Project title:

Development of a real-time information and monitoring system to support the risk assessment of engineered nanomaterials (ENMs) under REACH

Project Acronym: **NanoMONITOR**

Grant Agreement: **LIFE14 ENV/ES/000662**

Deliverable

DB1b. Report on nano-specific release factors and environmental release categories

Dissemination Level

Public / Restricted / Confidential

Document Information					
Associated action	B1	Development of a web based library of exposure scenarios and measured data on the exposure and release of ENMs			
Action Leader		ITENE			
Responsible Author		Name		E-mail	
		Beneficiary		Phone	

Rev. Nº	Date	Author	Beneficiary name
01			
02			

PROJECT CONSORTIUM INFORMATION

Beneficiary		Contact
ITENE (Packaging, Transport & Logistics Research Centre)		Carlos Fito cfito@itene.com Maida Domat maida.domat@itene.com
AXON Enviro-Group Ltd		Athena Progiou ap@axonenviro.gr
The Mediterranean Center for Environmental Studies (CEAM)		Jose Luis Palau joseluis@ceam.es
The REACH Centre		Judith Friesl / j.friesl@thereachcentre.com Stella Stoycheva / s.stoycheva@thereachcentre.com

List of acronyms

AC:	Article Category
CES:	Contributing Exposure Scenarios
ECHA:	European Chemicals Agency
EHS:	Environmental, Health and Safety
ENM:	Engineering Nanomaterial
ERC:	Environmental Release Category
ERC:	Environmental Release Categories
ES:	Exposure Scenario
GES:	Generic Exposure Scenarios
IU:	Identified Uses
LEV:	Local Exhaust Ventilation
NM:	Nanomaterial
NOAA:	Nano-Objects and their Agglomerates and Aggregates
OC:	Operative Conditions
PC:	Chemical Product Category
PEC:	Predicted Environmental Concentration
PNEC:	Predicted No Effect Concentration
PPE:	Personal Protective Equipment
PROC:	Process Category
RA:	Risk Assessment
REACH:	Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals
RMM:	Risk management measures
RMMs:	Risk Management Measures
SD:	Source Domain
SU:	Sector of Use category

Summary

Present deliverable aims to provide a list of at least 10 refined release factors and 10 well described environmental release categories specifically described for the life cycle of ENMs, factors relevant for the characterization of the risk characterisation ratios on a regulatory basis.

The action has been carried out as a continuation of the actions A3 and B1.1 and B1.2, where a throughout study of all the available data on exposure to ENMs was undertaken and classified by scenario and risk level.

More than 13 nanospecific release categories were outlined along with the classification of the probability of release of ENM in each of them, taking into account the RMMs present for the specific case and considering always the worst case scenario. All the life cycle stages, from production to disposal were analysed.

The review brought as well a classification of the liberation of NM into the environmental compartments, air, water and soil. It was concluded that the majority of ENMs are disposed in landfills, with a significant fraction going to soils and the atmosphere. These data will be reviewed and updated as new information becomes available.

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1. Scope and goal of the deliverable

Action B1 was aimed to develop an on-line inventory of exposure scenarios and exposure monitoring data to ease and promote the use of the data from the project under the risk assessment process established by REACH. To this end, in previous deliverable **DB1a** "**Report on the determinants of exposure and exposure scenarios over NMs Life Cycle"** it was developed an on-line library of data on the levels of ENMs in indoor industrial environments and relevant environmental compartments, with updated/refined nanospecific exposure scenarios, to provide a complete description of the specific determinants of exposure across the life cycle stages of the ENMs for the definition of nanospecific ERCs.

Present deliverable **DB1b "Report on nano-specific release factors and environmental release categories"** is proposed as a continuation of the previous work to create a compendium of nanospecific environmental release categories (**nanoERC**) in the context of REACH to support the derivation of the predicted environmental concentration (PEC) of ENMs in relevant environmental compartments.

The release categories are calculated taking into account Risk Management Measures and Operational Conditions (RMM/OC) and can be properly refined linking the amount of material used with the actual concentration of the same material in a determined environmental compartment.

The data on the concentration of ENMs, either measured or retrieved from literature sources or questionnaires, are organized and structured to link the concentration measured with a defined combination of risk management measures, operational conditions and amount of ENMs used at industrial scale. Due to the lack of previous information, default worst case release factors resulting from the analysis conducted will be proposed when using ENMs.

A list of **at least 10 refined release factors** and **10 well described nanoERC** will be accessible via the project web site to support the direct consultation by stakeholders and risk assessors, and will be continuously updated as new information becomes available.

2. Introduction

2.1. Release factors and environmental release categories on a regulatory context

Environmental release category (ERC) are a key REACH use descriptor to define the release factors of a chemical substance in a specific use exposure scenario. Chapter R16 of the REACH Guidance on Information Requirements & Chemical Safety Assessment (IR&CSA guidance) introduces the ERCs as generic, broadly applicable emission scenarios. They define the fractions of a substance emitted during a process/application, and provide default assumptions for the local environmental properties.

The ERCs describe the broad conditions of use from an environmental perspective, based on those characteristics that give a first indication of the potential release of the substance to the environment. They are also used in modelling tools such as ECETOC-TRA and EUSES to derive environmental exposure estimates.

A list of the main ERCs along with a brief description of each can be seen in **annex A4** of DB1a. Note that the ERC 1 - 7 and 12 are related to industrial activities, while the ERC 8 - 11 are related to consumer or professional uses. Some examples of typical ERCs include **ERC1:** manufacture of substance, **ERC2:** formulation of preparations, **ERC6a**: Industrial use resulting in the manufacture of another substance (use of intermediates), **ERC8a**: Wide dispersive indoor use of processing aids in open systems or **ERC11b**: Wide dispersive indoor use of long-life articles and materials with high or intended release (including abrasive processing).

Environmental release categories (ERCs) specify default values of the:

- number of emission days;
- fractions of the amount released to water, air and soil;
- dilution factor;
- fraction of the tonnage being used in a region and a point source.

An industry evaluation concluded that ERCs wee useful for standardization and crucial for deriving environmental exposure estimates, however leaded to unrealistically conservative emission estimates. Since default emission values associated with ERCs are often very conservative and unrealistic, **Specific Environmental Release Categories (spERCs)** have been developed. SPERCs correspond to sets of information describing specific good practice conditions of use and the corresponding release estimates (to water, air, soil and waste). They are developed by sector groups of chemical industry and their downstream customer industries to refine the emission estimates obtained by using the ERCs' release factors, taking into account specific operational conditions and RMMs applied for the use in the sector.

Generally, **the default ERCs do not take into account nano-objects**, and there is an urgent need to set up for exposure scenarios in the case of spERCs and the necessity of modelling and measurement techniques for ENMs are demanded for exposure assessment an estimation of release factors of nanoproducts[1]. However, the amount of product applications and potential ENMs species and physico-chemical treatments is widely broad and difficults a case-by-case approach. The use of exposure scenarios tends to simplify this complexity challenge[2].

