

EXPOSURE SCENARIO LIBRARY AND DATA ON THE CONCENTRATION OF ENMs IN WORKPLACES

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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 $1.0x10^6$

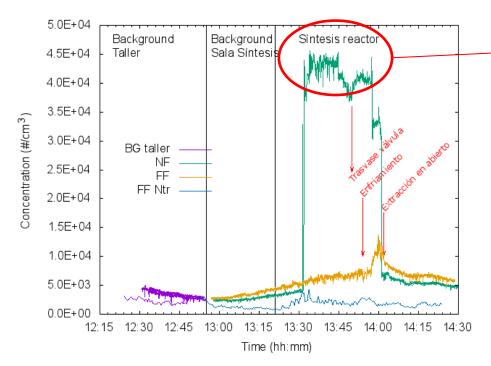


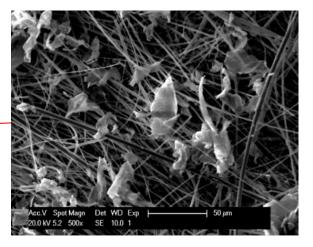


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Motivation & Background Information

In the occupational context, workers may be exposed to nanomaterials via three main routes: inhalation, ingestion or through dermal contact.





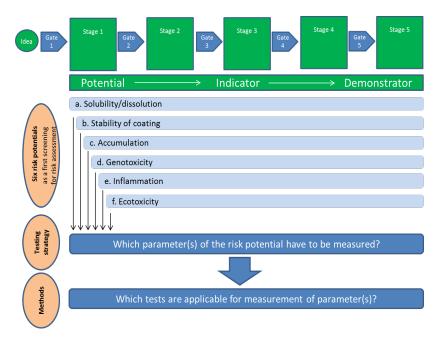
	Near Field			FF		
	Conc (#/cm3)	Desv. Est.	C _{activity} /C _{BG}	Conc (#/cm3)	Desv. Est.	C _{activity} /C _{BG}
Background	2,000	3,11E+02	1,06	2,34E+03	3,70E+02	0,74
Operation	20,000	1,77E+04	8,07	4,65E+03	9,80E+02	1,47

Graphene production. Source: ITENE

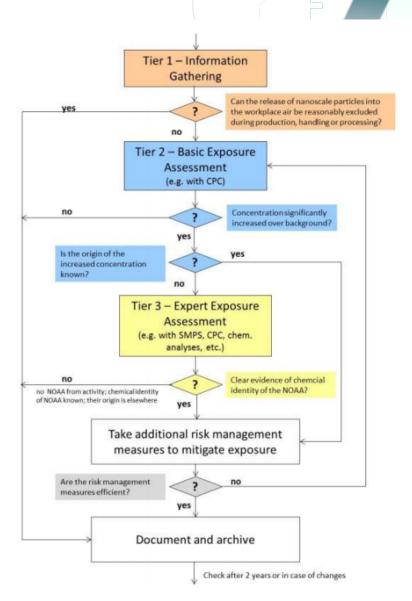
1. Introduction

Motivation & Background Information

Recent publications by relevant bodies recommends a proper exposure characterization + proven risk management measures in the risk assessment process.



Source: NANoREG framework for the safety assessment of NMs



Source: OECD 2015

1. Introduction

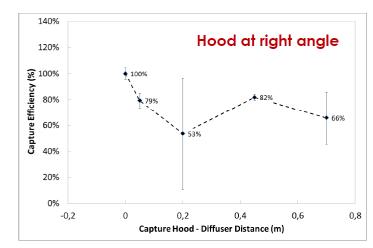
Concerning risk management approaches (RMM), knowledge, data, and test methods on common risk management measures for NMs are still very limited, which implies a severe knowledge gap on the effectiveness of currently available RMMs during nanomaterial production and handling processes

