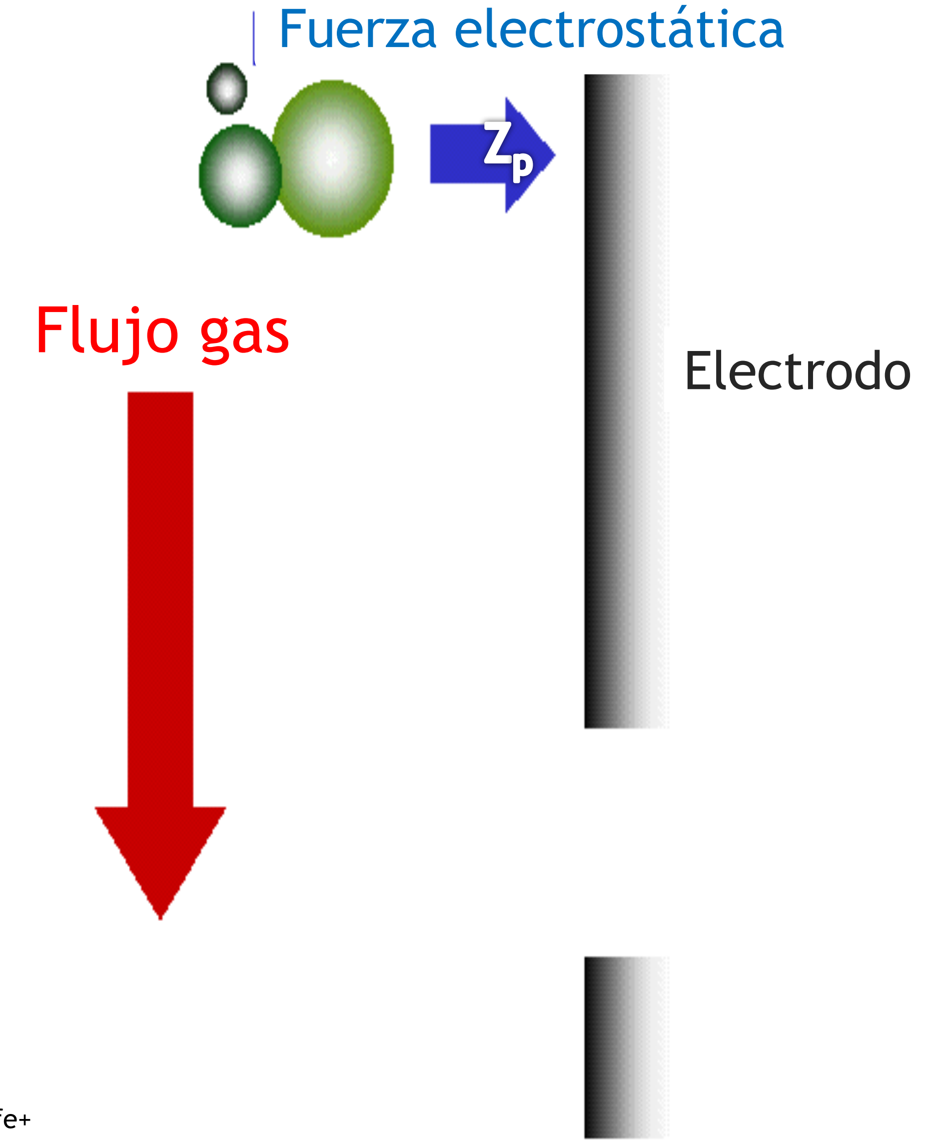

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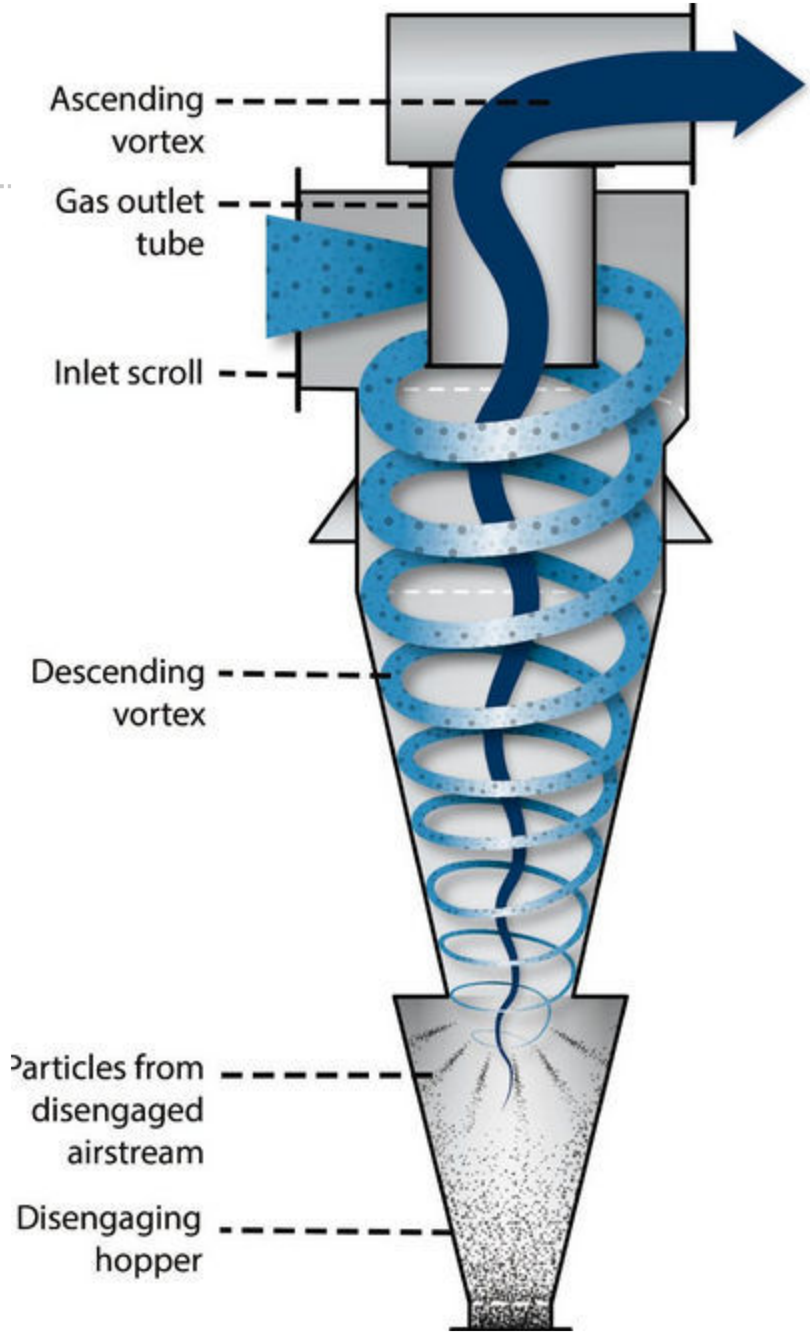

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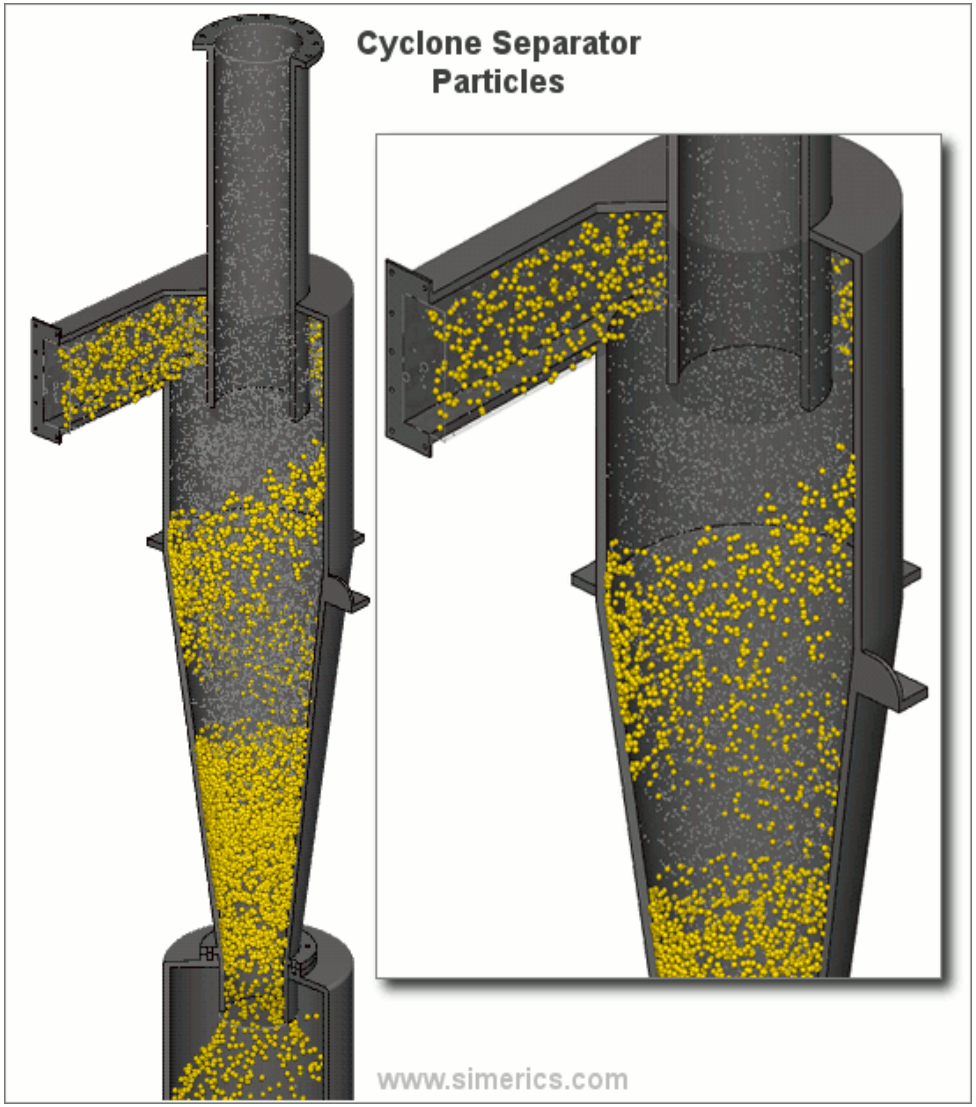

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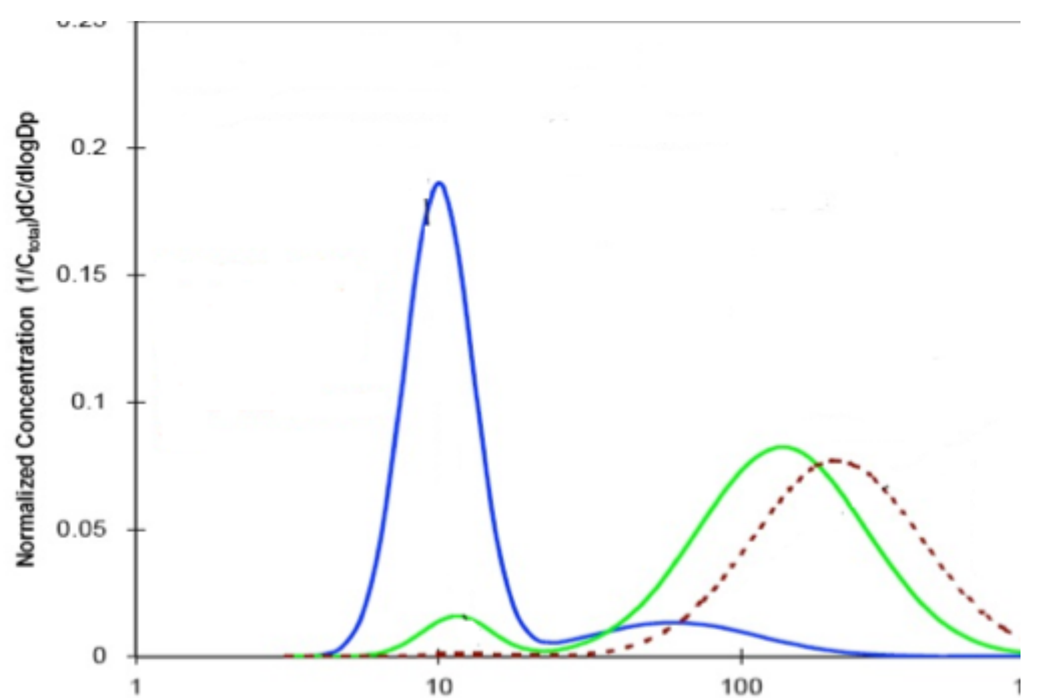
Different metrics:

- Particle number concentration (PNC)
- Pasticle Size Distribution (PSD)
- Mean Geometric Diameter (MGD)
- Mass distribution
- Surface area
- LDSA (Lung Deposited Surface Area)