The ERCs group the processes that can give rise to a certain emission to the air, water, and soil. The idea of B1b is to define the factors that influence the release and propose emission rates in % for operations and production processes of nanomaterials and nanoproducts. Processes and activities involving NMs have been identified in A3 and B1a, so they support in bibliography and can define a set of emission coefficients.

In the section R. 16, Estimation of Environmental Exposure, of the Guidance on Information Requirements and Chemical Safety Assessment of the EU[3] are given methodological tools and parameter values for quantifying the emissions into the environment, providing ERCs to surface water, wastewater, soil and air for a first generic estimation of the environmental emissions of chemicals. Estimated values can be seen in Table *1*.

Table 1: ERCs values estimated by the ECHA for all kind of chemicals.

DESCRIPTOR	ENVIRONMENTAL RELEASE CATEGORIES (ERC)	DEFAULT WORST-CASE RELEASE FACTORS		
		Air	Water (before STP)	Soil
ERC1	Manufacture of substances	5%	6%	0.01%
ERC2	Formulation of preparations	2.5%	2%	0.01%
ERC3	Formulation in materials	30%	0.2%	0.1%
ERC4	Industrial use of processing aids in processes and products, not becoming part of articles	100%	100%	5%
ERC5	Industrial use resulting in inclusion into or onto a matrix	50%	50%	1%
ERC6a	Industrial use resulting in manufacture of another substance (use of intermediates)	5%	2%	0.1%
ERC6b	Industrial use of reactive processing aids	0.1%	5%	0.025%
ERC6c	Industrial use of monomers for manufacture of thermo-plastics	5%	5%	0%
ERC6d	Industrial use of process regulators for polymerisation processes in production of resins, rubbers, polymers	35%	0.005%	0.025%
ERC7	Industrial use of sub-stances in closed systems	5%	5%	5%
ERC8a	Wide dispersive indoor use of processing aids in open systems	100%	100%	n.a.
ERC8b	Wide dispersive indoor use of reactive substances in open systems	0.1%	2%	n.a.
ERC8c	Wide dispersive indoor use resulting in inclusion into or onto a matrix	15%	30%	n.a.

[1] Environmental Release of and Exposure to Iron Oxide and Silver Nanoparticles: Prospective Estimations Based on Product Application Scenarios, Henning Wigger, PhD thesis, Springer (ISBN 978-3-658-16791-2) 2017.

[2] Praetorius et al., Development of environmental fate models for engineered nanoparticles--a case study of TiO_2 nanoparticles in the Rhine River, Environ Sci. Technol. 2012, 46(12):6705-13

[3] ECHA, Guidance on information requirements and chemical safety assessment, chapter R.16: Environmental Exposure Estimation, European Chemicals Agency, 2010.

ERC8d	Wide dispersive outdoor use of processing aids in open systems	100%	100%	20%
ERC8e	Wide dispersive outdoor use of reactive substances in open systems	0.1%	2%	1%
ERC8f	Wide dispersive outdoor use resulting in inclusion into or onto a matrix	15%	5%	0.5%
ERC9a	Wide dispersive indoor use of substances in closed systems	5%	5%	n.a.
ERC9b	Wide dispersive outdoor use of substances in closed systems	5%	5%	5%
ERC10a	Wide dispersive outdoor use of long-life articles and materials with low release	0.05%	3.2%	3.2%
ERC10b	Wide dispersive outdoor use of long-life articles and materials with high or in-tended release (including abrasive processing)	100%	100%	100%
ERC11a	Wide dispersive indoor use of long-life articles and materials with low release	0.05%	0.05%	n.a.
ERC11b	Wide dispersive indoor use of long-life articles and materials with high or intended release (including abrasive processing)	100%	100%	n.a.
ERC12a	Industrial processing of articles with abrasive techniques (low release)	2.5%	2.5%	2.5%
ERC12b	Industrial processing of articles with abrasive techniques (high release)	20%	20%	20%
ERC12c	Use of articles at industrial sites with low release	0.05%	0.05%	n.a.

The specific information that needs to be considered for the quantification of release estimation to the environment during the life cycle stages of a chemical is mainly:

- Tonnage of substance used or produced
- Life cycle stage
- Type of use in the life cycle stage
- Distribution of production volume in the market
- Emission pattern – distribution in time and special scale
- Emission pathways (air, soil, water)
- Multiple emissions
- Emission factors
- Receiving environmental compartments
- Risks management measures (RMM) to reduce emissions

The use of the ERCs is of great importance for predicting relevant emissions to the environment and link them to occupational activities, but also for grouping substance uses from an environmental perspective. Input parameters from substances with analogous use and exposure patterns or analogous properties, together with product tonnage and RMMs, can be used to calculate releases during the life-cycle of an unknown substance.

2.2. Strategies to support the definition of release factors and environmental release categories

3. Current approaches on the evaluation of the environmental release of ENMs

3.1. Considerations for emission assessment of ENMs

The European Chemical Agency (ECHA)[4] provides guidance on how to carry out environmental exposure assessment in the context of REACH3.

The procedure relies upon three fundamental preliminary actions:

1. collection of information on relevant substance properties: physical-chemical, fate, as well as (eco)toxicological properties
2. hazard assessment, based on representative measured data and/or model calculations: in this step, data are used to derive **a predicted no effect concentrations (PNECs)**
3. mapping of uses: identification of all the possible uses and conditions of use of the substance

Step 3 implies that the whole exposure assessment is built upon the definition of the life-cycle stages of the substance and the characterization of the release/exposure in each one of them. At this point, the exposure assessment can start with:

1. determination of operational conditions and risk management measures (RMMs), including, for example, the amount of the substance, availability of filters, scrubbers, municipal sewage treatment plants etc.
2. release estimation consisting in the determination of the release rates to different environmental compartments for each use.

The meaning of step 2 means that the estimation of the exposure values has to pass through the assessment of the emission- or release- of the substance to the environment. After that, the environmental fate is determined by modelling what happens to the material in terms of transport, partitioning, degradation and transformation.

The released quantity of substance is then divided by the reference volume of the environmental media under consideration, to evaluate the **predicted environmental concentrations (PECs)** of the substance, which are the outcome of the procedure. At this point, the risk characterization phase can take place by comparing them with the outcome of the hazard assessment (the PNECs values).

When suitable predicted no-effect concentrations (PNECs) are available, a quantitative risk characterization can take place for each use. The PNEC of a substance indicates the value of concentration below which exposure to it is not expected to cause adverse effect to species in the environment. The idea is to compare the exposure concentration in each compartment (air, water and soil) with the relevant PNEC. **Environmental Risk Characterization Ratios (RCRs)** can be derived by means of the equation

$$RCR = \frac{PEC}{PNEC}.$$

[4] ECHA Guidance on information requirements and Chemical Safety Assessment, Chapter R.16: Environmental exposure assessment, Version 3.0, February 2016.

