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EXPOSURE SCENARIO LIBRARY AND GUIDELINES ON SAMPLING METHODS AND ANALYTICAL TECHNIQUES

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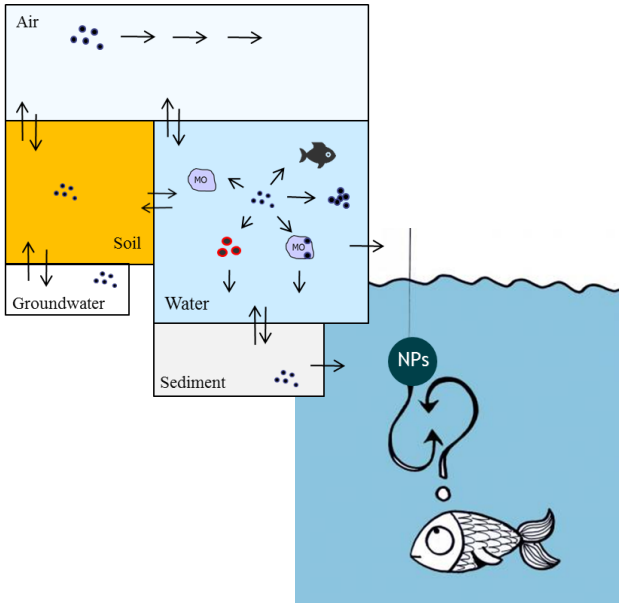
NanoMONITOR 1st stakeholders' day

1 INTRODUCTION

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.



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 $1.0x10^6$

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).	

Motivation & Background Information

- REACH implementation

REACH task	Actor	Action
Authorisation	MS, ECHA	Preparation of Annex XV dossiers: Identification of SVHC
	Information on persistency, bioaccumulation, background concentrations and timelines as criteria for inclusion into Annex XIV.	
	Interested parties	Comments on Annex XV dossiers for authorisation
	Information on persistency and bioaccumulation. Support of PBT / vPvB assessment.	
	M, I, DU	Voluntary monitoring programmes as argument for non-prioritisation of substances for inclusion in Annex XIV Application for an authorisation (based on registration dossier of substance (incl. PBT assessment)
	Proposal for in-house monitoring, local and regional monitoring	
Restrictions	MS, ECHA	Preparation Annex XV dossiers for restrictions proposal
	Interested parties	Comments on Annex XV dossiers for restriction
	Information on persistency and bioaccumulation. Support of PBT / vPvB assessment Information on critical exposure situations (PEC/PNEC >1)	
II. Success control (mostly related to specific substances)		
RMMs, SDSs	M, I, DU, CA	Self-monitoring/success control authorities (enforcement)
Authorisation and restrictions	M, I, DU	Self-monitoring of emission control measures
	CA	Control by authorities (enforcement (single companies),success control (regional/national/EU scale)
III. REACH Regulation as a whole (related to the total impact of all chemicals on human health and the environment)		
Information/ Art. 117, 121	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, they are not excluded and can be important to answer the key questions given above.	

