NSC Review Meeting

Exposures, Transformation and Life Cycle

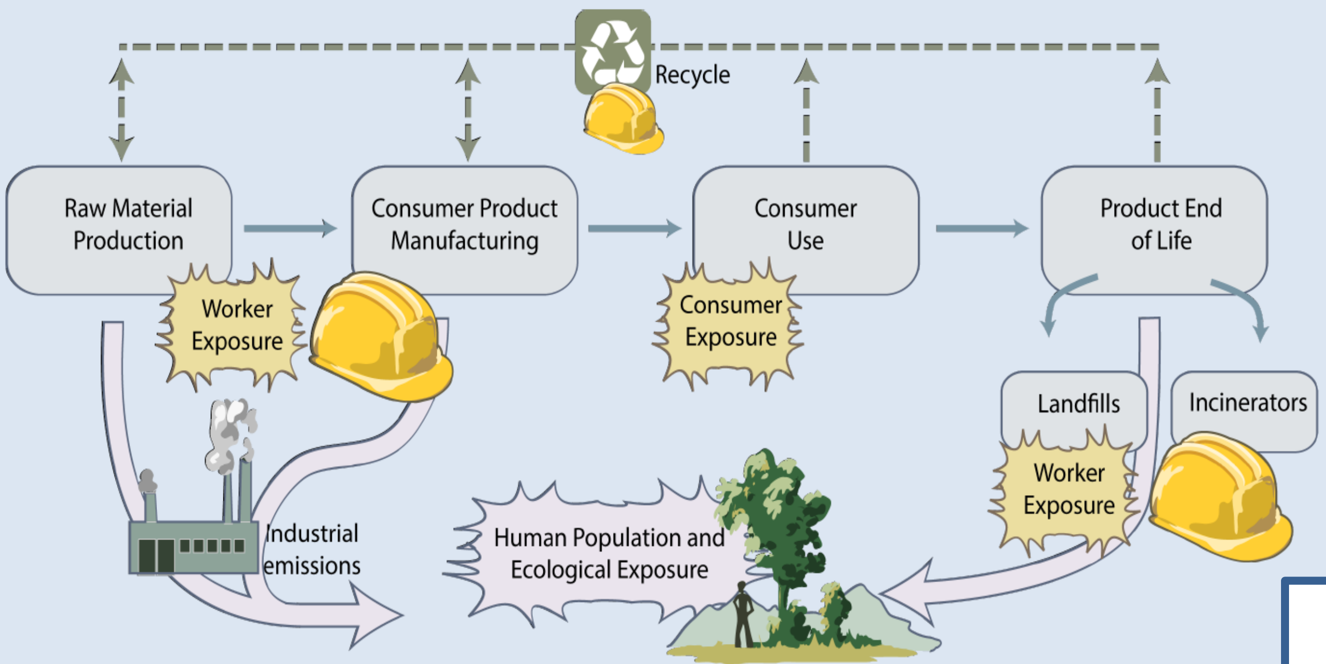
by

S. Vázquez-Campos, C. Svendsen, D. Brouwer, J. Rose

Human and Environmental Exposures along nano-enabled products life cycle

Engineered Nanomaterial and Nanotechnology-Enabled Product Life Cycle Considerations

Human and environmental exposures to ENMs can occur at all life cycle stages of an NEP.



Adapted from the *2011 NNI Environmental, Health, and Safety Research Strategy*, www.nano.gov/sites/default/files/pub_resource/nni_2011_ehs_research_strategy.pdf.

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Accidental release
(*e.g.* spill, fire…)

REF: NATIONAL NANOTECHNOLOGY INITIATIVE STRATEGIC PLAN - National Science and Technology Council - Committee on Technology - Subcommittee on Nanoscale Science, Engineering, and Technology. February 2014

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Human and Environmental Exposures along nano-enabled products life cycle