An RCR greater than one means that the risk posed by the substance is not under control and that risk management measures are needed. This procedure can be reiterated. If it turns out that the applied risk management measures and operational conditions are not adequate to control risks, the exposure assessment may need to be refined. This refinement is possible at every step, by means of more realistic data, using alternative modelling approaches or including additional risk management measures.

The part about **emission assessment** is fundamental to correctly evaluate exposure levels. It poses serious difficulties even for ordinary and well-known chemicals and **constitutes a real challenge in the case of engineered nanomaterials**. The first issue with ENMs is that, since they are quite new to the market, there is no monitoring of production rates and societal stocks, which makes really difficult the estimation of their release from society to the environment[5,6]. Also the information about the exact content of nanomaterial in a given product is often scarce and very few sources of data regarding the production of nanoparticles is available[7]. The few existing basic sources (see the Report from the Royal Society[8] or from the United Nations Environment Program[9], for instance, or the more recent one from the Australian National Industrial Chemicals Notification and Assessment Scheme[10]) do not always provide information about the methods applied and the sources used to get the data. All this results in large uncertainties on the values of the emissions and produced quantities. Probabilistic methods applied to current fate models for ENMs try to overcome this difficulties accounting for these uncertainties, but it is clear that more accurate data are needed for a precise environmental exposure estimation.

3.2. Considerations for fate modelling of nanoparticles

Turning existing models currently used to describe and predict fate behaviour of conventional chemical substances into something applicable to nanomaterials is one of the major challenges in environmental risk assessment. Models based on probabilistic mass flow analysis have been suggested as the most suitable to this purpose. However, these models require input data which are not currently available, like, as mentioned in the previous section, the amounts of ENMs produced every year. Furthermore, the strong limitations in the techniques needed to measure the concentration of nanoparticles in the different environmental compounds makes really hard the calibration and validation of theoretical models.

The scientific community basically agrees on the fact that, in contrast to occupational and consumer exposure, the **evaluation of environmental release of ENM has to be done from a "life-cycle perspective"**, distinguishing between the different phases of the life-cycle. This means that production, incorporation processes into products and release during use, as well as discharge via sewage treatment plants, waste incineration plants, landfill or recycling and disposal, must be taken into account. Moreover, it must be kept in mind that the physico-

[5] R. Arvidsson *et al*., Impacts of a Silver-Coated Future: Particle Flow Analysis of Silver Nanoparticles, *Journal of Industrial Ecology*, 15(6): 844-854 (2011)
[6] R. Arvidsson *et al*., Particle Flow Analysis – Exploring potential use phase emission of TiO_2 nanoparticles from sunscreen, paint and cement*, Journal of Industrial Ecology*, 16(3): 343-351 (2012)
[7] KEMI Report No 9/13, A report from the Swedish Chemical Society: Exposure Assessment of nanoparticles in aquatic environments – considerations, review and recommendations
[8] *Royal Society,* Nanoscience and Nanotechnologies: opportunities and uncertainties, London (2004)
[9] UNEP, Geo Year Book – An overview of our changing environment, Nairobi, Kenya (2007)
[10] NICNAS, Summary of 2008 call for information on the use of nanomaterials, Sidney (2010)

chemical properties and the interactions with the environmental media of the ENM may change during the life-cycle, due to aging and degradation[11].

During the production phase of the ENM, direct release can take place, for example through an open window when handling powders, from spills and transport accidents, into river through untreated or treated wastewater. The direct release rates can range from the worst case scenario's ones suggested by ECHA[12] (5% to air, 6% to surface water, 0.01%) to negligible values, depending on the production and maintenance procedures employed[13] [14].

Concerning the manufacturing stage, the situation is quite clear when talking about worker exposure, and, as stressed by Gottshalk and Nowack, there is no doubt that at a certain point the material released will reach the environment. Yet, it is impossible to establish to what extent it will happen as long as no information about the ENM flow into at least one environmental compartment is available. In Refs. 13 and 14, values of the release rates for formulation in mixtures equal to 2.5% to air, 2% to water and 0.01% to soils are assumed as default values. In the case of formulation in material, the equivalent values are 30%, 0.2% and 0.1 %.

The main source of release of ENM to the environment occurs, without any doubt, during use, recycling and disposal of products containing them. The release can be intentional, whose magnitude is known, or unintentional, due to product's alteration, degradation and recycling. The extent of phenomenon strongly depends on the physical state of the matrix the ENMs are embedded to: in the case of a liquid matrix (like sprays, sunscreens, cosmetics), the release is quick and almost complete, while it will occur more gradually in the case of solids (paints and textiles)[15]. Great part of the unintentional release will be into wastewater or solid waste, which makes of wastewater treatment plants and waste incineration plants important sources of ENMs release.

Besides life-cycle considerations, in order to fully understand the behaviour and fate of engineered NPs in the environment, their transportation, degradation, and persistence in air, soil, and water systems need to be studied. The conditions of the environmental system under consideration (*e.g.* pH, ionic composition, ionic strength, presence of natural colloids or nanoparticles and other contaminants[16]) as well as intrinsic physicochemical properties of engineered NPs such as surface area, size, and chemical composition, determine their transport in the environment and their bioavailability[17]:

[11] F. Gottchalk and B. Nowack, The release of engineered nanomaterials to the environment, J. Environ. Monit. 13, 1145 (2011)

[12] ECHA Guidance on information requirements and Chemical Safety Assessment, Chapter R.16: Environmental exposure assessment, Version 3.0, February 2016.

[13] F. Gottschalk *et al.*, Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions,Environ. Sci. Technol. 43, 9216-9222 (2009)

[14] F. Gottschalk *et al*., Engineered Nanomaterials in Water and Soils: A Risk Quantification Based on Probabilistic Exposure and Effect Modeling, Environ. Toxicol. Chem 29, 1036-1048 (2010)

[15] A. Koheler *et al.*, Green Processes for Nanotechnology: From Inorganic to Bioinspired Nanomaterials, J. Clean. Prod., 16, 927-937 (2008)

[16] J. R. Lead and K. J. Wilkinson, Aquatic colloids and nanoparticles: current knowledge and future trends. Environ. Chem., 3, 159–171 (2006)

[17] N. Senesi and B. Xing, Engineered Nanoparticles and the Environment -Biophysicochemical Processes and Toxicity, Wiley-IUPAC Series in Biophysico-Chemical Processes in Environmental Systems (2016)

Fate in water:

aggregation, dispersion, dissolution, sedimentation, photochemical reactions due to sunlight, transformation reactions, degradation by living organisms, and interactions with natural colloids and other elements are some of the processes NPs can undergo in water. **Ionic strength** and **pH** are key factors for aggregation, while the presence of aquatic system components, such as **organic matter**, plays a fundamental role in stability and reactivity of ENPs: organic macromolecules can absorb ENPs, coating their surface and inhibiting agglomeration[18], making them more persistent. **Concentration** affects aggregation, dissolution and persistence, while oxidation and dissolution are both increased by **pH**[19] [20]. It has also been observed that the oxidation and dissolution are increased as the **NP size** decreases[21] [22]. Oxidation may occur not only for metal NPs. Though for chemical oxidation of CNTs, strong oxidative forces (normally not occurring spontaneously in the environment[23]) are needed, photo-oxidation reactions are possible. Moreover, some oxidants such as ozone (commonly used in wastewater treatment) may potentially affect the amount of CNTs released.