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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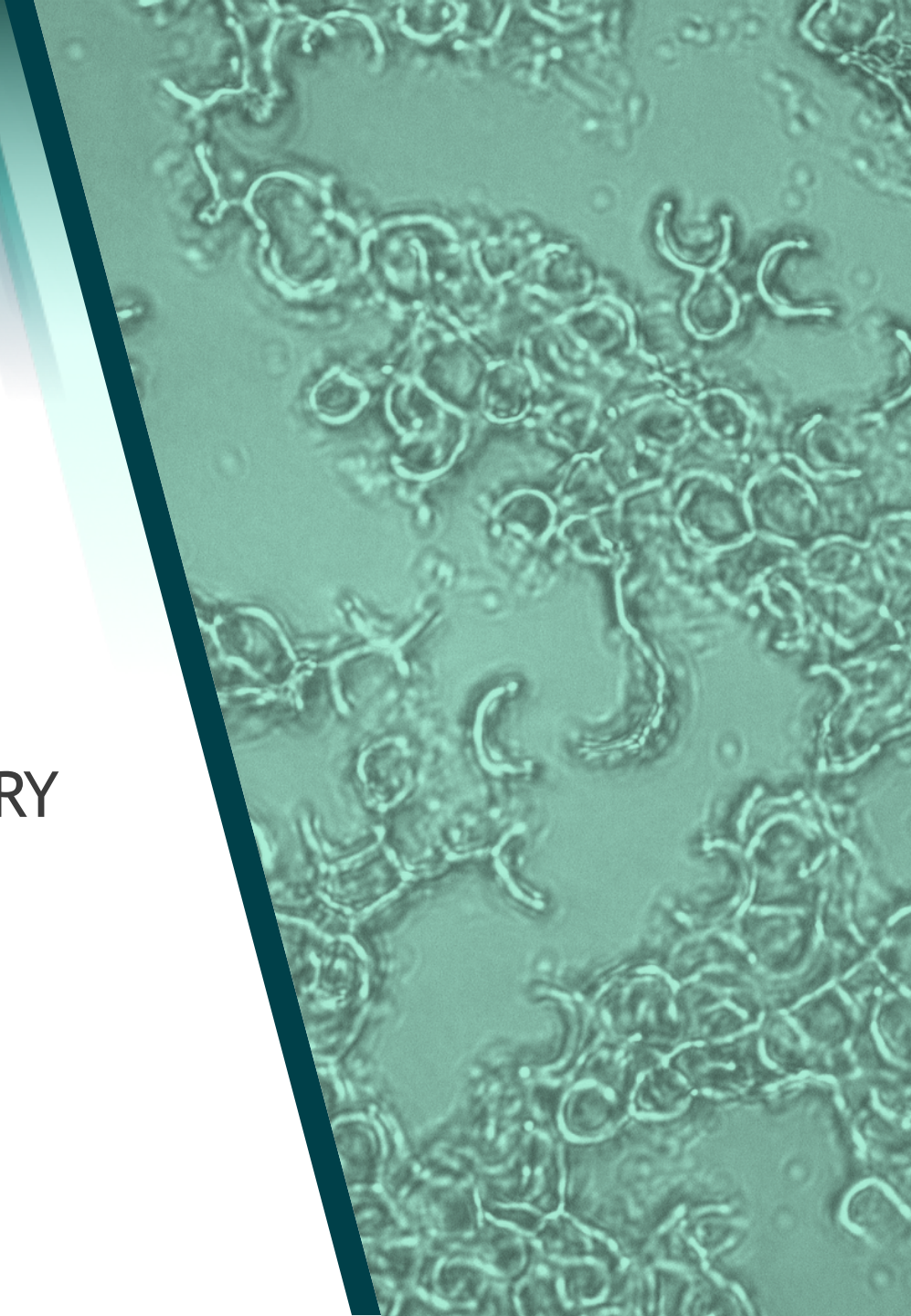
ESPOSURE SCENARIO LIBRARY

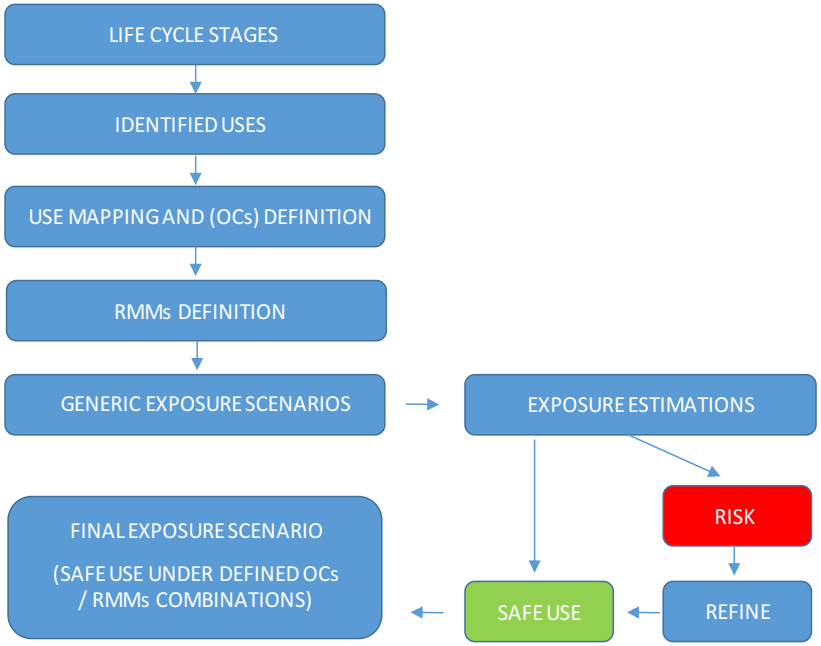


2. Exposure Scenario Library

- An ES is the cornerstone of the chemical safety assessment and the related communication in the supply chains under REACH.

- In occupational ESs, OCs and RMMs for workers are described for each handling activity. ESs for consumers should include information on the population exposed (e.g. children, adults), particular conditions of use (e.g. in spray, in cream), body parts exposed, and any behavioural advice to reduce exposure.

- For environmental ESs, OCs (e.g. river flow rate, STP size, and annual number of working days) and RMMs (e.g. oil skimmer, carbon filter) are described as part of "Specific Environmental Release Categories" (spERCs)



Source: P. A. Schulte.Journal Nanopartice Reseach (2016) 18:159

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2. Exposure Scenario Library

- The standard format of an exposure scenario can be found in the Guidance on information requirements and chemical safety assessment – Exposure Scenario Format in Part D: Exposure Scenario Building Part F: CSR Format.