RPD	Specifications	Measures	Standard Efficiency	Protection (NMs)	Reference particle
Filters	P2 Filter	Efficiency	94 %	99.83 %	NaCl
	P3 Filter	Efficiency	99.95 %	99.97 %	NaCl
Half Mask	New Mask P3 Filter	Efficiency	99.95%	99.47 ± 0.83 %	NaCl
	Aged Mask P3 Filter	Efficiency	99.95%	99.77 ± 0.29 %	NaCl
Full Mask	New Mask P3 Filter	Efficiency	99.95%	99.73 ± 0.25 %	NaCl
	Aged Mask P3 Filter	Efficiency	99.95%	99.78 ± 0.16 %	NaCl
FFP	FFP1	Efficiency	80%	75.63 %	NaCl
	FFP3 (Model a)	Efficiency	99%	99.77 ± 0.29	NaCl
	FFP3 (Model b)	Efficiency	99%	95.63 ± 4.39	NaCl









1. Introduction

Motivation & Background Information

REACH implementation

REACH task	Actor	Action			
I. Specific REACH m	echanisms (mostly related	to specific substances)			
Registration	M, I	Preparation of registration dossiers			
		support the evaluation of substance properties e.g. persistence, bioaccumulation, o)toxicity, PBT assessment. (Standard information requirements according to			
	Monitoring data may concentrations (local	support exposure estimations e.g. by delivering measured environmental and regional)			
Supply Chain Information	DU	Communication on Risk Management Measures and new hazardous properties			
	Use of monitoring da	ta to show adequateness of risk management measures			
	Use of monitoring da	ta to prove local accumulation / effects of substances			
Evaluation	MS, ECHA	Dossier and substance evaluation			
	Check of information Substance evaluation Information on emer	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).			





1. Introduction

Motivation & Background Information

REACH implementation

REACH task	Actor	Action			
Authorisation	MS, ECHA	Preparation of Annex XV dossiers: Identification of SVHC			
	Information on persis	tency, bioaccumulation, background concentrations and timelines as criteria for			
	inclusion into Annex 2	inclusion into Annex XIV.			
	Interested parties	Comments on Annex XV dossiers for authorisation			
	Information on persis	tency 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	Interested parties Comments on Annex XV dossiers for restriction			
	Information on persis	Information on persistency and bioaccumulation. Support of PBT / vPvB assessment			
	Information on critical exposure situations (PEC/PNEC >1)				
II. Success control (mos	tly related to specific s	ubstances)			
RMMs, SDSs	M, I, DU, CA	Self-monitoring/success control authorities (enforcement)			
Authorisation and	M, I, DU	Self-monitoring of emission control measures			
restrictions	CA				
III. REACH Regulation as	a whole (related to the	e 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:			
		n of environment and human health?			
	- Trends of concentra	tions of hazardous substances?			
	- (Local) Accumulatio	n of hazardous substances?			
	Art. 117 does not expl	icitly mention environmental monitoring activities. However, they are not excluded			
	and can be important	and can be important to answer the key questions given above.			

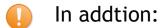




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Under REACH regulation, the risk assessment process is based on a comparison between the predicted/measured/estimated level of exposure and the predicted or derived no effect concentration levels of the substances of concern.



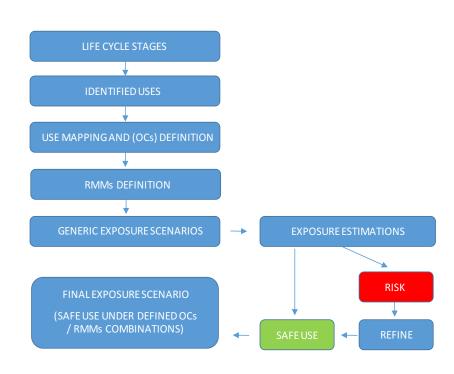
- 4,480 publications on toxicity
- 2,669 publications related with risk
- Up to 190 publications on occupational exposure
- Up to 65 publications on environmental exposure