Industrial sectors

- ENM Providers
- Plastics
- Textiles
- Paints
- Inks, …

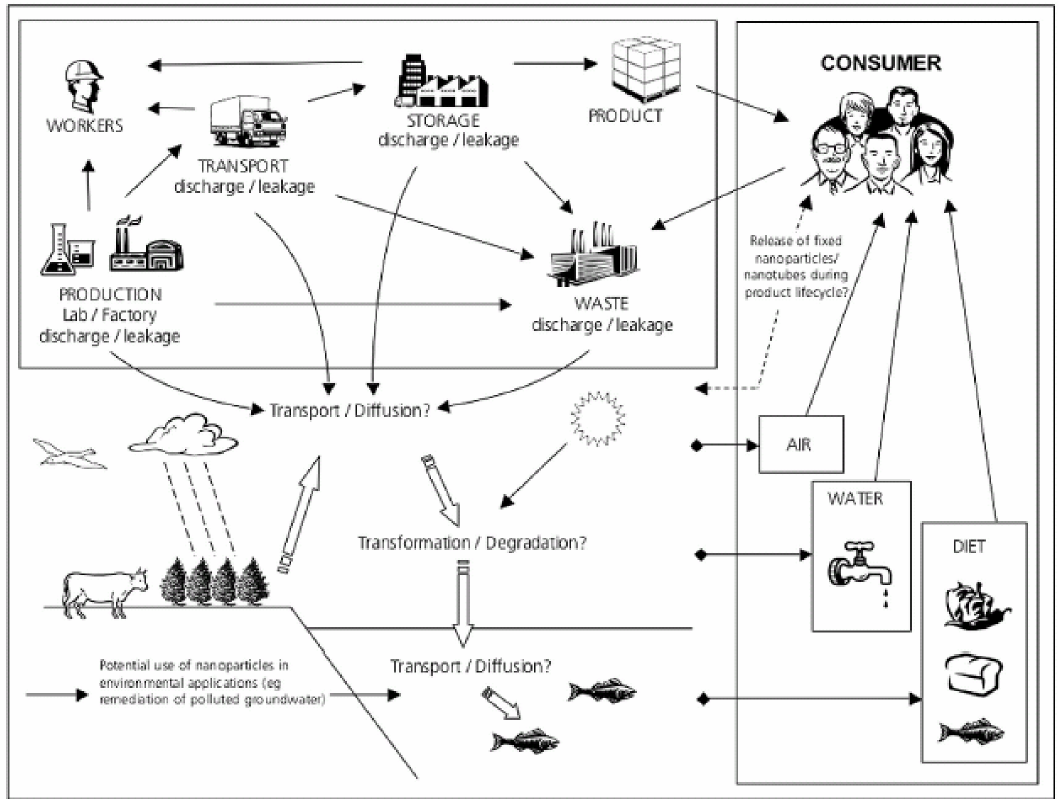
Life cycle stage

- Synthesis of ENM
- Manufacturing
- Use
- End of life

Accidental scenarios

Occupational, Consumer, Environmental Exposure

LCA of nanotechnology-based products



Environmental Transformations & Fate

Predictive models of exposure

Building blocks of exposure modelling

- ❑ The potential for release due to interaction of substance properties and activities or processes
- ❑ Emission to the (indoor) air compartment
- ❑ Transport of aerosols through the indoor air
- ❑ Immission and (personal) protection

Building/ developing exposure scenarios

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Occupational/ Consumer Exposure along nano-enabled products life cycle

Categories of exposure scenarios assessed

Synthesis of ENM, Manufacturing of products containing ENM, Preparation, mixing and product application on site, Assembly and machining, Demolition and disposal, Accidental

Exposure scenarios databases/ libraries

Processed data collection (ES Libraries)

Raw data collection (NECID)

Airborne exposure assessment

Aggregation/agglomeration patterns

Deposition factors

Risk mitigation strategies

To mitigate Exposure

To mitigate Hazard

Effectiveness of PPE/ ventilation/ filtration

Occupational/ Consumer Exposure along nano-enabled products life cycle

Standardized protocols, methods, devices and measurements strategies for ENM

- Testing, comparing and **validating current methods to measure** and characterize physicochemical properties of ENM, and demonstrate the feasibility and performance of systems both during normal operations and for management of accidental risks (NanoValid)

- **Development of protocols to measure dermal exposure**, methods to quantify nano-objects in fire effluents (Scaffold)

- Development of **validated methods and reference materials for the analysis of ENM in food and beverages** (Nanolyse, INSTANT) **and cosmetic** products (sunscreens and other creams, INSTANT)

- **Methods for the detection, identification, and measurement of ENM in complex matrices** in Consumer Products, in Food, in the Environment and in situ in Biota (Smartnano)

- **Development of novel, portable and easy-to-use devices** suitable for measurement, sampling and characterizing NP exposure at the workplace (NANODETECTOR, NANODEVICE, NANORISK)

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Occupational/ Consumer Exposure along nano-enabled products life cycle

PROJECTS	TYPE OF DATA							
	ES	Release	Dustiness	(transport)	Workplace	Personal	Consumer	Control
MARINA	X	X	(X)	X	X			
NanoValid		X	X		X			
NanoMicex	X				X	X		PPE/EPE
NanoSafePack	X	X	X		X	X		PPE/EPE
NanoRISK	X		X		X	X		PPE/EPE (library)
Scaffold					X			
SANOWORK		X	X		X			
NanoREG	X	X	X		X	X		
NanoIndex					X	X		
REACHnano	X				X			
SUN		X	X	?	X	(X)	X	PPE/EPE
GUIDEnano	X				X + Simulations		(X)	PPE/EPE
NanoDUST			X					

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Environmental Exposures along nano-enabled products life cycle

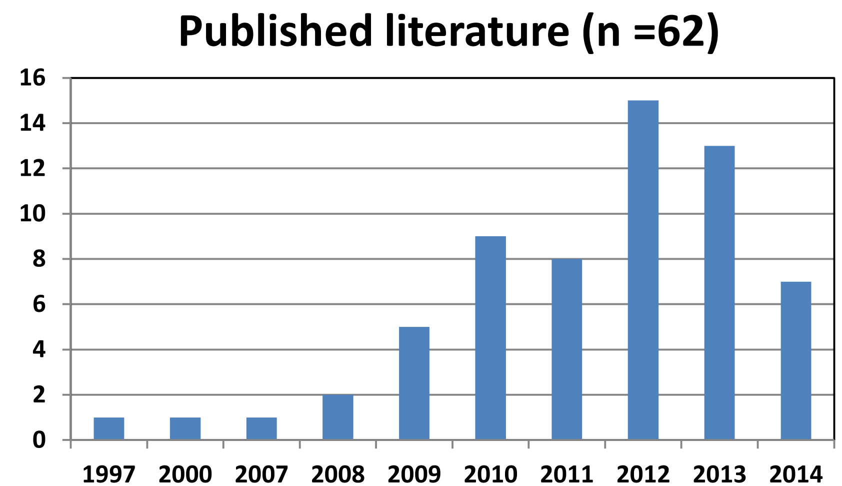
Release Assessment to Environmental Compartments

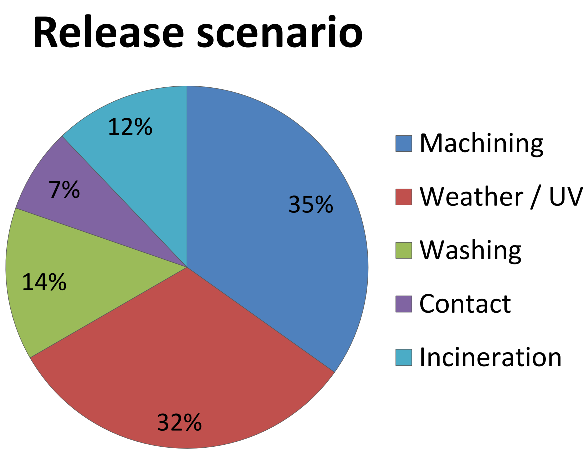
- Life cycle stages studied: Manufacturing, use, end of life, including recycling
- Experimental simulations for use phase
- Experimental simulations for end of life processes and recycling
- Collection and characterization of released materials
- Toxicological impact of released materials