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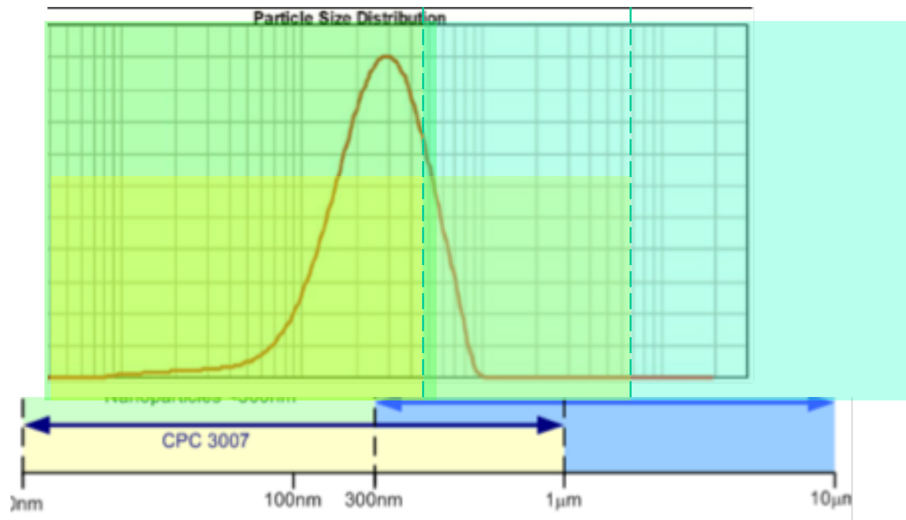
Different measuring ranges:

- 6 nm – 1 um
- 1 – 300 nm
- 300 nm – 10 um
- 10 – 300 nm
- 10^3 - 10^6 part/cm^3



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Different response times:

- Direct Reading: 1 sec – several min
- Indirect reading: samples to the lab

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- Mean Geometric Diameter (MGD)
- Mass distribution
- Surface area
- LDSA (Lung Deposited Surface Area)

Different measuring ranges:
- 6 nm – 1 um
- 1 – 300 nm
- 300 nm – 10 um
- 10 – 300 nm
- 10^3 - 10^6 part/cm^3

Different response times:
- Direct Reading: 1 sec – several min
- Indirect reading: samples to the lab

Different applicability:
- Personal monitoring
- Environmental monitoring
- Lab research systems

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Methodology

Instrumentation

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Based on aerosols technology

Different physical principles:
- Optical
- Eléctrical
- Gravimetric

Different metrics:
- Particle number concentration (PNC)
- Pasticle Size Distribution (PSD)
- Mean Geometric Diameter (MGD)
- Mass distribution
- Surface area
- LDSA (Lung Deposited Surface Area)

Different measuring ranges:
- 6 nm - 1 um
- 1 - 300 nm
- 300 nm - 10 um
- 10 - 300 nm
- 10^3 - 10^6 part/cm^3

Different response times:
- Direct Reading: 1 sec - several min
- Indirect reading: samples to the lab

Different applicability:
- Personal monitoring
- Environmental monitoring
- Lab research systems

Do not distinguish chemical composition!

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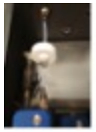
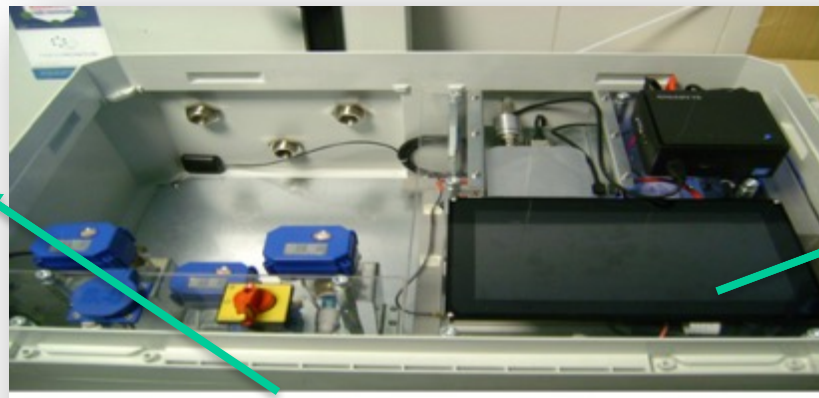
Methodology

NanoMonitor solution



Unattended filter sampling & nanoparticle characterization



PNC

Dpg

M

LDSA

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3 Exposure to NMs in occupational environments

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Exposure to NMs in occupational environments

Examples of exposure assessment

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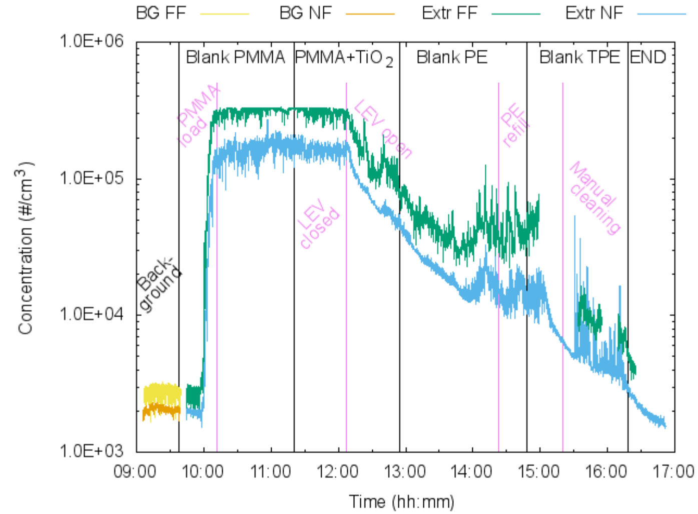
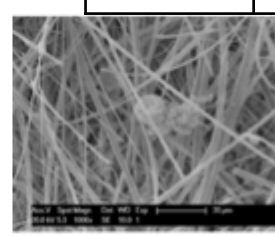
TiO2 NPs+ PMMA Extrusion



ES	Image Code number	Approx. Size of captured particles	Main elements detected
Background extrusion	2.1	40 µm	Si, Al, Cl, O
	2.2	20 µm	C
	2.3	30 µm	C, N
PMMA + TiO2 no LEV	3.1	20 µm	Ca, O
	3.2	20 µm	C, N
	3.3	40 µm	C, N
PMMA + TiO2 open LEV	4.1	20 µm	C
	4.2	20 µm	Si, Al
	4.3	30 µm	C, Ti, O



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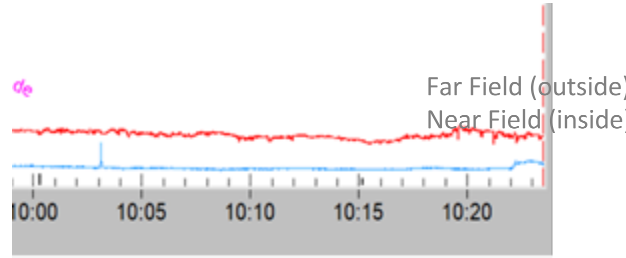
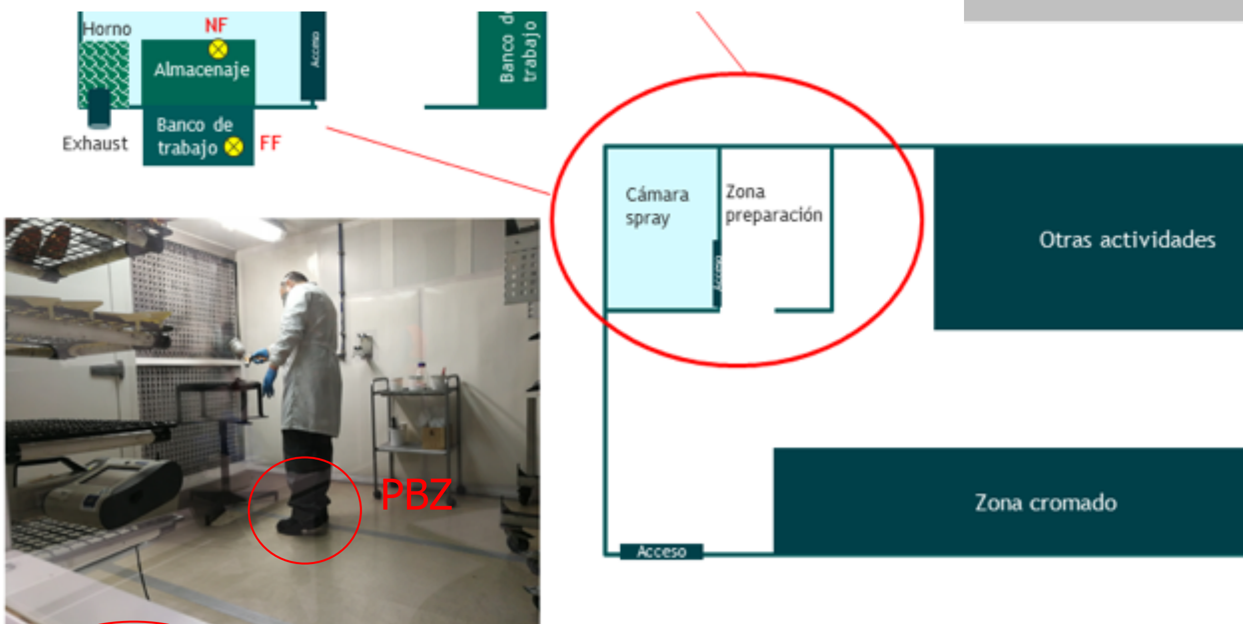
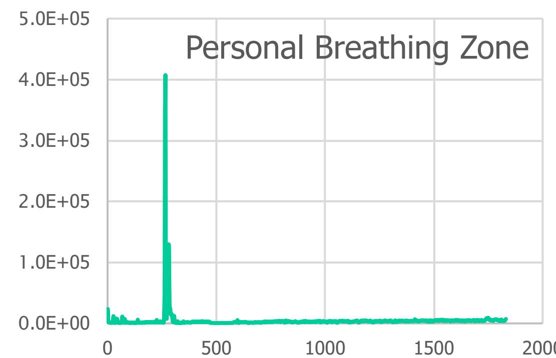
Exposure to NMs in occupational environments

Examples of exposure assessment

Spraying a dispersion with Al_2O_3 NPs within a spray booth – Pilot scale







Near Field

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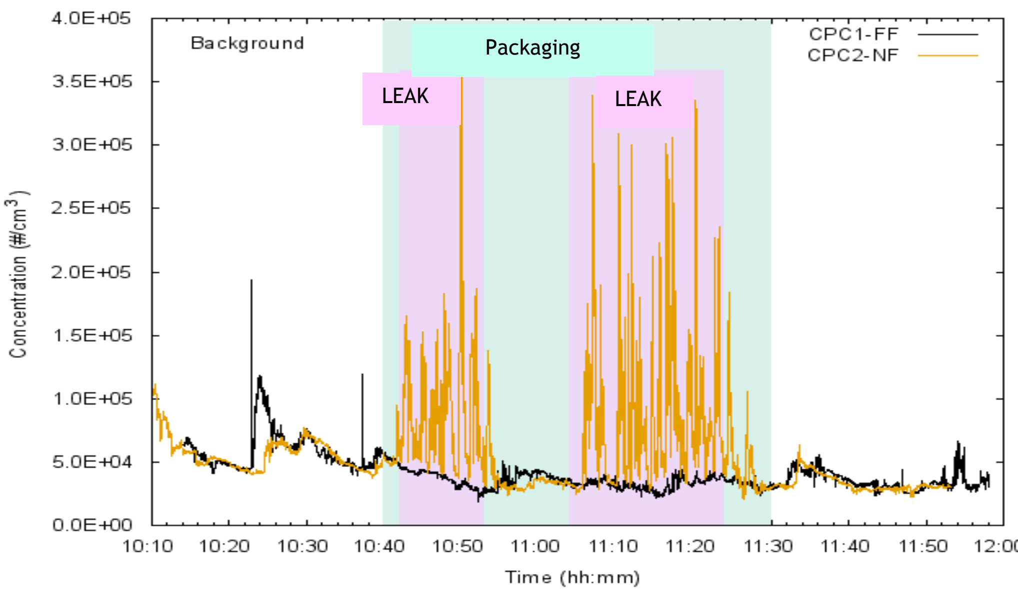
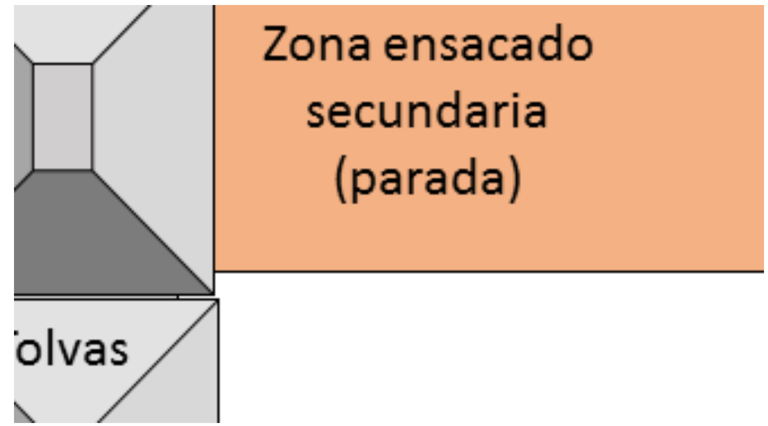
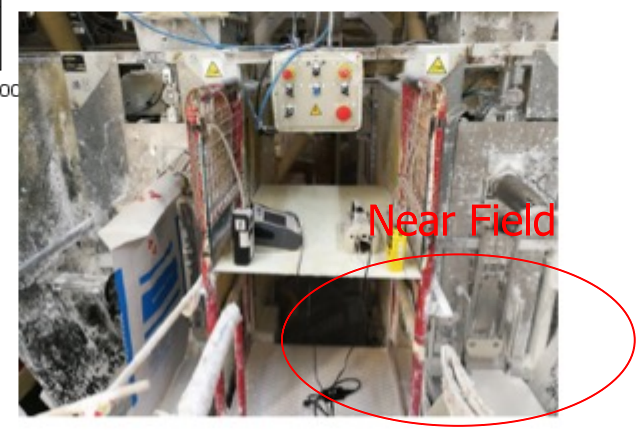
Exposure to NMs in occupational environments

Examples of exposure assessment

Industrial packaging of SiO2 NPs







Leaks in the hoppers before gravity packaging cause very high particle emissions

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4 Conclusions

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Conclusions

General recommendations

- ✓ There are no nano-specific regulations in the EU.
- ✓ Current chemical regulations can be applied to nanomaterials (REACH annexes).
- ✓ Nanomaterial *per se* does not mean higher release:
  - ✓ Certain NANO materials do not register increases in NPs concentrations during handling.
  - ✓ Some NON-NANO materials record increases in nanoparticle concentration → secondary sources
- ✓ The quantitative evaluation allows to determine the effectiveness of the risk control measures implemented.
- ✓ No instrument can detect specific chemical particles in ambient, combination of different measuring techniques + processes must be performed.
- ✓ NEAT technique + tiered approach is currently the best methodology for exposure assessment

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Thank you for your attention!