Fate in soil:

Bibliography concerning ENPs' fate in soil system is very scarce, mainly due to the technical limitations for investigating their interaction with different components[17]. Studies have shown that interaction with natural colloids, humic substances (HS, partially stable degradation products from plants and algae) and clay particles[24] can occurr. At low **ionic strength** and high **concentration of organic matter**, interactions of NPs with soils are less likely, increasing mobility. The **presence of HS** can improve the stability of NPs and reduce aggregation and sedimentation. The interactions of NPs with solids are determined by environmental conditions and physico-chemical properties. In porous media, the mobility is governed by Brownian diffusion[25] but in the case of aggregates and agglomerates, gravity becomes relevant, making these larger particles interact more with the soil surface. Soil and ENPs' **surface charge** controls electrostatic forces. When the soil system has the same charge of the NP, repulsion and thus higher mobility is observed[26]. These repulsive forces diminish at higher **ionic strength** conditions, promoting aggregation. Factors such as **pore size distribution** and **particle size** can influence p**article straining in porous media** (particles

[18] R. D. Handy *et al.*, The ecotoxicology and chemistry of manufactured nanoparticles, Ecotoxicology 17, 287-314 (2008)

[19] J. Fabrega *et al.*, Silver nanoparticles: behavior and effects in the aquatic environment, Environ. Int. 37, 517–531 (2011)

[20] C. Levard *et al.*, Environmental transformations of silver nanoparticles: impact on stability and toxicity. Environ. Sci. Technol. 46, 6900–6914 (2012)

[21] T. Phenrat *et al.*, Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions. Environ. Sci. Technol. 41, 284–290 (2007)

[22] W. X. hang, Nanoscale iron particles for environmental remediation: an overview, J. Nanopart. Res., 5, 323-332 (2003).

[23] E. J. Petersen *et al.*, Potential release pathways, environmental fate, and ecological risks of carbon nanotubes, Environ. Sci. Technol. 45, 9837–9856 (2011)

[24] T. Ben-Moshe *et al.*, Transport of metal oxide nanoparticles in saturated porous media, Chemosphere 81, 387–393 (2010)

[25] K. A. D. Guzman *et al.*, Influence of surface potential on aggregation and transport of titania nanoparticles, *Environ. Sci. Technol.*, **40**, 7688–7693 (2006)

[26] T. K. Darlington *et al.*, Nanoparticle characteristics affecting environmental fate and transport through soil, Environ. Toxicol. Chem., 28, 1191–1199 (2009)

trapped in soil pores)[27]. **Flow rate** must be also taken into account in transport studies, since it can affect deposition and agglomeration[28].

3.3. Review of current approaches

Despite the fact that REACH has not yet addressed any specific environmental release parameters for nanosized particles, the Scientific Committee on Emerging and Newly-Identified Health Risks concluded that no completely new methodology is needed and that the exposure research can be built on available knowledge about chemicals. However, available release factors are very conservative, and to what extent are they adequate for ENMs is still under discussion.

For each environmental compartment potentially exposed, the exposure concentrations are derived either by measurement (monitoring data) or by model prediction, taking into consideration distribution and fate processes after the chemical has entered the environment.

Most of the reports focus on emissions during the production and manufacturing stages of ENMs. However, results from worker exposure normally cannot be used for quantifications of the environmental release since the mass flow per unit time of ENMs reaching outdoor air or the water body are rarely specified. The improvement of current transfer modelling methodologies to approaches that consider explicitly nanospecific properties is of great importance, since currently none of the ENM exposure assessment models provide up to date convincing solutions for the environmental fate of ENMs in the environment[29].

The main problematic to overcome this gap is the lack of data. There are almost no empirical data available which describe these dynamics, and regarding the models, the majority only use mass-transfer simulations between environmental and technical compartments, which are not precise enough for processes involving transfer or degradation of particles, such as suspension/resuspension, agglomeration/aggregation dissolution or settling, among others.

Therefore, the review of the literature published in the last few years carried out in previous actions of the project is aimed to provide useful information with which to improve the results of environmental exposure models by more accurate input parameters. The compilation of the ENM environmental concentrations will be used to approach the ERCs to ENMs concentrations and it is reported in Table 2 together with a review of the existing models.

[27] Y. G. Wang *et al.*, Transport and retention of nanoscale C-60 aggregates in water-saturated porous media, Environ. Sci. Technol., 42, 3588–3594 (2008)

[28] T. K. Darlington *et al.*, Nanoparticle characteristics affecting environmental fate and transport through soil, Environ. Toxicol. Chem., 28, 1191–1199 (2009)

[29] Towards Efficient Designing of Safe Nanomaterials: Innovative Merge of Computational Approaches and Experimental Techniques, Ch. 12: Modelling the Environmental Release and Exposure of Engineered Nanomaterials (F. Gottschalk & B. Nowack), Ed. T. Puzyn & J. Leszczynski, The Royal Society of Chemistry 2012

Table 2 Review of exposure models for nanoparticles in the environment (reference list at the end of the deliverable).

Study	ENM	Sources of Emission	Compartments	Properties considered in fate modelling	Description	Estimated PECs
Arviddson *et al.*[i] [ii]	TiO_2, Ag	Production, use, waste handling	Water	None	Aims at assessing general emission to the environment from production, use and waste handling phases. Based on substance flow analysis (SFA) but applied to particle number. No particle property relevant in fate modelling taken into account.	NA
Arviddson *et al.*[iii]	TiO_2	Generic	Water	Particle size, density, collision efficiency (though this parameter also depends on the environmental media)	Applied to particle number. Based on stability and particle collisions theory[iv] [v]. Focused on agglomeration and sedimentation. Effects of the presence of natural organic matter can be included via collision efficiency when experimental studies are available.	NA
Boxall *et al.*[vi]	Ag, Al_2O_3, Au, CeO_2, C_{60}, SiO_2, TiO_2, ZnO	Direct input to surface waters, inflows from use of agrochemicals, runoff from contaminated soil, aerial deposition, release from wastewater treatment plants	Water, sludge, soil	None	Simplistic release model to calculate the emission of ENM via single products (pharmaceutical, cosmetics, paints, coatings…). Only applicable to individual and hypothetical usage scenarios. Non-comprehensive range of products and life-cycle stages.	<u>Water</u>(µg/L) Ag: 0.01-0.1 Al_2O_3: 0.0002-0.0025 Au: 0.14-1.43 CeO_2: <0.0001 C_{60}: 0.096-0.96 SiO_2: 0.0007-0.02 SiO_2 Organic: 0.005-0.05 TiO_2: 24-245 ZnO: 76-380 <u>Sludge</u> (mg/Kg) Ag: 0.29-2.90 Al_2O_3: 0.01-0.07