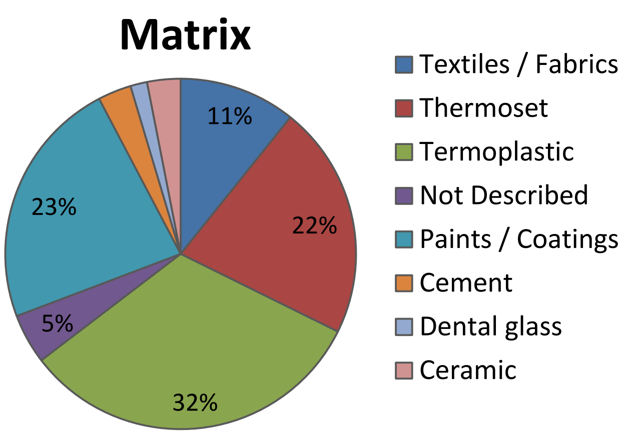
<u>Projects covering these issues</u>:

NEPHH, Nanopolytox, NanoHOUSE, NanoSustain, Nanosolutions, NanoMILE, NanoREG, GUIDEnano, SUN and ...

State of the Art: Release Studies







Particle and Fibre Toxicology 2014, **11:17 (review) complemented with own revision published articles (n = 60)*

Polymeric Nanocomposites: Outdoor Use (including Paints)

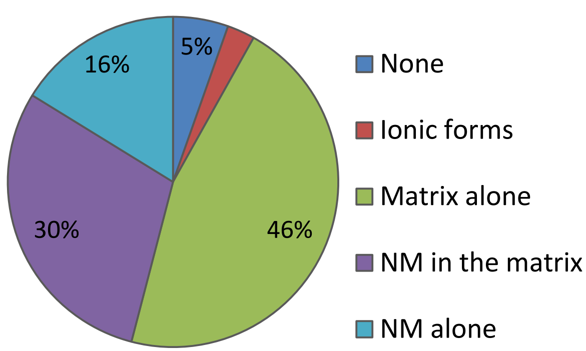
➢ More rigorous studies than any other release scenarios

WEATHERING

Most studies used common laboratory equipment, following **standardized protocols** (e.g. ISO Modified ISO 4892/06 for polymers) **simulating UV and /or rain weathering**, e.g. in climate chambers

<u>Released NMs Characterization</u>: ICP-MS, TEM/SEM, TGA, FTIR, DLS
Drawbacks: Collected runoff water should be pretreated, difficult to analytically quantify ions and ENM of the same element

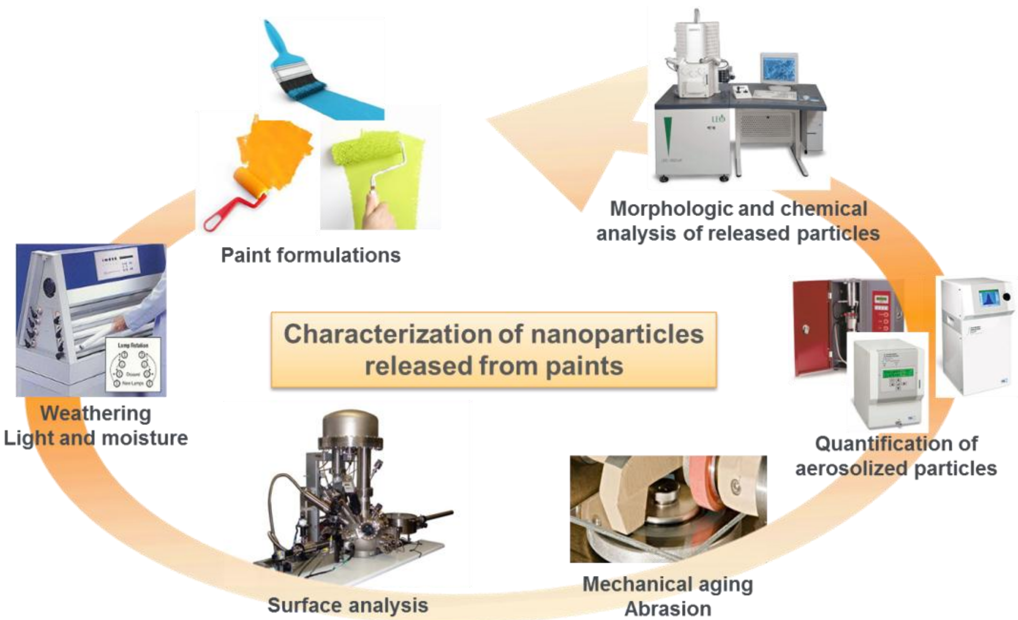
Released Materials

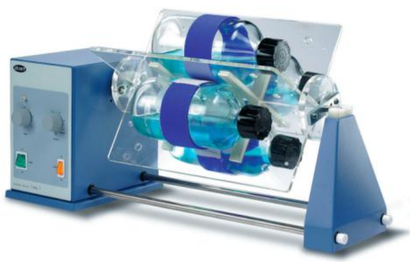


Run-off waters collection

Nanotechnology-based Paints: Outdoor use

WEATHERING AND ABRASION + LEACHING





- ❑ **Small amounts of ENM are released if they are effectively incorporated within the matrix.**
- ❑ **Nature of released ENM: Presence of aggregates of ENM embedded in the organic matrix, and very few dispersed single ENM**

Al-kattan *et al*. Environ. Sci. Process. Impacts **2013**, *15*, 2186
Zuin *et al*. J. Nanoparticle Res. **2013**, *16*, 2185