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LIFE NanoMonitor Webinar

13th December, 2018

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ENVIRONMENT
LIFE Programme

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Use of the Nanomonitor station prototype

Presenter: Francisco Alacreu / Jose Luis Palau

ITENE CEAM AIΦΩN yordas

Event name: LIFE NanoMONITOR Webinar - 13 December 2018

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ENVIRONMENT LIFE Programme

Outline

1. Prototype main components
2. Peripheral components
3. Control Software

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Prototype main components

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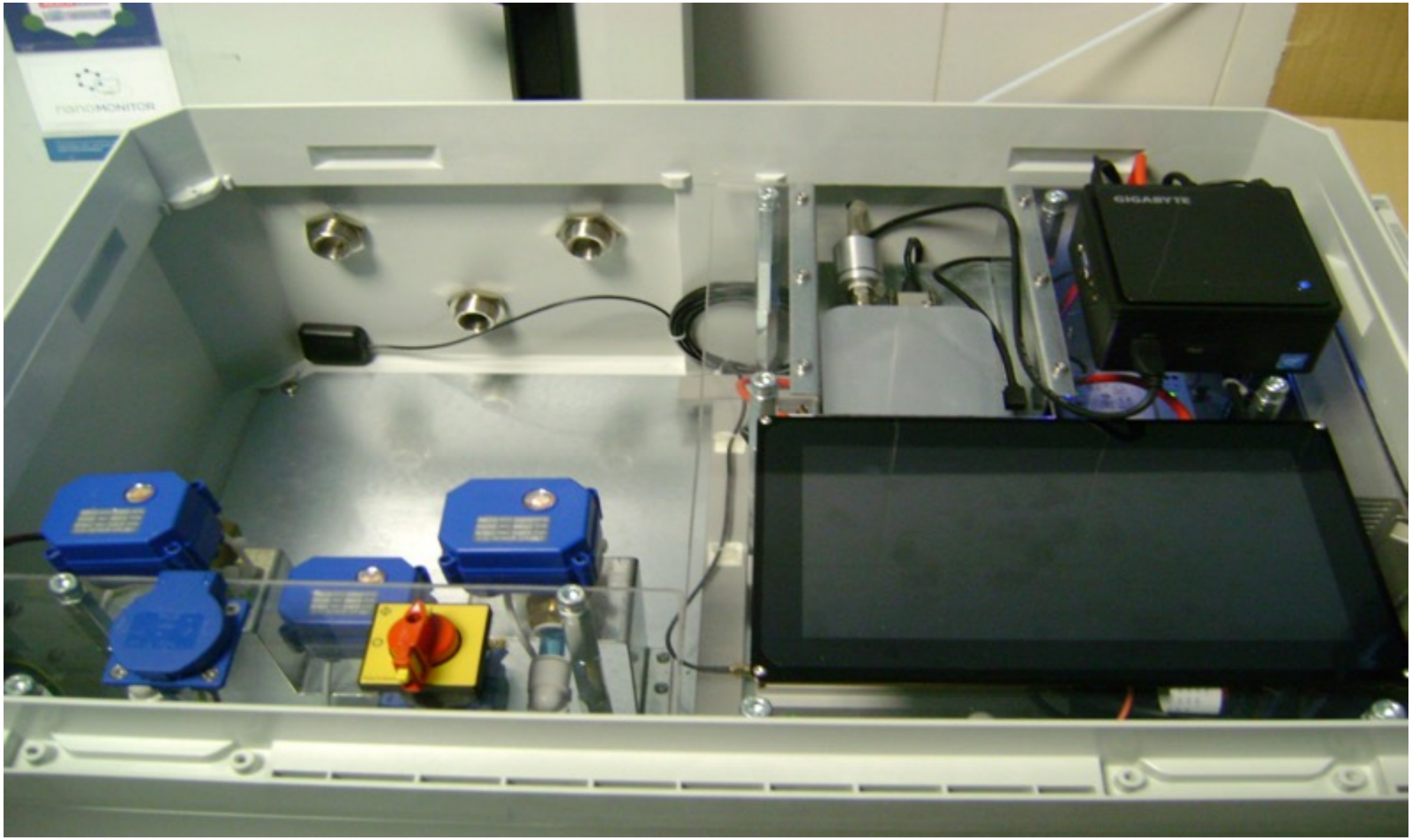
Prototype main components

General view



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Prototype main components

Real time measuring device

The real time device measures, at the same time:

- **Particle Number Concentration - 10^3-10^6 particles/cm^3**
- **Average Particle Size Range - 10-300 nm**
- **Particle Mass Concentration - mg/m^3**
- **Lung Deposited Surface Area - $\mu m^2/cm^3$**

All of them with
a resolution of 1Hz

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Prototype main components

Pneumatic module

The station allows the identification of chemical species through the collection of air samples in a physical support

- ❑ **Three independent air sampling lines**
- ❑ **Each controlled by a regulation valve**
- ❑ **The output of each valve converges in a unique line. An external pump should be connected to aspire the air through the filters**

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Prototype main components

Pneumatic module

Different holders for filters, as well as impactors or cartridges can be placed in the station

The chemical components collected in the samples can be identified using offline technique

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Peripheral components

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Other sensors

Measuring stations include other sensors:





- **An electronic external module with sensors to acquire relevant meteorological variables (T, P, RH)**
- **A GPS to locate the exact position of the station**

- **A cooling system (Peltier cell) to keep the internal temperature of the box in safe levels**

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Control software

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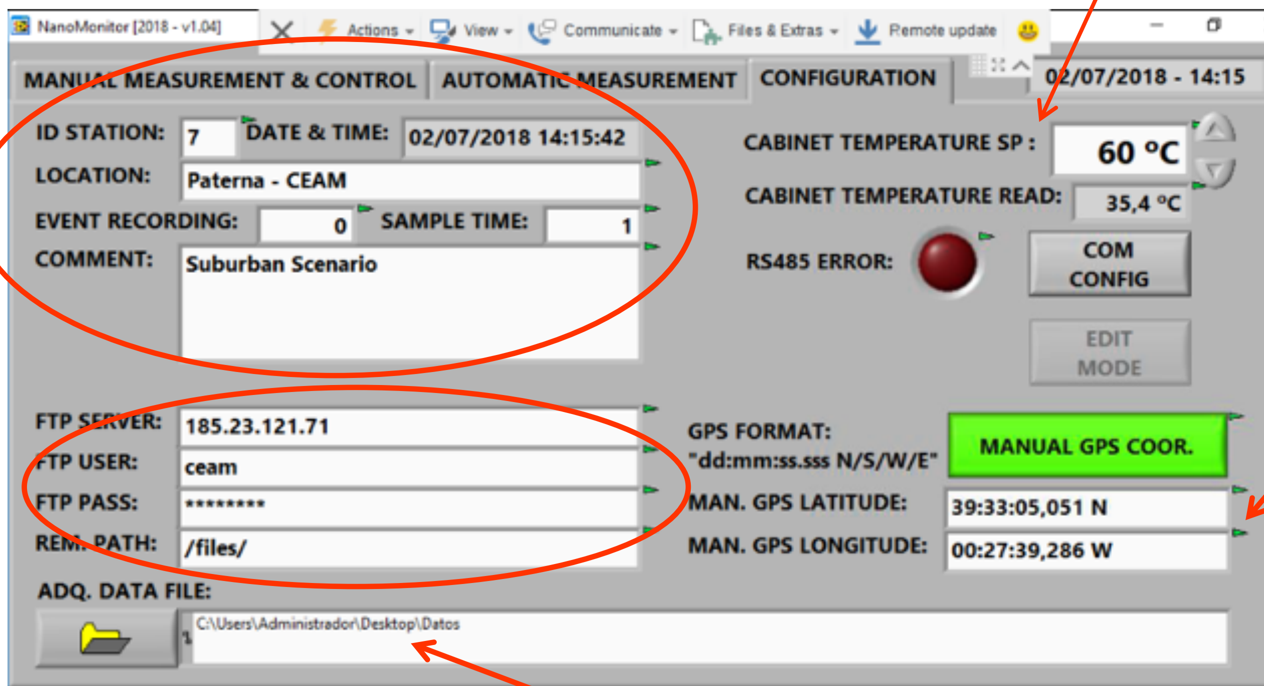
Information needed by the web application
to display in real time the data sent to the server

Cabinet temperature control



Configuration of the ftp protocol for server-station communication

Manual GPS coordinates

Acquisition data file path

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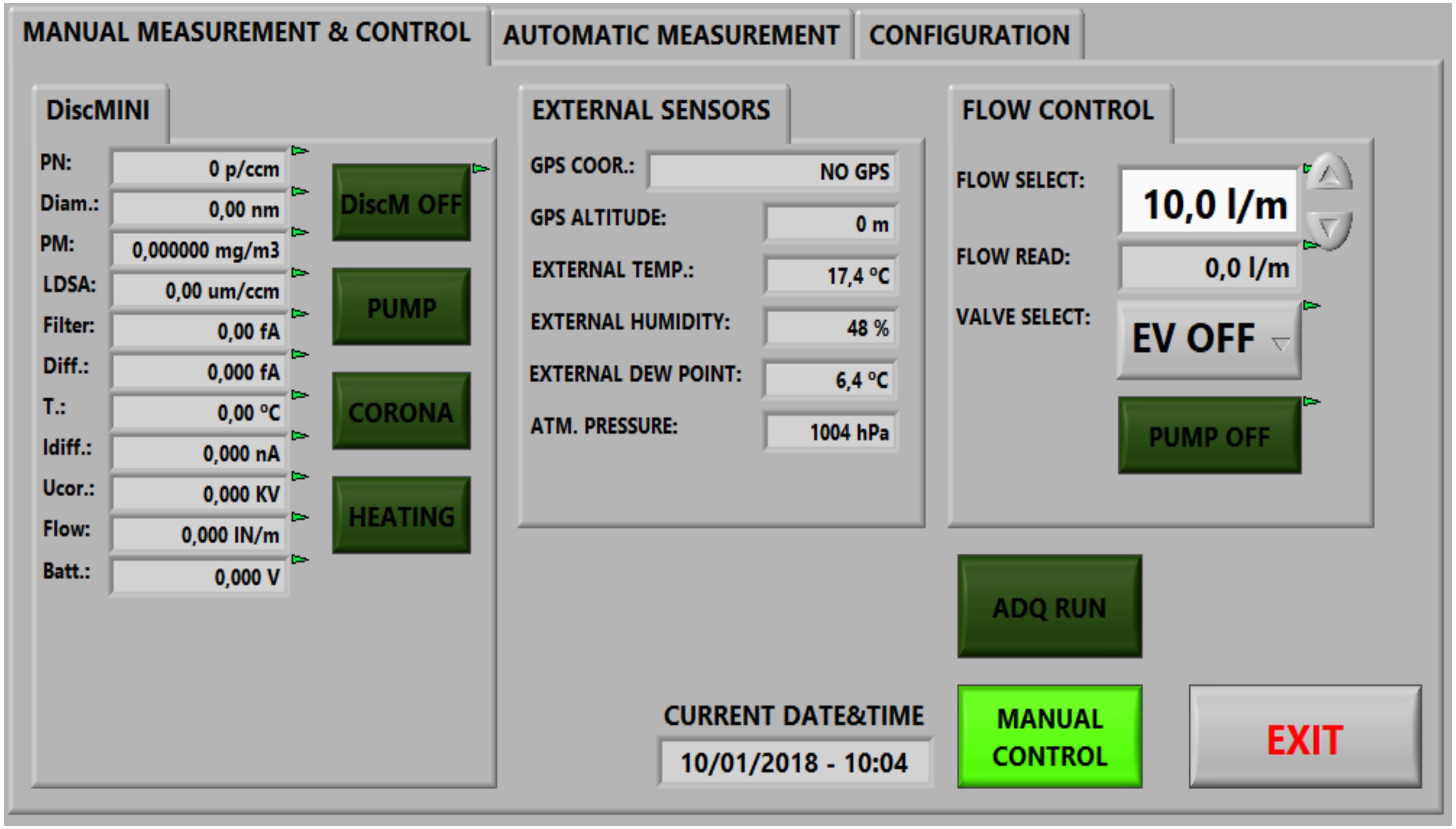
Control software

Tab 'MANUAL MEASUREMENT AND CONTROL'