						Au: 4.7-40.7 CeO_2: <0.01 Fullerenes: 8.94-894 SiO_2: 0.02-0.21 Organic SiO_2: 0.01-0.14 TiO_2: 701-7007 ZnO: 2172-10861 Soil (µg/Kg) Ag: 0.439-4.26 Al_2O_3: 0.01-0.1 Au: 5.99-59.9 CeO_2: <0.01 Fullerenes: 13.2-132 SiO_2: 0.03-0.31 Organic SiO_2: 0.02-0.21 TiO_2: 1030-10305 ZnO: 3194-31944
Park *et al.*[vii]	CeO_2	Release from fuel additives	Air, soil	None	ENM emission calculated based on established model for particle emissions.	NA
Mueller and Nowack[viii]	TiO_2, Ag, CNT	Production, use, waste handling	Air, water and soil	None	ENM release considered from a whole life-cycle perspective. Calculations based on a substance flow analysis (tons/year). High uncertainties due to lack of data on the amount of ENM produced.	Air: (µg/m^3) Ag: 1.7 10^{-3} TiO^2: 1.5 10^{-3} CNT: 1.5 10^{-3} Water: (µg/L) Ag: 0.03

						TiO^2: 0.7 CNT: 0.0005 Soil: (µg/Kg) Ag: 0.02 TiO^2: 0.4 CNT: 0.01
Gottschalk *et al.*[ix x]	TiO_2, ZnO, Ag, CNT, C_{60}	Production and consumption	Air, water, soil, sludge, sediments, groundwater	None	Extension of the model of Mueller and Nowack. PECs calculated based on a probabilistic material flow analysis from a life-cycle perspective. Uncertainties on the release coefficients considered by means of Monte Carlo algorithms. The most critical information needed is the ENM production volume. The lack of data leads to very large uncertainties.	Very large range of values, see reference for more details.
O'Brien and Cummins[xi]	Ag, TiO_2, CeO_2	Use phases of exterior paint, food packaging and diesel fuel	Air, surface waters	None	Semi-quantitative three level risk model based on the relations between material properties and their behavior in the environment.	Water: (µg/L) Ag: 0.029 CeO_2: 0.024
Johnson *et al.*[xii]	TiO_2	Use of sunscreen	Sludge	None	Calculations done using the Low Flows 2000 Quality[xiii] extension model, normally used to estimate release of contaminants from consumer products. It includes the same fate mechanism used for chemicals (removal during wastewater treatment, dilution and biodegradation) such that no specific fate mechanism characteristic of ENP or their physico-chemical properties are taken into account.	<8.8 µg/L
Musee[xiv]	Ag, TiO_2	Production and consumption, sewage treatment plants	Water and soil	None	The values of PECs are evaluated according to the risk assessment procedure for chemical recommended by ECHA. No direct fate mechanism or specific physico-chemical properties are included.	STP: (10^{-4}-10^{-1}) µg/Kg Soil: (5 10^{-6}-10^{-1}) µg/Kg

Quik *et al.*[xv]	Generic	Generic	Water	None	Mass based model implementing the same approach used to calculate exposure to chemical substances of aquatic organism. It includes three fate mechanisms: advection, dissolution and sedimentation. No attempt to evaluate the coefficients regulating the three processes from basic physicochemical properties is done. No PEC values reported.	NA
Praetorious *et al.*[xvi]	TiO_2	Production and consuption, sewage treatment plants, air, soil	Water	Particle size, particle density	PEC values estimated by means of a river model combined with a model for ENP environmental fate. The motel relies mostly on kinetic fate mechanism for particles, including agglomeration, sedimentation and advection. Mass-based model. Also the fractal dimension of the agglomerates is included.	<0.0055 µg/L

4. Proposed environmental system parameters and emission rates to support the calculation of the precited environmental concentration (PEC) of ENMs

Material Flow Models aim to predict the concentration levels of ENMs in a well-defined system, quantifying their flows between the different technical and environmental compartments. They allow to track the release of ENMs through the different stages of its entire life cycle, from production up to recycling and disposal of the product containing the ENM.

We propose a model including the following compartments: ENPs production, manufacturing of articles containing the ENM, nanoparticle usage (Use), waste incineration plant (WIP), sludge treatment plant (STP), filter, environmental water, environmental air, environmental soil. The material flow through the different compartments and stages of the material life cycle is schematically shown in Figure 7. Two fundamental assumptions underlie the model. The first one is that the main compartments (water, air and soil) are considered as homogeneous and well mixed. Secondly, equal flow rates between the different compartments are taken for all ENMs.

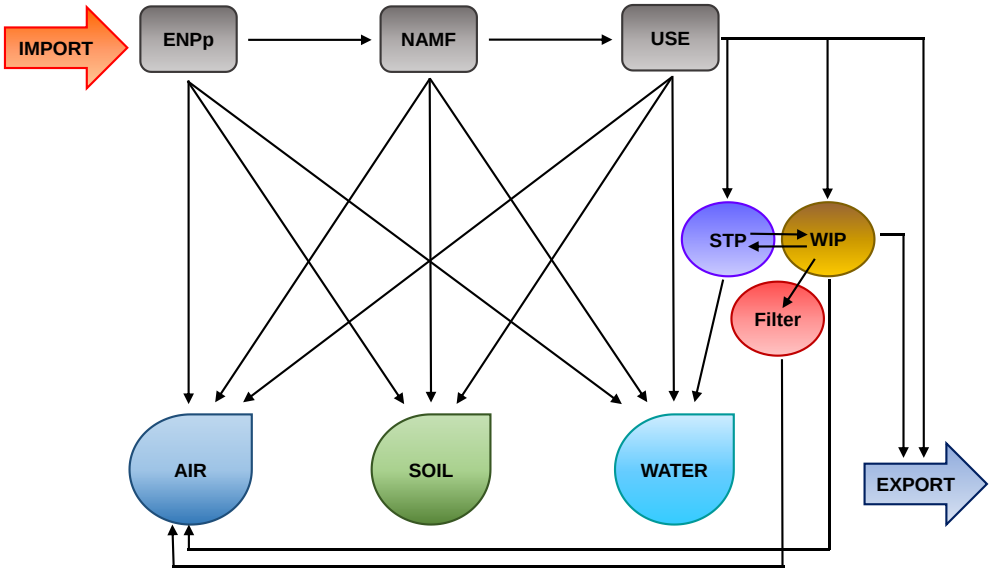

Figure 1: Simplified scheme of the material flow between the different compartments.

The model takes as input the amount of ENM introduced in the system. The percentages of ENMs flowing from one compartment to another are determined by means of **transfer coefficients (TC)**. For example, we can write the quantity of ENM transferred from the *i*-th to the *j*-th compartment using the following equation:

$$A_j = TC_{i\to j} A_i \ ,$$

where A_i and A_j are the amount of ENM in the compartments i and j respectively and $TC_{i->j}$ is the transfer coefficient between the two compartments.