Polymeric Nanocomposites: Indoor Use

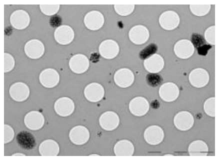
- **Covered by ≈50% of the studies, MWCNT the most investigated**
- **Two main methods applied to induce release: Abrasion, ageing (UV filtered, no rain)**

ABRASION

Non-standardized and typically hand-operated methods, including cutting, sanding…

Several standardized methods using Taber Abraser

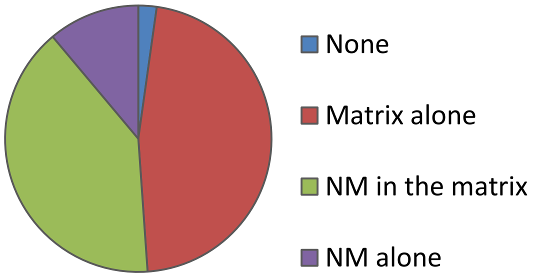
Abrasion resistance using the Martindale instrument (ISO 5470-2:2003) “**Textiles coated with plastic or rubber**”



Released ENMs characterization: Particle sizers /counters: CPC, APS, SMPS… combined with TEM/SEM, FTIR, TGA (of collected samples)

Drawbacks: no differentiation between NMs and matrix particles, also background. Therefore, qualitative characterization is commonly carried out by electron microscopy of NMs collected in filters or TEM grids.

Released Materials



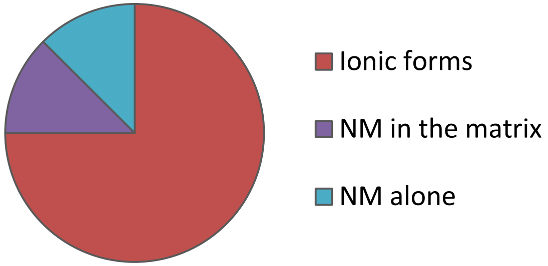
Nanotechnology-based textiles during their use

- Only for Ag and TiO_2 nanoparticles (antimicrobial, self-cleaning…)
- Studies do not generally describe textile nanocomposites

WASHING

Standarized protocols (ISO 105-C06:2010) for determining "**color fastness to domestic and commercial laundering**" has been adapted to assess release into the water compartment
<u>Characterization of released materials</u>: TEM-EDX, ICP-MS and Ion Selective Electrode to detect and quantify ions

Released Materials



Nanotechnology-based products: Proposed release studies

Antifouling paints containing ZnO NP

➡ Weathering in fresh / salt water

Lubricant oil with nanodiamonds

➡ Accelerated aging in car engine

Luminescent inks with CdTe QDs

➡ Printing process

Nanocellullose for food packaging

➡ Migration of nano-ingredient

TiO_2 NP Photocatalytic coating applied on roads

➡ Weathering in climatic chamber

➡ Abrasion produced by wheel traffic

And more…

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Final treatment and recycling of nano-enabled products

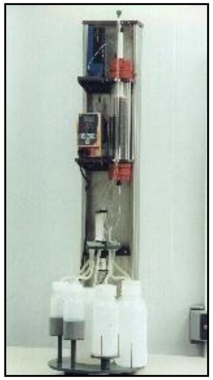
Few studies/projects have addressed these life-cycle stages. More information is needed about the final treatment of these products.

- Some projects have investigated recycling processes, focusing on both innovative technologies and possible release of ENM (e.g. nanocellulose in NANOSUSTAIN, polymer nanocomposites in NANOPOLYTOX).

- Regarding incineration and land-filling, little work has been done. Limited number of specific cases, e.g. TiO_2-based paint in NanoHOUSE and glass containing ZnO NPs in NANOSUSTAIN. From few studies it has shown that ENM in the incinerator (e.g. CeO_2) remain in the bottom ash (not for carbon-based materials).

- How these experiments performed in the laboratory reproduce real conditions is still unclear.

- Release is influenced by thermal and chemical stability of ENM. During recycling of construction materials, ENM might be formed when applying high shear forces.



Percolation test

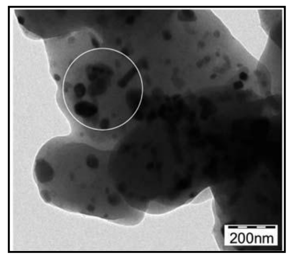
Zuin *et al*. Waste management. 2014, *34*, 1897
Bouillard *et al*. J. Nanoparticle Res. **2013**, *15*, 1519

Released ENM identification & quantification: ENM form determines both fate and hazard

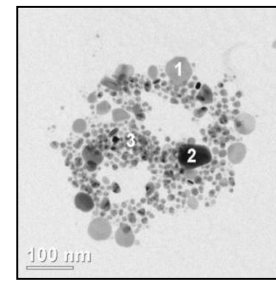
Released ENM

≠

Pristine ENM

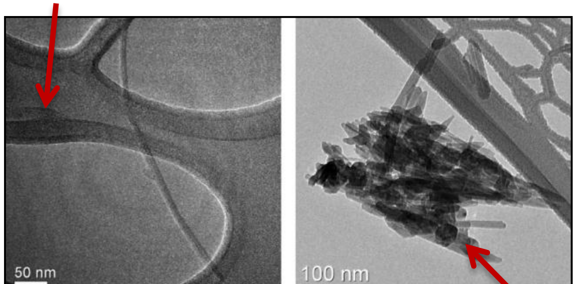


Wear from a **steel panel** with embedded ZnO NPs[1]



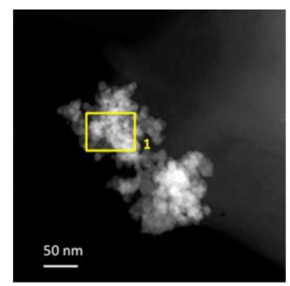
SiO_2 NPs in leaching liquids from **paints**[3]