Exposure Scenario Section		Description
1	Short title of the exposure scenario	Short title and included processes explanation using the use descriptor system of REACH. Describes which uses and activities with a substance are covered in the exposure scenario
2	Processes and activities covered by the exposure scenario	
Operational conditions of use		
3	Duration and frequency of use	Any action, use of tool or parameter state that prevails during manufacture or use of a substance (either in a pure state or in a mixture) that as a side effect might have an impact on exposure of humans and / or the environment.
4.1	Physical form of substance or mixture; surface to volume ratio of articles	
4.2	Concentration of substance in mixture or article	
4.3	Amount used per time or activity	Gas, liquid, powder, granules, massive solids; Surface area per amount of article containing the substance (if applicable);
5	Other relevant operational conditions of use	Temperature, pH, mechanical energy input; capacity of receiving environment (e.g. water flow in sewage/river; room volume x ventilation rate); wear and tear with regard to articles (if applicable); conditions related to service-life-time of articles (if applicable).
Risk management measures		
6.1	Risk management measures related to human health	Any action, use of tool, change of parameter state that is introduced during manufacture or use of a substance (either in a pure state or in a mixture) in order to prevent, control, or reduce exposure of humans and / or the environment
6.2	Risk management measures related to environment	
7	Waste management measures	

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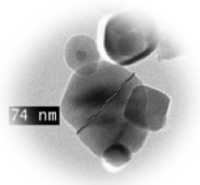
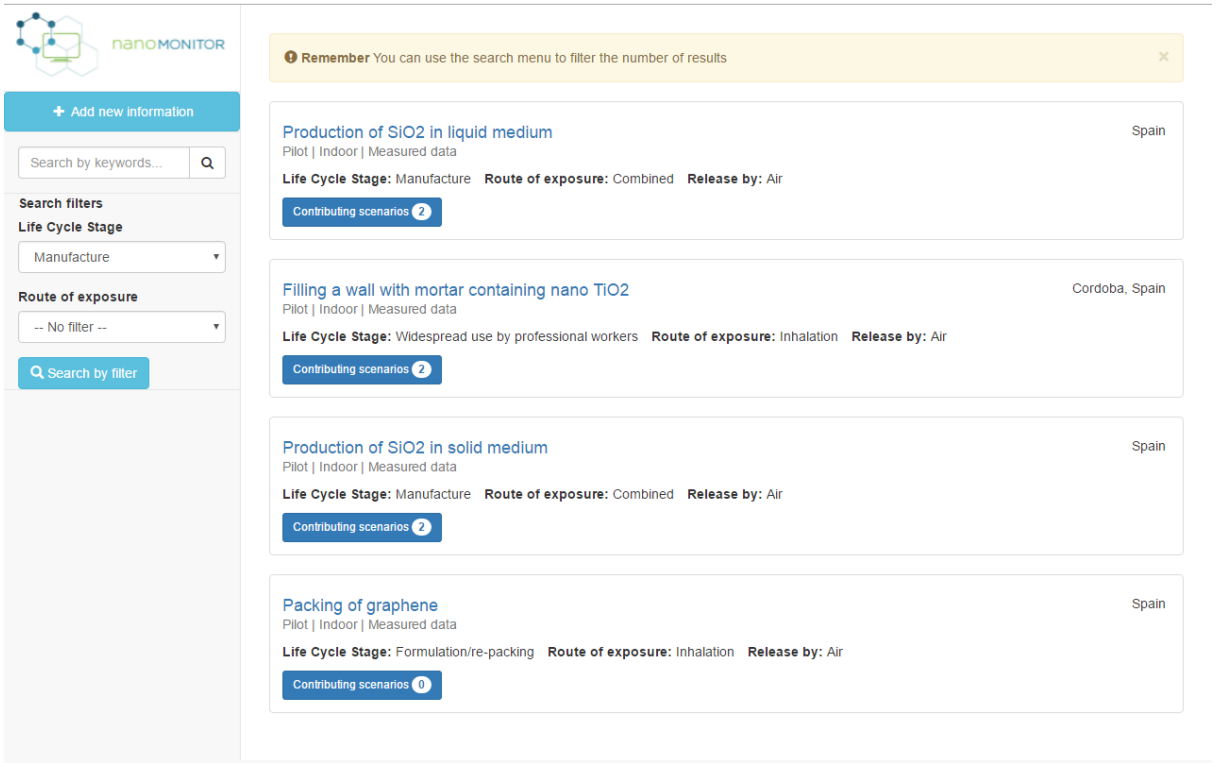
2. Exposure Scenario Library

- Within action B1, an on-line inventory of exposure scenarios and exposure monitoring data has been developed to ease the access and promote the use of the data generated within the project under the risk assessment process established by REACH.