The values we assumed for the transfer coefficients are listed in Table 3 and take into account all the stages of the ENM life cycle. They have been fixed according to the ECHA Guidance on information requirements and Chemical Safety Assessment.

The conversion from the released amount of ENMs water and soil to PEC values is done dividing the former by a reference volume of the environmental media. Since we are mostly interested in regional values of PECs, reference volumes will be related to geographic areas.

Table 3: Transfer coefficients

Flow		TC (%)
ENP production	→Air	5
	→Water	6
	→Soil	0,01
	→NAMF	89,99
Manifacturing	→Air	15
	→Water	1
	→Soil	0
	→USE	84
Use	→Air	5
	→Water	0
	→Soil	5
	→WIP	50
	→STP	5
	→Export	35
STP	→Air	0
	→Water	3
	→Soil	0
	→WIP	97
WIP	→Filter	30

	→Export	70
Filter	→Air	99
	→Export	1

5. Nano-specific release factors and categories for regulatory risk assessment of ENMs

This section defines a list of release categories based on information compiled from peer reviewed publications and data retrieved from measurements campaigns conducted by ITENE. A list of 12 nanoparticle release categories related with relevant activities and processes at all stages of the life cycle of ENP and nanoproducts have been defined.

The data retrieved from recent studies focused on the quantification of the release of ENPs in occupational settings, showing a significant release rate in processes involving the application of frictional forces and pressure, both resulting in the release of ENPs in quantities up to $2.0x10^{10}$ particles/cm^3. Mayor concerns are expected from wide dispersive applications such as the spraying of liquid dispersions containing ENMs and grinding processes. In these process, where the likelihood of release has been considered very likely, is highly recommended the implementation of controls to avoid the transport of the particles released from the source to the environment.

Other conventional processes such as harvesting and cleaning operations can generate a significant release of ENPs, being highly recommend to implement administrative procedures and controls aimed at reducing the release of ENMs to background levels.

A study from 2013[30] estimated that between 63–91 % of over 260000–309000 tons of the global ENM production of 2010 ended up in landfills, with the balance released into soils (8–28%), water bodies (0.4–7%), and atmosphere (0.1–1.5%). Regarding the manufacturing and production stages, total emissions from 0.1 to 2 % of the total production rate are estimated, from which between 10-40% of the total ends into air or water and 80-20% into landfill, correspondingly.

It must be noted that these release estimates are generic for all ENMs, given the lack of ENM-specific manufacturing information. Likewise, there is considerable uncertainty on the effect of the application of emission control measures in the different processes related to the ENMs, which adds higher imprecision to the estimates.

Table *4* contains a short description of the **NM release categories and related activities** based on a comparison of the actual ERCs and the information extracted from the literature review. These NP release categories reflect the combination of operations that may lead to a release of ENMs to the workplace environment. They are also classified by life cycle stage and release

[30] Global life cycle releases of engineered nanomaterials, A. A. Keller et al., J Nanopart Res (2013) ,15:1692

potential, coloured from lower to higher, along with an example of ranges extracted from the data compilation in DA3 and DB1b.

Table 4. Task Specific Nanoparticle release categories (NRC)

Stage	NRC	Activity	Description	Release potential	GM (#/cm³)
Production	**NRC1a**	Synthesis process Liquid-phase reaction and Flame spraying	Manufacture of ENPs by process Liquid-phase reaction and Flame spray pyrolysis.	**Low**	3900
	NRC1b	Top-down (milling) synthesis	Manufacture of ENPs by top down approaches	**Medium**	3865
	NRC2	Mechanical methods	ENPs are produced top down from larger particles	**Medium to High**	11200
	NRC3	Laser ablation	Laser ablation is the process of removing material from a solid (or occasionally liquid) surface by irradiating it with a laser beam	**Medium**	5900
	NRC4	Reactive Sintering	Process of compacting and forming a solid mass of material by heat and/or pressure without melting it to the point of liquefaction.	**Medium to High**	15300
	NRC5a	Transfer of pristine NP or mixtures into small containers at non-dedicated facilities	Filling and transfer of pristine NPs and mixtures in non-dedicated facilities.	**Medium to High**	17432
	NRC5b	Transfer of pristine NP or mixtures into small containers at dedicated facilities	Filling and transfer of pristine NPs and mixtures in dedicated facilities	**Medium**	6155
Formulation	**NRC6a**	Mixing or blending of powders for formulation of mixtures at laboratory scale (fume hood)	Mixing and blending of small amounts of ENPs into (chemical) mixtures in all types of formulating industries, such as paints, pigment paste, fuels, and household products.	**Low**	9400
	NRC6b	Mixing or blending of powders for formulation of mixtures at laboratory scale in open benches	Mixing and blending of ENPs into (chemical) mixtures in all types of formulating industries, such as paints, pigment paste, fuels, and household products.	**Medium**	9400
	NRC7	Formulation of ENPs in materials / Polymer preparations and compounds	Mixing or blending of ENPs which will be physically or chemically bound into or onto a matrix (material) such as plastics additives in master batches or plastic compounds.	**Medium to High**	22802
	NRC8	Spray application of powders	Spraying activities used to intentionally disperse powders on surfaces by using a pressure difference (e.g. dusting crops, powder coating).	**High**	50000
	NRC9	Polymeric nanocomposites manufacturing by extrusion / compounding	Activities where powders, granules, or pelletized material transformed by high temperatures, pressures or due to frictional forces in a molten state	**Medium to High**	16000