Single



CNTs from an epoxy-based **nanocomposite**[4]

Aggregated within the polymer



Washing solution (**textiles**) containing Ag NPs[2]

1 Gottschalk *et al*. J Environ Monit .**2011**, *13*, 1145
2 Lorenz *et al*. Chemosphere **2012**, *89*, 817
3 Zuin *et al*. J Nanopart Res. **2014**, *16*, 2185
4 Schlagenhauf *et al*. Environ. Sci. Technol. **2012**, *46*, 7366

State of the Art: Methodology

- The different methods must simulate those processes leading to ENM release, *e.g.*:
  - ➡ Paints for facades ⟶ Exposed to UV (sun) and rain cycles
  - ➡ Textiles ⟶ Washing machine + sweat + abrasion

- Generally, standardized protocols (ASTM, ISO…) to test materials resistance are used.

- ENM release can be quantified directly (*e.g.*: measure of nanoparticles in air) or indirectly (ENM quantification in the product before and after the ageing process).

- To quantify ENM release directly, standardized protocols are modified to include release collection:
  - ➡ Run-off water collection (rain, washer machine, sweat solution…)
  - ➡ Particle emission measures (CPC, OPC, SMPS…)
  - ➡ Collection in air or water filters

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State of the Art: Issues

- Lack of data, **inability to compare results**. Replicates and negative control experiments should be examined. NM characterization is poorly investigated.

- Need for **method validation** and **harmonization**.

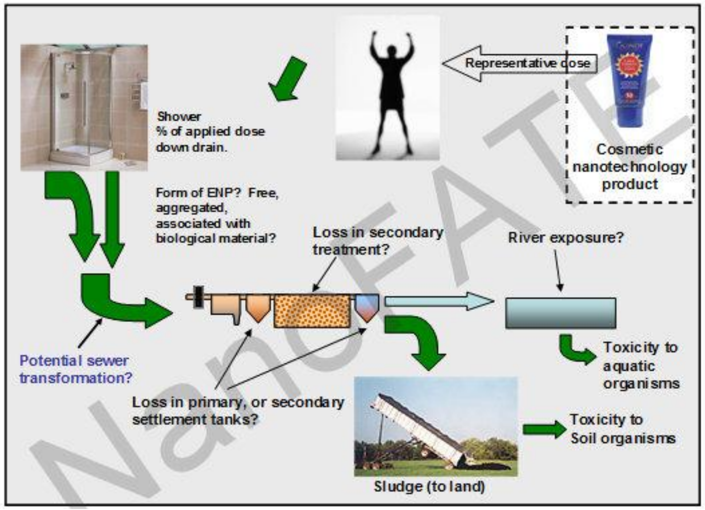
- **Different supply sources**: “worst case” nano-enabled products, other commercially available supplied by industry, and other lab-made. Therefore in most cases they **cannot be readily compared**.

- In general, **data might not necessarily be predictive of release**. Rather, it demonstrates which type of release particles one might expect**.**

- **Release** is frequent but **limited in volume**. Release of matrix particles with and without embedded ENM is common, free ENM is rare. While degradation occurs, ENM often remain tightly bound to the matrix (more likely to be released).

- Focus on scenarios where **multiple input energies are present**, with a **higher potential for release**.

Transformations and Fate of ENM along nano-enabled products life cycle



Taken from NanoFATE

NMs **Fate, transformation and behavior addressed across media** ranging from standard test media to environmental media:

- ✓ WWTP sludge and effluent,
- ✓ Natural waters and
- ✓ Soils

NanoFATE → CeO fuel additive ENPs via air into soils
ZnO ENPs and Ag ENP via WWTP into natural soils, river waters and six "standard EU waters"

ModNanoTox → Surface water, waste water and sludge

NanoRETOX → Simulated environmental (hard/soft freshwater, seawater)

NanoSustain → Surface water ????

Life Cycle Assessment (LCA) of nano-enabled products

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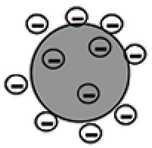
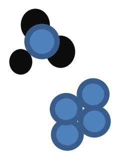
Environmental **fate models has been parameterized** with information on the priority ENM fate processes identified, namely:

Dissolution

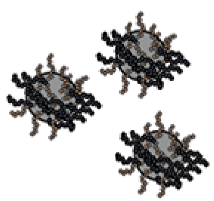


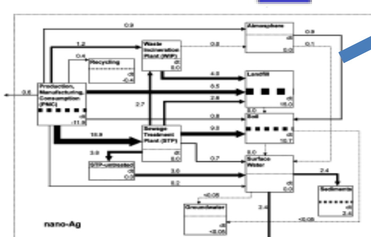
Agglomeration (homo- and hetero-agg.)



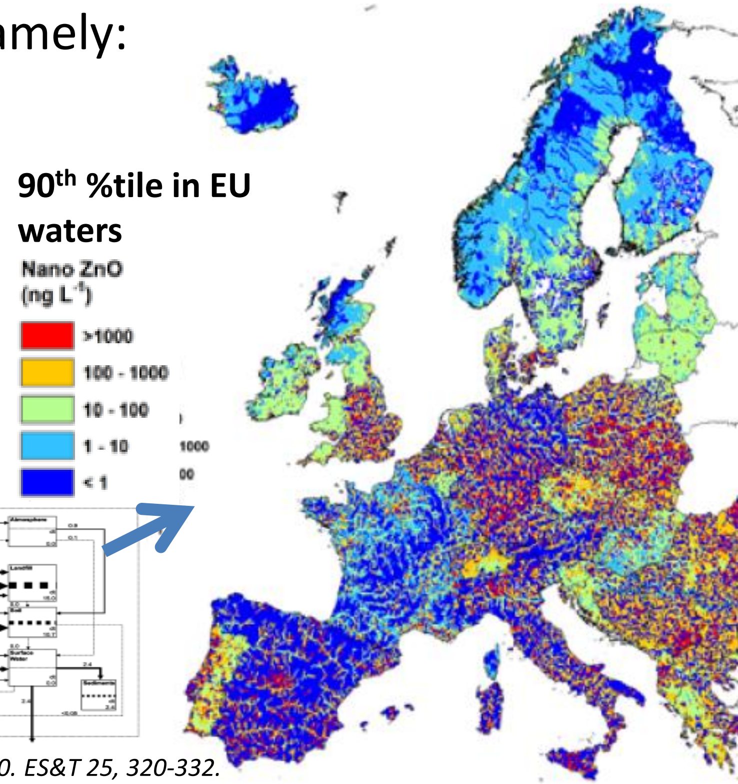
Sedimentation

Aging (transformations)