- 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)



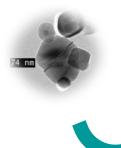
2. Exposure Scenario Library

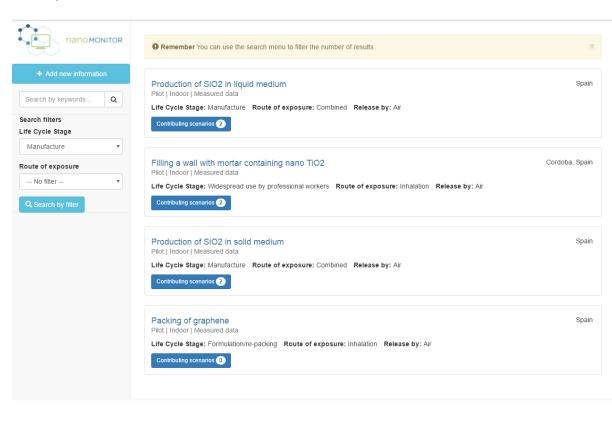
The standard format of an exposure scenario can be found in the Guidance on information requirements and chemical safety assessment - Exposure Scenario Format in Part D: Exposure Scenario Building Part F: CSR Format.

Exposu	re Scenario Section	Description
1	Short title of the exposure scenario	Short title and included processes explanation using the use descriptor
2	Processes and activities covered by the exposure scenario	system of REACH. Describes which uses and activities with a substance are covered in the exposure scenario
Operat	ional conditions of use	
3	Duration and frequency of use	Any action, use of tool or parameter state that prevails during manufacture
4.1	Physical form of substance or mixture; surface to volume ratio of articles	or use of a substance (either in a pure state or in a mixture) that as a side $ {\it effect might have an impact on exposure of humans and / or the } \\$
4.2	Concentration of substance in mixture or article	environment.
4.3	Amount used per time or activity	Gas, liquid, powder, granules, massive solids; Surface area per amount of
5	Other relevant operational conditions of use	article containing the substance (if applicable); 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 ma	anagement measures	
6.1	Risk management measures related to human health	Any action, use of tool, change of parameter state that is introduced during
6.2	Risk management measures related to environment	manufacture or use of a substance (either in a pure state or in a mixture) in
7	Waste management measures	order to prevent, control, or reduce exposure of humans and / or the $\ensuremath{environment}$

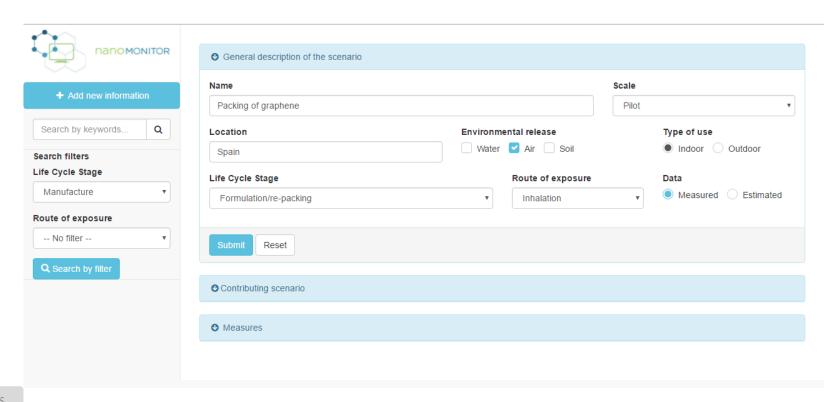


- Within action B1, an on-line inventory of exposure scenarios and exposure monitoring data has been developed to ease the access and promote the use of the data generated within the project under the risk assessment process established by REACH.
- Exposure scenarios will be updated as new information becomes available during the project.