Manufacture	**NRC10a**	Weighing of powders at laboratory scale (fume hood)	Weighing of small amounts of ENPs in powder forms in fume hoods	**Low**	35
	NRC10b	Weighing of powders in open benches	Weighing of ENPs in powder forms in open benches	**Medium**	15946
	NRC11a	Cosmetic manufacturing process of powdered or granulated material	Handling and transfer of powdered or granulated nano-enabled products	**Medium**	3300
	NRC11b	Cosmetic manufacturing process of liquid NPs' dispersion	Handling and transfer of liquid NM dispersions either during manufacturing or application of nano-enabled products	**Low**	689
	NRC12	Vacuum transfer of powders or granules	Activities where a stream of powder is transferred from one reservoir (or container, vessel) to the receiving vessel. Transfer through a hose or tube with pressure (e.g. vacuum transfer).	**Medium**	6330
	NRC13a	Manual packaging (Bagging) of small containers	Packaging of ENPs into small plastic containers and plastic bags (e.g. zip closed plastic bag)	**Medium**	6155
	NRC13b	Semi-Automated packaging (Bagging) of containers and bags	Packaging of ENPs into plastic containers and plastic/paper bags.	**Medium to High**	19428
Use	**NRC14a**	Spraying operations (indoor)	Spraying of liquid formulations (e.g. paints, cleaners, lubricants and adhesives) / Indoor processing	**High**	31200
	NRC14b	Spraying operations (outdoor)	Spraying of liquid formulations (e.g. paints, cleaners, lubricants and adhesives/ Outdoor processing	**Very High**	50000
	NRC15	Dyeing and finishing of Textiles	Immersion operations such as dipping and pouring. ENPs is applied to a surface by dipping the article into a bath.	**Low**	2000
	NRC16	Mechanical cutting, grinding drilling or sanding of articles	Substantial thermal or kinetic energy applied to a nanoproduct by grinding, mechanical cutting, drilling or sanding.	**High**	40000
	NRC17a	Activities with liquid surfaces/ undisturbed (no aerosol generation)	Handling of liquids in a bath or reservoir (e.g. immersion of objects, manual stirring of paint, mixing and loading of cleaning products)	**Low**	120
	NRC17b	Activities with liquid surfaces/ agitated	Handling of liquids in a bath or reservoir (e.g. electroplating, gas bubbling, mechanical mixing of paint, aeration of waste water, boiling, shaking liquids)	**Medium**	1200
	NRC18	Bottom loading	Pressurized transfer of a stream of liquid product from one reservoir to the next.	**Low**	35
	NRC19	Use of textiles	Washing and wearing of textiles.	**Low**	10
	NRC20	Use of packaging materials		**Low**	660
	NRC21	Fracturing and abrasion of solid objects	Solid objects are broken into smaller parts or abraded by frictional forces (e.g. crashing, sewing, sanding)	**Medium to High**	9400
Disposal	**NRC22**	Filtering	Removal from fluids (gas or liquids) of ENMs by nano-, micro-filtration	**Medium**	-

		and reverse osmosis for aggregated and non-aggregated nanoparticles due to the high-pressure membranes or electrostatic filters can remove inorganic and organic contaminants		
	NRC23	Waste Incineration Plant	Harmful substances are eliminated via chemical processes or separated from the combusting flue gas via mechanical processes.	**Medium**	**-**
	NRC24a	Waste Water Treatment Plant	Removal of impurities from water and by-products from wastewater with a range treatments used alone or in combination, such as prechlorination, aeration, coagulation, flocculation, slow-sand filtration, sedimentation, disinfection...	**Low**	**-**
	NRC24b	Sludge Treatment Plant	Treatment and disposal of sludge accumulated in a wastewater by anaerobic or aerobic digestion or composting. Incineration is used to a much lesser degree.	**Low**	**-**
	NRC25	Disposal into landfills	Transfer of ENMs to landfills through ash, slag or biosolids.	**Medium**	**-**
	NRC26	Abrasive blasting	Removal of coatings using abrasive material on the surface at high velocity (e.g. grit blasting, sand blasting, water cutting, welding)	**Medium to High**	**18300**

LOW  HIGH

Release depends strongly on the use and physical and operational characteristics of the applications of the end product depending on its product category, e.g. electronics, textiles, paints, automotive products or cosmetics, among others. The same NM may have completely different release behaviour if is incorporated into a product for example as a surface coating, with high release potential during use and disposal, versus suspended into a solid, where it has low release during use, but very high during disposal and recycling.

Therefore, the estimation of amount of material released must be done taken into account that a number of factors can modify the release. For this reason, some authors prefer to work with ranges of released material, such as Keller et al. previously cited[30].

A Probabilistic Material Flow Model (PMFM) can be used to estimate the release of material in the different environmental media (air, water and soil). Material Flow Models aim to predict the concentration levels of ENMs in a well-defined system, quantifying their flows between the different technical and environmental compartments. The model tracks the release of ENMs through the different stages of its entire life cycle, from production up to recycling and disposal of the product containing the ENM. The model considers the main compartments (water, air and soil) homogeneous and well mixed, and equal flow rates between the different compartments are taken for all ENMs.

The percentages of ENMs flowing from one compartment to another are determined by means of **Transfer Coefficients**[3] **(TC)**, listed in Table 5 taking into account all the stages of the ENM life

cycle, although being independent of the characteristics of scenario under consideration, exception made for the amount of ENM used in the process. They have been fixed according to the ECHA Guidance on information requirements and Chemical Safety Assessment.

Table 5: Transfer coefficients of material from each life stage.

Stage	TC (%)		
	Air	Water	Soil
Production/Formulation	5	6	0.01
Manufacture	15	1	0
Use	5	0	5
Disposal	0	3	0

In order to estimate the quantities of ENMs released, especially during use and waste, the availability of information on ENM containing products on the market is crucial. The release factors of Table 5 could be also modified by the presence of emission control technologies or combinations of them. The higher the efficiency of the RRMs taken into account, the lower the multiplicative reduction coefficient.

An estimate of the releases into each compartment can be calculated by the following equation:

$$M_{EC} = M_{tot}\left[TC_{A,B} * \sum F_{A,B}\right]$$

Where M_{EC} is the mass transferred to the Environmental compartment respect to the total mass M_{tot} of the ENM production, TC the transfer coefficient from process *A* to *B* and F the released fraction from *A* to *B*, e.g., fraction released into WWTP during disposal or fraction released into landfill during manufacturing.

From the above information and the data compiled in DA3 and DB1a, an assessment of the release coefficients for ENMs into the environmental compartments is proposed (*Table 6*). The coefficients are estimated for each nanospecific category within each life cycle stage of the NM. Estimations are based as well on the ratios given by Keller et al (2013)[30].

Table 6: Percentages of release material to the environmental compartments in each of the nano-specific categories classified.

Stage	NRC	Air (%)	Water (%)	Soil (%)
Production	**NRC1a**	0,05619	6,74275	0,01124
	NRC1b	0,05615	6,73755	0,01123
	NRC2	0,05	0,06	0,00010
	NRC3	0,05	0,06	0,00010
	NRC4	5E-06	0,06	0,00010
	NRC5a	0,00562	6,74404	0,01124
	NRC5b	0,05565	6,67773	0,01113
Formulation	**NRC6a**	0,00561	6,72923	0,01122
	NRC6b	5,60769	6,72923	0,01122
	NRC7	5,61525	6,73829	0,01123
	NRC8	0,05	0,06	0,00010
	NRC9	0,05	0,06	0,0001

Manufacture	**NRC10a**	0,01086	7,14956	0,57817
	NRC10b	10,86905	7,15276	0,57843
	NRC11a	0,0000000	0,01	0
	NRC11b	0	0,001	0
	NRC12	0,0010	0,0715	0,0058
	NRC13a	0,48970	32,22657	2,60610
	NRC13b	10,85635	7,14441	0,57775
Use	**NRC14a**	0	0	**0**
	NRC14b	4,89923	0	4,89923
	NRC15	4,19918	0	4,19918
	NRC16	0,13395	0	0
	NRC17a	1,8	0	1,8
	NRC17b	5,0	0	5,0
	NRC18	1,8	1	
	NRC19	5,0	0	0
	NRC20	0,5	0	5,0
	NRC21	5,0	0	5,0
Disposal	**NRC22**	44,51640	0	0
	NRC23	0	0,12211	0
	NRC24a	0	0	14,83880
	NRC24b	0,05619	6,74275	0,01124
	NRC25	0,05615	6,73755	0,01123
	NRC26	0,056	6,74	0,011

An overview of the data can be seen graphically presented in Figure *2*. It can be seen that the majority of ENMs are disposed in landfills, with a significant fraction going to soils and the atmosphere. Regarding the use, there is a quite homogeneous release to all compartments in almost all categories, except the one considered indoors (NRC8).