Gottschalk et al. 2010. ES&T 25, 320-332.



NanOFATE

Dumont et al Environmental Pollution (in press)

→ Nano specific mechanistic and classical fate and transport models **are technically relatively easy to couple** as they have compatible parameters.

→ **Heteroagglomeration** of the engineered NMs with natural particles (colloids) in the river water is the most important reaction (NanoFATE, ModNanoTox, Marina)

Transformations and Fate of ENM along nano-enabled products life cycle

✓ **Development and application of techniques and tools** used to characterise and analyse the behaviour of metallic NMs in natural aquatic media and integrate with environmental exposure modelling (e.g. NanoDefine, Marina, NanoADJUST).

	Inorganic NM	Organic NM
Aquatic systems	• TEM-SEM • DLS • **spICP-MS** • FFF-spICP-MS	• TEM - SEM • FTIR (CNT) • HPLC (C60)
Terrestrial systems	• Extraction, filtration • Backscatter SEM	• HPLC (C_{60})

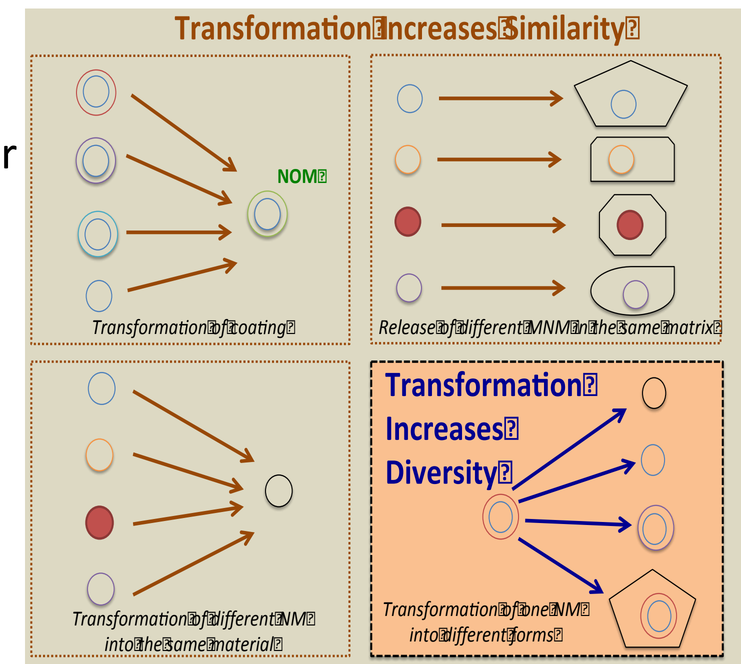
From Geert Cornelis Univ of Gothenburg (GUIDEnano, Marina)

Still heavy focus on size.

*Detecting **speciation** at early stages (e.g. SEM-Raman)*

Effective coating – future development

✓ **Continued development of novel modelling approaches** aiming to understand and accounting for NMs behavior in natural systems including possible transformation reactions (GUIDEnano, SUN, NanoMILE)



EU FP7 NanoMILE D3.1 “Report on environmental transformation reactions” Denise Mitrano & Bernd Nowack (EMPA), Sylvie Motellier and Simon Clavaguera (CEA) – Submitted to ES&T

Transformations and Fate of ENM along nano-enabled products life cycle

✓ **Use of Novel labelling methods** to provide new information on the release rates to air, surface fresh and marine water, waste water and soil, monitor and control their dispersion and stability in various test media and environmental matrices (NanoRISK, NanoMILE and NanoSAFEPACK).

✓ **Comprehensive knowledge hub and database** to improve existing models on transport and fate of ENPs in the environment (including bioaccumulation, persistence, bioavailability and life cycle impacts onto all forms of biota)

✓ Deliver more realistic fate, exposure and risk **prediction maps at the local, regional and European scale**

Limitations

Most projects on the topic have been focused on hazard identification that may occur at high concentrations, most of data currently available refer to ENM presentations and chemistries that will never occur in the real world environment.

Characterization technique available are not sensitive enough to work at environmental realistic concentrations e.g. find and characterize the hetero-agglomeration (ENM with other particles) compared to the homo-agglomeration (ENM-to-ENM).

Predicted environmental concentrations (PECs) hence the **models** cannot be validated until analytical methods in real environmental matrices are improved.