- Exposure scenarios will be updated as new information becomes available during the project.





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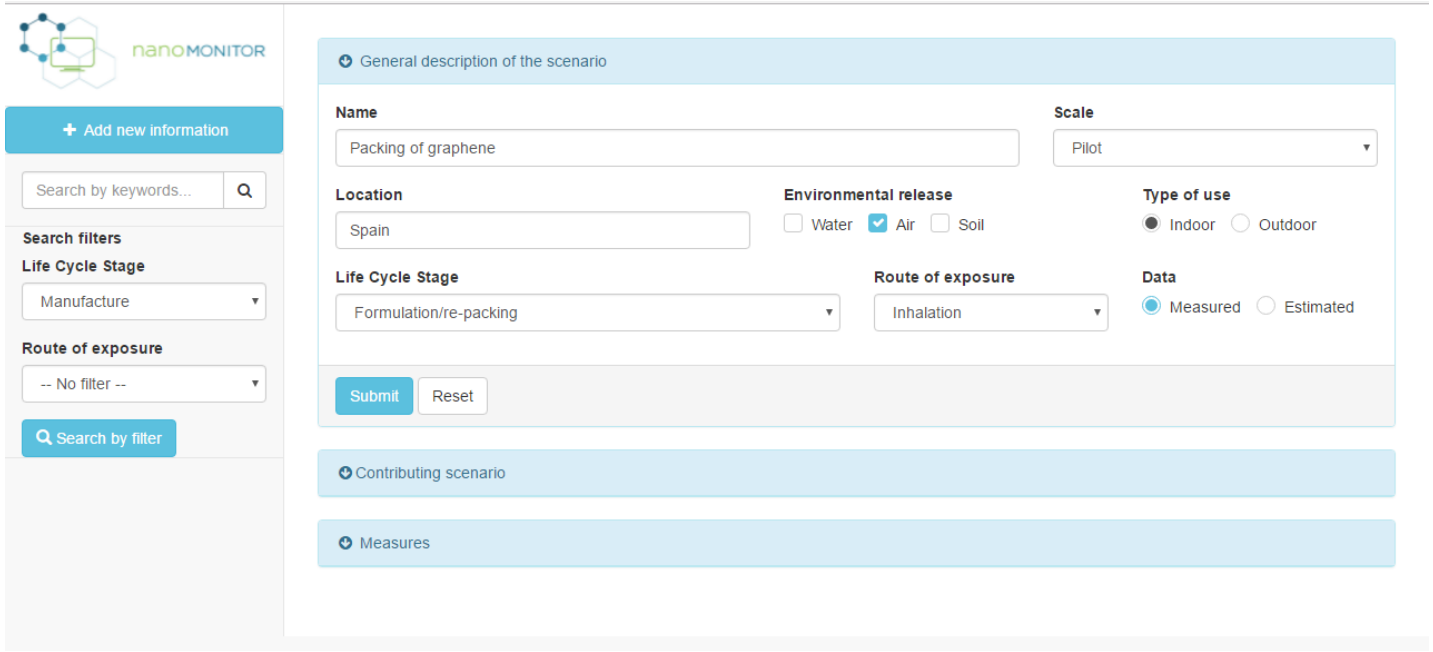
2. Exposure Scenario Library

- This tool is intended to guarantee a proper transference of the current knowledge on ENMs concentration
- Only authorized users will be able to complete on-line public ES
- Stakeholders are able to search and read information



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2. Exposure Scenario Library

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+ Add new information

Search by keywords...

Search filters

Life Cycle Stage

Manufacture

Route of exposure

-- No filter --

Search by filter

General description of the scenario

Save as PDF

Name: Production of SiO2 in liquid medium

Scale: Pilot

Location: Spain

Environmental release: Water [ ] Air [x] Soil [ ]

Type of use: Indoor ( ) Outdoor ( )

Life Cycle Stage: Manufacture

Route of exposure: Combined

Data: Measured (•) Estimated ( )

Contributing scenarios 2

Adition of the material and discharge of the end product | Cleaning

Contributing scenario title: Cleaning

Name of the ENM used: SiO2

Physical state of the material: Aglometares

Primary particle size: 160 nm

CAS Number: 112926-00-8

Shape of the ENM: Spherical

Surface area of the ENM: m^2/g

Density of the ENM: Unknown kg/m^3

Concentration in formulation: 97 %

Amount: 1kg-10kg

Frequency (aprox.): Unknown

Duration of use / Usage: 1min-30min/day

Operational conditions affecting exposure/release

Describe the activity in terms of the energy applied to the process: Unknown

Temperature at which the process is carried out: °C

Site conditions

Room volume: 339 m^3

Temperature: 16,5 °C

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2. Exposure Scenario Library

Contributing scenario

Select the scenario for

6. Packing of graphene

Contributing scenario title

Scenario 1

Name of the ENM used

Graphene

Unknown

Physical state of the material

Aglometares

Primary particle size

5 nm

CAS Number

Ex. 112926-00-8

Shape of the ENM

Spherical

Surface area of the ENM

[number] m^2/g

Density of the ENM

-- Select-- kg/m^3

Concentration in formulation

%

Amount

Unknown | <1g | 1g-1kg | 1kg-10kg | 10kg-100kg | >100kg

Frequency (aprox.)