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Control software

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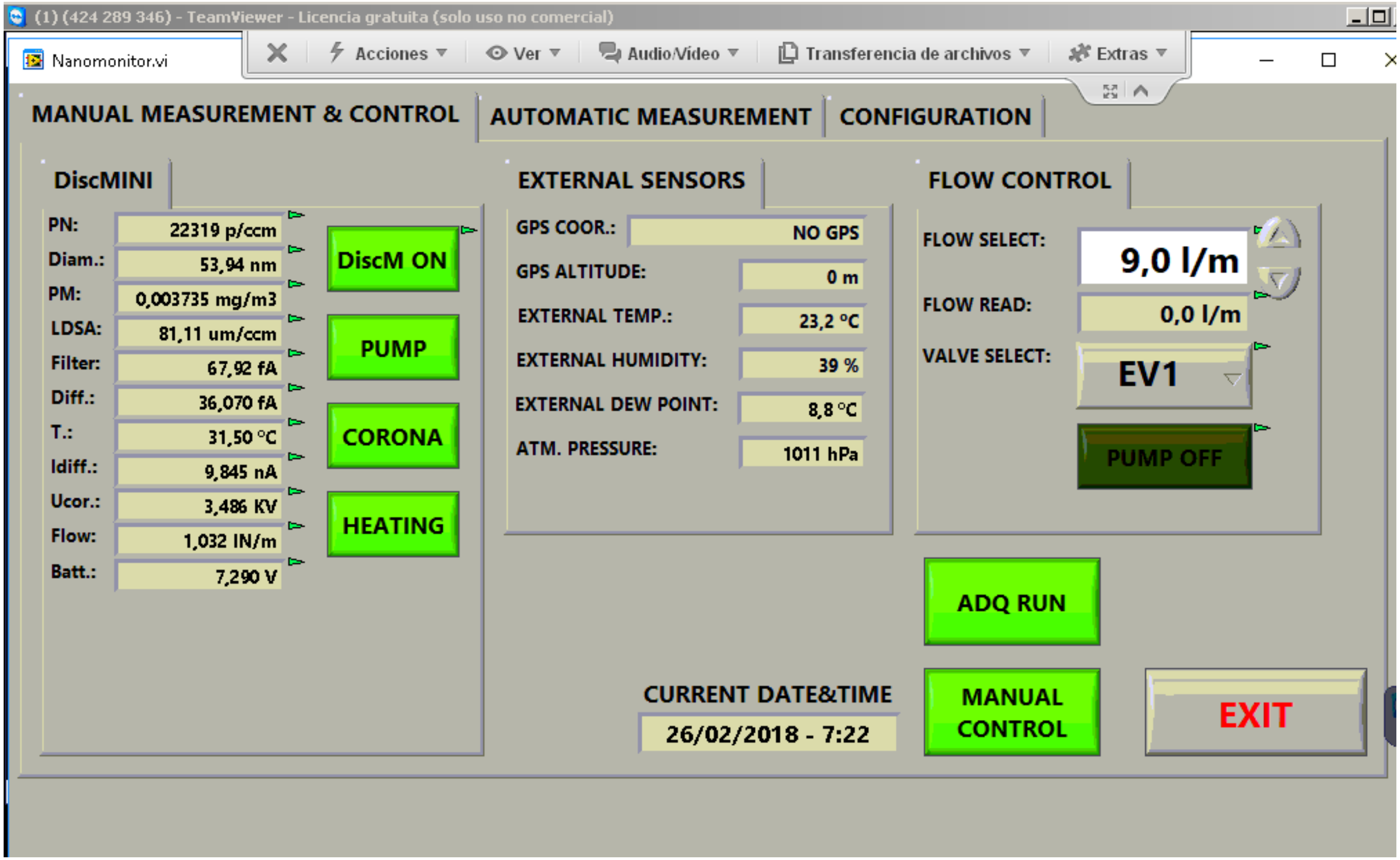

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Control software

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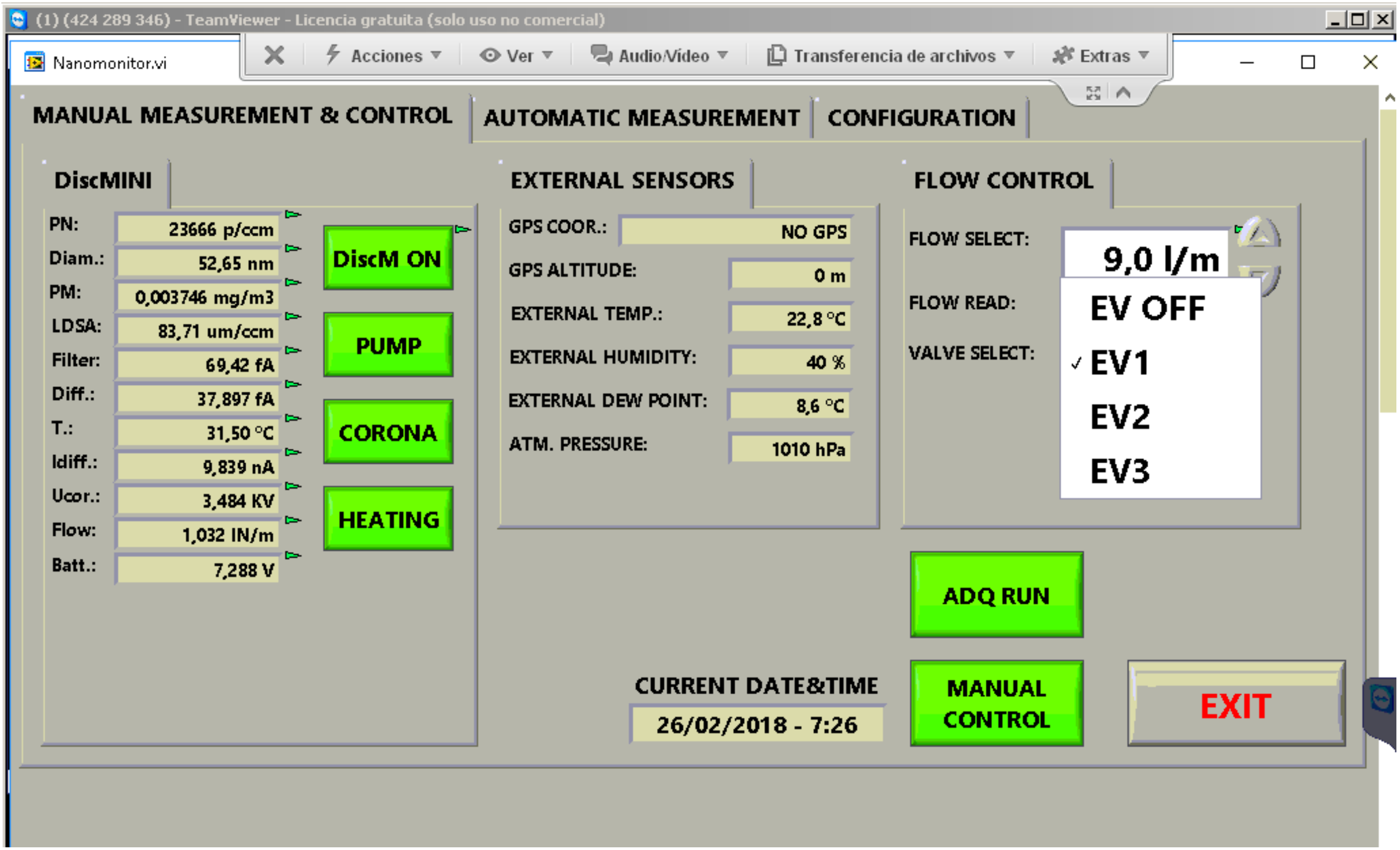

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Control software

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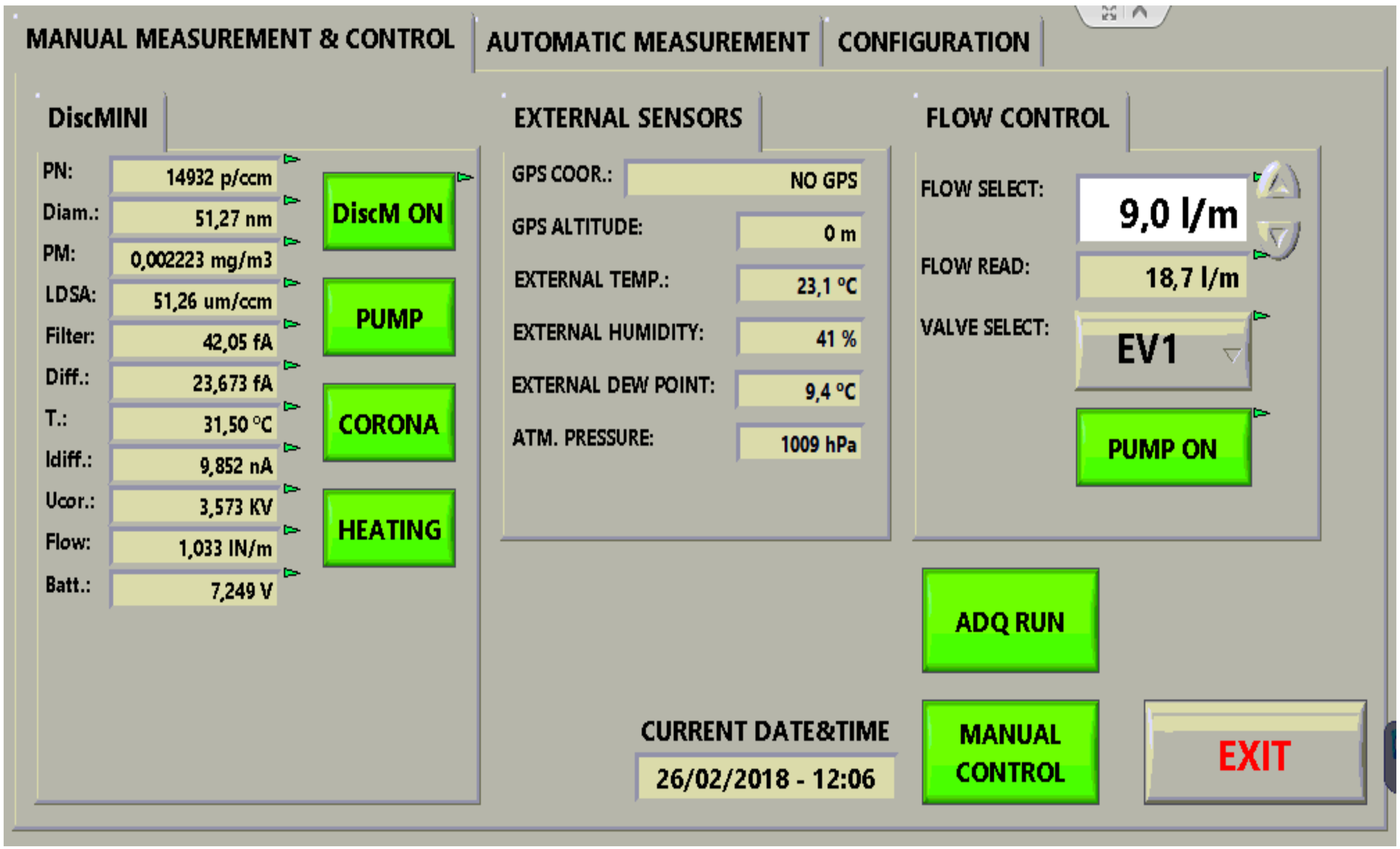

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Control Software

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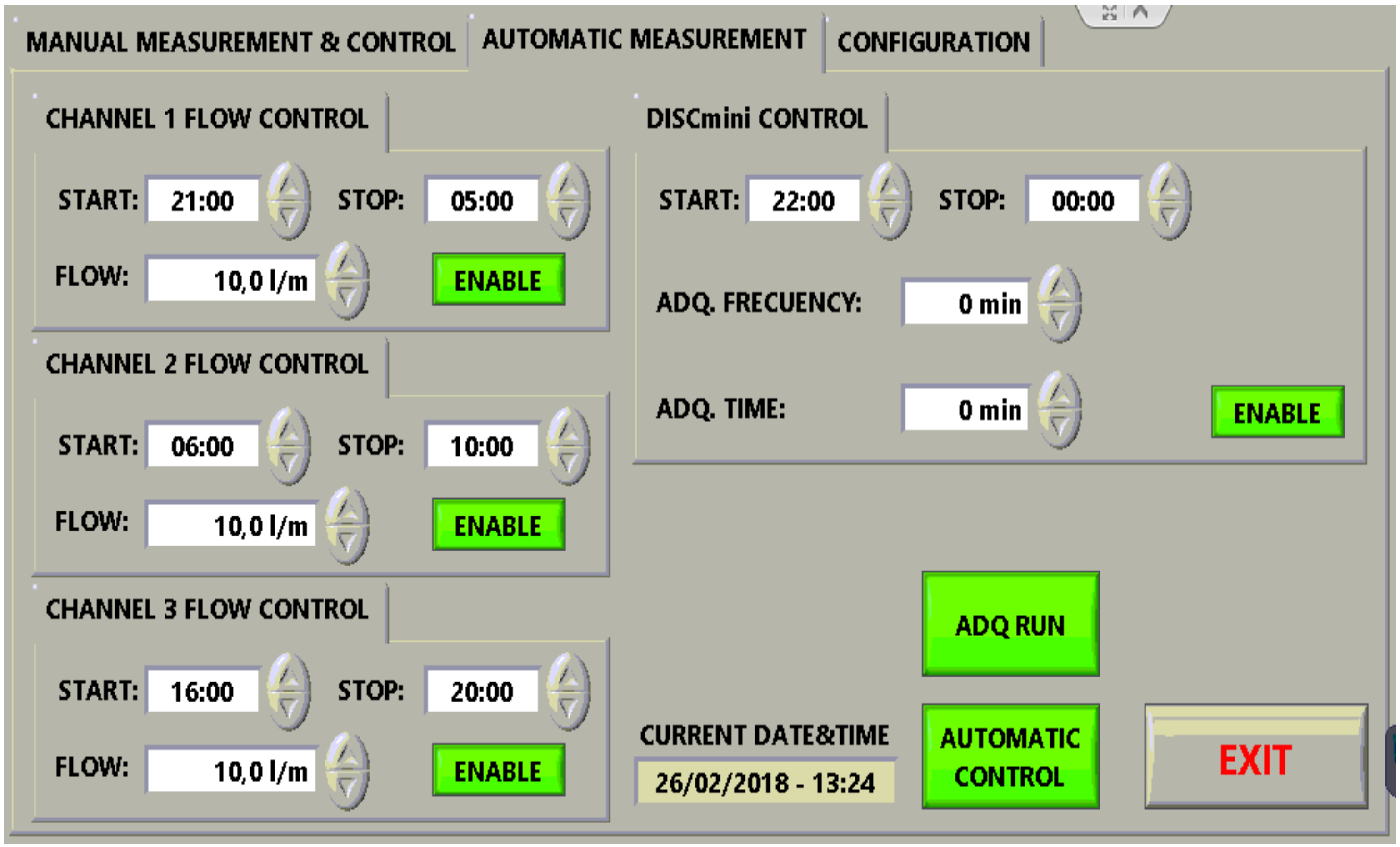

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Thanks for your attention!