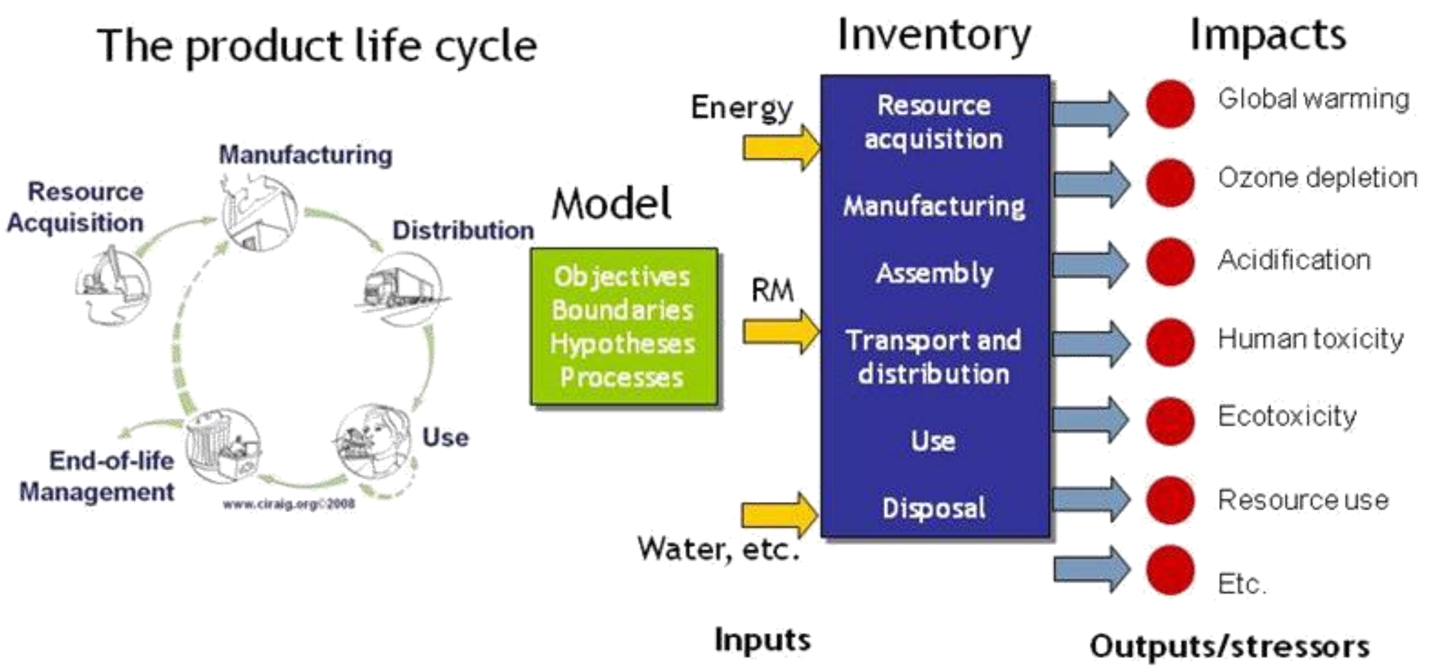
Future challenges

Characterization of fate and transformations in more environmental realistic exposure scenarios (low concentrations in complex matrices).

Life Cycle Assessment (LCA) of nano-enabled products

- Life Cycle Assessment (**LCA**) is **a comprehensive analysis tool** which is used **to evaluate how a product or material**, from the start of production to its end-of life, **potentially affects ecosystems and human health**

- Definition of LCA (ISO 14040 14044): "The collection and evaluation of the inputs, outputs and the **potential environmental impacts of a product system throughout its life cycle**"



MAIN GAPS OF LCA ON NANOTECHNOLOGY

- Synthesis and production processes:
  - Wide **variety in the production processes of ENM** and evolving fast
  - The **information** is also often **confidential and proprietary**
  - Different synthesis methods, different properties: **CASE BY CASE**
- **Limited knowledge on release of ENM** (especially during use phase and end-of-life phase)
- How to evaluate **exposure from release** data?
  - Limited knowledge on the transformations and concentrations of ENM in the environment.
  - **Lack of an environmental fate modelling of nanomaterials**: Need for adaptation of existing models (developed mainly for organic compounds)
- **Uncertainty in toxicity**: surface properties, functionalization, interaction with environmental media…

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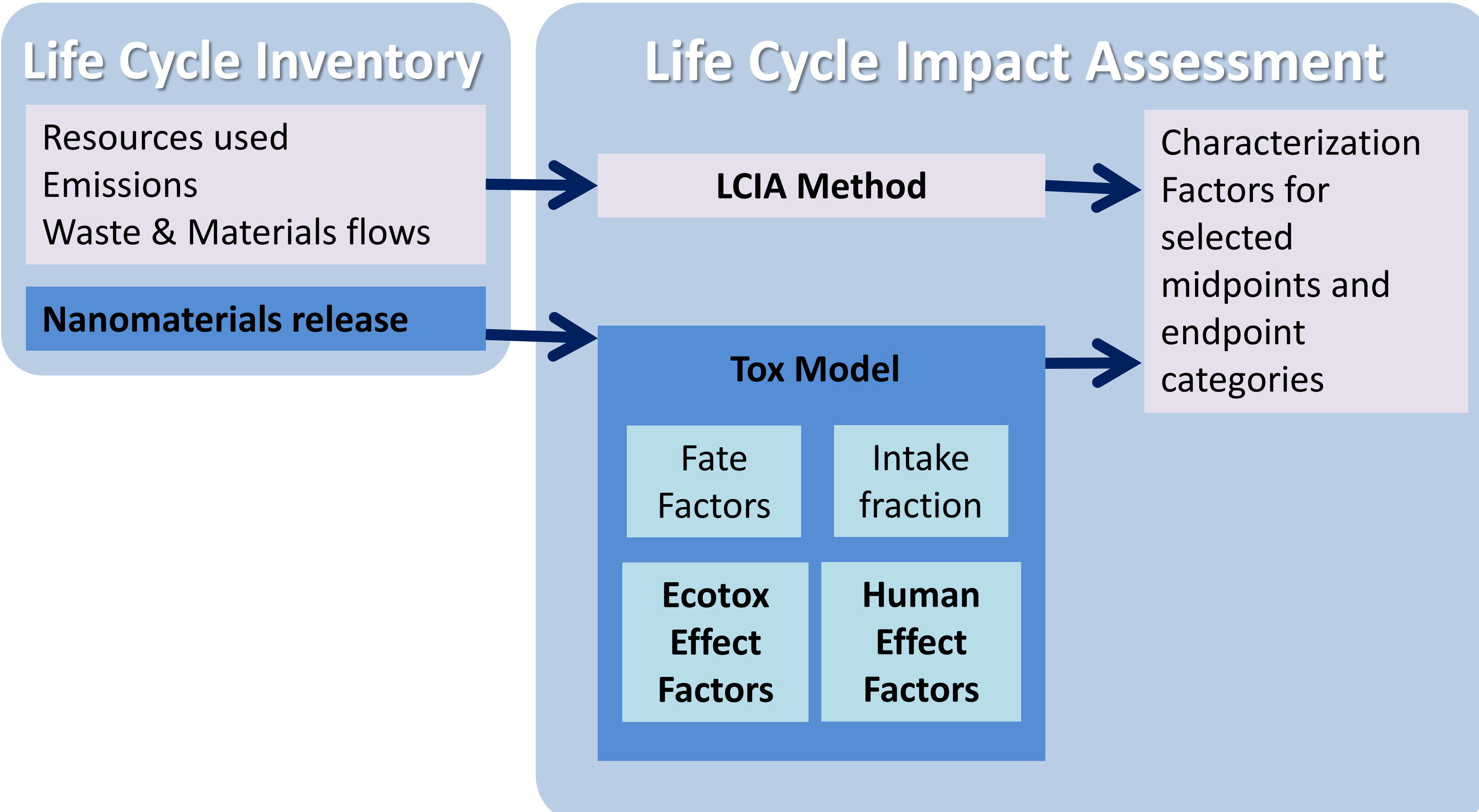
Life Cycle Assessment (LCA) of nano-enabled products