Unknown | 1day/year | 1day/month | 1day/week | 2-3days/week | 4-5 days/week

Duration of use / Usage

Unknown | 1min-30min/day | 30min-2h/day | 2h-4h/day | 4h-8h/day

Operational conditions affecting exposure/release

Describe the activity in terms of the energy applied to the process

Unknown

Temperature at which the process is carried out

Enter the temperature °C

Presence of a secondary source of non ENMs (NM release from the equipment used, or other substances used in the processes)

Yes No

Which secondary enms?

Site conditions

Room volume

338 m^3

Temperature

16.4 °C

Pressure

Enter the pressure Pa

Relative humidity

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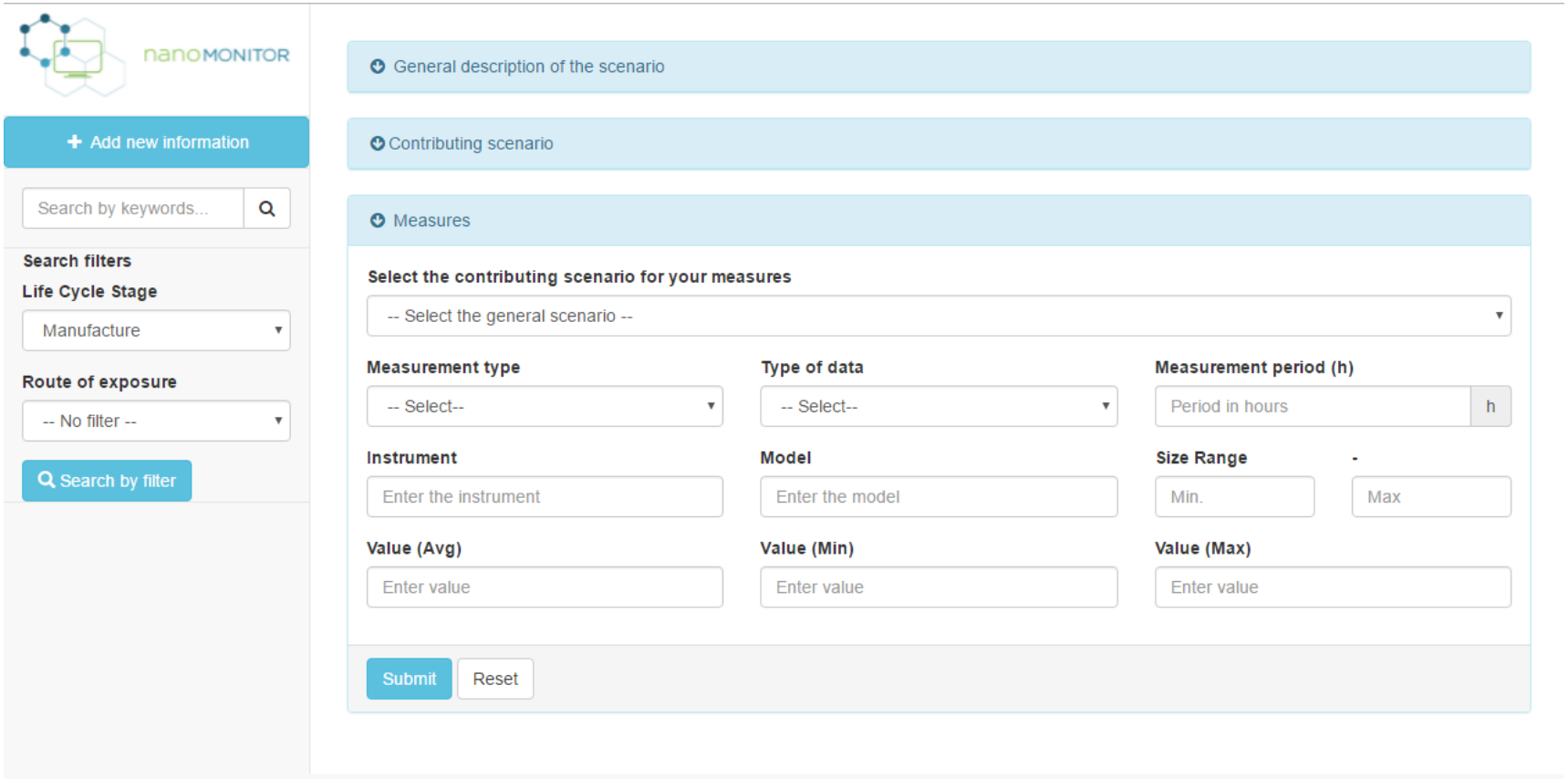
2. Exposure Scenario Library