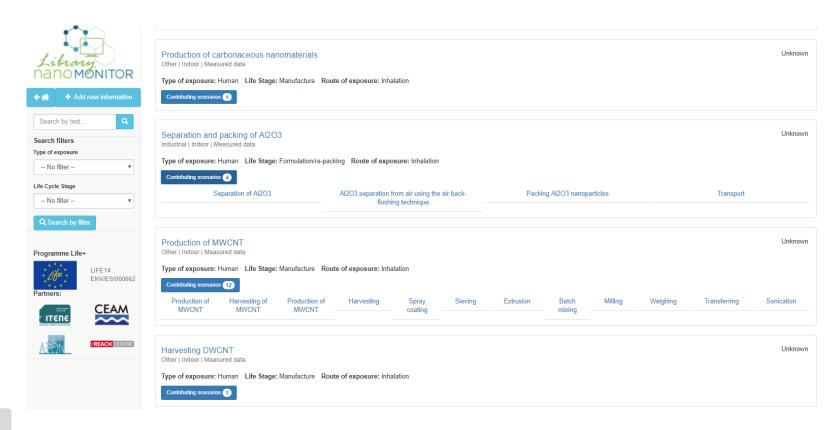




- This tool is intended to guarantee a proper transference of the current knowledge on ENMs concentration
- Only authorized users will be able to complete on-line public ES
- Stakeholders are able to search and read information.



- Stakeholders are able to study common contributing scenarios
- Up to 160 contributing scenarios avalible + more than 548 reference values
- Data retrieved from the monitoring stations will included