LCIA: ReCiPe Methodology

Midpoint impact category name	Abbr.	Endpoint impact category* HH	ED	RA
climate change	CC	+	+	
ozone depletion	OD	+	–	
terrestrial acidification	TA		+	
freshwater eurotrophication	FE		+	
marine eurotrophication	ME		–	
NM ⇨ human toxicity	HT	+		
Photochemical oxidant formation	POF	+	–	
particulate matter formation	PMF	+		
terrestrial ecotoxicity	TET		+	
NM ⇨ freshwater ecotoxicity	FET		+	
marine ecotoxicity	MET		+	
iosnising radiation	IR	+		
agricultural land occupation	ALO		+	–
urban land occupation	ULO		+	–
natural land transformation	NLT		+	–
water depletion	WD			–
mineral resource depletion	MRD			+
fosil fuel depletion	FD			+

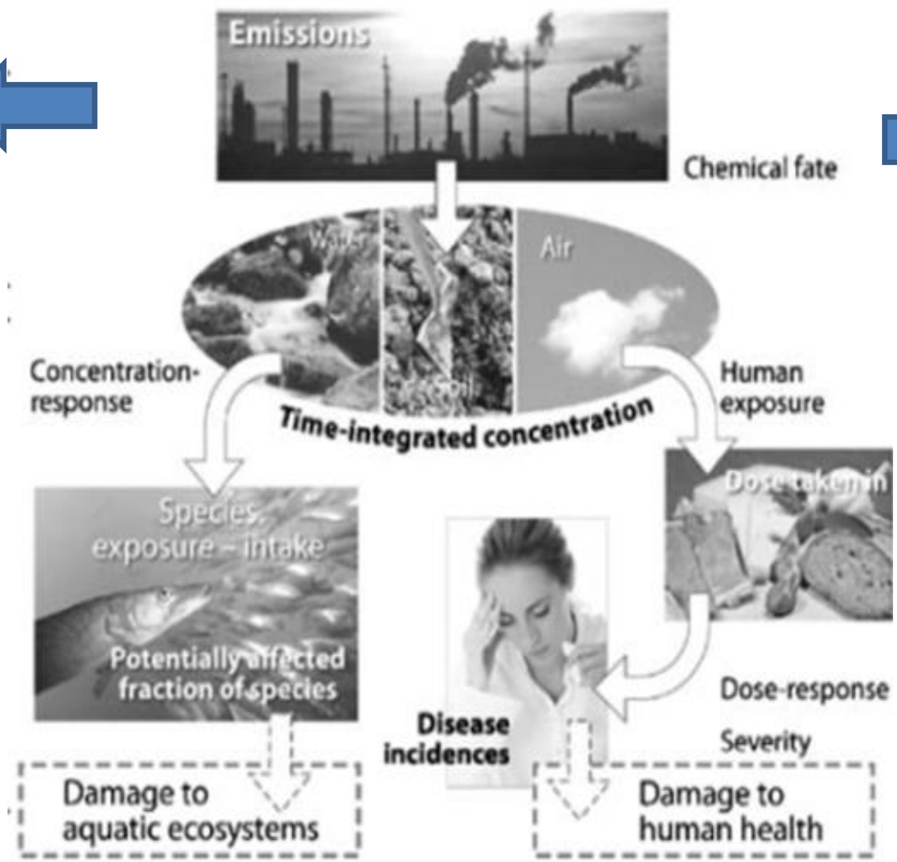
* **HH**: Human Health Damage; **ED**: Ecosystems damage; **RA**: Resource Availability Damage
+: Quantitative connection has been established in ReCiPe 2008 for this link; **–**: No quantitative connection has been established for this link in ReCiPe 2008

Life Cycle Impact Assessment (LCIA) of nano-enabled products

From Rosenbaum *et al*. Int. J. LCA, **2008,** 13, 532-546

Release

Ecotoxicity



Environmental distribution

Intake Fraction

Toxicity

Projects covering these issues:

NEPHH, Nanopolytox, Nanohouse, NanoSustain, NanoFATE, PROSUITE, Nanomicex, REACHnano, Nanosolutions, LICARA, ...

Thank You

Acknowledgements to:

C. Svendsen, D. Brouwer, J. Rose and A. Vilchez, M. Diez

For their contributions