Workplace exposure data inventory

ES	CES	Background	Surface ($\mu m^2/cm^3$)	Mass (mg/m^3)	Number ($\#/cm^3$)	Ratio
Production of SiO_2 in liquid medium	Addition of the material and discharge of the end product	3900 (N)	-	-	6019	1.5
	Cleaning	3900 (N)	-	-	8321	2.1
Production of SiO_2 in solid medium	Poured of the SiO_2 into the mixer	10237 (N)	-	-	14062	1.4
	Discharge of the functionalized SiO_2	10237 (N)	-	-	14062	1.4
	Cleaning	10237 (N)	-	-	10400	1.0
Sieved of SiO_2	Sieved of SiO_2	10237 (N)	-	-	14062	1.4
	Cleaning	5570 (N)	-	-	7946	1.4
Production of mortar with TiO_2		22581 (N)	-	-	23023	1.0
Packing graphene		5700 (N)	-	-	6610	1.2
Packing graphene platelets	Weighting and packing	5700 (N)	-	-	29165	5.1
	Cleaning	5700 (N)	-	-	12680	2.2
Packing mortar with nano TiO_2		-	-	-	57710	-
Packing SiO_2 in bags (20 kg)		9041 (N)	-	-	29816	3.3
Packing SiO_2 in bags (25 kg)		9041 (N)	-	-	26874	3.0
Packing SiO_2 in bags (500 kg)		12176 (N)	-	-	24191	2.0
Filling a wall with conventional mortar	Kneaded of the mortar	12400 (N)	-	-	15000	1.2
	Application of the mortar	12400 (N)	-	-	14200	1.1
Filling a wall with mortar containing nano TiO_2	Kneaded of the mortar	12400 (N)	-	-	20000	1.6
	Application of the mortar	12400 (N)	-	-	19000	1.5
Application of conventional paint using a roller		7200 (N)	-	-	8900	1.2
Application of a paint containing nano TiO_2 using a roller		7200 (N)	-	-	9000	1.3
Application of a photocatalytic product with nano TiO_2 using a roller		6630 (N)	-	-	10000	1.5
Spraying a conventional paint		7000 (N)	-	-	8700	1.2
Spraying a paint with nano TiO_2		11000 (N)	-	-	16000	1.5
Spraying a product with nano TiO_2		12400 (N)	-	-	50000	4.0

Workplace exposure data inventory

ES	CES	Background	Surface ($\mu m^2/cm^3$)	Mass (mg/m^3)	Number ($\#/cm^3$)	Ratio
Production of carbonaceous materials		34694 (N)			105856	3.1
Production of carbonaceous materials		34694 (N)			63130	1.8
Production of carbonaceous materials		57000 (N)		81000		1.4
Production of carbonaceous materials		57000 (N)		85000		1.5
Separation and packaging of Al_2O_3	Separation	19000 (N)			43000	2.3
	Packaging	19000 (N)			34000	1.8
	Transportation	19000 (N)			56000	2.9
Separation and packaging of Al_2O_3	Separation	50 (M)		200		4
	Packaging	50 (M)		460		9.2
	Transportation	50 (M)		510		10.2
Separation and packaging of Al_2O_3	Separation	18 (M)	77			4.3
	Packaging	18 (M)	57			3.2
	Transportation	18 (M)	93			5.1
Production of MWCNT	Production	2900 (N)	8.8	0.026	30700	10.6
	Harvesting	30700 (N)	24.7	0.032	31800	1.0
Harvesting of DWCNT		2900 (N)	33.5	0.032	31800	10.9