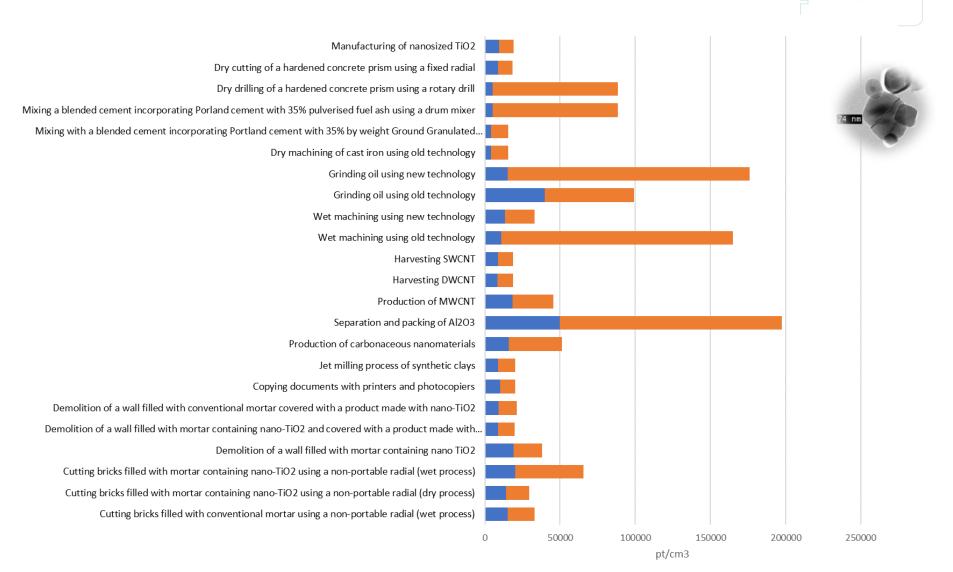


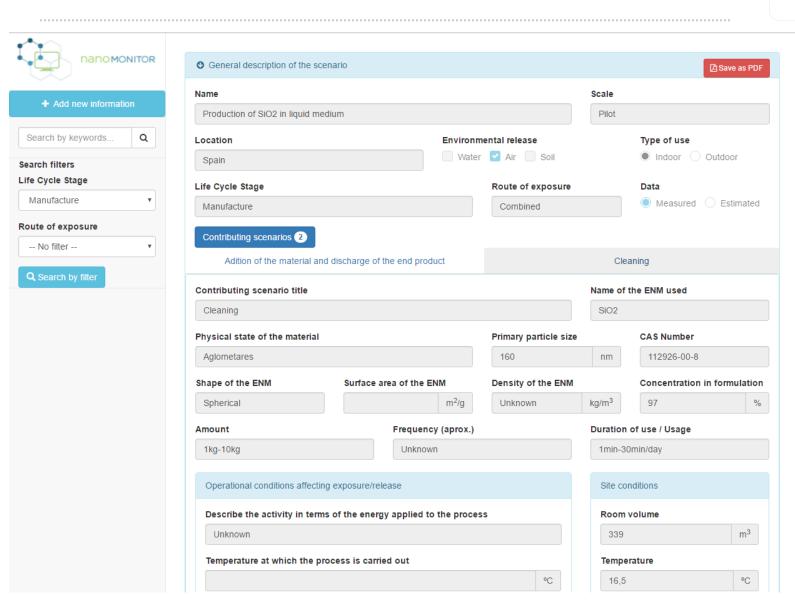
- 160 "activities" currently available, including:
 - Production of SiO2 nanoparticles, MWCNTs, Al2O3, TiO2, nanoAg, CeO2
 - Harvesting / Packing of graphene, MWCNTS, and metal oxide NPs
 - Mixing operations, drilling and cutting at industrial sites
 - Packing of construction products "mortar" with TiO2
 - Application of paints formulated with ENMs (Spray / roller)
 - Application of photocatalytic coatings (Spray / roller)
 - End-of-life processes in the construction sector: cutting, sanding, demolition
 - Printing and 3D printing operations
 - Jet milling

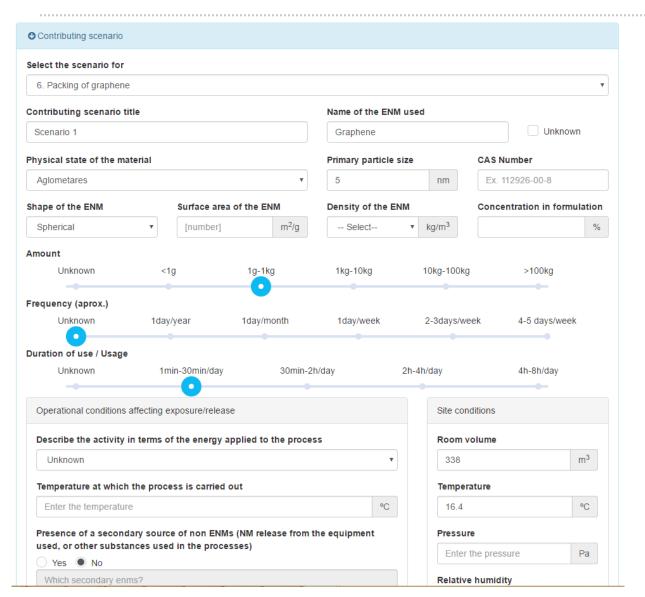


2. Exposure Scenario Library

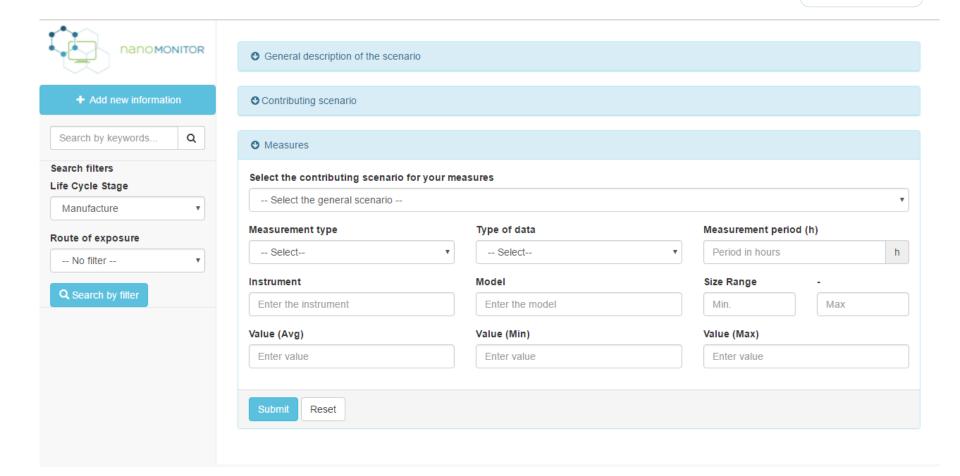
Data on the exposure concentration (PBZ)