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Hands on Training on Analytical Techniques for the Monitoring of ENMs in the Environment

nanoMONITOR

Carlos Fito López. Project Coordinator
R+D Area. Nanosafety Research group -ITENE
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December 13th 2018

NanoMONITOR – Project Review Meeting

NanoMONITOR is partly funded by the European Commission Life+ with grant agreement LIFE14 ENV/ES/000662

Outline

1 INTRODUCTION

2 SAMPLING METHODS AND ANALYTICAL TECHNIQUES

3 REPLICABILITY, TRANSFERABILITY AND SUSTAINABILITY

4 SUMMARY CONCLUSION

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ENVIRONMENT
LIFE Programme

1. Introduction

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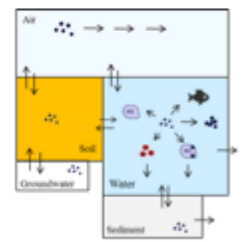
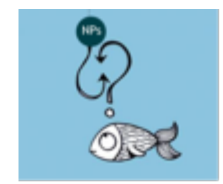
Motivation & Background Information

- Despite the scarcity of information on the environmental risk associated with ENMs, it is now accepted that **nanostructured materials can be released into the air, soil, and water** in common industrial processes and /or accidental events and ultimately accumulate in the environment.

- It is currently not possible to precisely asses the ecological impacts of the release of ENMs into the environment, which is mainly due to:
  - The lack of understanding of the **inherent physicochemical properties of ENMs** and mechanisms driving exposure and release.
  - A wide range of **analytical tools** is available, however, the most commonly used detection and characterization techniques are not adequate for the study of ENMs.
  - The **lack of techniques** suitable for collecting, preserving, and storing samples containing ENMs.





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NanoMonitor. Hands on Training on Analytical Techniques

1. Introduction

Motivation & Background Information

- Studies conducted so far point out that a **significant release of submicron sized particles**, including single particles, aggregates and agglomerates (< 1000 nm) and embedded in a solid matrix (i.e. polymers) , can be expected during the production and downstream use of ENMs.

- The availability of **reliable exposure data** is generally very limited and mostly focused on the workplace. This dearth of data implies that in the vast majority of cases, exposure levels must be estimated by making use of exposure estimation models.

Emission Source	NPs Type	Measured levels range
Primary / SD1		
Liquid-phase reaction	PGNP	$4.0x10^4$ to $11.0x10^6$
Flame spraying	PGNP	$4.7x10^3$ to $1.0x10^6$
CVD	PGNP	Non-significant
Top-down (milling)	ENPs / PGNP	$3.0\ 10^3$ to $1.0x10^6$
Secondary NP aerosol / SD2		
Weighing of powders	ENPs	$2.0X10^4$ to $7.0x10^4$
Harvesting	ENPs	$2.0X10^4$ to $5.0x10^4$
Manual packaging (Bagging)	ENPs / PGNP	$20.0x10^4$
Bag emptying of powders	ENPs	Significant increase
Melt Blending	ENPs / PGNP	> $1.0x10^5$
SD3a / SD3b		
Spraying of liquid	ENPs	$2.0x10^8$
Spraying (gas)	ENPs	$1.6x10^5$ to $2.0x10^{10}$
Injection Molding	ENPs	> $8.0x10^5$
Brushing and rolling	ENPs	> $6.0x10^5$
Sonication of nanodispersions	ENPs	> $8.0x10^6$
Tertiary NP aerosol / SD4		
Abrasion of nanoproducts	PM / EMNP	$8.0x10^3$ to $2.0x10^4$
Drilling	PM / EMNP	$4.0x10^4$
Grinding	PM / EMNP	$3.0x10^3$ to $1.0x10^6$

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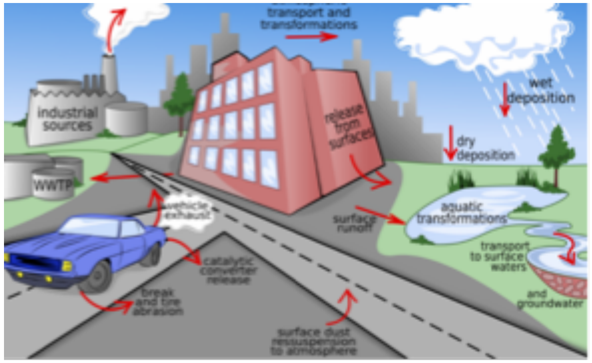
- Accidental spills during production or later transport of nanomaterials, and release from wear and tear of materials containing ENMs **may lead to potential exposure** in urban areas

- Incidental nanomaterials (INMs) can also be generated in **outdoor urban environments** by automobiles, power plants and urban based industries

- Existing evidence suggest **that subway systems** may be also of interest, including elevated levels of fine (PM2.5) and coarse (PM2.5 -10) particulate air pollution, as well as ultrafine particles (UFP), understood as particles smaller than 100 nm, with a chemical composition based on elements such as Fe, Mn, Si, Cr, Cu, Ba, Ca, Zn, Ni and K.



Source:Sources and pathways of outdoor urban nanomaterials in the environment (Baalousha, et al., 2016)

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Motivation & Background Information

- REACH implementation

REACH task	Actor	Action
I. Specific REACH mechanisms (mostly related to specific substances)		
Registration	M, I	Preparation of registration dossiers
	Monitoring data may support the evaluation of substance properties e.g. persistence, bioaccumulation, biomagnification, (eco)toxicity, PBT assessment. (Standard information requirements according to Annexes I, VI – XI)	
	Monitoring data may support exposure estimations e.g. by delivering measured environmental concentrations (local and regional)	
Supply Chain Information	DU	Communication on Risk Management Measures and new hazardous properties
	Use of monitoring data to show adequateness of risk management measures	
	Use of monitoring data to prove local accumulation / effects of substances	
Evaluation	MS, ECHA	Dossier and substance evaluation
	Dossier evaluation: Monitoring data for priority setting in dossier evaluation. Check of information on persistency and bioaccumulation potential	
	Substance evaluation: Information on emerging new pollutants from monitoring for priority setting. Art. 46(1). Request to the registrant to deliver further information (e.g. monitoring data).	

Source:Sources and pathways of outdoor urban nanomaterials in the environment (Baalousha, et al., 2016)

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Motivation & Background Information

- REACH implementation

nterested parties	Comments on Annex XV dossiers for authorisation
nformation on persistency and bioaccumulation. Support of PBT / vPvB assessmer	
M, I, DU	Voluntary monitoring programmes as argument for non-pric substances for inclusion in Annex XIV Application for an authorisation (based on registration doss PBT assessment)
Proposal for in-house monitoring, local and regional monitoring	
MS, ECHA	Preparation Annex XV dossiers for restrictions proposal
nterested parties	Comments on Annex XV dossiers for restriction
nformation on persistency and bioaccumulation. Support of PBT / vPvB assessmer nformation on critical exposure situations (PEC/PNEC >1)	
related to specific substances)	
M, I, DU, CA	Self-monitoring/success control authorities (enforcement)
M, I, DU	Self-monitoring of emission control measures
CA	Control by authorities (enforcement (single companies),suc (regional/national/EU scale)
whole (related to the total impact of all chemicals on human health and the envir	
MS, Commission	Evaluation of efficiency of the REACH Regulation

Monitoring data may provide information on the following key questions:
- Sufficient protection of environment and human health?
- Trends of concentrations of hazardous substances?
- (Local) Accumulation of hazardous substances?

Art. 117 does not explicitly mention environmental monitoring activities. However,

REACH Compliant
1907/2006/EU

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Motivation & Background Information

- Under REACH regulation, the risk assessment process is based on a comparison between the predicted/measured/estimated **level of exposure** and the **predicted or derived no effect concentration** levels of the substances of concern.

- In addtion:
  - 4,480 publications on toxicity
  - 2,669 publications related with risk
  - Up to 190 publications on occupational exposure
  - Up to 65 publications on environmental exposure

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2. Sampling methods and analytical techniques

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Action B4 will work on the definition of standardized protocols to assist stakeholders on the characterization of the concentration of ENMs in surface water, groundwater, soil, sediments and air:

- SOPs for detecting, quantifying, and characterizing metal oxide ENMS in surface water, ground water, wastewater, sediments, and soils
- SOPs for detecting, quantifying, and characterizing carbon based ENMs in surface water, ground water, wastewater, sediments, and soils
- SOPs for detecting, quantifying, and characterizing background concentrations of ENMs in surface water, ground water, wastewater, sediments, and soils
- SOPs for characterizing the particle size distributions, aggregation and dissolution rate of ENMs in surface water, ground water, and wastewater
- SOPs for characterizing the particle size distributions, mass concentration, surface area, and aggregation of airborne ENMs in industrial settings

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2. Sampling methods and analytical techniques

- SOPs for characterizing the particle size distributions, mass concentration, surface area, and aggregation of airborne ENMs in indoor urban environments
- SOPs for characterizing the particle size distributions, mass concentration, surface area, and aggregation of airborne ENMs in industrial areas (outdoor monitoring)
- SOPs for characterizing the particle size distributions, mass concentration, surface area, and aggregation airborne ENMs in natural environments (outdoor monitoring)

- Standard Operating Procedures for Data Management
- Standard Operating Procedures for Data Reporting

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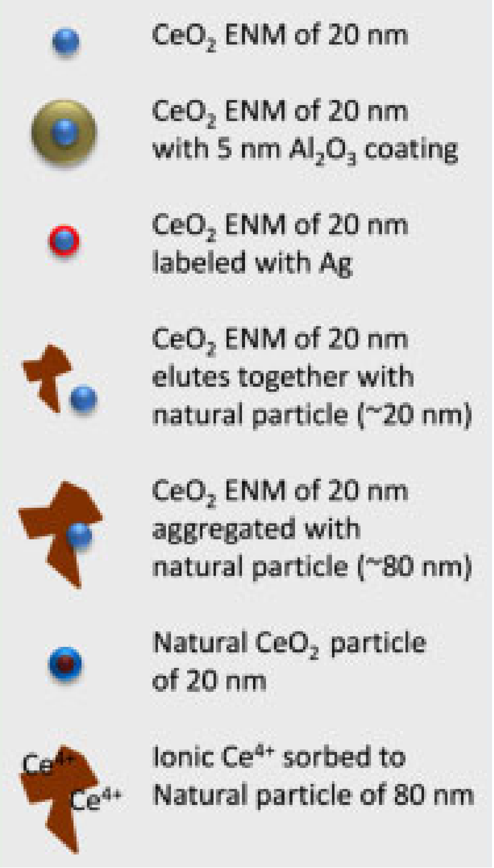
Data on environmental concentration

- Sample collection preservation and storage is likely the weakest link in the analytical workflow and has received little attention in the literature.
- Current techniques that are rapid, such as dynamic light scattering, may not be sensitive (LODs) or specific enough to be applied at environmentally or toxicologically relevant concentrations, depending on the material in question.
- The analysis of NPs in different matrices should not be limited to determination of composition and concentration, since their potential behavior, toxicity and ecotoxicity can be affected by particle number, size, distribution, structure and shape.
- New analytical techniques under development: recent studies have shown promising results when using field flow fractionation coupled to analytical detection methods (e.g. FFF-ICP-MS and FFF-ICP-AES) for the detection of ENMs in liquids.