Workplace exposure data inventory

ES	CES	Background	Surface ($\mu m^2/cm^3$)	Mass (mg/m^3)	Number ($\#/cm^3$)
Production of MWCNT	Production	12300 (N)	63.4	0.044	15300
	Harvesting	12300 (N)	55.2	0.037	12100
	Spray coating and sieving	12300 (N)	30.4	0.012	32100
Production of MWCNT	Sonication		30.8		10
	Weighing		16.1		510
Production of MWCNT	Extrusion	0.029 (M)	148.3	0.107	16000
	Batch mixing	0.029 (M)		0.033	9400
	Milling	0.029 (M)		0.016	6800
Mixing with a blended cement incorporating Portland cement with 35 % by weight Ground Granulated Blastfurnace Slag using a drum mixer		5260 (N)			21270
Mixing with a blended cement incorporating Portland cement with 35 % Pulverised Fuel Ash using a drum mixer		1980 (N)			30970
Production of SWCNT	Production	40200 (N)	64	0.046	43600
	Harvesting	5800 (N)	15.6	0.017	5900
	Cleaning	5800 (N)	24.4	0.022	14300
Dry drilling of a hardened concrete prism using a rotary drill		69850 (N)			279110
Dry cutting of a hardened concrete prism using a fixed radial		127320 (N)			732270

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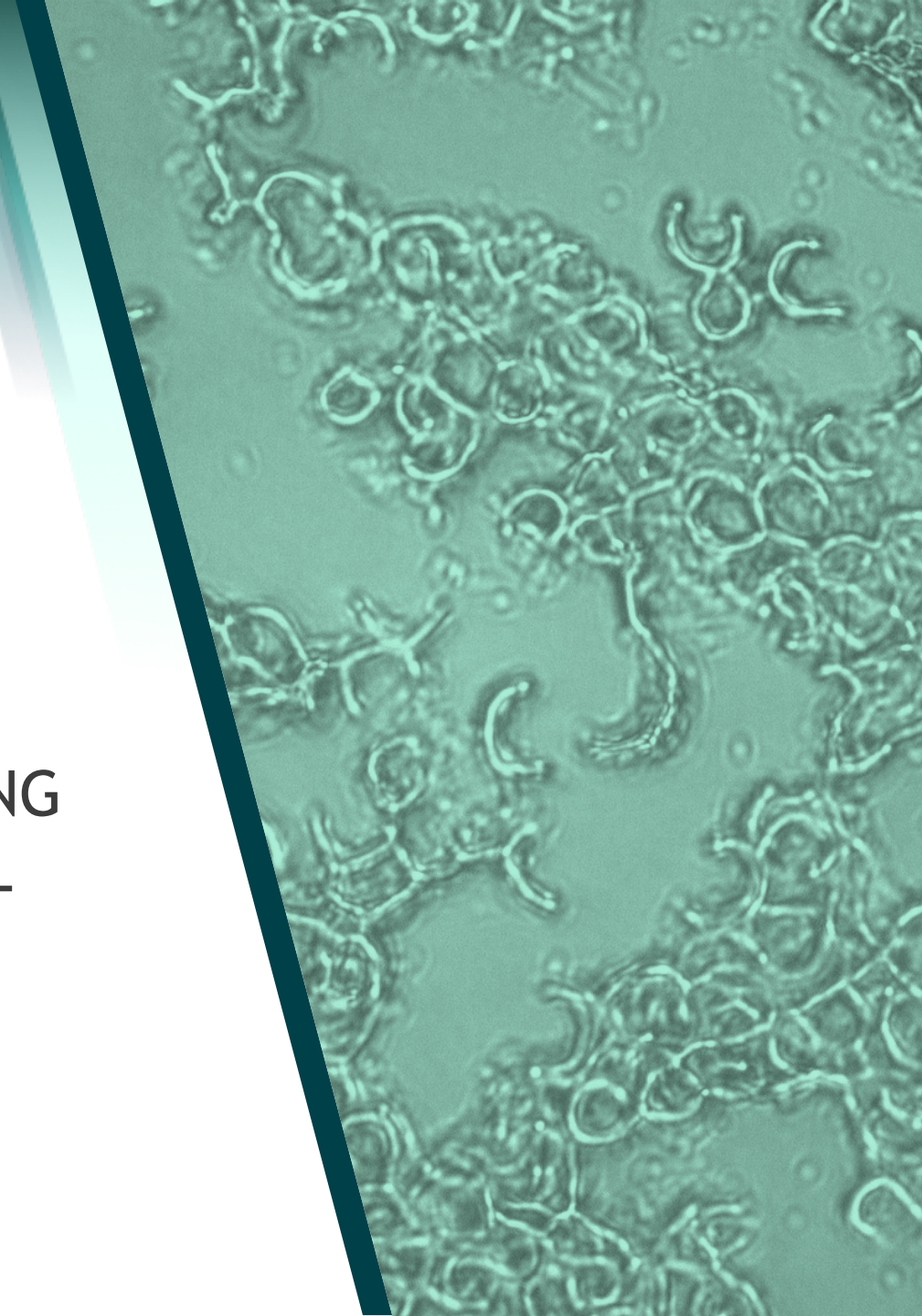
DEVELOPMENT OF SAMPLING METHODS AND ANALYTICAL TECHNIQUES