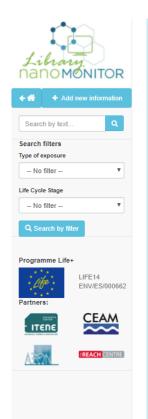


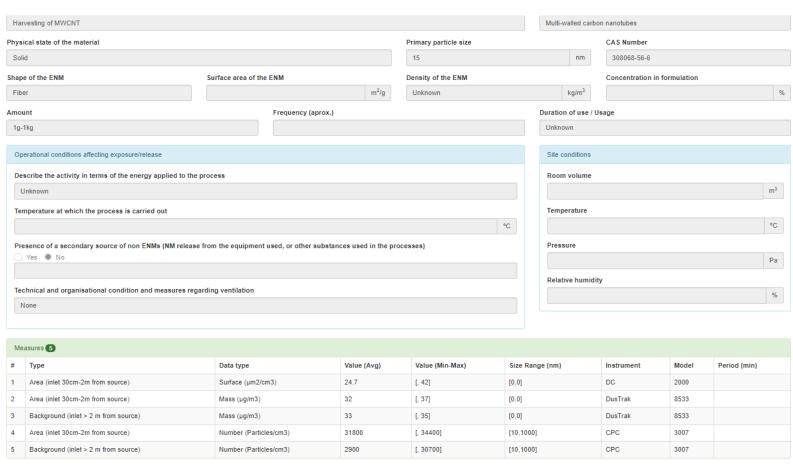












2. Exposure Scenario Library

Workplace exposure data inventory

ES	CES	Background	Surface (µm²/cm³)	Mass (mg/m³)	Number (#/cm³)	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
	Poured of the SiO ₂ into the mixer	10237 (N)	-	-	14062	1.4
Production of SiO ₂ in solid medium	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
Sieved of SiO ₂	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
Packing graphene platelets	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 well with conventional marter	Kneaded of the mortar	12400 (N)	-	-	15000	1.2
Filling a wall with conventional mortar	Application of the mortar	12400 (N)	-	-	14200	1.1
Fillian II ith	Kneaded of the mortar	12400 (N)	-	-	20000	1.6
Filling a wall with mortar containing nano TiO ₂	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 ${\rm TiO_2}$ using a roller		7200 (N)	-	-	9000	1.3
Application of a photocatalytic product with nano ${\rm TiO_2}$ 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

2. Exposure Scenario Library

Workplace exposure data inventory

ES	CES	Background	Surface (μm²/cm³)	Mass (mg/m³)	Number (#/cm³)	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	19000 (N)			43000	2.3
Separation and packaging of Al ₂ O ₃	Packaging	19000 (N)			34000	1.8
	Transportation	19000 (N)			56000	2.9
	Separation	50 (M)		200		4
Separation and packaging of Al ₂ O ₃	Packaging	50 (M)		460		9.2
	Transportation	50 (M)		510		10.2
	Separation	18 (M)	77			4.3
Separation and packaging of Al ₂ O 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
Production of MWCN1	Harvesting	30700 (N)	24.7	0.032	31800	1.0
Harvesting of DWCNT		2900 (N)	33.5	0.032	31800	10.9