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Data on environmental concentration

Qualitative analysis of nanoparticles

- Microscopic techniques
  Near-field scanning optical microscopy (NSOM): NMs aggregates
  Confocal laser scanning microscopy (CLSM): colloids
  Transmission electron microscopy (TEM) / TEM -EDS
  Scanning electron microscopy (SEM) / SEM-EDS
  Atomic force microscopy (AFM)
  Environmental SEM (ESEM)

- Separation methods
  Size-exclusion chromatography (SEC) /SEC combined with detection techniques
  Capillary electrophoresis (CE)
  Hydrodynamic chromatography (HDC)
  Field-flow fractionation (FFF)

- Light-scattering techniques
  DLS: sizing NPs and determining their aggregation in suspensions
  Small angle X-ray scattering (SAXS)
  Laser-induced breakdown detection (LIBD): detect trace amounts of NPs (<100 nm) in aqueous suspensions

- Spectroscopic methods
  Nuclear magnetic resonance (NMR): 3D structure of samples
  X-ray spectroscopy: crystallographic information
  Raman spectroscopy: structural characterization
  Combinations: CE with NIR-fluorescence or Raman spectroscopy

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3. Sampling methods and analytical techniques

Data on environmental concentration

- **Quantitative analysis of nanoparticles**

ICP-MS
Cloud-point extraction (CPE) coupled to TEM/ SEM/UV: environmental samples
Liquid chromatography (LC) combined with MS, time-of-flight (TOF)-MS
Liquid-liquid extraction (LLE) LC method
Quantitative LLE followed by LC coupled to electrospray ionization MS (LC-ESI-MS)
Accelerated solvent extraction (ASE) followed by LC-UV: soil

- **Elemental** (UV-vis, ICP-MS, ICP-OES, EDX/EDS)
- **Crystal Structure** (XRD, SAED)

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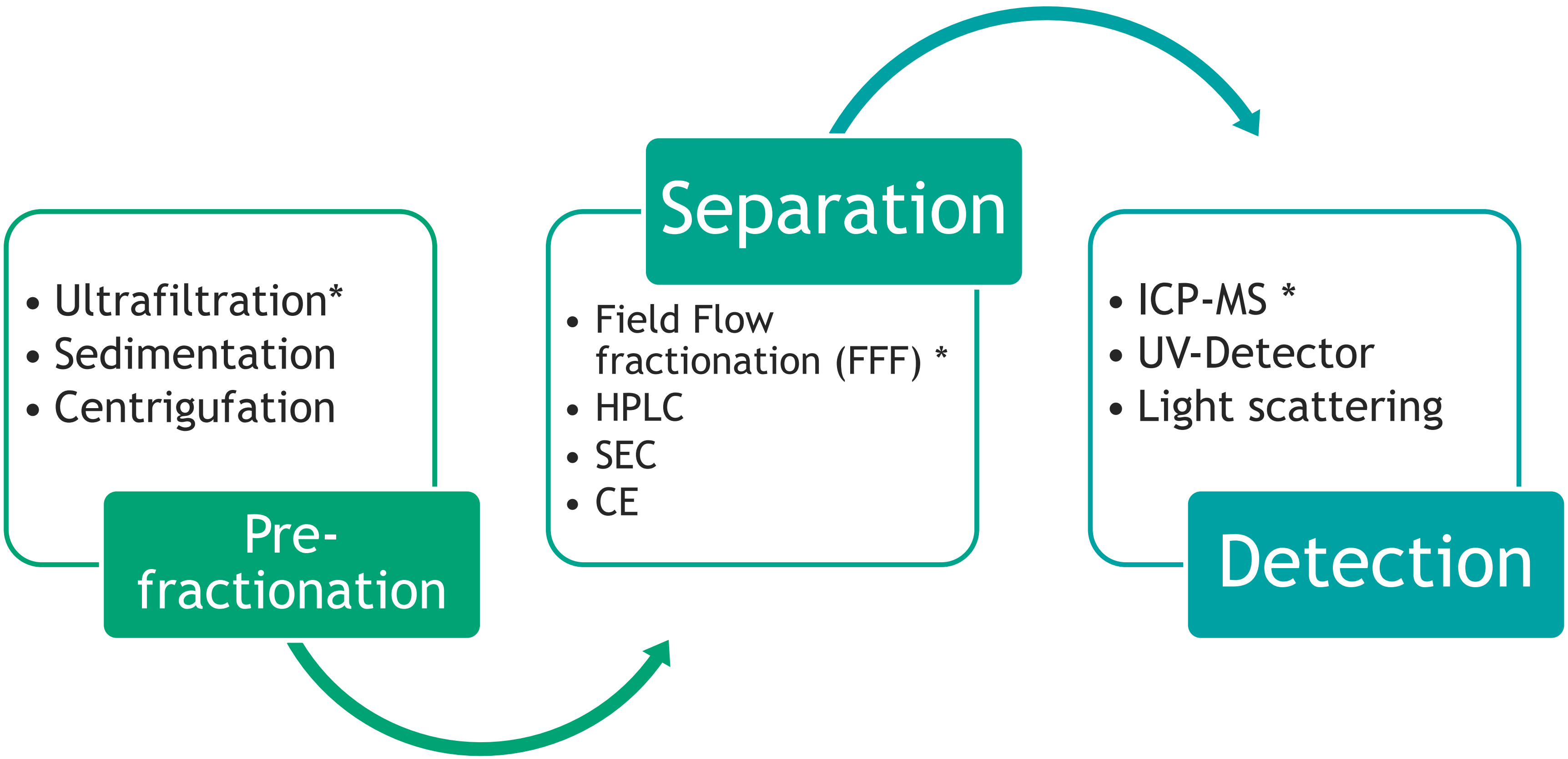
2. Sampling methods and analytical techniques



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2. Sampling methods and analytical techniques

ANALYSIS OF CURRENT KNOWLEDGE ON THE CONCENTRATION LEVELS OF ENMS IN INDOOR WORKPLACES AND THE ENVIRONMENT

3.1 Sources and forms of ENMs in target compartments

Airborne nanosized particles can originate from naturally occurring and incidental sources in addition to the engineered particles (ENMs) sources typically of interest in occupational settings. A highest exposure potential exists for workers in workplaces, where these materials are produced, used, or handled (*Asbach, 2015*).

The information on the concentration levels of ENMs in urban areas and/or ecosystems is still scarce, with a limited number of studies available. However, the number of published data on the levels of exposure to ENMs in the workplace has increased substantially over the last five years, including data on the particle number concentration (particles/cm3) and mass concentrations (µg/cm3) measured using real-time measurement devices.

The sources of ENMs in workplaces are related with the type of processes and work practices conducted in the industrial facilities. Schneider et al. proposed a classification based on the definition of four source domains (table 2) based on the life cycle stages, from production, downstream use, to end-of-life treatments.

The form and amount of the ENMs released in workplaces are determined by the activity emission potential and the substance emission potential. The activity emission potential is commonly related with the number of products (i.e. ENPs or nanoproducts) used, energy applied in the process and level of containment. Common forms of ENMs releases in workplaces include single particles and aggregates < 1000 nm, large agglomerates with a size range from 1 to 20 µm, as well as ENMs embedded into a solid matrix.

The substance emission potential can be considered specific of each ENM or nanoproduct. For ENMs in powder form, the emission potential will be determined by the dustiness of the material. In the case of colloidal dispersions containing ENMs, the concentration of the solute, diameter of dispersed ENMs, and viscosity of the mixture are key parameters influencing the emission potential.

Concerning urban areas, the study of the magnitude of the exposure to ENMs in cities is already a challenge. The main sources of release include unintentional emission from nano-enabled products used in urban building and other infrastructures, and industrial emission that can reach the urban areas due to complex transport process in the atmosphere.

Table 2. Examples of emission sources

EMISSION SOURCE	RELEASE POTENTIAL	SPECIFICATIONS
1. Point source or fugitive emissions		
Liquid-phase reactions	Likely	Single particles
Flame spraying	Likely	Single particles
CVD	Not Excluded	Single particles
Top-down (milling)	Not excluded	Single particles
2. Handling and transfer of bulk manufactured nanomaterial powders with relatively low energy		
Weighing of powders	Likely	Single particles and aggregates < 1000nm
Harvesting	Likely	
Manual packaging (Bagging)	Likely	
Bag emptying of powders	Likely	Single particles and aggregates < 1000nm Large aggregates 1 to 20µm
Melt Blending	Likely	Embedded particles. Limited release of fully dissociated NPs
3. Dispersion of either (liquid) intermediates containing highly concentrated (> 25%) nanoparticales or application of (relatively low concentrated < 5%) ready-to-use products		
Spraying of liquid	Very Likely	Single aggregates as well as large agglomerates
Spraying (gas)	Very Likely	
Injection Molding	Very Likely	Single particles and aggregates < 1000nm Embedded particles Limited release of fully dissociated NPs
Brushing and rolling	Very Likely	
Sonication of nanodispersions	Very Likely	Single particles and aggregates < 1000nm
4. Activities resulting in fracturing and abrasion of manufactured nanoparticles-enabled end-products		
Abrasion of nanoproducts	Not excluded	Embedded particles. Limited release of fully dissociated NPs
Drilling	Possible	
Grinding	Possible	

At present, there are few studies on revealing the concentration of ENMs in urban areas, however, ENMs are currently widely incorporated in new applications and products such as building façade paintings, fuel additives, photocatalytic concrete pavements or antireflection layers for road signs and pane, which means that a bigger number of ENMs that are likely to be released in the indoor and outdoor urban environments.

The effect of wind and rain, as well other weather conditions, triggers ENMs erosion that can lead to air/water transport and deposition, which implies a potential exposure to ENMs of citizens. In addition, as indicated in the previous chapter, incidental nanomaterials (INMs) can also be generated in the outdoor urban environment by automobiles, power plants and urban based industries. In this regard, INMs can be released due to road traffic via engine combustion exhaust, brake pad and tire abrasion, with average particle diameter below 300 nm (Kumar et al., 2014), and compositions ranging from metals and metal oxides to phosphates. These INM contribute to a negligible portion of the total mass of particulate matter (PM), but they are the dominant fraction in terms of particle number (Kukutschová et al., 2011).

Rail traffic is also a potential source of INMs, being mainly generated by the motion of trains movements and activities of commuters and subway staff, air ventilation and various stationary processes (Vania Ferreira, 2016). Evidence suggest that although abrasive forces between wheels, rail, and brakes can generate coarse and fine particles due to sharing, ultrafine particles can be generated via the high temperature of friction at interfaces between these components, with subsequent vaporization of the substrate (Sundh et al., 2009).

As an example, the levels of ultrafine particles measured with a condensation particle counter (CPC, TSI model 3007) reached an average value of 14.200 pt/cm3 for the metro systems of Toronto, Montreal, and Vancouver, in Canada (Van Ryswyk K, et al., 2017). In the subways system of Helsinki, UPF concentration reached levels rather similar to those in outdoor ambient air (31.000 pt/cm3).

A non-exhaustive list of the sources and types of ENMs in urban system is depicted in table 3.

Table 3. Examples of emission sources and types of ENMs in urban areas

SOURCE	EMISSION TYPE	MAIN USES OF ENMs
Nano-enabled products	Unintended releases during use	Metal and Metal Oxides (Ag, Cu, TiO_2, ZnO, SiO_2, CuO) Carbonaceous materials (Graphene) ENM particles heteroaggregated with background aerosols
Industrial emissions (Wet/dry atmospheric deposition in cities)	Direct release and transportation	Metal and Metal Oxides (Ag, Cu, TiO_2, ZnO, SiO_2, CuO) ENM particles heteroaggregated with background aerosols
Industrial emissions	Direct release and transportation	
Road Traffic		
Brakes/tires abrasion	Direct releases of Incidental Nanomaterials (INMs)	SiO_2, CeO_2, Zn, Mn, Fe, Co, Ni, Cd and Pb
Engine combustion exhaust		
Resuspension		
Rail Traffic		
Brakes/tires abrasion	Direct releases of Incidental Nanomaterials (INMs)	CuO Al, Ba, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, I, Pb, S, Si, Ti and Zn
Resuspension		

4. Summary conclusions

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3. Summary conclusions

- Measured data will be of prime importance to support REACH implementation when dealing with ENMs
- The ES Library will assist companies on the evaluation of the likelihood of exposure under similar situations
- Despite the current lack of analytic techniques, standardization will support comparability and reliability of data in complex matrices, in particular water and soil compartment
- Guidance on the sampling methods and analytical techniques for the measurement and monitoring of ENMs in the environment expected in December 2017
- Measured data from peer reviewed publications, on going/finalized project reports and voluntary data providers to be permanently upload into the NanoMONITOR platform.
- Training sessions on exposure assessment (workplace) and environmental monitoring (outdoor) expected in May-June 2018.

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NanoMONITOR – Project Review Meeting

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ENVIRONMENT
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Nanomonitor Web Portal

Dr. Athena Progiou AXON Enviro-Group Ltd.