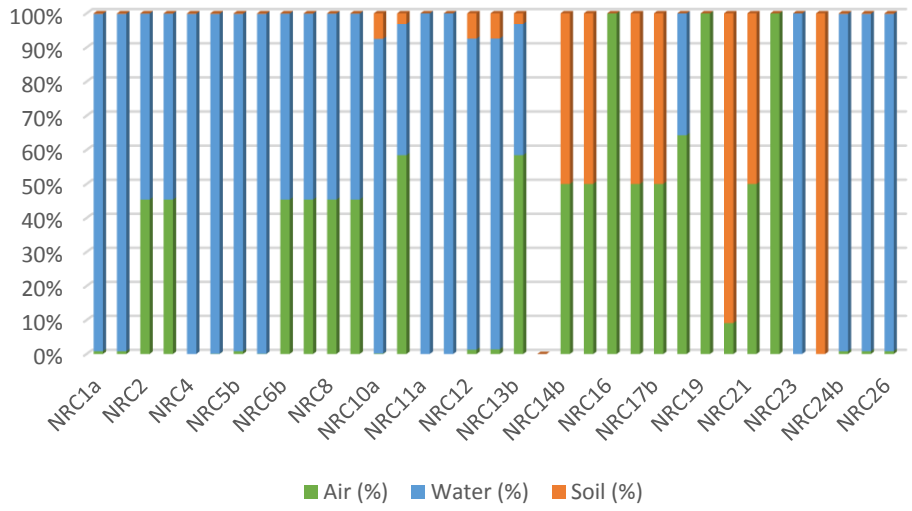

Figure 2: Representation of the release percentages to the environmental compartments from the nano-specific categories.

As stated previously, this fact is due to the absence of contention measures which are able to modify greatly the release of ENMs, and although in general RMMs are not considered, some processes are normally carried out with some mean of contention, e.g. NRC3a vs NRC3b, reducing up to the half the emissions to the environment.

The last but not least factor to take into account to estimate the amount of released material into each compartment is the time after emission, since there are several transport and transformation processes can occur once is liberated into the environment, changing its location among compartments. A brief scheme is shown in Figure *3*. Little knowledge is available about the fate and behaviour of ENMs throughout these processes, since several transformations of the ENM can occur[31,32]:

- ENMs are removed or destroyed due to waste during use or disposal (e.g. combustion)
- ENMs are captured by a treatment system and detected afterwards in the fly ash or other residues.
- Combination or reaction with other substances to form new particles (e.g. $CaCO_3$ to CaO and CO_2).
- Bigger particles decompose and turn into new, smaller particles or even ENMs.
- Agglomeration of ENMs forming bigger particles and not being detected by nano-measuring devices.

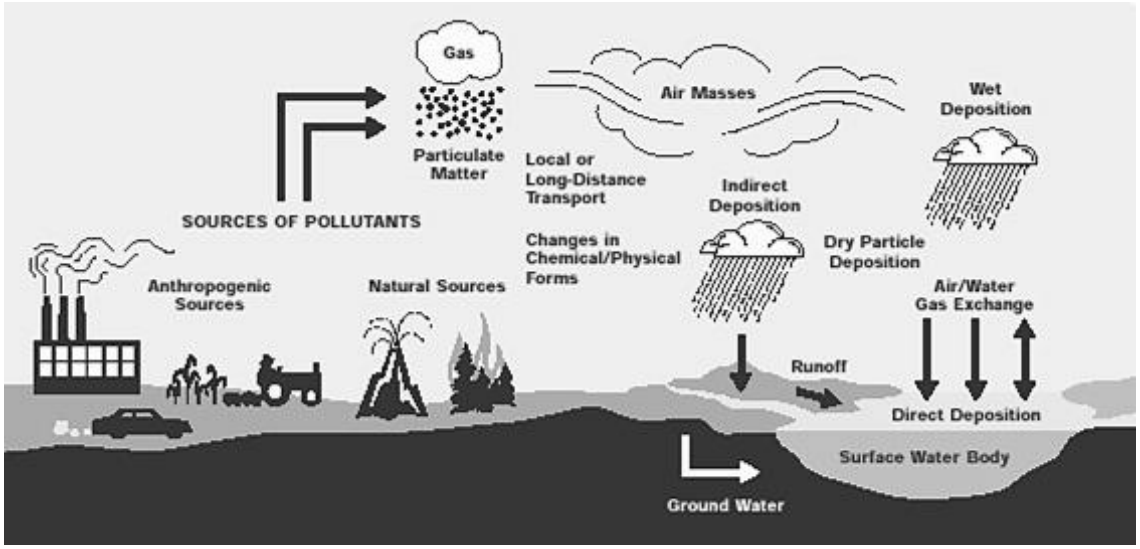

Figure 3: Atmospheric emission, transport and deposition processes[33].

Therefore, the coefficients can be used to quantify emissions at the local level, as inputs for fate and transport models to estimate concentrations in different environmental compartments, but always taking care of the processes, amounts and RMMs involved.

[31] Incineration of Waste Containing Nanomaterials, Working Party on Resource Productivity and Waste, OECD (2015)
[32] The Fate of Engineered Nanomaterials in Sewage Treatment Plants and Agricultural Applications, Working Party on Resource Productivity and Waste, OECD (2015)
[33] EPA, 2000c. Deposition of Air Pollutants to the Great Waters: Third Report to Congress. EPA-453-R-00-005. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

6. Conclusions

A list of at least of more than 13 refined release factors and their corresponding described environmental release categories (ERC) has been given. The estimation embraces the whole life cycle of the ENM, from the production, use and disposal.

The nanospecific release categories have been structured after compilation of emission and exposure data from literature and project outputs performed in previous tasks, and categorized among the risk of release of ENMs. It has been assumed that all ENMs produced will eventually release into the environment, and that once released a large fraction of them will transform (e.g., aggregate/agglomerate, dissolve or oxidize). Only in cases where specifically stated, RMMs are included.

Default worst case release factors resulting from the analysis conducted were selected, and the list of release factors and environmental release categories (ERC) will be continuously updated as new information becomes available. The relevancy of this action relies on the fact that both exposure scenarios (ES) and environmental release categories (ERC) are key elements in the characterization of the risk characterisation ratios (RCRs), being key to support the proper use of measured data on a regulatory basis.

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