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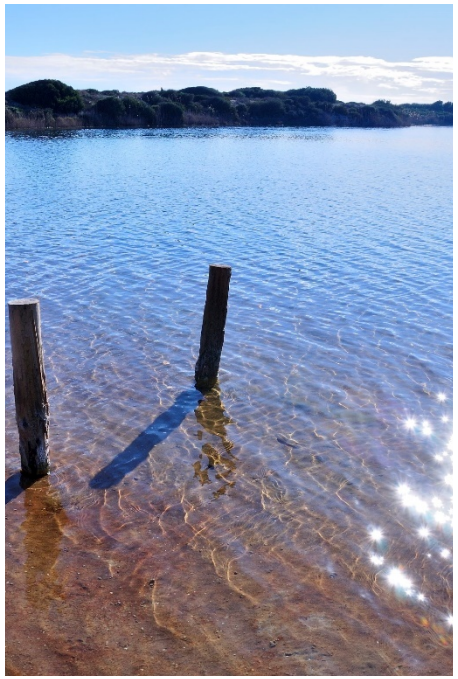
3. Sampling methods and analytical techniques

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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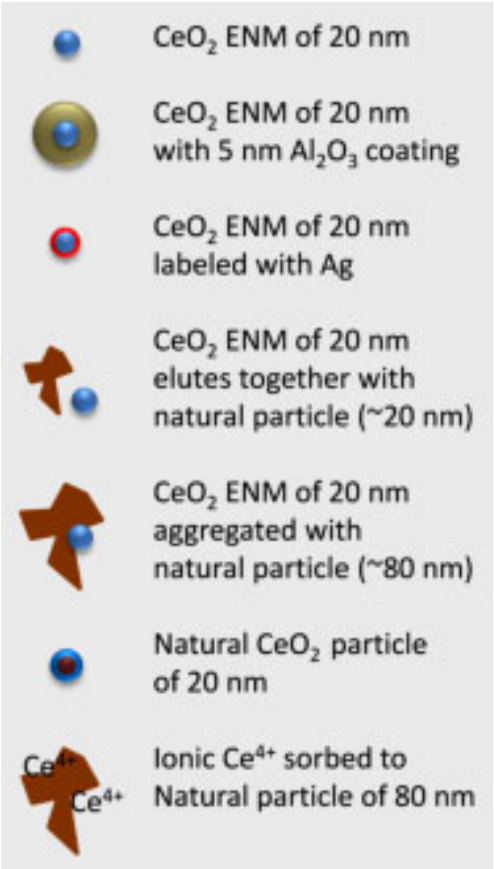
3. Sampling methods and analytical techniques

- 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

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.



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)

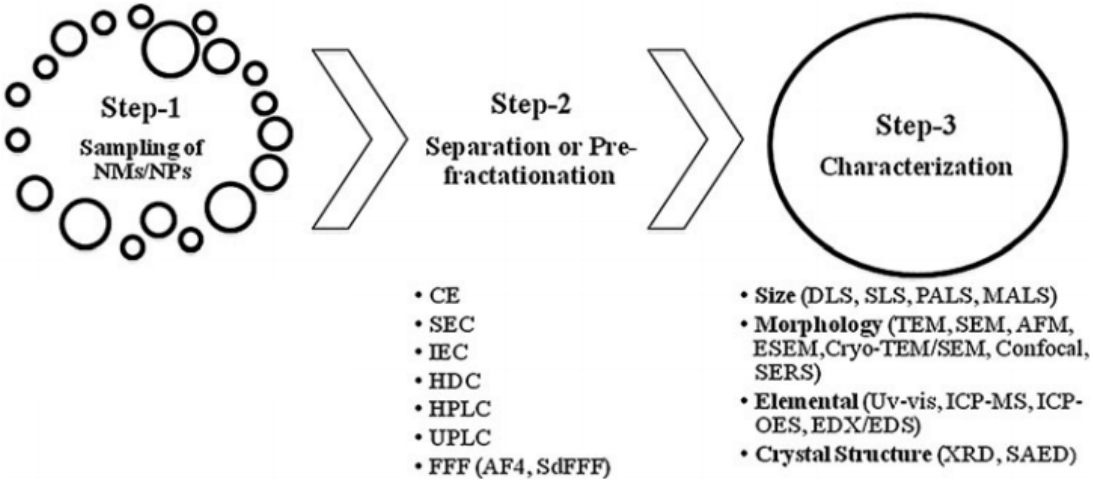
- Light-scattering techniques
  DLS: sizing NPs and determining their aggregation in suspensions
  Small angle X-ray scattering (SAXS)
  Laser-induced breakdown detection (LIBD): detect trace amounts of NPs (<100 nm) in aqueous suspensions

- 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

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



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SUMMARY CONCLUSIONS

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SUMARY 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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Thank you for your attention !

CARLOS FITO
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