2. Exposure Scenario Library

Workplace exposure data inventory

ES	CES	Background	Surface (μm²/cm³)	Mass (mg/m³)	Number (#/cm³)
	Production	12300 (N)	63.4	0.044	15300
Production of MWCNT	Harvesting	12300 (N)	55.2	0.037	12100
Production of Niweni	Spray coating and sieving	12300 (N)	30.4	0.012	32100
Production of MWCNT	Sonication		30.8		10
Production of MWCN1	Weighing		16.1		510
	Extrusion	0.029 (M)	148.3	0.107	16000
Production of MWCNT	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	40200 (N)	64	0.046	43600
Production of SWCNT	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



3. Sampling methods and analytical techniques

Action B4 focusses 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



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

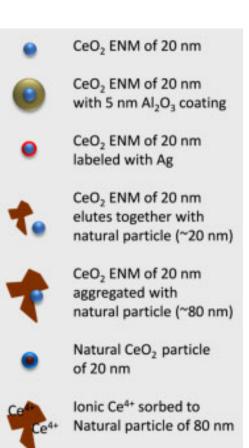




3. Sampling methods and analytical techniques

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.



3. Sampling methods and analytical techniques

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



3. Sampling methods and analytical techniques

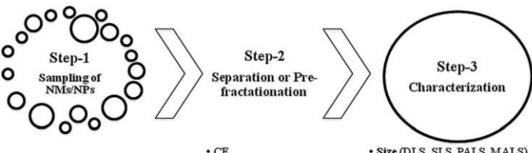


Quantitative analysis of nanoparticles

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



- · CE
- · SEC
- IEC
- · HDC
- · HPLC
- · UPLC
- FFF (AF4, SdFFF)

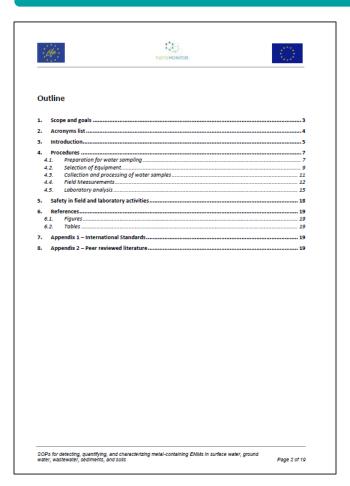
- · Size (DLS, SLS, PALS, MALS)
- · Morphology (TEM, SEM, AFM, ESEM, Cryo-TEM/SEM, Confocal, SERS)
- Elemental (Uv-vis, ICP-MS, ICP-OES, EDX/EDS)
- · Crystal Structure (XRD, SAED)





3. Sampling methods and analytical techniques

Protocols



	Properties / metrics	Instrumentation / methods		
and	Particle size	TEM, SEM, ICP-MS, UV-vis, DLS, FI-FFF, Sed- FFF, HDC, NTA, SLS, PALS, MALS		
ibution	Particle number concentration	spICP-MS, NTA		
distr	Particle diameter	EM/AFM/Flow-FFF/DLS		
: maize distr morphology	Morphology	TEM, SEM, AFM, ESEM, Cryo-TEM/SEM, Confocal, SERS		
Particle size Particle number concentration Particle diameter Morphology Aspect ratio		Microscopy, combination of light scattering methods or different FFF methods		
Pa	Crystal Structure	XRD, TEM-XRD (SAED)		
ä	Surface area / porosity	BET		
urfac tical ties	z-Potential	ELS		
Particle surface and optical properties	Surface Charge / Surface groups	Electrophoretic mobility, NMR, FTIR		
Part ar pı	Reflection, absorption, transmission	UV-vis spectroscopy		
Chemical compositio	Elemental composition	SEM/EDX, ICP-MS, ICP-OES, UV-vis, EDX/EDS, XAS		
n and	Mass	LC/ESMS		
concentrati on	Crystal Structure	XRD, TEM-XRD (SAED)		
OH	Purity	TGA		
	Moisture content	TGA		





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 March 2018
- 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.





Thank you for your attention!

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