NanoMONITOR Webinar

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The Concept

The NanoMONITOR web portal has two specific objectives:

1. **To store, manage and elaborate data**

2. **To disseminate knowledge to the scientific community, the stakeholders and the general public.**

url: **http://185.23.121.71/nanomonitor/index.php**

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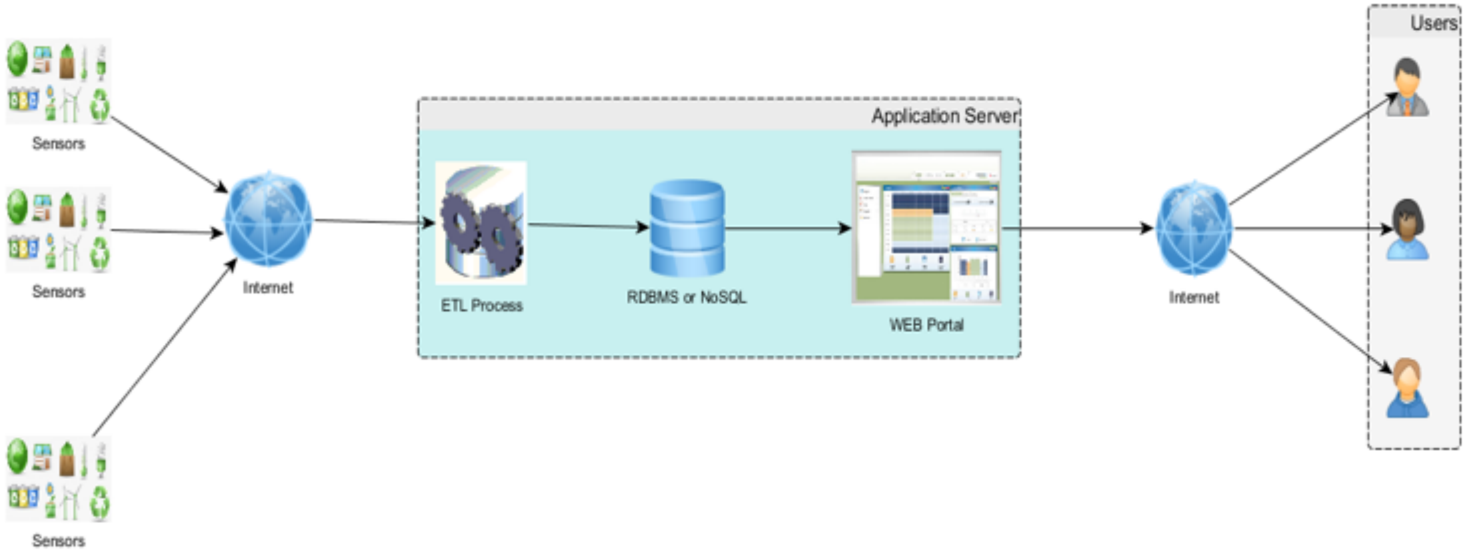
Nanomonitor Web Portal – System Architecture

A high level diagram of the solution in relation to the external entities



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Functionality of the Open Platform [1]

- Accessible over the Web and user friendly
- With pluggable computational modules
- Making use of processed data from various environmental sensors
- Not limited, scalable and expandable.

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Functionality of the Open Platform [1]

- Internet access with password for scientists, and/or authorised users
- Auto-storing function to avoid loss of data
- Availability of versions for PCs, tablets and mobile devices
- Use of alerts when improving the software features
- Data downloadable in excel sheets
- Ensure cooperation with main browsers

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Data sources

- ❑ There are two methods to receive sensor data.
- ❑ Both methods push data TO the data repository server.

Method 1: Real time (MAIN)

- ❑ JSON data are pushed from each sensor to the server for processing

Method 2: Off-line mode

- ❑ CSV data are pushed to the server by an operator (an authenticated user).

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User types

General Public

No registration, access to general data, no access to statistical elaboration.

Stakeholders

Access to all data and to the statistical tools.

Data providers / Partners / Scientists

Access to all data and to the statistical tools.

Administrator

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Input data file

According to the available specs every 10 secs a new record will be created from each sensor, thus, for every time instance t_i, the following values will be available in the DB.

- Station ID
- Date, Time
- Temperature (ambient) T
- Pressure
- Wind Speed, Wind Direction
- PN (number of particles) and Concentration C_A
- Diameter $\overline{d}$ (the monitoring station measures, for every time instance, the average diameter of the particles detected.)
- PM, PM10, PM2.5, O_3, CO, SO_2, NO_X

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Data Analysis [1]

- ✓ Trends
- ✓ Max values (*MAX*)
- ✓ Min values (*MIN*)
- ✓ Average value ($A\overline{VG}$)
- ✓ Percentile (*P*)
- ✓ Variance (*VAR*)
- ✓ Standard deviation (*s*)
- ✓ Correlation (*r*)
- ✓ Covariance (*COV*)
- ✓ Forecast (*F*)

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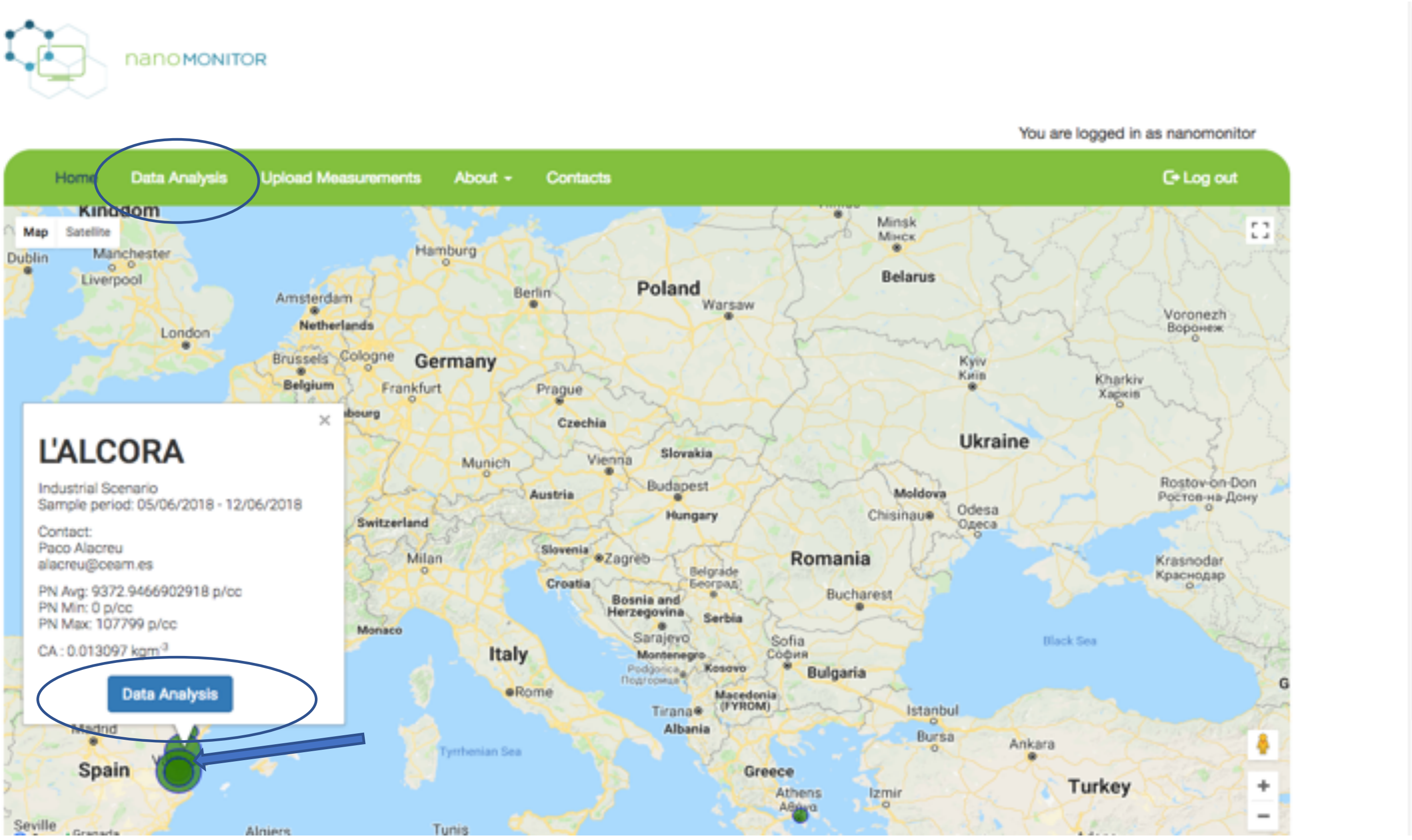
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You are logged in as nanomonitor
Home
Data Analysis
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L'ALCORA
Industrial Scenario
Sample period: 05/06/2018 - 12/06/2018
Contact:
Paco Alacreu
alacreu@ceam.es
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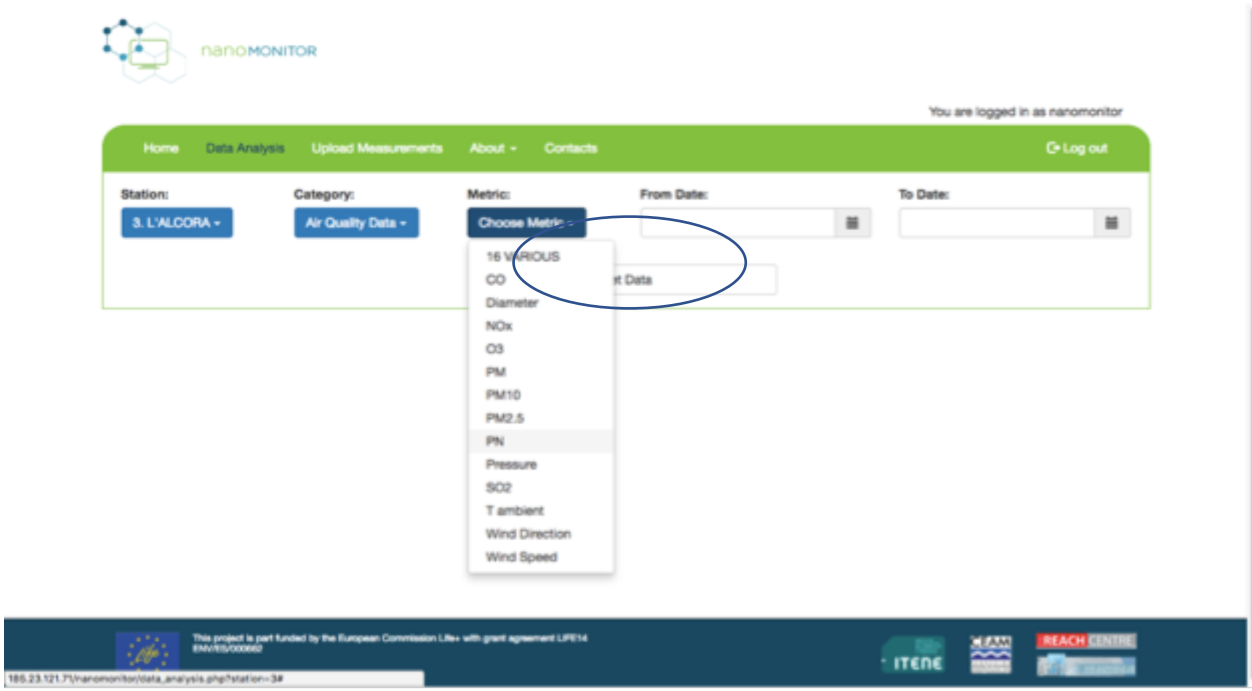
Data Analysis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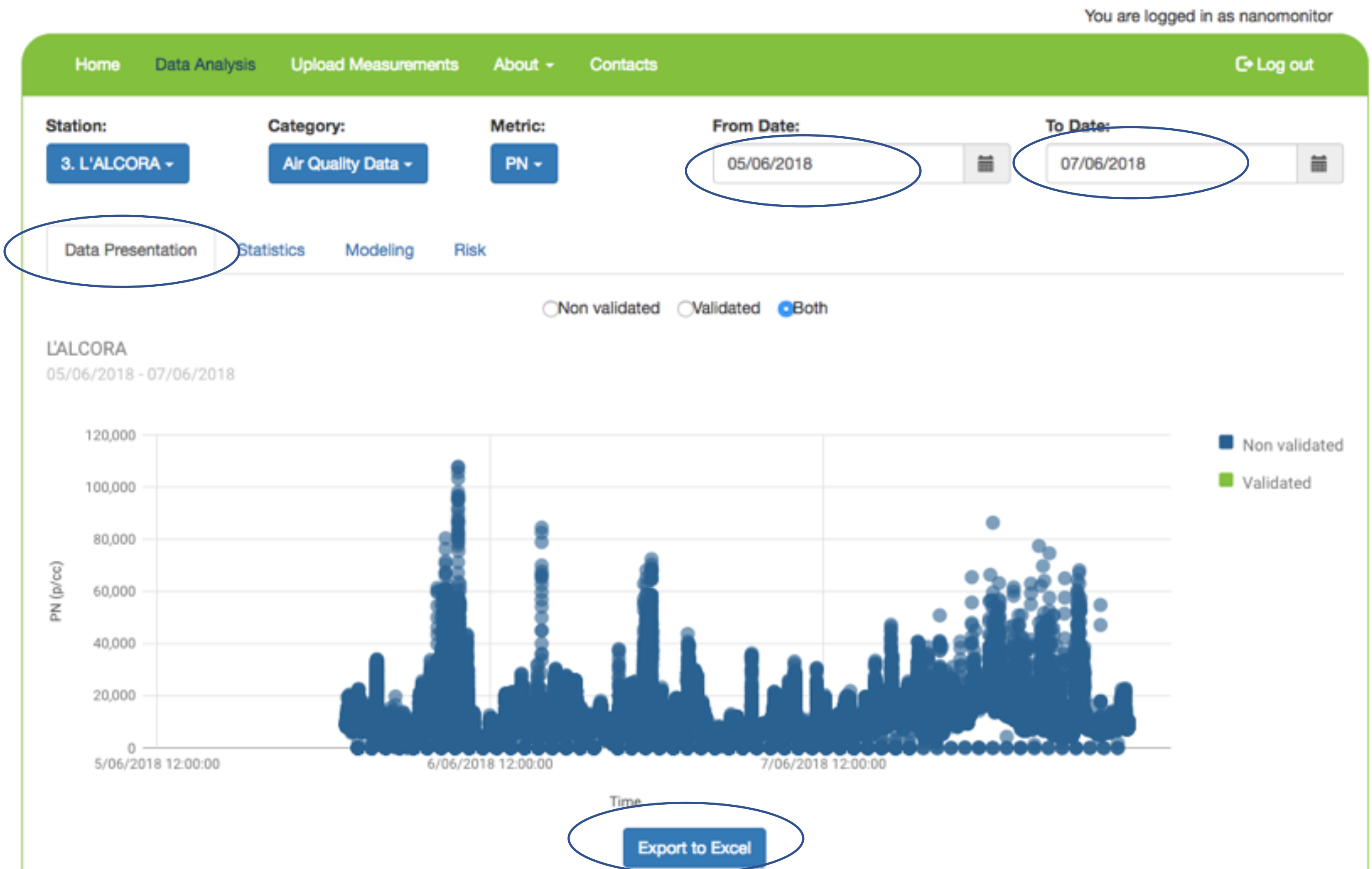

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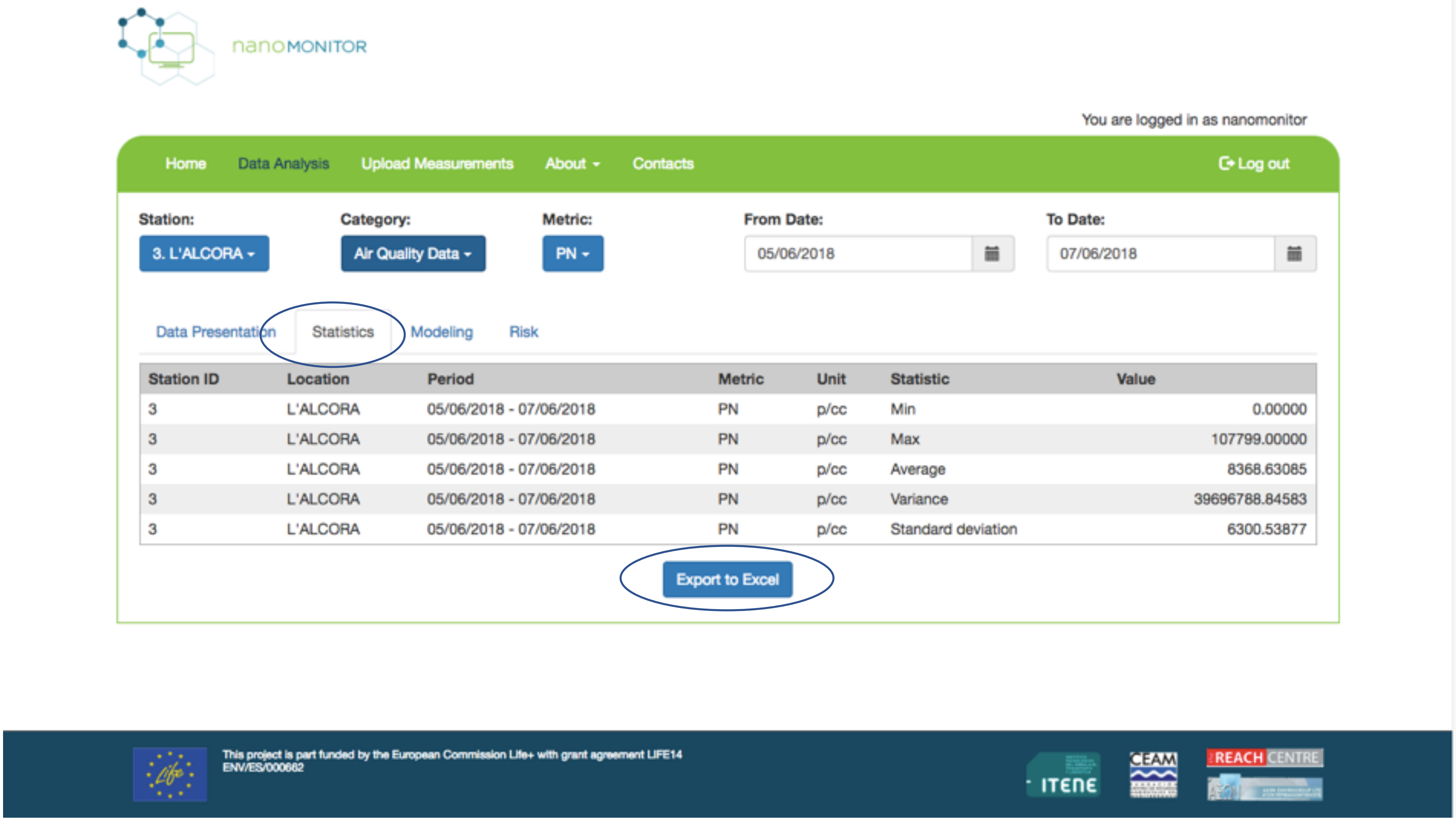
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3. L'ALCORA
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Air Quality Data
Metric:
PN
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To Date:
07/06/2018
Data Presentation
Statistics
Modeling
Risk
Station ID Location Period Metric Unit Statistic Value
3 L'ALCORA 05/06/2018 - 07/06/2018 PN p/cc Min 0.00000
3 L'ALCORA 05/06/2018 - 07/06/2018 PN p/cc Max 107799.00000
3 L'ALCORA 05/06/2018 - 07/06/2018 PN p/cc Average 8368.63085
3 L'ALCORA 05/06/2018 - 07/06/2018 PN p/cc Variance 39696788.84583
3 L'ALCORA 05/06/2018 - 07/06/2018 PN p/cc Standard deviation 6300.53877
Export to Excel
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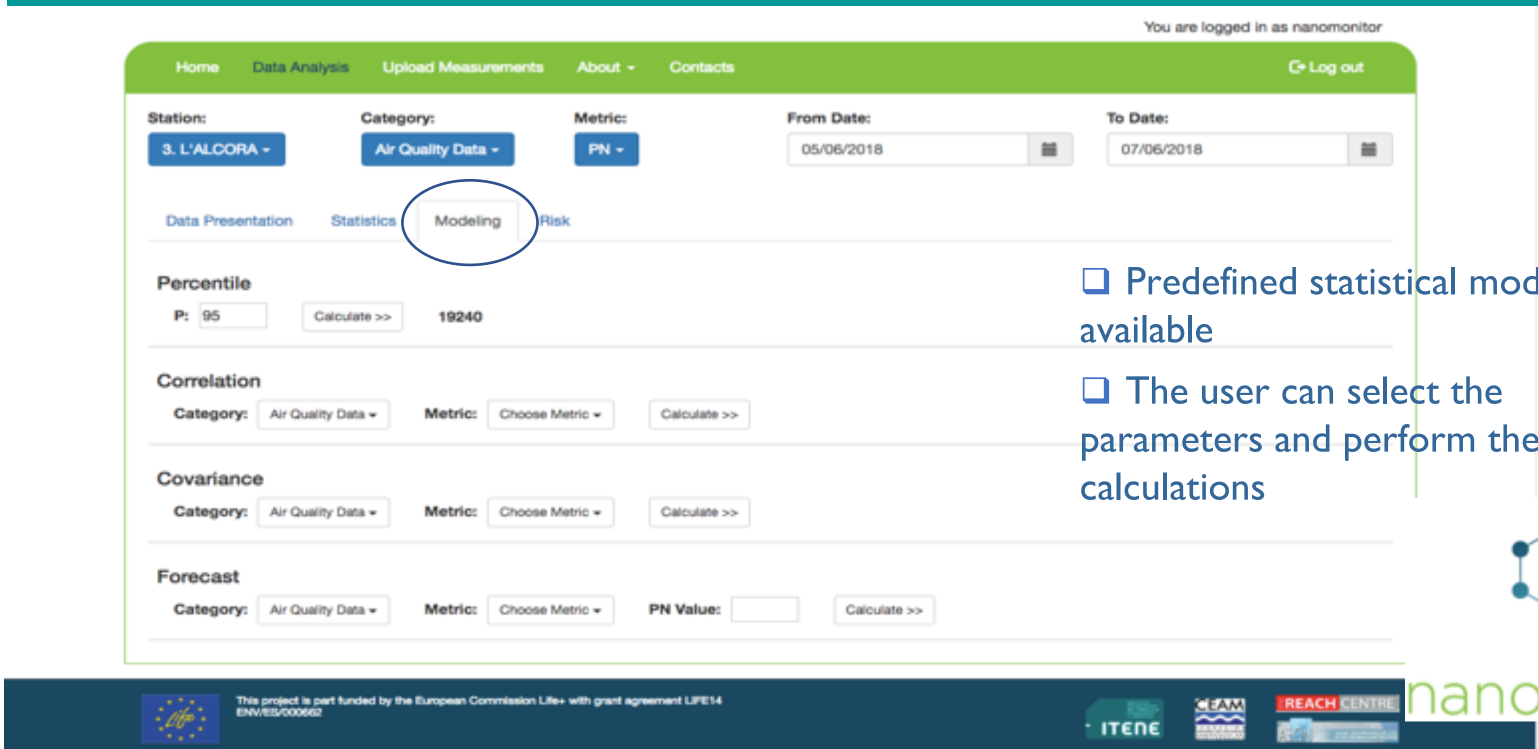
Data Analysis [2]



- ❑ Predefined statistical models are available
- ❑ The user can select the parameters and perform the calculations

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Data Analysis [3]

Predicted Environmental Concentrations in air, water and soil

$$PEC_A = \overline{C_A} = \frac{1}{n}\sum_{i=1}^{n} C_A(t_i) \qquad (1)$$

$$PEC_W = \overline{C_W} = \frac{1}{n}\sum_{i=1}^{n} C_W(t_i) \qquad (2)$$

$$PEC_S = \overline{C_S} = \frac{1}{n}\sum_{i=1}^{n} C_S(t_i) \qquad (3)$$

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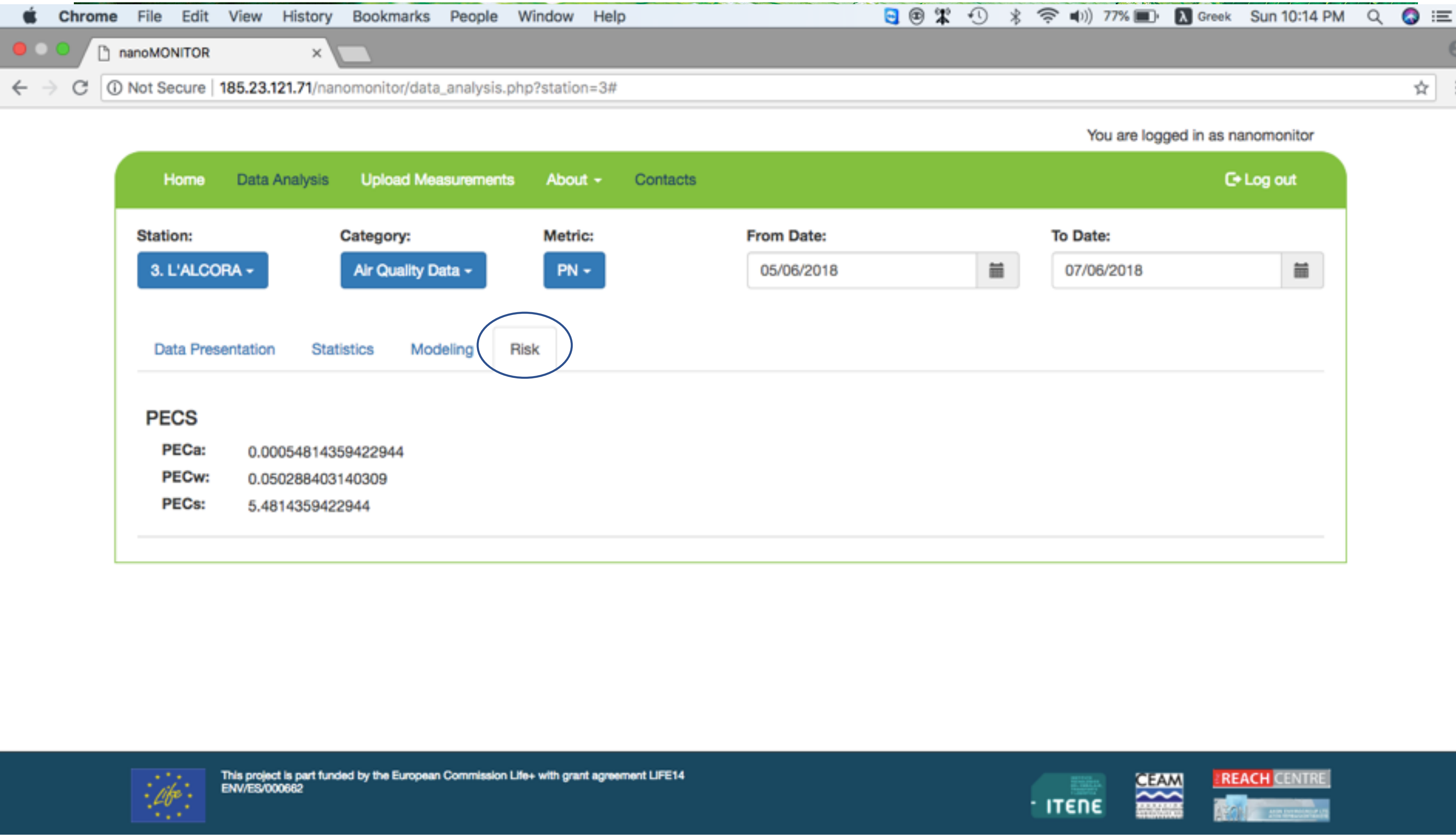
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Metric:
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From Date:
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Data Presentation
Statistics
Modeling
Risk
PECS
PECa: 0.00054814359422944
PECw: 0.050288403140309
PECs: 5.4814359422944
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Discussion

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Thank you!

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